Advances in Karst Science

William B. White
Janet S. Herman
Ellen K. Herman
Marian Rutigliano *Editors*

Karst Groundwater Contamination and Public Health

Beyond Case Studies

Springer

Advances in Karst Science

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Editors

Karst Groundwater Contamination and Public Health

Beyond Case Studies

Proceedings of a Conference Held in San Juan, Puerto Rico, January 27 to February 1, 2016

Organized by the Karst Waters Institute

Springer

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Preface

The conference **Karst Groundwater Contamination and Public Health** took place in the Hilton Condado Plaza Hotel in San Juan, Puerto Rico, on January 27–30, 2016. The 76 attendees were 45 professionals, 26 students, and 5 family members. The attendees came from seven countries: Austria, Denmark, France, Italy, Germany, Switzerland, and the United States. There were 30 oral presentations, 20 poster presentations, and 12 short, “snap” talks. The presenters were invited to contribute written versions of their presentations to this volume.

The conference was organized by the Karst Waters Institute, and the program and an initial set of abstracts were published as KWI Special Publication 19, available on-line at the KWI website. Special Publication 19 also contains information on the mid-conference field trip and the guidebook for the two-day field trip that followed the conference.

This volume presents the written contributions. In order to preserve a complete record of the conference, all presentations are included except for some of the snap talks. They are of three varieties:

Full papers: These were reviewed by the editors and, if necessary, by outside reviewers. Authors were asked to revise their papers as needed.

Extended Abstracts: Authors who did not wish to publish their complete work in the Proceedings were invited to prepare a summary as an extended abstract. These extended abstracts, essentially short papers, contain figures and references and should be considered citable sources of information. The extended abstracts were reviewed by the editors and modified as necessary.

Additional Papers: A few authors who did not wish to contribute to the Proceedings are represented by their original program abstracts. These have been combined into a single document that appears in the Summary section of the book.

In addition to the formal papers, the book contains introductory chapters that set forth the expectations of the conference and its interdisciplinary framework. The conference closed with an open discussion of needed research directions and opportunities. A summary of this discussion appears in the final chapter of the book.

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February 2017

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Part I

Introduction to the Conference

Contaminated Groundwater in Karst: Why Is It an Issue? An Introduction to the KWI San Juan Conference

William B. White, Janet S. Herman, Ellen K. Herman, and Marian Rutigliano

Abstract

The Karst Waters Institute sponsored a conference on karst groundwater contamination and its impacts on public health. The objective was to facilitate communication between hydrogeologists and the biomedical community, especially those dealing with public health issues. This volume contains the papers presented at the conference.

1 The Issue

If one were to compile a list of the necessities for a healthy human population, a source of pure water would be in the top tier of the list along with clean air, nutritious food, adequate shelter, and reliable sanitation. Pure, drinkable water is a priceless resource that is in limited supply on Earth, and it is vulnerable to contamination from the very beings who depend upon it.

Humans produce a wide variety of substances deleterious to health when introduced into water supplies. Surface streams, rivers, and reservoirs are easily contaminated, and as a result, water supplies drawn from surface sources require extensive filtration and treatment before introduction into water distribution systems. Water supplies drawn from wells for individual homes and farms often receive no treatment, and water supplies from municipal wells require much less treatment than water from surface sources. This comfortable assumption of safety without treatment does not apply to karst aquifers where surface water and groundwater are intermixed in a complicated way that is highly specific to individual aquifers. But karst aquifers are not to be ignored. Although hard data are limited, it has been claimed that 40 or more percent of the groundwater drawn for domestic and public water supplies in the USA is drawn from karst aquifers. Consider the number of towns that have grown up around the proverbial "big spring."

2 Karst Aquifers: What's Special?

Karst aquifers are those for which the host rock has significant solubility in water. Suitable host rocks for karst development are mostly carbonates and evaporites. Of these, only aquifers in carbonate rocks, limestone and dolomite, are likely to have a sufficiently low concentration of dissolved solids to be useful as water supplies. Dissolution of the host rock by infiltrating meteoric water enlarges pore spaces, widens fractures, and develops integrated systems of conduits that act as drainage networks. The process may have begun as early as the mid-Miocene although the active parts of the systems frequently date only from the late Pliocene or early Pleistocene. The consequence of the dissolutional modification of the aquifer host rock is that the hydraulics of groundwater flow in karst aquifers is often remarkably different from the hydraulics of porous media.

Because of the open pathways along fractures and conduits and the generally high flow velocities, karst aquifers can

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transmit contaminants and sediments that are not even a threat to porous media aquifers. Pathways from contaminant sources to actual or potential water supplies are complex and poorly predictable. 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, even less attention has been given to the actual impact of contaminated karst aquifers on public health. It can be established that a karst aquifer is contaminated, but what is the threat to the people who are using the water?

3 The Conference

It was to provide a comprehensive overview of groundwater contamination in karst aquifers and its impact on public health that this conference was convened in San Juan, Puerto Rico. The Puerto Rico karst is an especially appropriate setting for this meeting in that it provides drinking water for private residences and municipal water supplies and, at the same time, has been significantly impacted by unlined landfills and industrial outfalls. The conference consisted mainly of invited speakers with a poster session available for contributed papers. Invited speakers were chosen to provide the broadest possible coverage and the widest possible range of points of view. Thus, there are papers on the hydrogeology of karst aquifers, mechanisms of contaminant transport, the epidemiology of contaminated groundwater, and the impact of contaminated groundwater on public health.

The storage and movement of water in aquifers, including karst aquifers, is the province of the geological sciences and the community of hydrogeologists. The investigation of the effects of contaminated water on public health is the realm of the biomedical community who have little occasion to communicate with the earth science community. The conference was designed to encourage cross-disciplinary discussion by the selection of keynote speakers and by such devices as long coffee breaks, a poster session with a bar and snack table, and a mid-session field trip for all participants. The keynote papers are published together in the first section of the book and illustrate the range of topics discussed.

4 How to Address the Issue of Contaminated Karst Groundwater

4.1 Step One: Characterize the Specific Karst Aquifer of Interest

The term "karst aquifer" is not a label for a specific thing. Rather, karst aquifers represent a large and complex family of aquifers ranging from those little different from aquifers in sandstone or river gravel to "aquifers" that are little more than roofed-over surface streams. As might be expected, the devil is in the detail, and the first task of those evaluating contaminated aquifers is to delineate the hydrogeology, the effective boundaries of the aquifer—the groundwater basin—and the characteristics of its internal drainage. To this end, a large number of tools have been developed over the past decades (see, e.g., Goldscheider and Drew (2007) or Kresic (2013)). Some conference papers illustrated contemporary approaches to the hydrogeology of karst aquifers and are collected under the heading "Aquifer Studies."

4.2 Step Two: How Do the Various Types of Contaminants Move?

The usual suspects that would be a threat to surface waters and to groundwater in non-karstic aquifers comprise the list of contaminants that might impact a karst aquifer. The fundamental differences are the mechanisms by which the contaminants move and are stored in the aquifers, i.e., their fate and transport. There are water-soluble contaminants, of which nitrate is the most widespread, but also agricultural chemicals and leachates from dumps, landfills, and tailings piles. There are non-aqueous phase liquids—gasoline, fuel oil, chlorinated solvents, and many others—that have movement and storage mechanisms that may be quite different from the movement of water in the aquifer. There are microorganisms—bacteria, viruses, and protozoa—that move easily through the karst system. There are particulates, ranging from colloids to cobbles, some benign and some not, that are washed through the system by flood pulses. Cleanup of many of these contaminants ranges from difficult to impossible.

Investigation of contaminant fate and transport is an extremely active area of research. Many of the papers presented at the conference dealt with identification and characterization of contaminated groundwater and with techniques for evaluating the transport of the contaminants by the groundwater. These appear in the section labeled "Karst Groundwater Contaminants and Tools for Their Evaluation."

4.3 Step Three: What Is the Threat to Public Health and What to Do About It?

To return to the initial question: What is the issue? The motivation for this conference was to bring health sciences professionals into a conversation with environmental scientists to focus on karst groundwater, its contamination, and consequent health outcomes. A particular aspect of this intersection of perspectives requires recognition of exposure levels and timescales. Although public health professionals are frequently addressing acute health problems, it is often true that exposure to contaminants of concern in drinking water is a chronic issue. The distinction between exposure to a high concentration of contaminant over a short time and long-term exposures to a ubiquitous background contaminant at low concentrations but over a very long time is crucial to making the connection between contaminated water and human health. Unfortunately, the cumulative effects of long exposures are much more difficult to identify and evaluate. The conference was fortunate to have the participation of the Puerto Rico Testsite for Exploring Contamination Threats (PROTECT), a large and long-term investigation of the effects of low levels of contamination on preterm birth in the north karst belt of Puerto Rico. There were multiple papers from the PROTECT group in the conference. These contributions along with other papers addressing the driving question about health outcomes are found in "Contaminant Exposure and Public Health."

The synthesis of all the scientific contributions to the conference is an attempt to answer the question, "What do we do about it?" Why should groundwater contamination in karst aquifers be treated any differently than contamination of groundwater in any other aquifer, or for that matter, from contamination of surface streams and reservoirs? The contaminants will be from the same sources, have the same properties, and have the same effects on public health regardless of the source from which the contaminated water is drawn. There are three primary reasons why karst aquifers should be treated differently, both from a management and from a regulatory point of view.

(1) The much larger apertures in karst aquifers, ranging from a few millimeters in solutionally widened joints to tens of meters in master conduits, permit the passage of much larger solid contaminants than would be possible in porous media. Bacteria and other microorganisms, for example, can easily pass through a karst aquifer to the point of drinking water extraction, whereas they would have been filtered out during flow through the porous medium of a sand aquifer.
(2) Very short travel times. If a tanker truck full of chlorinated solvents goes off the highway, rolls down an embankment, and breaks open in a river, the authorities know they have an emergency, especially if the accident took place only a few kilometers upstream from the intake to a city water supply. A similar wreck above a non-karst aquifer is a more leisurely affair. The authorities will have to quickly constrain surface runoff, but infiltrating solvent will form a slowly diffusing plume that can be evaluated and treated. However, if a tanker truck spills its load into a sinkhole, the travel to the spring will not take much more time that the flow down the river. Spills in karst regions are as much of an emergency as spills into rivers.
(3) Ready communication between the surface, the localization of all human activities, and the groundwater in a karst aquifer. Wastes from the production of food, mining, energy, and manufacturing, as well as septic, sewage, and urban storm water, are all easily directed to recharging the groundwater via karst features of sinking streams, sinkholes, and thin soils. Taken all together, the inescapable realization is perhaps the most important outcome of the conference: Both the public and the responsible authorities must treat water supplies from karst aquifers with the same level of suspicious evaluation and environmental protection that would be given to a surface water supply. There is a certain nostalgia about "pure mountain spring water," harking to a time when grandmother carried water from the spring in an oaken bucket. Karst springs are usually beautiful, but beautiful does not mean that they should be piped directly into the community's water mains. The most important threat from contaminated karst aquifers may be the lack of understanding on the part of planners and regional authorities and also on the lack of a regulatory framework that takes the peculiarities of karst aquifers into account. This critically important topic is addressed in the collection of papers on "Risk Assessment and Regulatory Issues."

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Public Health and Karst Groundwater Contamination: From Multidisciplinary Research to Exposure Prevention

Heather F. Henry and William A. Suk

Abstract

Karst aquifers account for up to 20% of the world land area and are a source of drinking water for much of the world. Despite the critical value of these aquifers as a drinking water source, there are a growing number of incidences of karst aquifer contamination worldwide, including inadvertent spills, dumping, industrial discharges, or sewage seepage events. Given the porous nature of carbonate rocks, the hydrogeology of karstic aquifers is extremely complex, making it difficult to predict movement of contamination in these aquifers and to identify exposure risks. These contamination events—together with emerging issues such as climate change, exposures to infectious agents, as well as the increase in informal mining practices—indicate the need to explore linkages between karst groundwater, contamination, and health. Accordingly, the issue of karst groundwater contamination presents a unique global public health challenge requiring a multidisciplinary problem-solving approach. The National Institute of Environmental Health Sciences (NIEHS) Superfund Research Program's (SRP) multidisciplinary approach serves as a model for integrating expertise across health, engineering, geological, and community-based approaches to solve problems. Using examples relevant to karst contamination, NIEHS SRP grantees are engaged in research endeavors to address issues of drinking water safety—from remediation to well-testing best practices. It is recommended that continued research addresses karst contamination, with particular attention given to identifying people at risk of exposures and to developing proactive means to prevent further exposures. This is particularly important in the USA, where two-fifths of the population's drinking water comes from karst aquifers. Furthermore, over 40 million US citizens are on private well water for drinking, yet testing for contamination in these wells is often not required. Given the challenges predicting contaminant transport in karst and the lack of uniform private well water testing regulations, there is a need to promote awareness of risks for people living in karst areas among public health, hydrogeology, and government officials, and to use community-based approaches as models for intervention and exposure prevention.

1 Introduction: Karst Contamination—A Global Concern

Public health implications for contamination in karst aquifers are of global concern. It is estimated between 12.5 and 20% of the Earth's land surface that is composed of carbonaceous rocks (Fig. 1) (Williams and Fong 2014; USGS 2016b).

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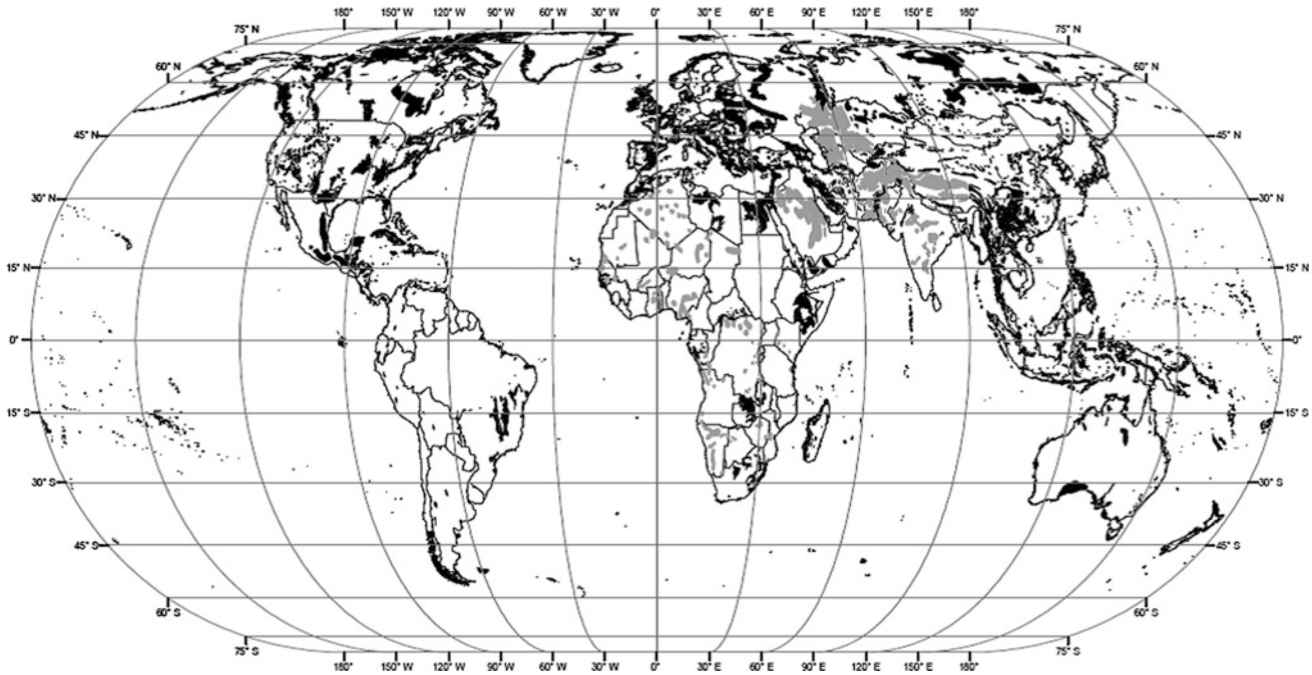

Fig. 1 Karst aquifers worldwide based on Ford and Williams (1989). From Williams and Fong (2014)

These rock formations—limestone and dolomite—form karst, meaning the rock material is slowly dissolved through time leaving behind caves, springs, sinkholes, etc. Unlike non-carbonaceous rock formations, karst hydrogeology is governed by small cracks and fractures as well as larger conduits. These complicated networks of channels create difficulty in predicting transport of water through karst, as well as anything transported along with water, such as contaminants or pathogens (USGS 2016b). Given the porous nature of carbonate rocks, the hydrogeology of karstic aquifers is extremely complex, making it difficult to predict movement of contamination in these aquifers and to identify exposure risks.

Numerous studies report contamination impacts in karst aquifers throughout the world (Du Preez et al. 2016; Xu et al. 2016; Li et al. 2016; Morasch 2013; Krejcova et al. 2013; Huang et al. 2013; Metcalfe et al. 2011). Some studies indicate linkages to increased risk of disease and dysfunction as a result of contamination of aquifers by hazardous substances (Rodriguez et al. 2015; Huang et al. 2013; Long et al. 2012; Hu et al. 2011). There are several emerging global issues that would also overlay with the concerns of contamination in karstic aquifers. Transport of infectious agents through karst aquifers is well documented throughout the world (Somaratne and Hallas 2015; Sinreich et al. 2014; Arcega-Cabrera et al. 2014; Bauer et al. 2013; Wampler and Sisson 2011; Khaldi et al. 2011; Dussart-Baptista et al. 2007). There is growing evidence that co-exposures between contamination and infectious agents confer heightened risk of disease and dysfunction—above what would be expected from exposure to the contaminant alone (Boldenow et al. 2015; Jaligama et al. 2015; Notch et al. 2015). In the way that large above ground metal processing shows impacts to karst aquifers (Du Preez et al. 2016; Deng et al. 2009, 2011), it should be noted that informal mining practices may release mixed contaminants that could impact drinking water resources. Activities on the rise, such as electronic waste (e-waste) mining (Heacock et al. 2016; Grant et al. 2013) as well as informal precious metal mining (Maier et al. 2014), have potential to contaminate water resources, and those in karst aquifers are particularly vulnerable. Lastly, several karst researchers are investigating the impacts of severe weather events related to climate change (Polemio 2016; Thomas et al. 2016; Dura et al. 2010). These surge events impact the movement of contaminants in karst—leading to unanticipated sewage contamination and toxicant transport.

2 Understanding Karst Contamination Issues Requires Multidisciplinary Research Framework

The issue of karst groundwater contamination presents a unique global public health challenge requiring a multidisciplinary problem-solving approach. The National Institute of Environmental Health Sciences (NIEHS) Superfund Research Program's (SRP) multidisciplinary approach serves as a model for integrating expertise across health, engineering, geological, and community-based approaches to solve problems. One such multidisciplinary study is underway in the northwest karstic region of Puerto Rico (PR) where fate and transport modeling and environmental sampling of aquifer contamination are being studied as variables to understand the high incidence of preterm birth in PR (NIEHS 2015; Yu et al. 2015). They are applying state-of-the-art methods to study biological mechanisms involved in preterm birth related to environmental factors (Johns et al. 2015; Watkins et al. 2015; Cantonwine et al. 2014; Ferguson et al. 2014). The epidemiological research is complimented by bidirectional community and stakeholder engagement through providing culturally sensitive risk communication information to pregnant mothers, coordinating with organizations that promote karst conservation, and collaborating with health advocacy groups such as March of Dimes (NIEHS 2016).

The research in the northwestern karst region of Puerto Rico also touches on another issue of high relevance to mainland USA: Contaminant exposure varies widely depending on whether drinking water comes from public versus private sources. Under the Safe Drinking Water Act (SDWA) of 1974, all public drinking water facilities are required to ensure safety of drinking water through setting maximum contaminant levels (MCLs), testing for compliance with the MCLs, and maintaining effective operation of drinking water treatment and delivery systems. Hence, in cities, towns, and municipalities under public drinking water works, contaminant levels are tested for and controlled (assuming compliance with SDWA). However, a major concern stems from the fact that private well users are not protected under the testing and maintenance provisions of the SDWA. These SDWA regulations do not apply to the estimated 40 million US citizens reliant upon private well water for their drinking water (Maupin et al. 2014). For private well water users, rules and regulations for testing are not uniform and vary from state to state. In general, there may be some testing required at the time of well installation; however, these tests rarely account for toxicants that might be associated with discharges from current and/or legacy industry operations (e.g., toxicants such as heavy metals, chlorinated contaminants, or other hazardous substances), nor geogenic hazardous substances (e.g., naturally occurring arsenic). Furthermore, for much of the USA, testing of wells is not required after installation. As a result, the testing of private well water is largely the responsibility of the individual homeowner (EPA 2016a). This places private well water users in a particularly vulnerable position. They may not be aware that well testing is their own responsibility and would not necessarily be aware of contamination sources in their region that may impact their drinking water aquifer.

Hence, NIEHS SRP-funded research study in northwestern Puerto Rico is investigating linkages between karst aquifer and drinking water quality (whether private or public)—using these data as a model for better understanding fate and transport of contaminants in karst groundwater. Furthermore, the researchers are measuring for contaminant exposure utilizing innovative biomonitoring tools. With this integrated approach, hydrogeological research has advanced the understanding of movement of hazardous substances in the karstic groundwater and provided critical geospatial information useful for the epidemiological studies (Anaya et al. 2014). This multidisciplinary research approach is forging a new model framework to understand the interactions between contamination and human exposures in karst aquifers—and developing best practices for engaging communities and stakeholders to protect public health, to conserve these unique karst ecosystems, as well as protecting these vulnerable karst aquifers.

3 Future Directions: Drinking Water Protections in the USA and Karst Aquifers

Given the uncertainty of risk from contaminant transport through karst aquifers, there is need to develop new policies, integrate data networks, and expand outreach to those potentially vulnerable to exposures. Using the USA as an example, there would be a tremendous benefit to focus policy, research, and outreach to states/communities/regions with a high percentage of private well use (Fig. 2) drawing from karst aquifers (Fig. 3). Overlaying karst aquifer regions with data about private well usage in the USA can be used to identify states and communities that would benefit from targeted communication campaigns to bring awareness about the nature of karst aquifers in terms of contaminant transport.

Bringing together stakeholders from multiple sectors is a first step to identify risk factors for environmental exposures and to develop effective interventions to prevent further exposures. The Karst Waters Institute's "Karst, Groundwater Contamination & Public Health: Moving Beyond Case Studies" 2016 meeting in Puerto Rico brought to light concerns from multiple stakeholders, including community groups, karst conservation groups, health researchers, government regulators (from the USA and worldwide), as well as experts in hydrogeology and engineering (KWI 2016). The need for maintaining this community of practice is evident, as the exchange between and across disciplines is invaluable for practical solutions such as modeling contaminant transport in karst aquifers, developing effective guidance for private well users, as well as engaging communities. Another recent focus group was convened by the North Carolina Environmental Health Collaborative (NC EHC) titled "Safe Water from Every Tap" held in North Carolina in 2015. This summit identified critical barriers to well testing by convening a multistakeholder group of local

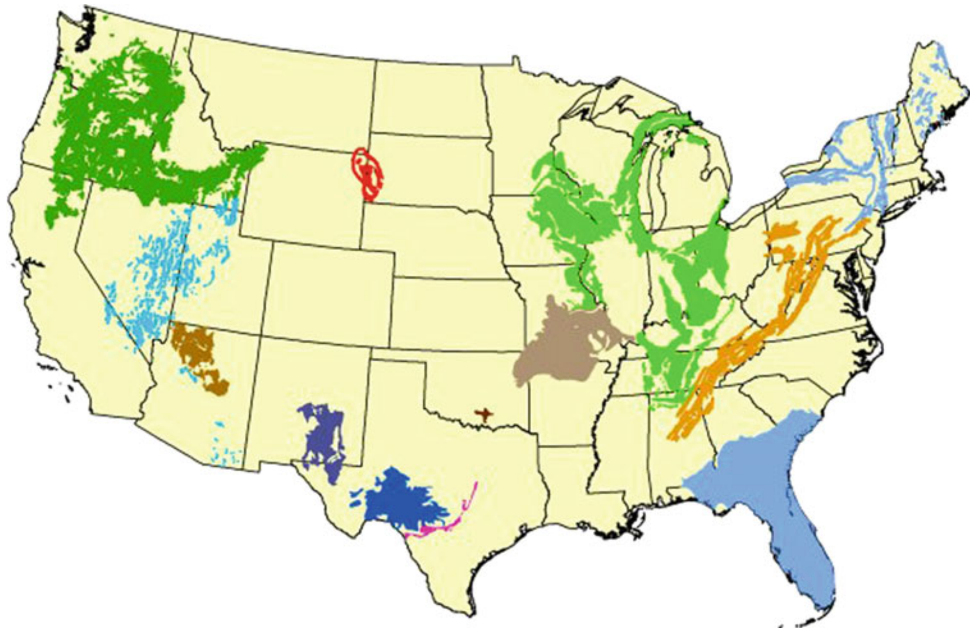

Fig. 2 Principal karst aquifers of the USA (USGS 2016a)

health departments, state and federal agency representatives, water utilities, and industries (RTEHC 2015). In addition to the recommendation to expand efforts to better inform communities about well testing, the summit also identified new well-testing regulations and policies that may be used as models to reduce the gap of regulation for private well users. An example is the Private Well Testing Act (PWTA) of New Jersey (2011), a consumer information law requiring private drinking well testing for real estate transactions (prior to closing) and for rental properties (every five years). The PWTA is a model of new policy relevant to contaminant transport risks—regardless of the aquifer type—because the test includes 32 contaminants of human health concern (metals, hydrocarbons, chlorinated contaminants). Another provision of the PWTA is that data are incorporated into a statewide groundwater quality analysis database maintained by the NJ Department of Environmental Protection (NJDEP) (Atherholt et al. 2009). This additional effort by NJDEP, to maintain and analyze their data, addresses challenges identified in both the Karst Waters Institute and the North Carolina Environmental Health Collaborative conferences. Access to groundwater data is difficult and becomes a limiting factor in reaching out to those who may be at greatest risk.

It follows that well-testing communication efforts might prioritize outreach to families, communities, and counties where drinking water comes from private wells in karstic aquifers. In terms of data integration, there are several tools, such as geographical information systems (GIS), that can be used to overlay multiple data layers—such as hydrogeological layers, contaminant-release information, or locations of Superfund sites (Hollingsworth et al. 2008; NLM TOXMAP 2016). Tools like these are being used to explore the extent of contamination in karst, and in one such study, it is estimated that as many as 23% of Superfund sites are found in karst regions (Cotto-Ramos 2015). Despite the availability of hydrogeological and hazardous substance mapping databases, there remain challenges to identifying those most at risk in terms of an intersection between karst, contamination, and private well users. This is because state and county records of private well locations are not always available in database form; furthermore, these data are not often publicly available. Established collaborations between researchers (i.e., health, geospatial, environmental monitoring) and staff at state departments of health and environment (where records are often located) can be critical to identifying those who may be at greatest risk for environmental exposures. An example of such collaboration is the NIEHS SRP-funded research project mapping high areas of arsenic and locations of private wells in the state of North Carolina, a project made successful by interactions between the researchers and the NC Department of Health (Sanders et al. 2011). The researchers identified areas of high risk of exposure to arsenic from private wells—and they have since followed up with outreach to these vulnerable communities. This reinforces the need for coordination and integration between multiple sectors: government, health, geological, and community outreach expertise.

Lastly, translating research findings to stakeholders—as well as impacted individuals and communities—is important to bring awareness to the connections of karst, contamination, and public health. The US EPA provides Web sites with general guidance for private well owners to help identify symptoms indicative of well water contamination

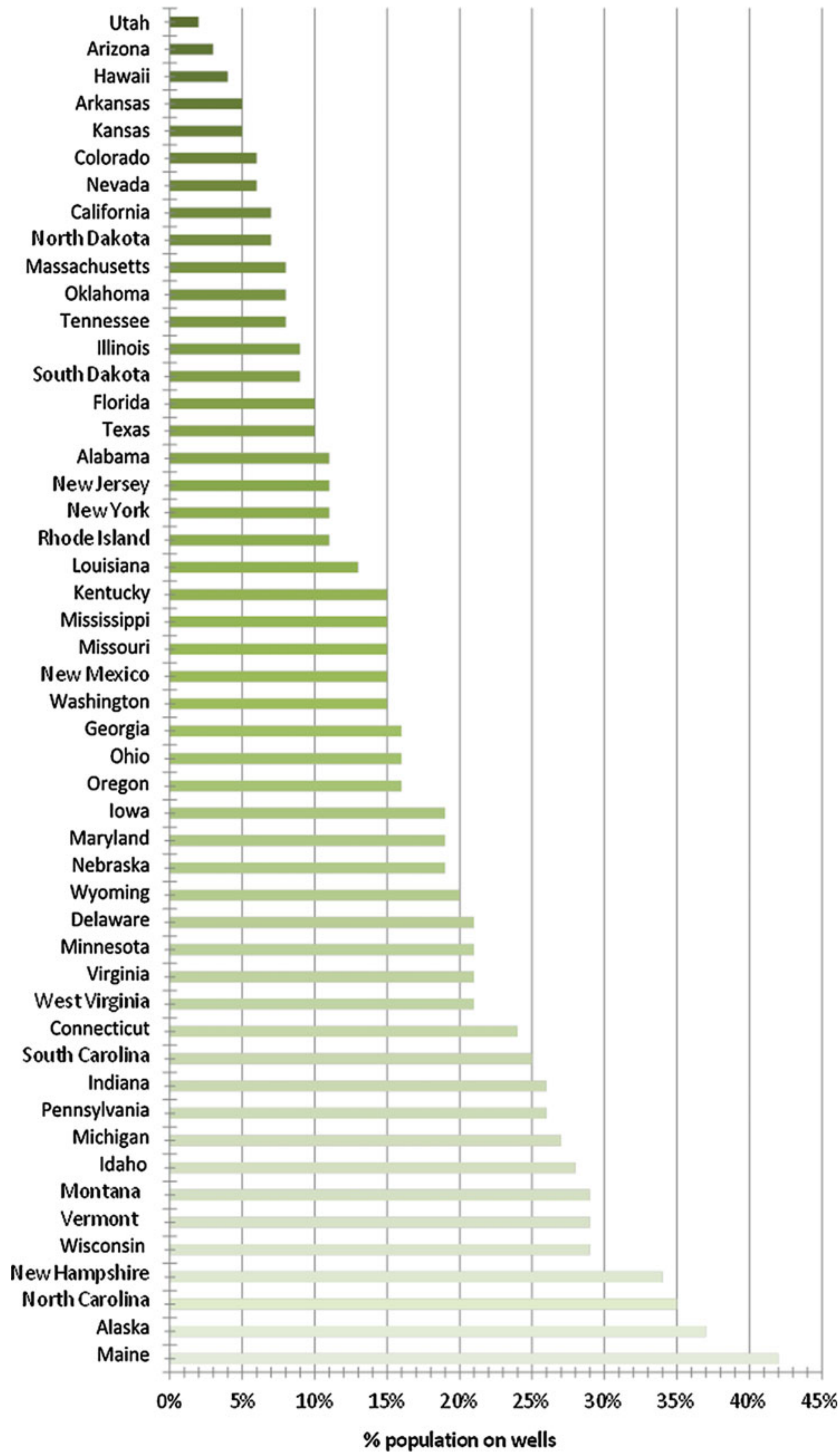

Fig. 3 Percentage of residents on private well drinking water based on data from Maupin et al. (2014) and Research Triangle Environmental Health Collaborative (2015)

(EPA 2016a, b). They have also developed the Drinking Water Mapping Application to Protect Source Waters (DWMAPS) as a resource for communities to answer questions about potential contaminant impacts on their water supply (EPA 2016c). The DWMAPS mapping tool integrates information about pollution sources, which can help a private well user identify potential exposure risks. These are helpful resources for state and county offices to understand whether there is cause for concern for their communities—and for community members who are already aware of potential contamination concerns with their water.

However, as mentioned previously, many of the 40 million private well users may not be aware that well testing is their own responsibility and would not necessarily be aware of contamination sources in their region that may impact their drinking water aquifer. For this reason, a more proactive approach to reaching out to communities at potential risk is ideal. Utilizing a multidisciplinary framework incorporating health, monitoring, and community engagement research studies, several NIEHS-funded Superfund Research Centers are engaging with communities to develop effective communication approaches to help private well owners navigate the process of well testing. Their efforts range from using geospatial databases to identify private well-using communities in areas of elevated groundwater arsenic (Sanders et al. 2011); identifying socioeconomic patterns that reveal barriers to testing (Flanagan et al. 2016a, b, c; Flanagan et al. 2015a, b; Lothrop et al. 2015); developing communication campaigns to appeal to most vulnerable citizens; and providing non-technical information about the advantages and disadvantages of testing and treatment products on the market (Paul et al. 2015). Through their successful efforts, it is clear that working within communities to tailor community-specific outreach campaigns is essential to inspire individuals to be proactive about well testing.

4 Summary and Conclusions

Karst aquifers are an important source of drinking water for much of the world; however, incidences of karst aquifer contamination worldwide impact global public health. These contamination events—inadvertent spills, dumping, industrial discharges, or sewage seepage events—co-occur with growing emerging issues such as the impact of climate change on karst flow, infectious agents, and informal mining. There continues to be a need to explore linkages between karst groundwater, contamination, and health. Using a multidisciplinary approach, NIEHS SRP grantees are engaged in the research endeavors needed to make the connection between karst aquifer contamination and the potential health impacts. In addition, NIEHS SRP researchers design studies to identify communities of potential high risk of exposure leading to a possible negative health outcome—and then translate findings to practitioners (such as state public health staff) and develop prevention opportunities with impacted communities. For example, several NIEHS SRP community engagement leaders have initiated outreach campaigns for well testing among private well users where exposure to naturally occurring arsenic may be possible. This type of outreach is important to promote public health in that private well users are responsible, sometimes unknowingly, for testing and treating their own wells to ensure safe drinking water quality. Of relevance to karst aquifer contamination, there would be a public health benefit to utilize these effective community engagement practices to tailor well-testing communications for private well water users in karst aquifers, where movement of contaminants are difficult to predict.

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Part II

Keynote Papers

Team Science Applied to Environmental Health Research: Karst Hydrogeology and Preterm Birth in Puerto Rico

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Abstract

Understanding the interaction of environmental contamination and its impact on human health stretches the disciplinary demands required for effective research. Team science is required to understand the origin of contaminants, their pathways to human, their health effects, and for development of effective mitigation. We describe a team science model applied to the study of preterm birth in a region of karst hydrogeology, the Puerto Rico Testsite for Exploring Contamination Threats (PROTECT). This research program uses an innovative, holistic, source-to-outcome transdisciplinary approach that integrates epidemiological, toxicological, analytical, fate-transport, and remediation studies, along with a unified sampling infrastructure, a centralized, indexed data repository and a data management system. PROTECT is contributing new knowledge about the risk that contaminants may pose in pregnancy resulting in preterm birth, how these contaminants reach karst aquifers, and what are the biological mechanisms by which environmental contaminants may promote preterm birth. PROTECT also is developing novel remediation approaches that will target removal of contaminants linked to preterm births from ground water. These integrated efforts offer unique opportunities to address a serious public health problem and its solution would result in a healthier population and a healthier environment.

1 Introduction

Conducting environmental health research today requires a diverse research team that can address the breadth of disciplines needed to understand the complex dynamics of the environment and its interaction with human populations. Where biology and chemistry might have once sufficed, research teams must now include a broad array of disciplines to (1) identify routes of human exposure to chemicals, (2) understand the health effects resulting from human

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exposure to these chemicals, (3) recognize their impacts on public health, and (4) develop effective interventions to remediate contamination and improve the health of the impacted population. A transdisciplinary approach, implemented in a team science management structure, can provide a platform to understand the interactions between the environment and human populations and translate research findings into strategies to improve human health and the environment. Project PROTECT (Puerto Rico Testsite for Exploring Contamination Threats) is currently ongoing in Puerto Rico.

The study of groundwater contamination is an important component as it is a major threat to water resources and consequently human health. Understanding the fate and transport of contaminants in groundwater, that may lead to human exposure and adverse health outcomes, is needed to understand health impacts and to develop intervention strategies. Aquifers in karst systems are highly heterogeneous, which complicates understanding fate and transport of contaminants (Fig. 1). Karst groundwater systems develop in soluble rocks and are typically characterized by well-developed conduit porosity and high permeability zones. These characteristics make aquifers in karst areas highly productive and an important freshwater resource for human consumption and ecological integrity. Exposure from contaminated karst aquifers is very relevant to the U.S. as about 40% of the groundwater used for drinking comes from karst aquifers (USGS 2013). Worldwide, karst aquifers contribute about 25% of the drinking water; these aquifers are distributed throughout Asia, Europe, other parts of the Caribbean, and Australia (Hartmann et al. 2014). Karst aquifers present highly susceptible pathways for contamination of water supplies due to the presence of fissures, sinkholes and sinking streams that can rapidly inject contaminants at or near the land surface. Once in the aquifer, the contaminants can be readily transported via solutional openings in the subsurface such as conduits and underground streams. Filtration processes that can retard contaminant movement, commonly found in alluvial aquifers, are rarely present in karst aquifers. There is a significant lack of understanding of contaminant transport in karst and a critical need for development of remediation strategies for such complex and potentially deleterious systems. This is particularly relevant where availability of water resources from highly productive aquifers in karst regions spawn industrial and urban development, which promotes economic growth but increases the potential for extensive contamination of the groundwater resources. The dynamics of the solubility, flow, and exposure to contaminants through karstic groundwater is made more complex by the presence of some contaminants as non-aqueous phase liquids (NAPLs) and interactions between different contaminant groups.

In Puerto Rico, risk of exposure to contaminants thorough groundwater is high because many waste sites exist, particularly on the north coast. Eight of the 16 Superfund sites, and many of existing unlined landfills in Puerto Rico, exist over karstic aquifers in the northern part of the island. Such high level of contamination is a public health threat on the island. An overlay of Superfund sites (EPA 2013) on karst regions in the U.S. (Tobin and Weary 2004) shows that 23% of all Superfund sites are located in karst areas. In Puerto

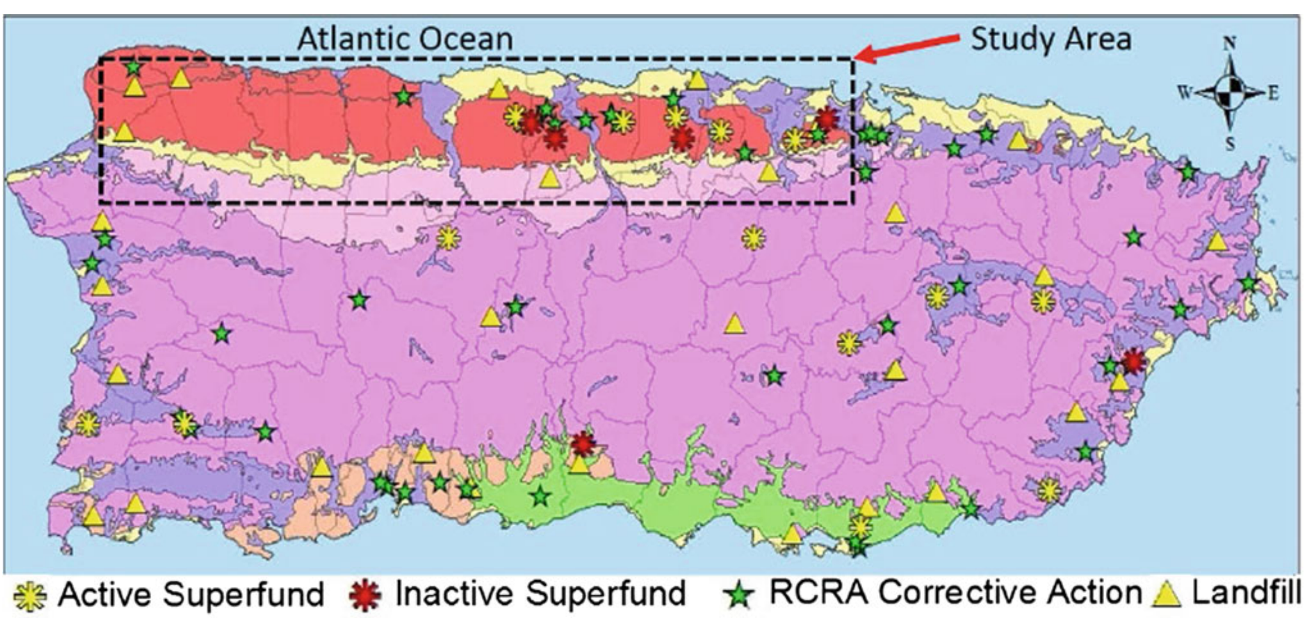


Fig. 1 Hydrogeology and major potential contamination sites in Puerto Rico. North coast limestone aquifer in *orange* and *light pink*

Rico, 45% are within the northern karst region of the island (Fig. 1). This region has been affected by a long history of toxic spills into the subsurface (EPA 2011; Hunter and Arbona 1995; Zack et al. 1987) and is coincidentally among the areas with the highest groundwater extraction in Puerto Rico (Molina-Rivera and Goméz-Goméz 2008). Serious contamination has prompted inclusion of 16 National Priority List (NPL) and 15 corrective action sites within the Resource Conservation and Recovery Act (RCRA) in the north coast region of Puerto Rico between 1983 and 2012. Recent (Padilla et al. 2011) and past (Guzmán-Ríos et al. 1986) studies in this region have consistently reported the presence of organic contaminants in the karst groundwater system. In spite of the known contamination, the connection between exposure to a complex mix of environmental factors, including drinking water contamination in karst regions, and the high rates of adverse health outcomes for children in Puerto Rico has not been comprehensively or integratively investigated.

From the human population perspective, Puerto Rico has the highest rate of childhood asthma in the U.S., more than twice that of Hispanic children on the mainland (16.5% vs. 7.9%) and its preterm birth rate increased dramatically in 1990s and the first decade of the 21st century. In 2009, Puerto Rico had the highest rate of preterm birth in the US, and the third highest rate in the world in 2012 (Blencowe et al. 2012). Infants born preterm are more likely to die in the first year of life, and those who survive can suffer serious short- and long-term disabilities, including blindness, deafness, cerebral palsy and development disorders. Early studies found that traditional risk factors for preterm births did not explain the high rate observed (Cordero and Mattei 2009) and placed the focus on potential environmental factors. The island has suffered extensive hazardous waste contamination over the years and has the highest density of hazardous waste sites per square mile than any other jurisdiction in the US. Those findings raised questions about the role of environmental contaminants in the high rate of preterm births in Puerto Rico.

PROTECT addresses critical gaps identified in the 2007 Institute of Medicine report on preterm birth (Behrman and Stith Butler 2007). Preterm birth is the second leading cause of death in children under the age of 5 worldwide (Blencowe et al. 2012), and the leading cause of perinatal and infant mortality in the U.S. (Klebanoff and Keim 2011; Callaghan et al. 2006). Reducing preterm birth rates will help save babies, improve their quality of life, and minimize the escalating costs of health care. For the U.S. alone, the most recent estimate is that preterm births cost society over $26 billion annually in 2005 (Behrman and Stith Butler 2007), not including the costs of medical care beyond early childhood or the total cost of special education services and lost productivity (Klebanoff and Keim 2011). The causes of preterm births remain largely unexplained, and interventions geared toward known causes are projected to result in a reduction in preterm births of only 5% by year 2015 (Chang et al. 2013). New approaches are needed to identify modifiable risk factors. Environmental pollutants as potential contributing factors to preterm birth have been greatly understudied (Behrman and Stith Butler 2007). Thus, establishing links between environmental exposures and preterm birth would have major public health significance since many exposures may be modifiable through new policies or interventions at the individual, community, clinical, and state or federal level. Furthermore, by demonstrating that a common toxicological effect—oxidative stress—activates pathways associated with parturition, PROTECT combines new knowledge of biological mechanisms by which environmental contaminants may promote preterm birth. Knowledge of these mechanisms, combined with new information on toxicant-stimulated responses using in vitro model systems, is leading toward to the development of assessment tools for toxicological evaluation of potential chemical risks for preterm birth.

To address these questions, PROTECT, a Superfund Research Program (SRP) Center, was developed and initiated its research program in 2010. PROTECT employs an integrated, transdisciplinary approach and team to study the fate, transport, exposure, health impact and remediation of contaminants, with particular attention to phthalates and chlorinated solvents, both suspect and model agents for the high preterm birth rates in Puerto Rico. To do so, PROTECT uses an innovative, holistic, source-to-outcome structure, integrating epidemiological, toxicological, analytical, fate-transport, and remediation studies, along with a unified sampling infrastructure, a centralized, indexed data repository and a data management system. Administrative, research translation, training and community engagement cores engage and inform stakeholders, provide knowledge-transfer activities to the greater SRP and environmental health community, and provide extensive cross-disciplinary training. In a nutshell, PROTECT is a transdisciplinary model of team science that is responsive to NIEHS, EPA and CDC strategic goals, and addresses priority areas identified by the Institute of Medicine Committee on preterm birth (Behrman and Stith Butler 2007).

2 Approach

PROTECT is a multi-institutional research center with collaborating researchers from Northeastern University; the University of Puerto Rico (Medical Sciences Campus—UPR-MSC, and Mayaguez Campus—UPRM); the University of Michigan; the University of Georgia, West Virginia University, Silent Spring Institute and Earth Soft Inc. The central theme of PROTECT is the study of exposure to Superfund hazardous chemicals and their potential contribution to preterm birth, focusing on Puerto Rico as a testsite with dynamic contamination exposure pathways through aquifers in karst regions.

Effort is centered around the problem-based, solution-oriented theme, to address three goals: (1) define the contribution of environmental chemical exposure to preterm birth, (2) develop new technology for discovery, transport characterization, and green remediation of Superfund hazardous chemicals in aquifers in karst region, and (3) engage stakeholders to support environmental public health practice, innovation and policy; professional development; and awareness around our theme.

The Center is composed of eleven integrated components: five biomedical and environmental research projects, two research support cores and four enrichment cores. PROTECT encompasses five interrelated research projects. **Project 1** is a targeted molecular epidemiology study of phthalate exposure and preterm birth in Puerto Rico. This project is conducting a prospective cohort study to identify novel risk factors for preterm birth, with a focus on exposure to phthalates. It utilizes state-of-the-art methods to estimate phthalate exposure and assess intermediate biomarkers of effect, to provide much needed human data on environmental and other predictors of preterm birth in Puerto Rico, and the biological pathways involved. **Project 2** on mechanistic toxicology explores toxicant activation of pathways of preterm birth in gestational tissues. This project identifies toxicological mechanisms for epidemiologic associations between exposure to select environmental contaminants and adverse birth outcomes through studies of toxicant actions on placental and extraplacental tissues. **Project 3** conducts non-targeted chemical analysis with a focus on discovery of xenobiotics associated with preterm birth. This project seeks to discover xenobiotics that contribute to preterm birth by advancing and applying non-targeted chemical analysis by mass spectrometry to urine from pregnant women in Puerto Rico, placenta (human and animal) and water (tap and groundwater; before and after remediation). **Project 4** focuses on fate and transport and studies dynamic transport and exposure pathways of contaminants in karst groundwater systems in Puerto Rico. This project is characterizing the fate and transport regions and dynamic mechanisms controlling the mobility, persistence, and potential pathways of target contaminants toward exposure and/or remediation zones in karst groundwater in Puerto Rico. **Project 5** focuses on the development of a solar-powered remediation process for contaminated groundwater. The project is developing a novel, environmentally-friendly in situ groundwater remediation technology using solar-powered electrolysis to regulate groundwater redox for transformation of contaminants.

These projects are supported by a human subjects and sampling research support core and by a data management and modeling core which provides effective management of collected data and modeling support. These projects have common requirements of human subject recruitment, collection of human and environmental samples, and management of large volume of data and led to the development of the Research Support Cores. The human subjects and sampling core recruits pregnant women to the cohort, and collects, stores and distributes biological and environmental specimens and data for use by projects. The data management and modeling core provides efficient collection, cleaning, integration and effective management of biomedical and environmental data being collected and analyzed across the PROTECT Center. This core provides support for modeling, GIS, multi-dimensional data mining and visualization, and provide customized user interfaces for efficient and accurate data entry and analysis.

The four enrichment cores include Administration that provides integration, coordination, and operational support, Training, a major component that ensures the development of the next generation of researchers, Research Translation that facilitates the application of research findings into practice, and the Community Engagement Core that ensures a direct connection to the communities of the Northern karst region and the participants in the study with a model report-back system. Figure 2 describes the interaction and integration of the projects and cores into the overall PROTECT model.

3 Integration of Disciplines

PROTECT's strong integration of biomedical (epidemiology, toxicology) and environmental (analytical chemistry, engineering, hydrogeology) disciplines is evident in its goals, each of which requires a highly collaborative approach with significant interaction and sharing of samples, testing and results (Fig. 3). The Research Support Cores are a critical part of the interdisciplinary approach and of the integration of the research activities across disciplines and projects. The Data Management and Modeling Core, through which the projects share and mine results, allows us to test new hypotheses that are based on integration of the multidisciplinary data from multiple projects. This core provides a unified system for data entry, and supplies complex multidisciplinary datasets in a readily usable format, as well as technical assistance with multi-layered data management inquiries, and a centralized repository for all data collected and analyzed (Fig. 4). Importantly, this core is enabling us to cross-index these datasets, carry out database queries and perform data mining, analysis and multilayered mapping and modeling. The Human Subjects and Sampling

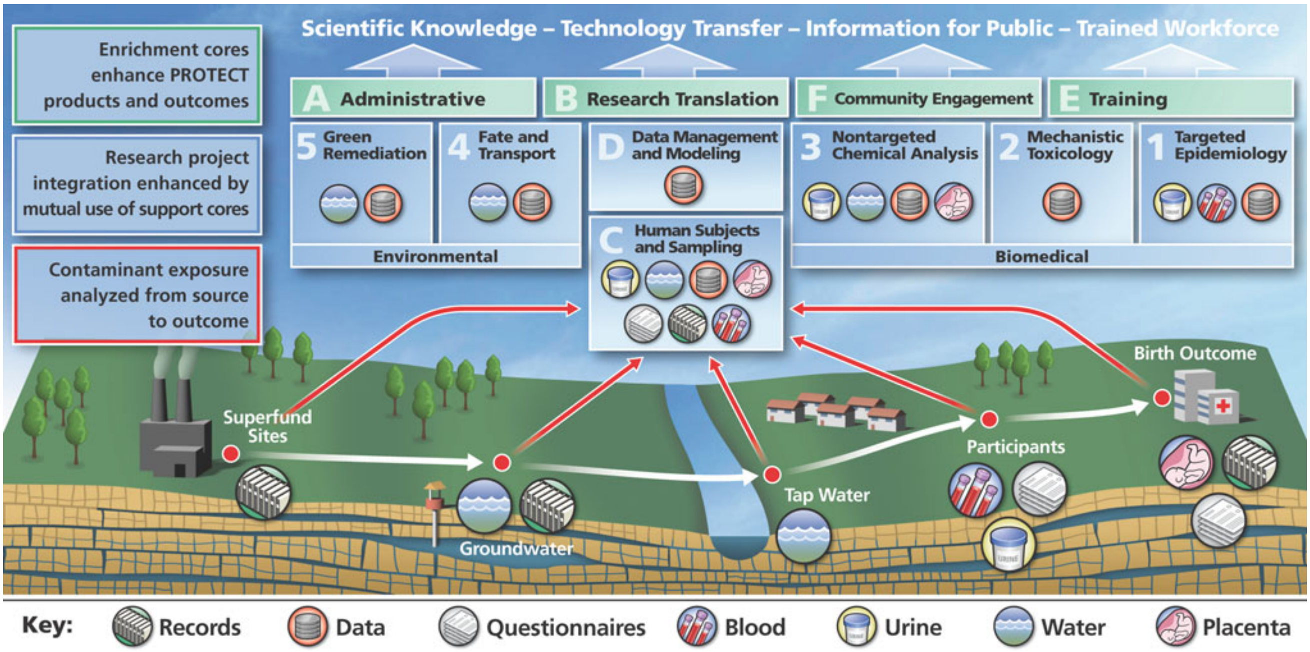
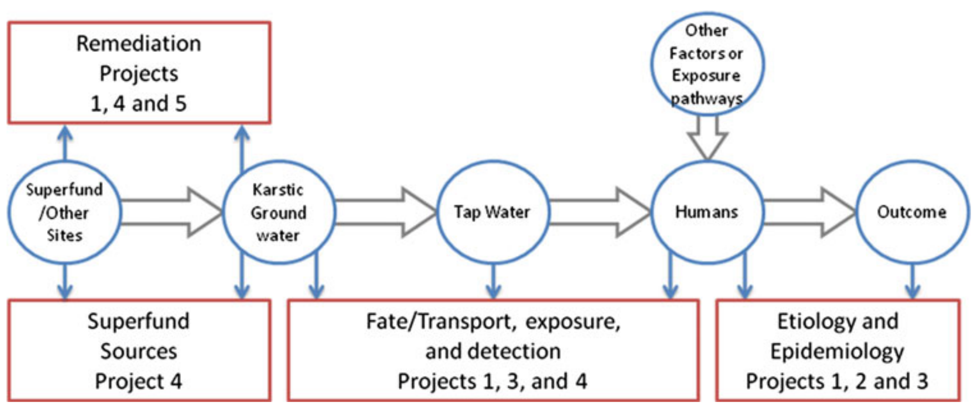


Fig. 2 PROTECT uses a holistic system of research, training, and stakeholder engagement to study contaminant exposure and its potential contribution to preterm birth in Puerto Rico

Fig. 3 Flow chart highlighting relevance of the project to the program



Core systematically unifies the sampling process for all projects. These samples, comprising tap water, groundwater, urine, blood, hair, and placenta, although diverse and for different projects, are consistently and uniquely indexed so that data retrieval and mining is multidisciplinary and consistent for all projects. Many of PROTECT's key outcomes rely on the ability to access both biomedical data and environmental data in a unified, coherent data management and assessment framework (Fig. 4). A critical advantage of using a centralized data repository is the ability to evaluate the relation between multiple causes. PROTECT has the ability to assess cumulative and synergistic risk factors.

In addition to the significant role that the research support cores play in integration of the projects, there are significant bidirectional collaborations and integration directly among the projects. Sharing of samples, data, and results is integral to the projects. For example, the project on mechanistic toxicology provides bidirectional collaboration with epidemiologic investigations and provides mechanistic links for epidemiologic associations observed in the targeted epidemiologic project. Toxicology studies conducted in collaboration with the non-targeted analysis project identified oxidative stress as a response produced by a phthalate metabolite in human placental cells (Tetz et al. 2013a). Stimulated by those findings, the targeted epidemiologic studies found associations between urinary phthalate metabolite concentrations and biomarkers of oxidative stress (Ferguson et al. 2011, 2012). The mechanistic toxicology project collaborates with non-targeted chemical analysis project to provide further insight into toxicological

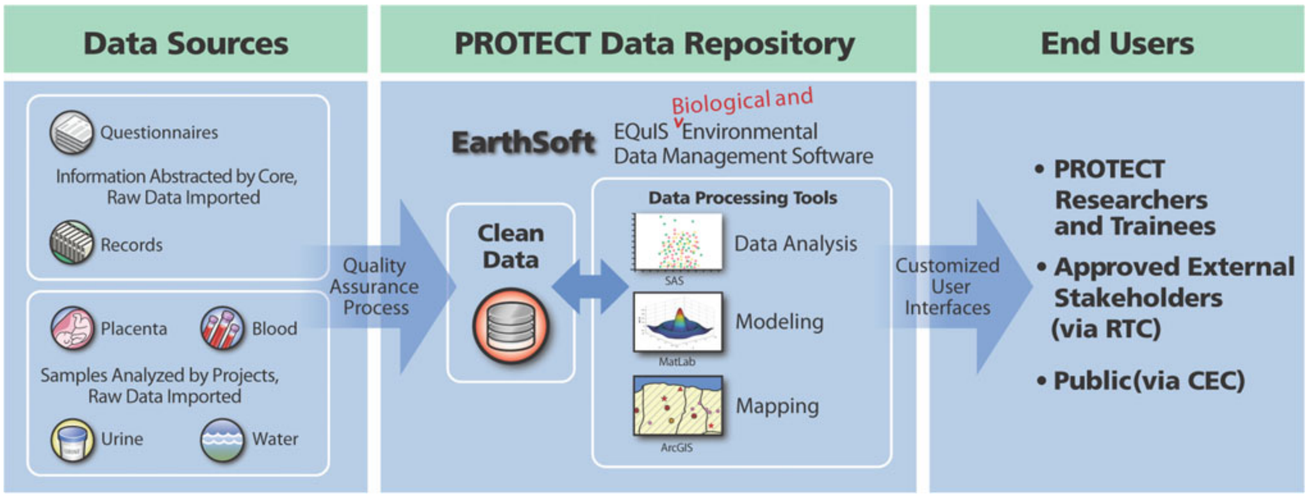


Fig. 4 The centralized multidisciplinary data core will play a major role in PROTECT integration. Information is abstracted and data imported directly into the data repository while samples are analyzed by the projects and data from that analysis is imported as well (*left panel*). Data processing tools (*center panel*) that access biological and environmental data simultaneously are available to end-users (*right panel*)

mechanisms with additional potential to identify new toxicants of interest through discovery analysis and pathway identification, respectively. The non-targeted chemical analysis project also provides insight into defining the objectives and scope of remediation (Mao et al. 2011, 2012a, b, 2013) by helping set performance targets for remediation techniques developed in the green remediation project. The non-targeted chemical analysis project is examining xenobiotics and DNA adducts from a subset of women to further relate it to the mechanistic toxicology studies of preterm placenta in Puerto Rico, and to potentially increase the number of chemicals tested by the targeted epidemiology project. Contamination and water quality data collected and analyzed the fate and transport project provides data for the exposure assessment in the targeted epidemiology project. The fate and transport project also provides data on phthalates in groundwater and tap water which are vital to the targeted epidemiologic project's aim to identify key sources of phthalate exposure. The fate and transport project provides information on the dynamics of episodic fate and transport processes in karst groundwater, which greatly affect the kinetics of electrochemical transformation in green remediation development and has implication for the design and analysis of targeted epidemiologic studies. A key activity of the green remediation group is a pilot-scale field test conducted in coordination with the fate and transport group. The green remediation project uses groundwater samples collected from the study area in Puerto Rico by the Human Subjects and Sampling Core. Samples collected before, during, and after treatment are sent to the non-targeted chemical analysis project for detection of xenobiotics, which will guide toxicity assessments in the green remediation project.

In addition, a well-defined management approach has successfully been implemented to maintain cross-disciplinary interactions and activities. Timely, inexpensive, and useful Information Technology (IT) and communication tools facilitate and expedite communication among trainees and investigators, and across disciplines and institutions. This is valuable for integration of activities and maximizing interactions between trainees within and from different institutions. The enrichment cores (Administrative, Research Translation, Training and Community Engagement) provide several venues for integration of activities and collaboration among projects. These activities include weekly meetings or conference calls, project town-hall meetings, an annual retreat, and conferences.

4 Preliminary Results

Our research documents significant contamination in the study area and compelling preliminary epidemiologic and mechanistic toxicology associations between target contaminants and preterm birth.

4.1 Contamination in the Study Area

Analysis of historical contamination patterns in the karst region of northern Puerto Rico (Padilla et al. 2011) shows significant contaminant distribution beyond the demarcated sources of contamination (Fig. 5) and a strong capacity of the karst groundwater system to store and slowly release contamination. These historical data show that groundwater sources in the north coast of Puerto Rico have been

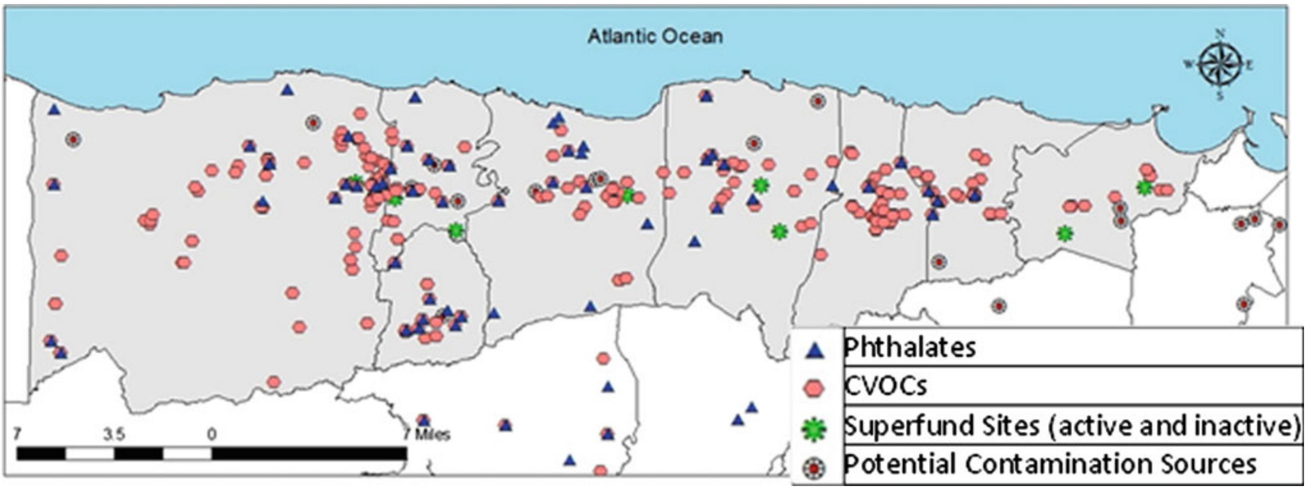


Fig. 5 Sources and detections of CVOCs and phthalates in the study area

contaminated for over 40 years and that chlorinated volatile organic compounds (CVOCs) were detected in 57% of all samples and 72% of all sampled wells (based on historical data). Current field sampling and our Center analysis show the continued presence of CVOCs and phthalates in groundwater and tap water (Fig. 5), which indicates that contamination remains in the groundwater in the area long after major sources have been controlled. CVOCs were detected in 38% of groundwater samples, 60% of the sampled wells and in 51% of tap water samples. Additionally, phthalates, including di-2-ethylhexyl phthalate (DEHP), dibutyl phthalate (DBP) and diethyl phthalate (DEP) were detected in 70% of the groundwater sites, and 57% of the tap water sites. Comparison of CVOC in groundwater and tap water samples suggest that groundwater contamination is reaching drinking water sources and is a potential mode of exposure.

4.2 Epidemiologic Association Between Target Contaminants and Preterm Birth

We conducted a pilot study within a long-standing birth cohort study in Mexico City (Meeker et al. 2009). Urine samples collected during the third trimester from 30 women who delivered preterm were compared with samples from 30 randomly selected controls who delivered at term. We found that urinary phthalate metabolite concentrations were higher among cases than controls, along with significantly or suggestively elevated odds of delivering preterm in relation to exposure. We also conducted a much larger case-control analysis among a birth cohort study in Boston with strikingly similar results with regard to exposure and elevated adjusted odds of preterm birth (Ferguson et al. 2016).

We also explored publicly-available data from the United States National Health and Nutrition Examination Survey (NHANES) for the years 2009–2010 and found a number of relationships (significant or suggestive associations in hypothesized directions) between urinary phthalate metabolites and intermediate biomarkers of mechanisms that may be relevant to preterm birth. These mechanisms include oxidative stress, inflammation, and endocrine disruption (Ferguson et al. 2011, 2012; Meeker and Ferguson 2011).

Through the PROTECT cohort study, we analyzed 373 urine samples from 139 women for a suite of 11 phthalate metabolites and compared results with those reported among women ages 18-40 years in US NHANES 2009–2010. The results (Table 1) suggest that phthalate exposure of women in northern Puerto Rico is higher than the U.S. general population, highlighting the need for detailed human health studies of the effects of phthalate exposure among this at-risk population. Most striking was the observation that the geometric mean concentration for MEHP, the bioactive metabolite of DEHP, was more than twice as high among women in PROTECT ($p < 0.05$). We have found strong associations between several phthalate metabolites and two sensitive markers of oxidative stress (8-OHdG and isoprostane) when adjusting for urinary specific gravity and other important covariates. We have also observed significant or suggestive evidence for increased levels of pro-inflammatory cytokines (IL-1β and IL-6) or CRP, and decreased thyroid hormone levels, in relation to multiple phthalates. These results are an important linkage to our mechanistic toxicology work and provide further evidence for potentially diverse yet overlapping impacts of phthalates on multiple pathways relevant to preterm birth in our study population. They also serve as further justification to assess the impact of exposure to multiple phthalates as mixtures as well as individually.

Table 1 Distribution of selected urinary phthalate metabolite concentrations (ng/mL) in PROTECT women (N = 139) compared to women of reproductive age from NHANES 2009–2010 (N = 341)

Analyte	Population	GM (95% CI)	50th	75th	95th
MEHP	PROTECT	3.3 (3.0, 3.7)	3.7	7.4	17.5
	NHANES	1.6 (1.4, 1.9)	1.6	3.2	11.0
MECPP	PROTECT	19.6 (18.0, 21.3	19.9	34.4	76.0
	NHANES	17.9 (14.9, 21.5	17.5	32.3	95.3
MnBP	PROTECT	19.2 (17.0, 21.7	20.9	42.0	117
	NHANES	15.7 (13.2, 18.6)	18.5	32.9	83.0
MiBP	PROTECT	10.9 (9.8, 12.1)	11.0	20.3	63.5
	NHANES	8.8 (7.4, 10.5)	9.6	18.6	42.0
MEP	PROTECT	102.2 (85.4, 122)	99.2	388	1880
	NHANES	76.5 (60.3, 97.0)	72.5	205	1286

GM grand mean; *CI* confidence interval. Final three columns give percentiles

4.3 Mechanistic Association Between Target Contaminants and Preterm Birth

Our mechanistic toxicology study showed that a metabolite of DEHP (MEHP) stimulates reactive oxygen species (ROS) formation, induces oxidative DNA damage and activates apoptotic cell death and prostaglandin pathways in human placental cells in vitro (Tetz et al. 2013a). Likewise, our data showed that a metabolite of TCE (DCVC) activated oxidative stress, inflammatory, cell death, and prostaglandin pathways in human placental cells in vitro (Tetz et al. 2013b). The DCVC-stimulated release of the pro-inflammatory cytokine IL-6 was inhibited by co-treatment with the antioxidant Vitamin E, suggesting a role for ROS in the IL-6 response. Moreover, we found that the model pro-oxidant chemical *tert*-butyl hydroperoxide (TBHP) stimulated ROS generation and increased expression and release of parturition-activating pro-inflammatory cytokines and prostaglandins in human placental cells. The latter TBHP-stimulated responses were blocked by antioxidant treatments and an inhibitor of the p38 MAPK pathway. In vivo, TCE significantly decreased rat pup weight at a dose relevant to human occupational exposure, with evidence of increased cell death and suggestion of oxidative DNA damage in the placenta.

5 Discussion

The PROTECT program demonstrates how team science based on a well-integrated transdisciplinary platform that can advance the knowledge of the karst hydrogeology and its impact to human and environmental health. Results to date provide first-hand evidence of significant contamination in Puerto Rico and justify the need for a complete evaluation of the exposure to Superfund hazardous chemicals and impact on preterm birth. PROTECT has recruited nearly 1200 pregnant women and it is on track to recruit 1800 women by the end of 2019. This will provide the data needed for a comprehensive study of environmental, demographic, behavioral, psychosocial and other predictors of preterm birth in Puerto Rico using the state-of-the-art and novel epidemiological methods of Project 1. Continued investigation by Project 2 is needed to better understand the toxicant actions of suspect chemicals on placental and extraplacental tissues that can promote preterm birth. The nontargeted chemical analysis investigation of urine, placenta and water samples collected from a subset of the study participants, conducted by Project 3, is needed to discover additional chemicals, beyond phthalates and chlorinated solvents, that contribute to preterm birth. Project 4 will expand its multi-scale experimental models and field experiments, and extend its evaluation of historical contamination in Puerto Rico, to characterize transport and exposure of contaminants in the karst groundwater system of concern. To develop solar-powered remediation, Project 5 will improve electrochemical transformation of contaminants by innovative electrodes, assess the transformation pathways and their associated effects on groundwater toxicity, and measure the performance in field-scale testing.

Ultimately, PROTECT is a response to community concerns about the increasing rates of preterm birth in Puerto Rico. The Puerto Rican chapter of the March of Dimes (MOD) was very involved in defining our goals at the initial stages of proposal preparation. The local community and government have been engaged in our efforts and play major roles in our activities, including serving on our Advisory Committees (Caribbean EPA, USGS and MOD), collecting groundwater samples (USGS), providing access to extensive historical Superfund data (EPA), providing water quality and well data (EPA and PRASA—Puerto Rico Water Authority), and assisting in recruiting participants for our cohort (MOD). The role to date of MOD has facilitated creation of a ground-up framework for the Community Engagement Core that is engaging PROTECT participants and community groups with a novel system of reporting back test results at an individual basis and the broad results at a community level. This process will enhance and accelerate the translation of PROTECT findings into lower rates of preterm births and a recovered environment.

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Flow Routing in the Karst of Puerto Rico

Thomas E. Miller, Gilles Brocard, and Jane Willenbring

Abstract

90% of Puerto Rico's 2400 km^2 of karst is located near the Atlantic Coast. The north coast limestone aquifer consists of Tertiary carbonates with an unconfined upper aquifer and a confined lower aquifer. The transmissivity of the lower aquifer is an order of magnitude smaller than the upper aquifer. About half of the recharge is rainfall on karst uplands that travels north to near-coast springs and wells. Approximately 148,000 m^3/day is withdrawn from the lowland areas, some of which contain a variety of chemical contaminants (e.g., phthalates) introduced in the populated lowlands. Widespread use of septic tanks and of caves and dolines for trash disposal is also a threat of unknown magnitude to water quality. Although the general flow paths of the upper recharges are known, and scores of streams in caves (of hundreds) have been mapped in higher elevations, the specific routes to the final discharges are not well understood. Dye traces, and isotope comparison of different sectors of the lower discharge area, have not proved particularly useful to identify them, so some efforts have focused on defining the characteristics of accessible cave system flows to see whether they can provide useful analogs. Geologic strike and dip are major controls of cave passage orientations, followed by faulting or major joint sets.

1 Introduction

For its size, Puerto Rico has a large background of karst literature (dominated by Watson Monroe's papers [e.g., 1976] and geologic maps), although most of this concerns surface features, and much less (except for accounts of exploration) reference to the hundreds of known caves. The climate is humid tropical, with rainfall of about 1.8 meters per/year on the north karst, and perhaps 1.4 m in the rain-shadowed south. Some features such as mogotes, cockpits, ramparts, 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 has arched the island, exposing older plutonic and metamorphic rocks in the cordillera and likely contributing much of the jointing in the carbonate rocks (Lewis and Draper 1990). Cosmogenic dating of surfaces in the Luquillo Mountains of the east indicates that this occurred by about 5 My BP (Brocard et al. 2016). Uplift of the Tertiary carbonates was probably less than 600–700 m; high points of the northern karst reach only an elevation of 530 m a.s.l. today (Lugo et al. 2001). Tectonic activity on the Atlantic Coast 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.

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2 Karst Areas

2.1 North Karst

The mouths and valleys of the major streams on the north coast have alluviated during sea level rise to as much as 120 m, decreasing inland. The lowered sea levels of the Pleistocene significantly enhanced the relief and undoubtedly encouraged karst development below current sea level. As a result, the second largest spring on the island—Aguas Frias, the discharge of the Rio Encantado System—descends in a water-filled passage to below sea level (15 km inland), before ascending 30 m to resurge on the banks of the Río Grande de Manatí. These karst areas comprise 90% of those on the island.

The northern rocks [dominantly limestone, and minor dolomite, with a tiny exposure of karren developed on granodiorite in the southeast (Beck and Cram 1977)] mostly dip as a homocline gently northward 4–5° to the Atlantic, where differential erosion has produced scarps, and/or long chains of mogotes (steep-sided relict hills) along the E–W strike. Large level areas are covered with remnants of the reddish "Blanket Sands" (quartz and clays), likely from past longshore drift during uplift phases. Rugged expanses of mogotes that drain to cockpits (deep depressions between the mogotes that are the most active sites of infiltration and solution) dominate most of the remaining area, although less-soluble beds and facies of the diverse Cibao Formation produce expanses of rolling hills, as well as confine the lower aquifer largely formed in the Lares Limestone. Some streams of the Cibao drain down-dip to swallets and caves of the Aguada Limestone, part of the upper aquifer. An interesting observation by Monroe (1976) is that many mogotes appear to have a slope and shape asymmetry correlated with the prevailing NE winds, appearing steeper on the leeward side. Monroe attributed this to case-hardening of porous limestone due to solution of calcite during rainfall in brief showers, followed by calcite deposition in the hot sun. Conversely, Day's (1978) detailed measurements in one cockpit karst found no asymmetry.

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 in the Lares Limestone. With care, the "chaos" of cockpit karst is often recognizable as relics of former valleys that had crossed the karst, and which were then progressively dissectioned via cockpit development along the thalwegs. The few modern 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 four major karst blocs of the north (Fig. 1) (Miller 2009). The two best known caves are those of the Rio Camuy and Rio Encantado systems, each with somewhat more than 20 km in mapped length.

Most large caves, then, are found near the southern boundary of the North Karst, or in the uppermost units of the Cibao. A common sequence is that following initiation of a major conduit, a series of vertically superposed galleries develop as base levels migrate downward in response to vertical uplift or widespread base-level erosion (Troester 1994). Recent ^{10}Be–^{26}Al cosmogenic dating (Brocard et al. 2016) of cave sediments in the famous Rio Camuy System indicates that by at least 4.7 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. (Miller 2004a, 2010).

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. The cave development and environment is currently of interest because of the presence of phthalates and other endocrine disruptors of the human birth process. Cave passage orientations are mostly controlled by the strike and dip, with occasional faulting or major joint sets playing a role (e.g., Miller 2004b). The locations of the cockpits and other surface features, and the major cave conduits, are largely independent of each other. As noted by Renken et al. (2002), "Regional groundwater movement from the upper aquifer is to the major rivers, wells, coastal wetlands, coastal nearshore, and offshore springs, or as seabed seepage. Hydraulic conductivity of the upper aquifer generally increases in a coastward direction and reflects lithologic control, karstification in the upper 30–100 m of the section, and enhanced permeability in a zone of freshwater and saltwater mixing." Dye tracing has had local successes in identifying unknown courses of the major cave passages, but this success has not extended out into the lower-lying karst.

2.2 Karst of the South Coast Tertiary Rocks

Most of the remainder ($\sim$9%) of the island's karst areas are young rocks near the south coast; cave streamflows here (if any) are to the Caribbean. These rocks are broadly contemporaneous with the north, but are more faulted and inclined. Although the areas of limestone can be extensive, caves are limited: The east–west Central Cordillera axis is asymmetrical, so that catchments and invading stream flows are smaller on the south side, plus the southwest is in the island's rain shadow, with rainfall of only about 800–1400 mm/yr.

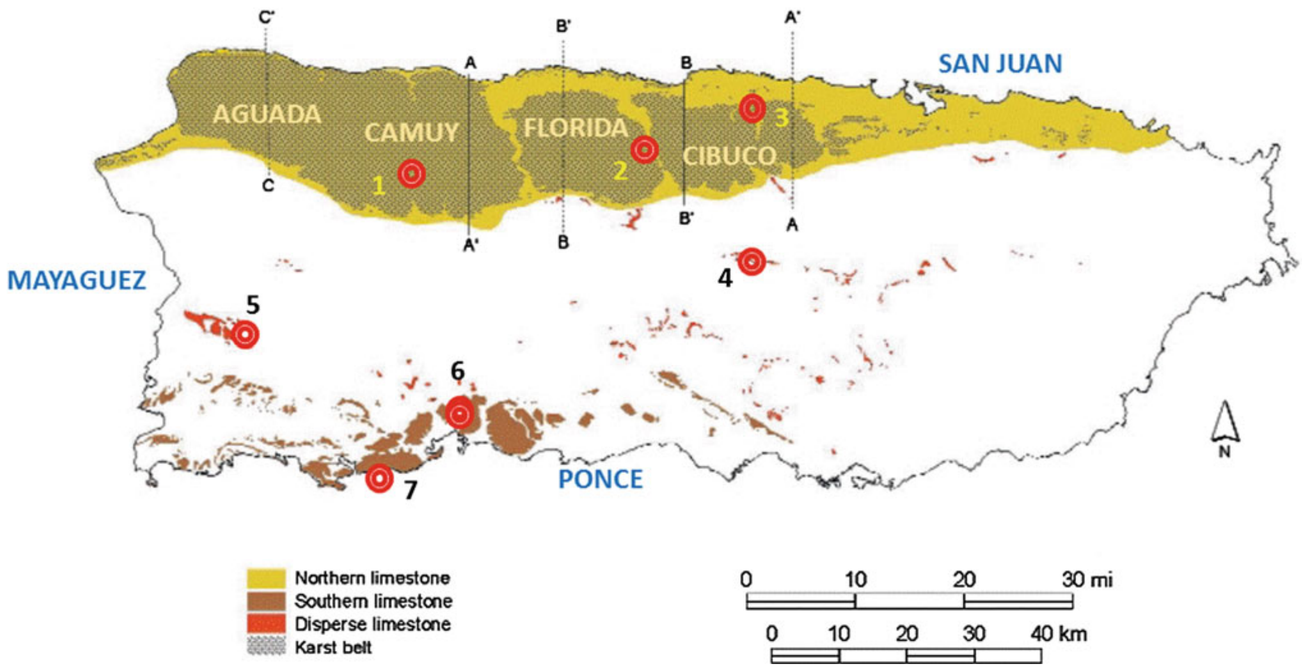

Fig. 1 Karst locations in Puerto Rico (after Lugo et al. 2001). *Blue labels* are major cities. *Yellow areas* are the four major blocs of the North Karst. *Red circles* are karst features mentioned in the text: *1* the Rio Camuy Caves; *2* the Rio Encantado system and Aguas Frias Spring; *3* the caves of Carmelita; *4* Aguas Buenas Group; *5* Cueva Viento; *6* Cueva Convento Group; *7* Guanica caves and aquifer

The Cueva Convento network, in the Juana Díaz Formation, is the largest known of the cave systems in south coast Tertiary rocks. It consists of a single active stream source, with passages likely developed from the neighboring higher, larger, and older phreatic complex of Cueva El Viento, and Cueva Mapancha, which contains one of the largest cave chambers on the island. This area is the only south-side Tertiary limestone that receives allogenic waters from the Cordillera to the north.

The area of the Guanica dry forest reserve contains a seaward-sloping aquifer, accessible in several locations through caves (such as the large Cueva Murcielagos).

2.3 Karst of the Interior Cretaceous Rocks

The remaining 1½% of soluble outcrops are the older carbonates: relatively hard, well-bedded, and commonly steeply dipping. They formed as smaller reefs or pods in an episodically volcanic environment. Absent on the north coast, they are widely scattered on the island and in places on the south-side border the Tertiary limestones. Because of their limited exposures, and because they are frequently summit formers (more resistant than igneous rocks in this climate), it is uncommon for them to contain dolines, although they usually have well-developed karren. However, they are located in more humid areas than the southern Tertiary limestones and have had a longer exposure history, so caves are common, often large, and most are relict and often multilevel. Common features of the larger caves are levels that preserve evidence for relative groundwater lowering of 40–60 m, with passages dominantly guided by the dip and strike (Miller 2004b).

In the hills south of San Juan, for centuries the Aguas Buenas caves were the best known of Puerto Rico (Gurnee et al. 1968). The caves combine a series of related caverns in a well-developed karst with enclosed depressions of as much as 50 m deep. Including the as-yet-unconnected Cueva Múcara segment, they are about 2–3 km in length, with a vertical range of 100 m. The Aguas Buenas Limestone is about 90 m thick and strongly metamorphosed, with a dip of about 5° NW. The rock is probably fault-bounded and is separated into two blocks, each with its own group of caves.

There are two main passages offset several hundred meters; the upper is dry with abundant clay deposits, and large volcanic stream cobbles. Shafts of about 35 m connect it to the lower cave stream, and numerous other vadose shafts pierce the ceilings throughout the cave. The levels are likely the result of tectonic rejuvenation, which is not yet complete as shown by several waterfalls in the modern stream course. The limestone contains volcanic dikes, which are aligned with a prominent joint set where they intersect cave passages; flow from this cave is to the north as a tributary of the Rio Grande de Loiza.

Sistema Vientos in the Peñones Limestone is one of the island's most intricate caves. The orientations of horizontal passages are parallel either to the strike or internal strata that dip generally at 30–60°, with considerable horizontal shifting of the strike (up to 45°) due to fault offsets. An unusual feature of this cave is at least ten vertical series of vadose shafts and pits of 70–80 m that pierce through four horizontal galleries from the surface and follow small vertical faults and clastic dikes. They indicate an active phase of surface karst development that has fortuitously intersected a preexisting cave of much greater age (still in adjustment from a previous drainage system perhaps 40 m higher). The bottom level contains a small active stream, which flows south to Rio Guanajibo, then west to the Mona Channel.

3 Cave Conduits as Trash and Contaminant Pathways

It is worth noting that 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.

Fig. 2 The Carmelitas Karst. **a** Septic tanks emptying directly into the Carmelitas Caves and **b** same doline, seen from the cave below, filled with about 10 m of appliances and trash

The common types of trash are typical of households, e.g., washing machines, refrigerators, stoves, used tires, and mattress beds. Mobility of these trash sites can be 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 stays in situ.

Septic tank use in the North Karst is in the tens of thousands, often constructed with complete disregard of EPA regulations and common sense. The classic example is that of the Carmelitas urbanization 25 km west of San Juan. This area with hundreds of residents contained at least 37 known collapse sinkholes prior to construction. Most of these lead to thin-roofed caves 5–10 m below ground, in which many connect beneath homes and buildings. Surface septic tanks discharge directly into these caves, the majority of whose entrances are also filled with voluminous trash (Fig. 2a, b).

Large numbers of bats supply significant amounts of phosphates and nitrates in some cave systems. At least one bat species appears to remove significant amounts of rock in cave ceiling roosts, forming upward-growing bellholes (Miller and Figueroa-Mulet 2009). Most high CO_2 concentrations in the caves (>5000 ppm) are primarily associated with dense bat populations or larger cave rivers transporting trees, bamboo, and other vegetation.

4 Summary

Flow in the karst aquifers of Puerto Rico is largely controlled by the gradient of the potentiometric surface as locally influenced by strike and dip and less commonly affected by faulting, folding, and clastic dikes. The cave streams often inherit a favored route as a result of successive vertical abandonment of low gradient galleries/levels and may follow these favored routes for millions of years. Although cave conduits almost certainly developed in the near-coast karst during glacial periods, they would have been both alluviated by rising base levels and flooded by sea waters, with development of a largely near-static water table. Such factors have so far made it difficult to predict such subsurface flow routes with any accuracy. Contaminants introduced into the karst waters are largely of human origin.

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Fate, Transport, and Exposure of Emerging and Legacy Contaminants in Karst Systems: State of Knowledge and Uncertainty

Ingrid Y. Padilla and Dorothy J. Vesper

Abstract

It is well known that the same characteristics that make karst groundwater systems highly productive 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 is 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 focuses 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.

1 Introduction and Background

The hydrogeological characteristics of karst aquifers make these systems highly productive and important freshwater resources, and they also impart a high vulnerability for contamination. High aquifer productivity and water availability in karst regions promote industrial, agricultural, and population growth that enhance socioeconomic conditions, but also increase the potential for contamination, resource degradation, and exposure. This paper addresses the state of knowledge, modeling capabilities, and sources of uncertainty on the fate, transport, and exposure of contaminants in karst systems. Particular examples are provided on contamination of legacy and emerging contaminants in karst aquifers of eogenetic character, such as those found in northern Puerto Rico, and discuss how they may compare to other contaminated aquifers in the continental karst. It addresses chlorinated volatile organic compounds (CVOCs) as legacy contaminants from industrial and waste disposal sources, and phthalates as emerging contaminants from personal care and consumer goods.

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1.1 Karst Environments

Karst terrains are underlain by soluble rocks, primarily limestone and dolomite, which undergo considerable dissolution to create joints, fractures, bedding planes, and other openings in which groundwater flows (Fig. 1). These terrains show distinctive surface and subsurface features associated with sinkholes, springs, caves, and sinking, losing, and gaining streams (Ford and Williams 2007). Sinkholes, sinking streams, and other surface features provide for direct recharge into karst aquifers, which are characterized by well-developed conduit porosity and highly transmissive zones. These characteristics make groundwater systems in karst areas highly productive and important freshwater resources for human consumption and ecological integrity of streams, wetlands, and coastal zones. Underlying about 20% of the planet's ice-free continental areas, karst areas provide roughly 20–25% of the global population's water needs (Ford and Williams 2007). In the USA, karst systems (Fig. 2) underlay about 18% of the continent (Weary and Doctor 2014) and provide over 40% of the groundwater used for drinking purposes (Veni et al. 2001).

Groundwater in karst aquifers moves down-gradient through fractures, conduits, and the rock matrix. Differences in flow capacity through these regions give rise to a spectrum of flow modes, which range between the diffuse and conduit-flow end members. Although one type of flow may predominate in a system, most carbonate aquifers are characterized by a mixture. Diffuse-dominated flow is common in karst aquifers with significant primary porosity and permeability, such as those in eogenetic karst systems, and regions of well-interconnected fractured zones. Carbonate rocks in eogenetic systems have not undergone deep burial and are under active meteoritic diagenesis (Vacher and Mylroie 2002). As a result, fractures and conduits develop in a highly porous rock matrix; both conduit and matrix flow could contribute to flow in these carbonate aquifers. Eogenetic karst aquifers are widely distributed near the warm, low-latitude environments and include (1) karst islands, such as Bahamas, Bermuda, Barbados, and Guam; and (2) karst formations in larger islands, such as Puerto Rico and Jamaica, and continental settings, such as those found in the Floridan, Yucatan, and Edwards aquifers (Anaya et al. 2014). Flow in more diagenetically-altered carbonate rocks, such as those in telogenetic karst systems, is mostly concentrated in conduits, while the rock matrix serves mostly to store water (Martin and Dean 2001). Conduits in telogenetic systems develop in rocks that are exposed after porosity reduction of burial diagenesis (Vacher and Mylroie 2002) and are characterized by dense, low porosity rocks with well-developed conduit network (Bailly-Comte et al. 2010; Vacher and Mylroie 2002). These systems can range between diffuse and conduit dominated depending upon the degree of conduit development (Shuster and White 1971) and the recharge mechanism (Scanlon and Thrailkill 1987). Telogenetic karst systems are associated with continental karst (Vacher and Mylroie 2002), such as those found in southern France, Germany, and Kentucky, USA (Anaya et al. 2014).

1.2 Contamination, Fate and Transport, and Exposure in Karst Aquifers

Availability of water resources from highly productive karst aquifers promotes agricultural, industrial, and urban development, which increases the number of possible sources of contamination. The same characteristics that make karst aquifer systems highly productive also make them highly vulnerable to contamination (Göppert and Goldscheider 2008): surface features provide easy access for contaminants to enter the subsurface and contaminate large volumes of water; well-developed conduit porosity reduces the capacity for physical and chemical filtration and other attenuation processes and conduits increase the ability to transport contaminants at high flows and velocities. Contaminants can, therefore, move and disperse rapidly over long distances. The porous matrix of the karst rocks and the significant amount of sediments trapped in karst formations in many systems may provide high storage capacity for contaminants that can be slowly released for long periods of time. As a result, karst systems have an enormous capacity to store and convey contaminants from sources to potential exposure zones over long distances and periods of time, and can serve as an important route for contaminant exposure to humans and ecosystems (Padilla et al. 2011). This is reflected, for instance, in the large number of Superfund sites located in karst regions. An overlay of Superfund sites (USEPA 2013) on karst regions in USA (Tobin and Weary 2004) using geographic information systems (Fig. 2) shows that 23% of all Superfund sites are located in karst areas. In Puerto Rico, 48% of Superfund sites lie on the northern karst region of the island.

Extensive contamination of the groundwater system has been documented in karst aquifers for both legacy and emerging contaminants (Calò and Parise 2009; Einsiedl et al. 2010; Green et al. 2006; Guzmán-Ríos et al. 1986; Guzzella et al. 2005; Metcalfe et al. 2010; Padilla et al. 2011; Reh et al. 2013; Schwarz et al. 2011; Yu et al. 2015). Legacy contaminants are known, persistent, bioaccumulative, and toxic contaminants that are commonly monitored in the environment (Hutchinson et al. 2013). These include heavy metals, volatile organic compounds (VOCs), pesticides, polychlorinated biphenyls (PCBs), polyaromatic hydrocarbons

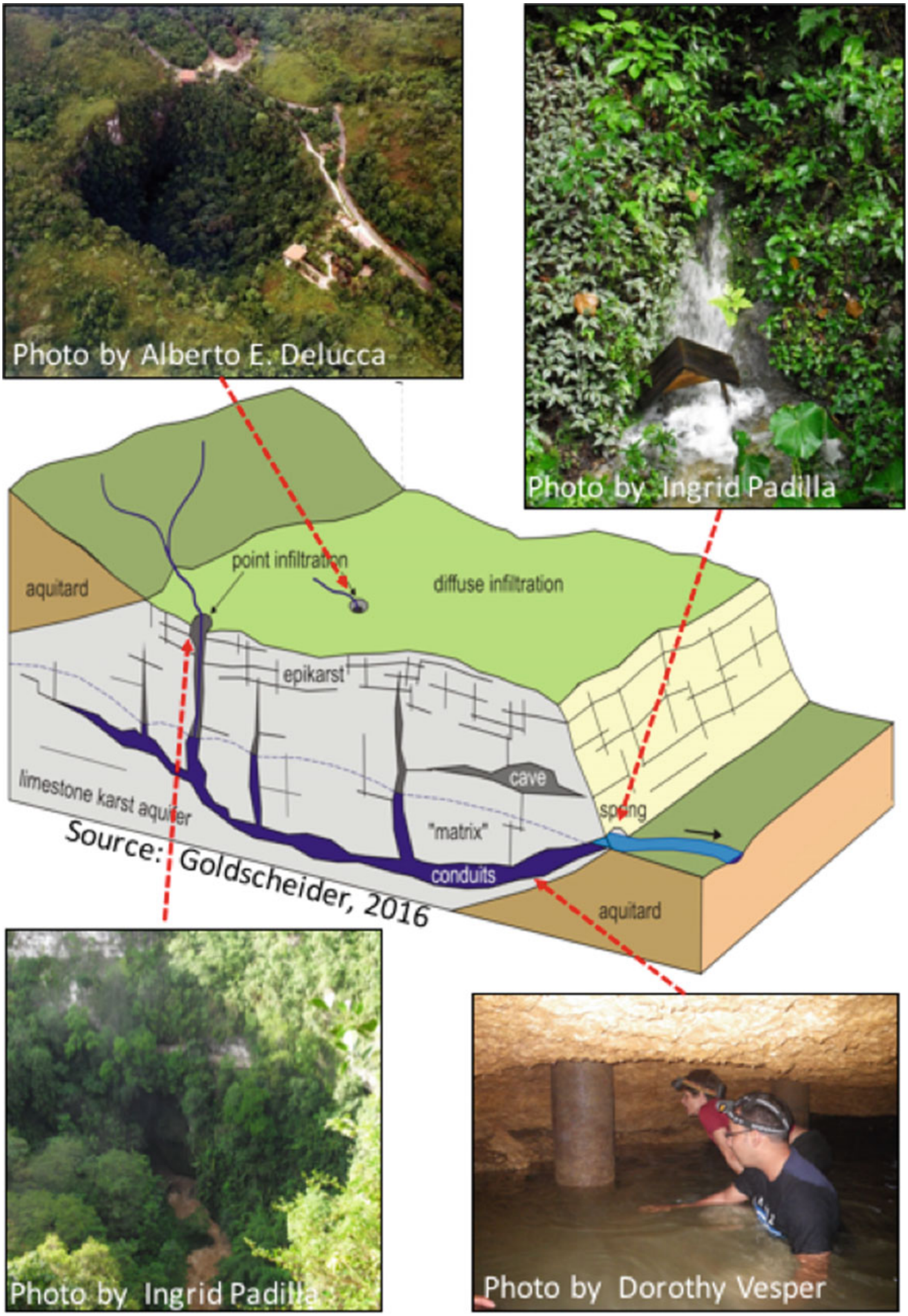

Fig. 1 Features in karst systems

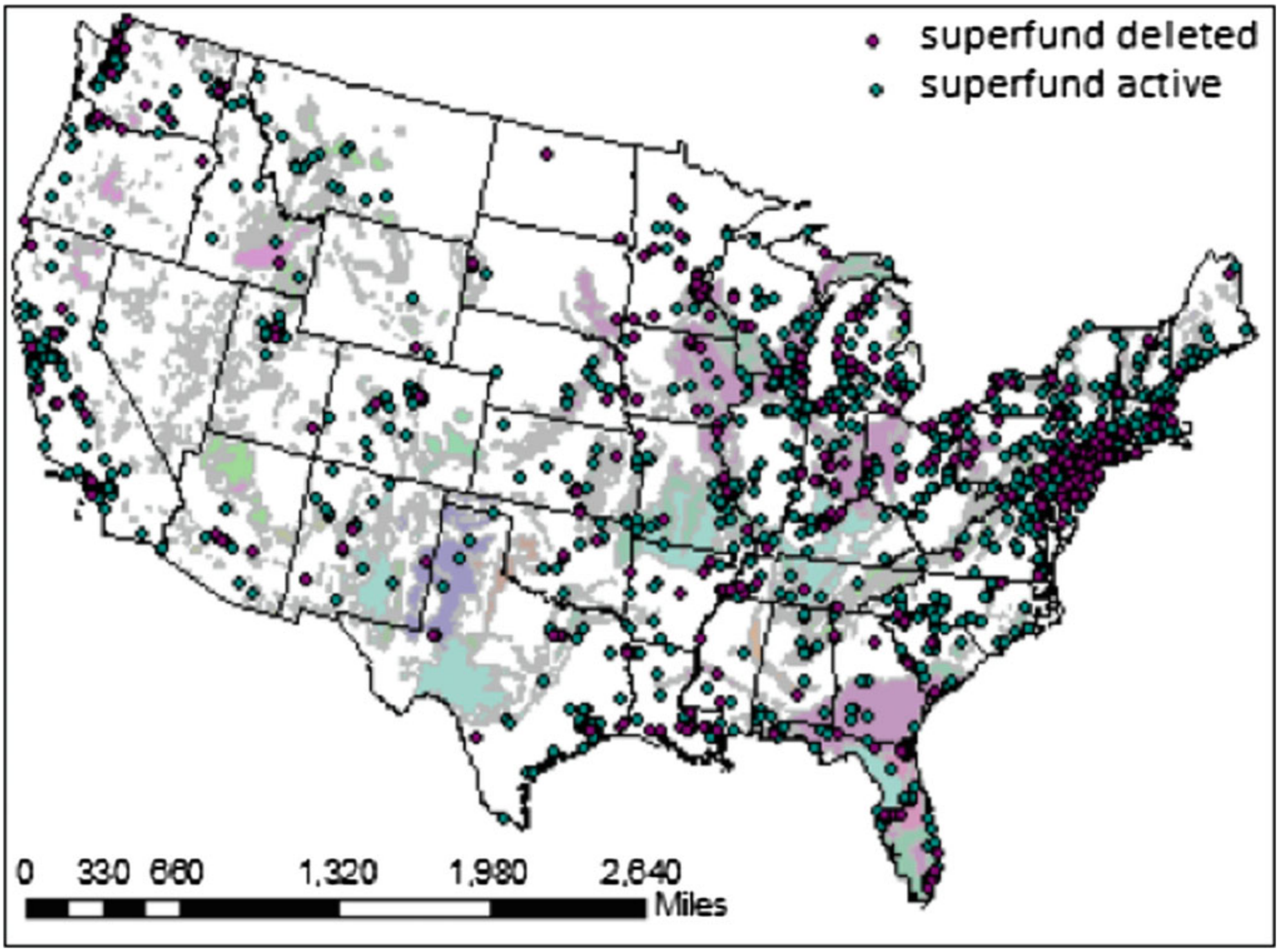

Fig. 2 Superfund sites (*circles*) and karst regions in USA. Distributed map *colors* representing type of karst rock

(PAHs), nutrients, and certain microorganisms. Emerging contaminants (ECs) are synthetic or naturally occurring chemicals or microorganism that are not commonly monitored in the environment, but have the potential to enter the environment and cause known or suspected adverse ecological and(or) human health effects (USGS 2016; Sorensen et al. 2015; Hmielowski 2016). ECs have been detected in the environment, many in karst systems (Reh et al. 2013), but their fate and biological impacts are poorly understood and currently not included in regulatory monitoring programs (Hutchinson et al. 2013). ECs include personal care products, pharmaceutical flame retardants, hormones, antibiotics, and plasticizer (USEPA 2016; Hmielowski 2016; Sorensen et al. 2015). Reported contaminants in karst groundwater include metals (Calò and Parise 2009), pharmaceuticals (Einsiedl et al. 2010; Metcalfe et al. 2010), personal care products (Metcalfe et al. 2010), pathogens (Green et al. 2006), VOCs (Guzman-Rios et al. 1986), chlorinated VOCs (Padilla et al. 2011; Padilla et al. 2015; Yu et al. 2015), herbicides (Guzzella et al. 2005; Metcalfe et al. 2010), and PAHs (Metcalfe et al. 2010; Schwarz et al. 2011).

2 Fate and Transport Processes

The mobility, persistence, and ultimate distribution of contaminants in karst systems are, as with other types of subsurface environments, controlled by fate and transport mechanisms (Fig. 3). Unlike many other types of aquifers, however, the highly heterogeneous character of karst media results in complex pathways that can store and transport significant contaminant mass for long periods of times (Loop and White 2001; NRC 2005). These pathways are influenced by the characteristics of the system, the contaminant, and contaminant sources.

Transport of contaminants in karst groundwater systems is highly influenced by the flow mechanism predominating in the aquifer. Conduit-flow-dominated systems tend to convey contaminants rapidly through the system without

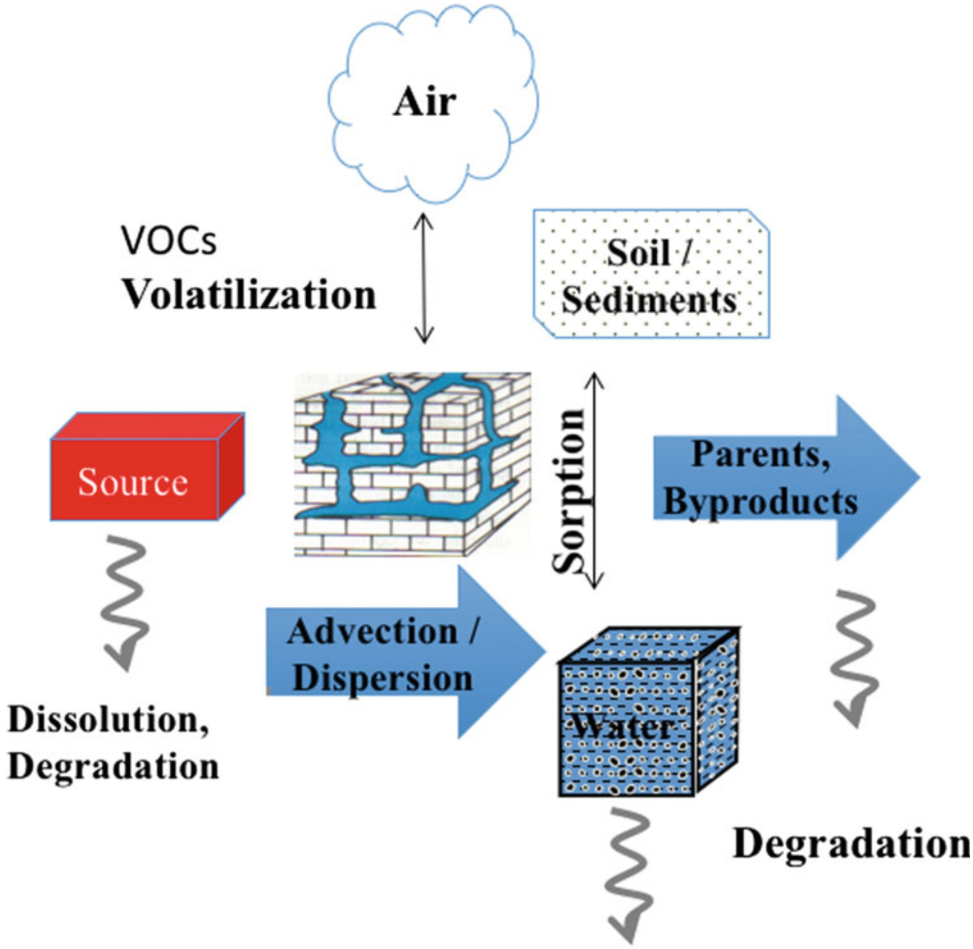

Fig. 3 Processes affecting contaminant fate and transport

much attenuation. Diffuse-flow systems can retard the movement and store large quantities of contaminants, causing a long-term release of contaminant to the environment. Combined conduit- and diffuse-flow transport mechanisms occur over a wide range of hydrogeological systems and flow conditions (Schilling and Helmers 2008; White 2002), but can be highly associated with karst systems with high matrix permeability, such as those found in carbonate aquifers of Puerto Rico (White 2002). In such systems, conduits can concentrate water and contaminants from direct sources and/or diffuse flow and convey them rapidly to potential exposure discharge points (e.g., springs). They can also convey contaminants to "trapping" diffuse-flow zones of greater contaminant storage capacity, where they can serve as a long-term storage areas and sources of contamination. Groundwater discharge and potential areas of exposure in combined-flow karst systems are not limited to a particular point of discharge, but can potentially act as a diffuse source and potential exposure path over large discharge zones. This makes karst aquifers are among the most challenging hydrogeological settings to characterize and manage (NRC 2005).

Depending on the flow, system, and contaminant characteristics, contaminants in karst groundwater may move as solutes, particulates (e.g., sediments, bacteria), non-aqueous phase liquids (NAPLs), colloidal matter, emulsions, sorbates (in moving particles), and vapor phase. They can be stored in the vadose or saturated zones as dissolved solutes, as soil sorbates, as pools along low permeability, as irregular surfaces, and as trapped phases in pores spaces, fractures, and solution cavities (Loop and White 2001).

Transport of dissolved contaminants in karst groundwater systems is controlled by advection and dispersion through the fissures and conduits, diffusion into the relative immobile pore water in the rock matrix (in the case, for instance, of telogenetic aquifers), retardation processes caused by sorption, and other biophysicochemical processes (Geyer et al. 2007). Slow mass transfer of solutes from dead-end fissures and immobile pore water in the rock matrix produces long-term release of contaminants. Advection in karst groundwater system is highly influenced by the discharge and flow velocities in the individual fissures or conduits in conduit-dominated systems, and by matrix and fracture permeability in diffuse-flow systems. Transport in combined-flow systems is influenced by conduits and rock matrix characteristics and discharge. In this case, the rock matrix can not only be thought of as an immobile compartment in which contaminants diffuse in and out, but also as regions of active transport that can be influenced by advection, dispersion, and contaminant mass transfer. Generally, as flow velocities increase, dissolved contaminants' travel times decrease, but concentrations may increase or decrease depending on the contaminant source and the mixing, dispersive, and dilution characteristics of the system (Vesper et al. 2001). Dispersive processes in karst systems are highly influenced by heterogeneity, as well as flow regime. Greater velocity variations in more heterogeneous and higher flows are expected to result in a greater dispersive capacity of the systems.

Transport of colloidal and suspended solids (or emulsified liquids in the case of NAPLs) is expected to be low or negligible during base flow characterized by diffuse-flow conditions (White 2002). During storm flow conditions, turbidity, suspended sediments, emulsified liquids, colloids, and bacteriological counts from rainfall runoff and material settled at the bottom of conduits are mobilized and transported through the system. Generally, the velocity and recovery of colloidal and suspended particles in karst conduit systems depends on the magnitude of flow, although they never fully recovered at discharge points (Göppert and Goldscheider 2008). Low recovery is attributed to rock matrix attachment and filtration mechanisms. These mechanisms, however, have not been quantified.

Retardation of dissolved and NAPL contaminants in karst aquifers can be significant in the rock matrix and fractures (NRC 2005), and highly influenced by diffusion mass transfer into diffusive-flow regions (Memon and Prohic 1989). Generally, sorption along enlarged openings has been assumed to be limited because of low reactive surface area and high velocities relative to the rates of sorption processes. Sorption of organic contaminants along the flow path may, however, be significant depending on the clay and organic carbon content of the rock and sediments (Langer et al. 1999), and geochemical properties. Sorption onto suspended particles and colloids in karst groundwater system has been conceptualized as an important process affecting the overall movement and storage of organic contaminants through the system (White 2002). Particle-facilitated transport of sorbed organic contaminants has been indeed shown for polycyclic aromatic hydrocarbons (PAHs, highly hydrophobic compounds with strong sorption capacity) in highly vulnerable karst system in southern Germany (Schwarz et al. 2011). A study in this system reveals that PAHs are commonly retained in the soils, except during high discharge events, when increasing concentrations are observed at the outlet of the karst catchment. Because these events are associated with increasing particle concentrations, the increase mobility of the PAH is attributed to particle-facilitated transport. In contrast, sorption of contaminants onto immobile sediments can retard transport or limit transport to periods of high velocity flow.

Other biophysicochemical processes influencing the fate and transport of dissolved contaminants in groundwater include speciation, degradation, volatilization, and mass transfer processes. Many inorganic contaminants, such as metals, exist as one or more species depending on the geochemical conditions (e.g., pH, redox, carbonate content, and other chemical components) of the system. The mobility of metals depends on their speciation. In addition to the transport in the dissolved phase, volatile compounds, such as trichloroethene (TCE) and other chlorinated volatile organic compounds (CVOCs), can move as vapors in the vadose zone. Their transport in the vapor phase depends on vapor pressure, volatilization rates, gaseous diffusion, and other partitioning properties. Volatilization rates are expected to increase at higher water velocities due to potential turbulent conditions. Organic compounds can also be degraded abiotically or biotically, resulting in reduced total mass of the original compound. They may also degrade into other contaminants resulting in an increased total mass of the degradation product. Degradation rates vary significantly among contaminants, and depend on biogeochemical conditions. Many organic compounds, such as TCE and many phthalates, have slow degradation rates and tend to persist in natural environments. Degradation rates are expected to be further limited by their lower residence times in karst conduits, but not as limited in the rock matrix where residence times are higher. Hydrophobic organic contaminants that have high sorption properties, such as many phthalates, tend to show even lower degradation rates due to the reduced bioavailability (Peterson and Stapples 2003). Although sorption characteristics of many organic compounds to limestone are unknown, it is commonly assumed to be low (Langer et al. 1999). Sorption to colloids and sediments in the karst may, however, induce enhanced transport and limit the bioavailability for biodegradation.

Mass transfer processes of contaminants in karst groundwater systems include dissolution, sorption/desorption and volatilization, and diffusion into and out of matrix rock, immobile water regions, and sediment piles. Volatilization is important for volatile contaminants either near or in the vadose zone, and it is expected to vary with flow regimes and velocities. Although vapor transport in unsaturated conduits and regions is expected to be high, very little work has been done on vapor intrusion in karst systems. Dissolution is a major mechanism affecting the transport of trapped NAPLs in groundwater. In the absence of degradation pathways, dissolution mass transfer controls the length of time that the NAPL is entrapped in fracture systems and the rock matrix (Dickson and Thomson 2003).

Modeling results have indicated that dissolution processes of DNAPLs in fractured systems are a function of flow and transport properties of the fracture network and the rock matrix (VanderKwaak and Sudicky 1996). Mass transfer between domains (mobile–immobile, conduit/fracture/matrix, water–NAPL, sediment water) in fracture systems occurs as concentration and hydraulic gradients are developed between advective flow paths and surrounding medium (Jardine et al. 1993). These processes are commonly diffusion-controlled and could serve as a slow, but continued and significant release of contaminants into zones of potential exposure.

Chlorinated solvents can form DNAPLs, which are heavier than and immiscible in water. DNAPLs move downward or laterally through fractures and available pore openings until local conditions favor their accumulation (Wolfe and Haugh 2001). As they migrate in the system, DNAPLs can be trapped in fractures, conduits, and cave passages and in the matrix rock (Loop and White 2001), where they can serve as a long-term source of contamination. Transport experiments using non-aqueous phase TCE in a laboratory-scale karstified limestone rock show that although DNAPLs tend to follow a downward path, they can be transported along non-vertical conduits when subjected to groundwater flow fields (Carmona De Jesús and Padilla 2015). The study also shows that once DNAPLs penetrate regions of preferential flow, subsequent injections tend to follow the same path. When they reach regions of limited flow, DNAPLs are accumulated and transported through diffusive processes after dissolution (Carmona De Jesús and Padilla 2015). In conduits and caves, DNAPLs tend to sink to the bottom, where they can be stored in pools or trapped in sediments deposited along the conduits. Pooled DNAPLs remain stationary under low-flow conditions, except for gradual loss by dissolution. Pooled DNAPLs dissolve at rates given by the exposed area of the DNAPL pool, the specific dissolution mass transfer properties of the particular compounds, and the flow regime. Flow regimes which reduce the concentration gradients near the NAPL tend to reduce dissolution rates. Similar to dissolved solutes, the transport and release of DNAPLs in karst systems tend to be highly dependent on flow regime (Loop and White 2001). During high (storm) flows, DNAPL pools can be dragged downstream or flushed as suspensions and emulsions at high flows (Vesper et al. 2001). As a result, flood flow can send previously immobilized DNAPLs to outflows points (potential exposure routes) in toxic pulses. If trapped in obstructed pathways, the DNAPL can be pressed against the conduit walls under pipe flow regimes, being forced into fractures and the rock matrix. DNAPLs that have become entrapped in conduits sediments, fractures, and the rock matrix are removed by dissolution, desorption, and diffusion-controlled processes (Carmona De Jesús and Padilla 2015). The rates at which entrapped contaminants are removed depend on contaminant and medium properties and flow regimes. For high matrix permeability rocks, numerical models indicate that DNAPLs in fractures will dissolve faster than those in matrix of low permeability or inaccessible to flow (Dickson and Thomson 2003; VanderKwaak and Sudicky 1996). Although conceptually framed, the overall transport behavior of DNAPLs and associated solutes in karst aquifers is poorly understood.

3 Potential Contaminant Exposure

The potential for humans and ecosystems to be exposed to contaminants in karst systems over space and time depends on an interrelated set of factors that affect the dimensional mobility, persistence, and mode of exposure. These factors include the hydrogeological characteristics of the karst system, type and properties of contaminants, and anthropogenic activities. Hydrogeological characteristics (e.g., recharge components, sinkhole density, permeability, conduit geometry and connectivity, rock–conduit interactions, matrix reactivity, geochemical conditions) and type (e.g., dissolved, volatile, non-aqueous) and properties of contaminants (e.g., state, solubility, volatility, degradability, speciation, sorptivity, particle size) affect the fate and transport processes that control the magnitude, direction, and rate of contaminant movement and storage. Anthropogenic activities that affect potential exposure are commonly related to land, water, waste, and contaminant use and management. These activities influence input sources of contaminants (type, location, density, distribution, rates, phase/concentration, mass flux), as well as water source, delivery, and discharge to other environmental compartments (e.g., rivers, coastal zones, wetlands, springs). In simplified conceptual models (Fig. 4), contaminants move from input sources to points of exposure, where, depending on their characteristics and land use/management, they can be inhaled as vapors, absorbed through the skin, and/or consumed as food or drinking water. In karst systems, where water is often available for use, input sources are abundant, and the hydrogeological characteristics support significant transport of water and contaminants, the potential for exposure is high. Yet, the ability of scientists and engineers to predict exposure point concentrations and reduce human and ecological exposure is limited.

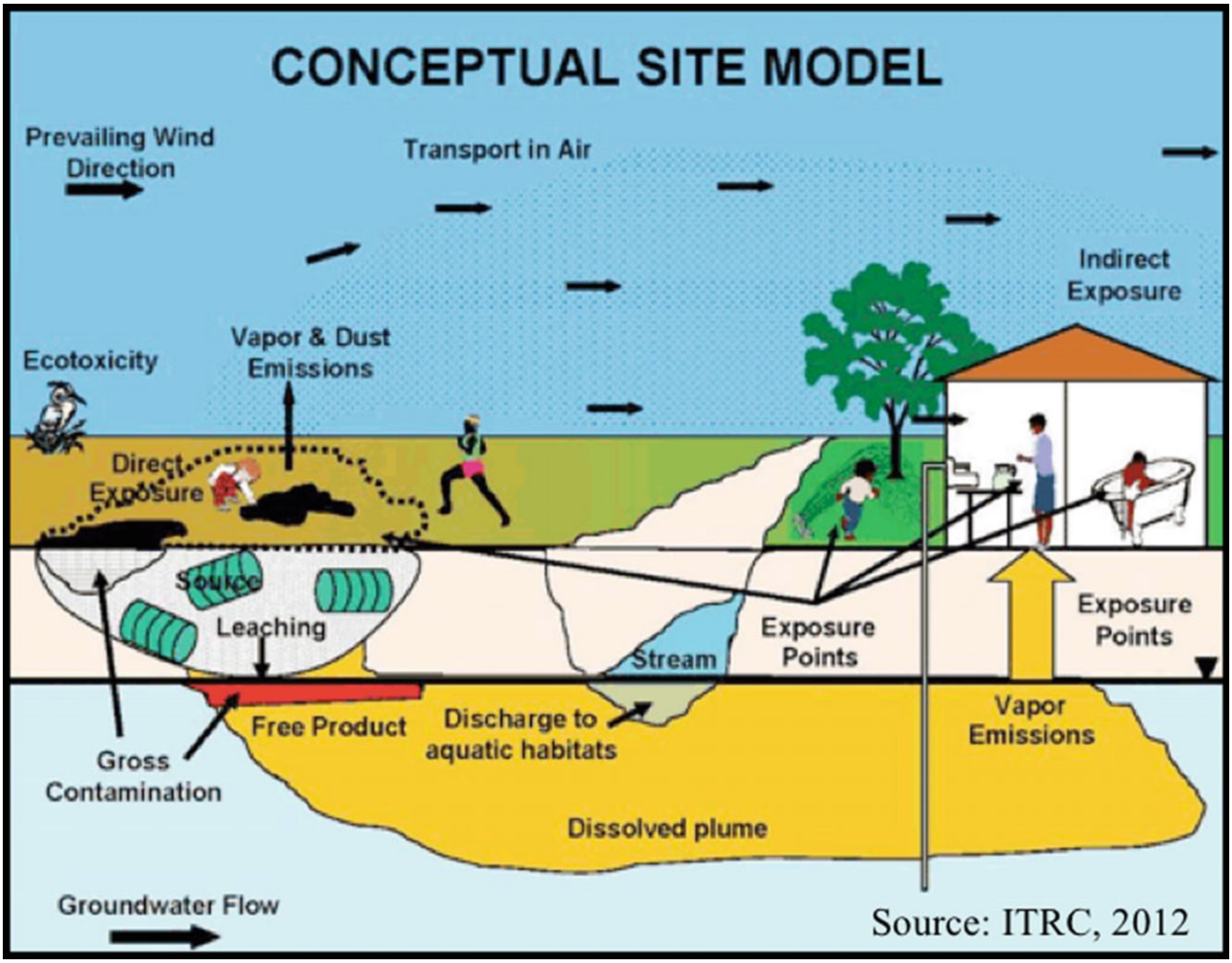

Fig. 4 Conceptual model illustrating contaminant pathways from source to human exposure points

4 Case Studies

4.1 Karst Region of Northern Puerto Rico (KRNPR)

The northern karst region contains two of the most extensive and productive freshwater aquifers in Puerto Rico (Lugo et al. 2001). These aquifers are characterized by well-developed conduit networks within eogenetic limestones having primary porosity as high as 30% and also high permeability. They have significant flow components along conduits and through the rock matrix (Renken et al. 2002). The karst aquifer system in this region comprises three major hydrogeological units (Fig. 5): the upper aquifer, which is mainly composed of the Aymamon and Aguada Limestone Members; the lower aquifer, which is formed by the Lares and Montebello Limestone Members; and a confining unit that separates the upper and lower aquifer, which is comprised by the Cibao Formation (Renken et al. 2002). The upper aquifer is unconfined and linked to the surface throughout most of its outcrop area. The lower aquifer is confined toward the coastal zone and outcrops to the south of the shallow aquifer, where it is recharged. The outcrop extents are much more vulnerable to contamination due to direct interaction with the surface.

KRNPR has had a long history of toxic spills, chemical waste, and industrial solvent release into the subsurface (Padilla et al. 2011; Hunter and Arbona 1995). The highly permeable characteristics of the aquifer system have prompted extensive groundwater contamination (Padilla et al. 2011, 2015; Yu et al. 2015) that results in high potential for exposure and significant adverse health impacts. Serious contamination in the KRNPR has caused the inclusion of 12 National Priorities List (NPL) and 15 corrective action sites within the Resource Conservation and Recovery Act (RCRA) between 1983 and 2016 (Fig. 5). There are many other sources of contamination, including unlined landfills and illegal waste dumps. Recent

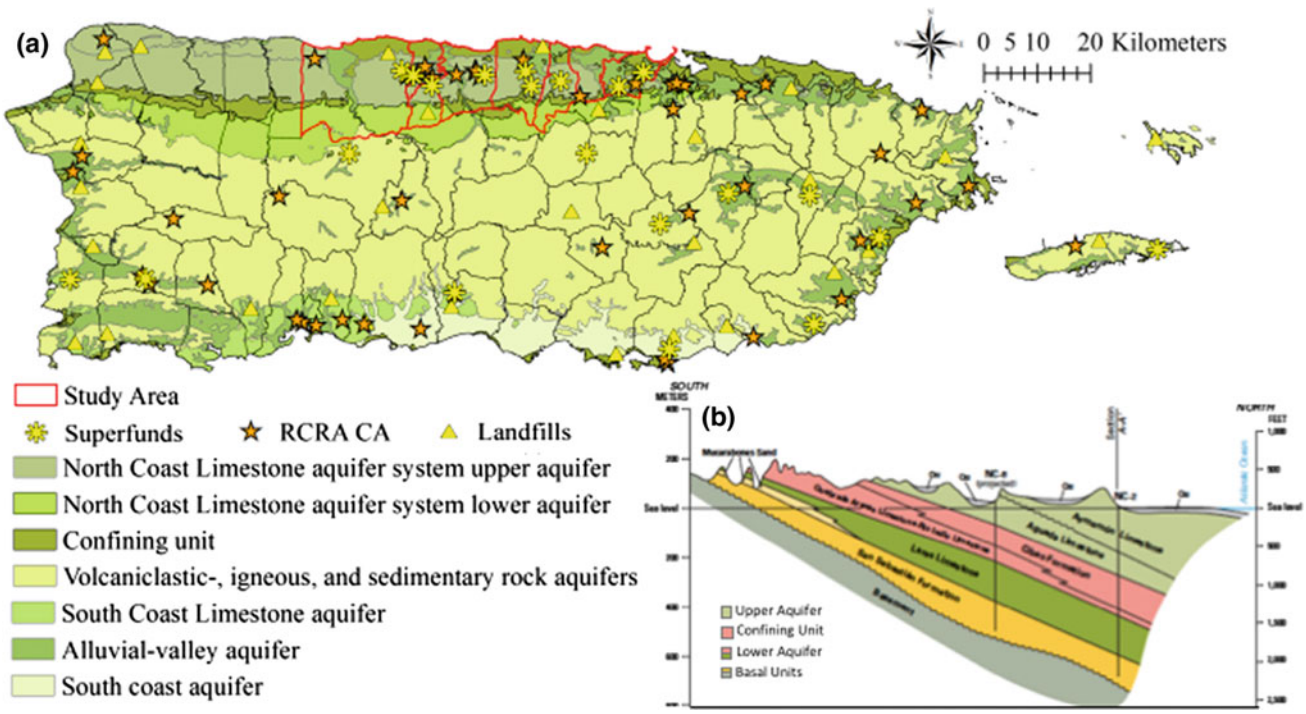

Fig. 5 Principal **a** hydrogeology and contaminated sites in PR and **b** hydrogeological cross section of the northern karst region of PR

(Padilla et al. 2011) and past (Guzmán-Rios et al. 1986) studies in this region have reported the presence of organic contaminants in the karst groundwater system. Of particular interest is the contamination with CVOCs and phthalates, including trichloroethene (TCE), tetrachloroethene (PCE), trichloromethane (TCM), carbon tetrachloride (CT), di-ethyl-hexyl phthalate (DEHP), Di-butyl phthalate (DBP), and di-ethyl phthalate (DEP) because they are ubiquitous in the environment and they have potential health impacts. The above-mentioned CVOCs are within the top 50 predominant contaminants in Superfund sites, with TCM and TCE listed as No. 11 and No. 16, respectively, in the EPA's 2015 CERCLA Priority List of Hazardous Substances (ATSDR 2016). Phthalates have been found in and around landfills and Superfund sites (Irizarry 2014). DEHP, the only regulated phthalate specie, is listed as No. 77 of predominant contaminant in Superfund sites and the most frequently detected phthalate compound in the northern karst region of Puerto Rico (Torres-Torres et al. 2016). CVOCs and phthalate contaminants have been identified as potential precursors of preterm birth complications (Meeker et al. 2009; Meeker 2012; Sonnenfeld et al. 2001; Forand et al. 2012), and are being evaluated as one of the causes for the extremely high rates of preterm birth rates in Puerto Rico (NCHS 2012) compared to other jurisdiction in the USA.

Spatiotemporal data of CVOCs in the KRNPR show a widespread distribution that varies in space and time (Figs. 6 and 7). The variability is attributed to (1) changes in contamination input sources; (2) dynamic fate and transport processes; (3) variation in remedial and monitoring schemes; (4) differences in spatial and temporal data resolution; and (5) changes in groundwater use. Although greater contamination is found in the upper aquifer, CVOCs are found in both the upper unconfined and lower confined aquifers. Greater detection in the upper aquifer is attributed to higher number of contaminant input sources and a much greater sampling density in the upper aquifer than the lower one. The principal detected CVOCs, which include TCE, PCE, DCE, CT, TCM (chloroform), DCA, and DCM, are associated with some known contaminated sites, but their spatial distribution extends beyond known sources of contamination. The large extent is attributed to rapid mobility of contaminants within conduits and high-permeability zones, delay in remedial response of highly contaminated sites, inability to capture the heterogeneous plume, and the existence of other potential sources of contaminations. The temporal distribution of CVOCs in the KRNPR shows a high capacity of the karst system to store and slowly release contaminants over long periods. Although in general, CVOCs concentrations tend to decrease over time (Fig. 8), percent detection has remained high for over 30 years of contamination. The concentration decrease is mostly associated with active remediation activities of the major Superfund sites, although some is due to degradation of major CVOC parents (e.g., TCE, CT) into other CVOCs (e.g., TCE and CT degraded to DCE and TCM,

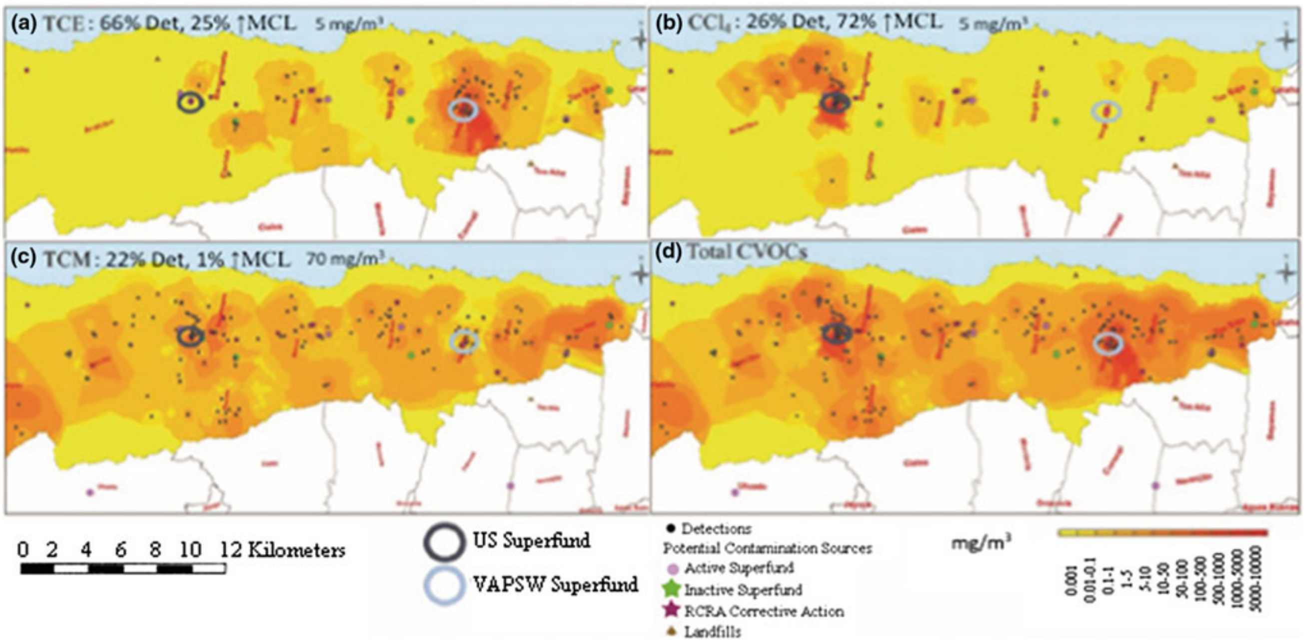

Fig. 6 Spatial distribution of average temporal concentrations for **a** TCE, **b** CCl_4, **c** TCM, and **d** total CVOCs over study area

respectively). It is important to note that, even under active remediation, CVOC concentrations have not reached regulatory levels and a significant number of samples still have concentrations above the maximum contaminant level (MCL).

The spatiotemporal data of phthalates also show widespread presence of these contaminants in the KRNPR (Torres-Torres et al. 2016), but their distribution is much less associated with highly contaminated sites. This is because sources of phthalates, which are contained in many personal care and consumer products, are much more widely distributed than CVOCs. As a result, areas of greater phthalate detection are more highly associated with hydrogeological properties and conditions of the region. In general, the detection of phthalates in groundwater is greater in the upper aquifer (similar to CVOCs) and in regions of higher hydraulic conductivities and sinkhole coverage. They are also detected at a higher percent in areas of high urban and industrial development. Like CVOCs, phthalates are found in both aquifers of the KRNPR.

The aquifer system of the KRNPR serves as a source of water to individual households, rural communities, municipal distribution systems, and industries. Initial assessment of potential population exposure from groundwater contamination in the KRNPR suggests that contaminants are reaching the drinking water system. Measurement of CVOC and phthalate contaminants in tap water across the KRNPR indicate that potential exposure at the point of use depends on various factors, including water use, storage, treatment, and distribution material, among others. It also depends on the type of contaminants. General comparisons between groundwater and tap water during a four-year study period (2012–2015) suggest that, except for TCM, concentrations and detection frequencies for CVOCs are generally higher in groundwater than tap water and that the distribution of major species also changes. Groundwater samples show greater detection of parent contaminants (TCE, PCE, CT), whereas TCM was the predominant specie in tap water. Detection of phthalates, on the other hand, tends to be higher in tap water than groundwater, with higher concentration predominance of DBP in groundwater and DEHP in tap water. These results indicate a complex relation between contaminants in groundwater and those found in tap water that must take into account potential losses and sources of contaminants, as well as fate and transport processes within the distribution system.

4.2 Continental Karst

Transport experiments and water quality measurements in continental karst aquifers of eogenetic character have shown significant transport of solutes between conduits and the rock matrix that results in high contaminant storage in these aquifer systems. Tracer experiments in the Biscayne Aquifer (an eogenetic karst system) in southeastern Florida show that solute transport in this karst limestone aquifer occurs over multiple flow paths that exhibit a wide range of fluid velocity (Shapiro et al. 2008). This results in an initial rapid transport of solutes through highly transmissive zones having greater

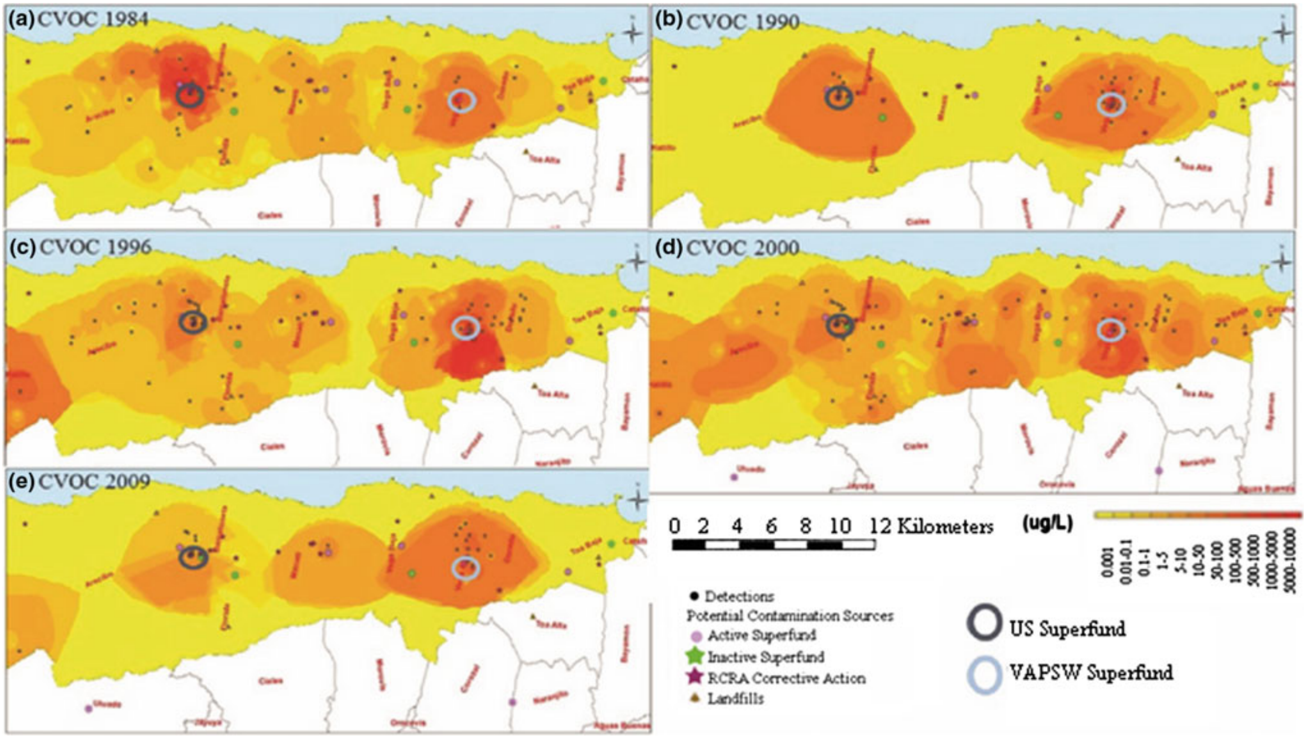

Fig. 7 Spatial distribution of total CVOC concentration distribution for **a** 1984, **b** 1990, **c** 1996, **d** 2000, and **e** 2009

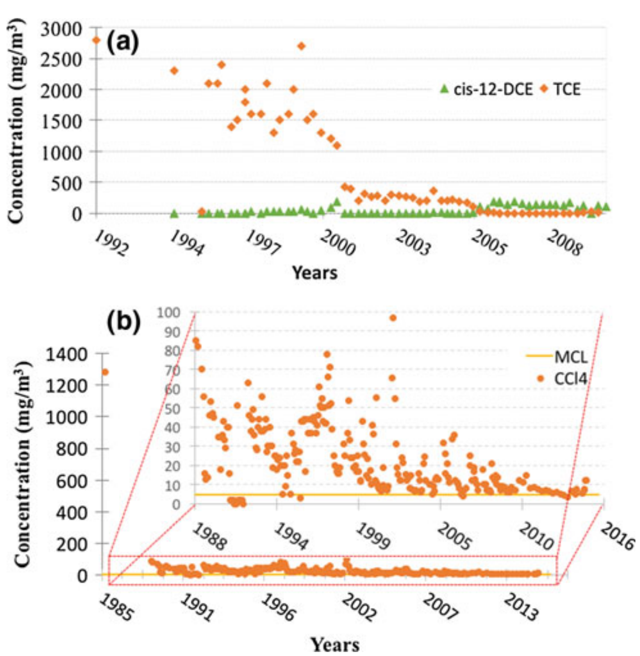

Fig. 8 Temporal distribution of **a** TCE and DCE concentrations in a Vega Alta well and **b** CCl_4 concentrations in an Upjohn well

advecting velocities, followed by chemical diffusion into immobile (or less mobile) water contained in less transmissive intervals of interparticle and separate-vug porosity that provide high aquifer storage (Shapiro et al. 2008). Flushing of the solutes after their input is terminated is, therefore, limited by mass transfer into immobile or slow advecting water and the high aquifer storage. Transport and hydraulic response of this aquifer suggests that it behaves as a dual-porosity medium; however, the results of the tracer test showed rapid transport similar to other types of karst (Renken et al. 2008). Tracer and water quality measurements at a local conduit system in the Floridan aquifer of north-central Florida show conduit-flow-dominated transport that is significantly influenced by exchange with rock matrix (Screaton et al. 2004). Although not directly comparable, transport of water and contaminants in these continental eogenetic aquifers reflects similar transport and storage characteristics as those found in the KRNPR.

Water and contaminant transport in more diagenetically altered carbonate rocks is commonly assumed to be concentrated in conduits (Martin and Dean 2001). This is, however, dependent on the level of karstification and connectivity among network of fractures and conduits. Tracer experiments in a highly karstified (conduit-dominated) system in southeastern Minnesota show, for instance, an advective-dominated transport with little mass exchange between the conduits and the rock matrix (Luhmann et al. 2012). Early arrival of suspended sediments relative to dissolved tracers during these experiments indicates that settled sediments within the conduits were re-suspended and transported preferentially along lines of higher flow velocities. Studies of a karstic dolostone aquifer system in Ontario, Canada, show, however, that transport in this aquifer system may be controlled by conduit- and diffusive-flow components (Perrin et al. 2011). The presence of karst geomorphological features, such as sinkholes, springs, and caves, suggests the existance of conduit-controlled flow and transport. Other work has, however, described the dolostone as a fractured system with variable hydraulic conductivity without mentioning the occurrence or influence of solution conduits (Perrin et al. 2011). Studies of areas showing significant contamination with polychlorinated biphenyls (PCBs), chlorobenzenes, TCE, and pesticides in the upper part of the dolostone aquifer have reported contaminant distributions and groundwater flow as having no influence from solution conduits. Other areas, however, show flow characteristics dominated by the influence of conduits, including troughs in the potentiometric surface, the presence of high hydraulic conductivities, rapid water level and hydrochemical responses to recharge events, and the existence of sinkholes and underground streams near the site. Tracer tests of the area show high velocities in conduits connecting a sinking stream and a spring, but much slower velocities in the shallow contaminated part of the rock. Analysis of well logs shows that, although conduits occur in the area, the flow system is governed by interconnected fractures with substantial hydraulic conductivities independent of the conduits. Detailed monitoring of distributed and point source contaminants further shows strong transverse dispersion and contaminant distribution consistent with transport by flow in a network of ubiquitous connected fractures that can be described by equivalent porous media models (Perrin et al. 2011).

A study of groundwater flow, transit times, and halogenated volatile organic compounds (HVOCs) levels in a karstic, fractured, carbonate-rock aquifer in West Virginia suggests that this system is dominated by diffuse flow through a network of fractures (Plummer et al. 2013). Although rapid advective transport of contaminants is shown through the system, ubiquitous detection of low-level concentrations of HVOCs suggests the presence of long-term external and internal persistent sources. Sources external to the carbonate rock include seepage from a closed landfill. The internal ones, including infiltration of HVOCs from the epikarst, exchange with low-permeability zones in the fractured rock, and upward leakage of older water containing HVOCs, indicate a high capacity of the system to store and slowly release contaminants over long periods of time.

A study in a complex carbonate aquifer of the Zechstein Formation in Germany shows frequent detection of emerging contaminants in groundwater samples (Reh et al. 2013). Their presence in the aquifer system is associated with urban and agricultural land use. Although emerging contaminants are detected in both aquifers, like the KRNPR, the upper aquifer generally exhibits higher number and seasonal variability of detections than the lower aquifer. Contamination in the lower aquifer is attributed to potential hydraulic connections between these two systems. Overall, greater detection of less degradable contaminants indicates that degradation processes are occurring over their residence time in the system. Residence time estimation of over 20 years for some of the emerging contaminants (Reh et al. 2013) indicates high storage capacity of the aquifer system. High storage capacity of contaminants in continental karst is also observed in a study looking at the occurrence and transport of pharmaceuticals in the karst groundwater system of the Franconian Alb in southern Germany. This aquifer consists of conduits, an epikarst, and a fracture network (Einsiedl et al. 2010). Conduits in this system transport water and contaminants at high velocities over long distances. The water and contaminant transport in the fracture systems is characterized by long mean transit times and strongly influenced by diffusion processes between the mobile fracture water and the more immobile rock matrix (Einsiedl et al. 2010). Low tracer recoveries and the frequent occurrence of pharmaceutical in groundwater at low concentrations in this aquifer show that most of the water, tracers, and contaminants go into storage in the fractured system and do not move rapidly and concentrated along the conduit to spring outlets (Einsiedl et al. 2010). Low contaminant concentrations are attributed to high dilution processes and storage properties.

5 Modeling Contaminant Transport in Karst Aquifers

5.1 Overview

Modeling karst groundwater flow and contaminant transport in karst systems pose particular challenges because of their highly heterogeneous nature, wide spectrum of flow regimes (ranging from laminar to turbulent flow), lack of proper data for accurate characterization, and limited applicable models, among others. In spite of these limitations, numerical models can be used to describe flow and transport trends, as long as they are applied within the limits of their realm. Particular challenges arise when trying to locally predict direction and rate of solute transport (Quinlan et al. 1996). This requires accurate knowledge about the distribution, geometry, and direction of subsurface fractures and conduits. These characteristics are often unknown at the local level. As a result, modeling of hydraulic heads, volumetric flows, general directions, and contaminant transport is often done at a regional scale, in which the size of the modeled area is large enough to approximate equivalent porous media (Scanlon et al. 2003).

Several modeling approaches exist for simulating groundwater flow and contaminant transport in karst aquifers. These approaches, which include lumped and distributed models, are briefly described here. Greater detail on these methods is provided by others (Ghasemizadeh et al. 2012; Hartmann et al. 2014; Scanlon et al. 2003). Lumped parameter models do not include spatial dimensions and inherently assume equivalent porous medium (Scanlon et al. 2003). These models require minimal data and are rapid, but cannot be applied to simulate spatial variability in hydraulic heads, water quality, contaminant transport, and groundwater directional flow. Distributed parameter models are used to simulate spatial variability in groundwater flow and can, therefore, simulate spatial transport of contaminants and resulting contaminant distribution. They discretize the model domain into a grid of homogeneous sub-units, with each sub-unit having specific properties (e.g., hydraulic, fate and transport) and conditions (Ghasemizadeh et al. 2012). The challenge of distributed models resides in the amount of system data to properly simulate the karst systems. Several distributed models have been applied to simulate karst groundwater. These include equivalent porous media, double porosity, discrete fracture or discrete conduit network, and hybrid models.

Equivalent porous media (EPM) models treat the fractured media with conduits as an equivalent porous media, using bulk parameters instead of the properties of the media and individual fractures and conduits, and do not account for strong heterogeneity (Ghasemizadeh et al. 2012) and rapid flow through conduits. These models do not do well at simulating direction and rates of groundwater flow and contaminant transport at local scales in highly karstified aquifers because they do not integrate detailed information on fracture and conduit architecture. EPM models have, however, been successful at simulating contaminant transport and distributions at the regional level in slightly karstified aquifers. Simulations of TCE transport in the karst region of northern Puerto Rico show that EPM models can be used to address general contaminant concentrations in observations wells at the regional level (Ghasemizadeh et al. 2012, 2015; Sepúlveda 1999). The models, however, cannot simulate irregular spatial distributions, nor high temporal concentration variations resulting from the presence of preferential flow paths in karst conduits at local levels.

Scanlon et al. (2003) show that EPM models can adequately simulate regional groundwater flow in the Edwards Aquifer, USA. In more karstified aquifers that are influenced by local conduit features, EPM models tend to underestimate the rate of contaminant movement. Tracer tests conducted in carbonate aquifers in Anniston, Alabama, USA, and Walkerton, Ontario, show higher tracer velocities than those predicted by the model (Quinlan et al. 1996). Similarly, an EPM model developed to assess the rate of contaminant movement in the groundwater system under the Oak Ridge Tennessee, USA, underpredicted the distance at which contaminants would move.

Double porosity (DP) models, also known as double continuum or two-region models, treat the heterogeneity of karst systems through the application of two interacting continua, one represents moderately karstified aquifer zones (diffuse flow, high storage capacity) and the other represents highly karstified zones with high flow, low storage capacities (Hartmann et al. 2014). Interactions between these continua are assumed to follow a linear exchange rate. It is applicable to moderately to highly karstified systems. These models generally represent the rock matrix as regions of relatively low or no flow, but high storage capacity, whereas conduits are represented by regions of higher relative water velocities with minimal storage capacity. Field and Pinsky (2000) have applied DP models to simulate solute transport in karst solution conduits. DP models, however, assume laminar flow and still suffer from the limitation of simulating rapid flow through the conduits.

Discrete fracture/conduit network (DF/CN) models simulate flow and transport within individual fractures/conduits or set of fractures/conduits under laminar or turbulent conditions (Ghasemizadeh et al. 2012). The DF/CN approach assumes negligible permeability in the rock matrix and attributes flow and transport only to the fractures or conduits. It is, therefore, not applicable to karst systems with significant transport within the rock matrix, such as those found in eogenetic karst systems. Discrete fracture and discrete conduit models differ only by the type of geometric data used to describe fractures or conduits, but both require detailed information of fracture or conduit geometry. These models are sometimes used interchangeably as many times detailed information of these features is not available. Large data requirements on fracture/conduit characteristics restrict the use of these models to local systems. The DF/CN approach has been used to simulate solute transport through sparsely fractured rock in Sweden (Dverstorp et al. 1992) and the hydraulics of a variably saturated large cave in Switzerland (Jeannin 2001).

Hybrid models (HMs) integrate discrete models and EPM. HMs simulate the matrix in a continuum in which the conduits are embedded as discrete elements. It is included in the widely used groundwater model MODFLOW (MODFLOW-CFP), but presently CFP cannot simulate solute transport or chemical reactions (Ghasemizadeh et al. 2012; Hartmann et al. 2014; Shoemaker et al. 2008). Another HM, the HFEMC, has been used to simulate groundwater flow and solute transport in systems influenced by both conduit and matrix transport (Orban et al. 2010). The model reproduces the spatial tritium and nitrate concentrations and the nitrate temporal trends in a regional chalk aquifer in the Geer basin in Belgium. Results show that the spatial distribution of the contaminants in the basin is related to the prevailing hydrodynamic conditions, and not to the local hydrodispersive processes (Orban et al. 2010). HMs are largely limited by the required knowledge on the characteristics of the matrix and the karst conduits, and have generally been applied to study synthetic situations related to flow, transport, and dissolution processes in karst aquifers (Ghasemizadeh et al. 2012).

5.2 Challenges in Coupling Contaminant Transport to Flow in Models

The challenges in modeling water flow in karst aquifers are further complicated when contaminant transport is added to the model. The assessment and prediction of contaminant fate, transport, and potential exposure in karst systems is greatly impacted by limited knowledge, scarcity of data and information, and limitations in efficient numerical modeling tools for these systems. Uncertainty is related to spatiotemporal variability on the hydrogeological and biochemical characteristics influencing the fate and transport processes, and to the anthropogenic activities acting on the systems. The uncertainty related to geophysical heterogeneities (e.g., location, geometry, extent, direction, connectivity of conduit networks), bulk hydraulic characteristics (e.g., hydraulic conductivity, anisotropy), and hydrologic components (e.g., internal and external runoff, recharge) is well known across the karst community. Other sources of uncertainty arise from limited knowledge on the biogeochemical processes (e.g., sorption, mass transfer, reactions, contaminant–particle interactions), storage properties affecting the mobility and persistence of contaminants in karst aquifers, the role of mobile and fixed sediments in the aquifer, and on the interrelated interactions of these processes and properties with the heterogeneous physical system and flow regimes. The high storage capacity of contaminants in karst aquifers is observed in the contamination observed in the karst region of northern Puerto Rico, as well as in most of the contamination examples provided in this paper.

High uncertainty also exists on local anthropogenic variables that affect fate, transport, and exposure processes, and hinder our ability to predict and minimize contaminant exposure. These include variables related to characteristics of contaminants input sources (e.g., rates, mass, location, period), groundwater extractions, water distribution systems, and water use and consumption.

6 Conclusions

This paper demonstrates that karst groundwater systems are easily contaminated, resulting in extensive contamination of the aquifer. The high storage capacity in these systems results in slow-release and long-term contamination and potential exposure. Modeling results have shown that most of the storage occurs at the rock matrix (Green et al. 2006). In general, fate and transport processes are highly heterogeneous, depending on local and regional characteristics of the hydrogeological system and the contaminant. CVOC and phthalate concentration distributions in the karst regions of northern Puerto Rico indicate that contaminant distributions are heavily influenced by input source characteristics, with emerging (e.g., phthalate) contaminant distributions much more extensive and difficult to assess than plumes of legacy (e.g., CVOCs) contaminants. Sources of these emerging contaminants are likely to be discontinuous in space and time, and there is generally less data available for emerging than legacy contaminants because of the lack of monitoring requirements. Higher detection frequencies of phthalates are more closely associated with hydrogeological properties and conditions of the region. Contaminant distributions for legacy contaminants are generally more defined and closely related to the sources of contaminations. Assessment of potential exposure indicates that the relationship between contaminants in groundwater and those in tap water is similarly, highly dependent on the contaminant and source characteristics.

The assessment and prediction of contaminant fate, transport, and potential exposure in karst systems is often limited by lack of data and information, and limitations in efficient numerical modeling tools for these systems. Uncertainty is related to spatiotemporal variability on the hydrogeological, biochemical, and anthropogenic characteristics influencing the fate and transport processes in the system. Uncertainty is also provided by the modeling approach applied. Solute transport at the regional scale in less karstified systems, such as those in eogenetic aquifers, can be generally simulated with EPM models. Contaminant transport at local scales and/or in highly karstified aquifers may require the use of more sophisticated models (e.g., DP, Df/DC, and hybrid models). Lack of parameters and high modeling uncertainty, however, limit their applicability.

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Puerto Rico's Karst Protection—Beyond the Laws and Regulations

Abel Vale-Nieves

Abstract

My lecture will briefly explain the process of karst conservation in Puerto Rico by Ciudadanos Del Karso. However, most of my lecture will question current anthropocentric views on Laws and Regulations and their limitations. The main objective is to take a hard look at those ideas, on which laws and regulations have been based, so that we can consider new ideas from new perspectives, and start thinking outside the box. Good evening and I hope that so far everyone has enjoyed the weather in Puerto Rico and the conference. It is a pleasure to be at this conference on Karst, Groundwater contamination and Public Health. On behalf of myself and the Board of Directors of Ciudadanos Del Karso, our deepest and most humble thanks to the Karst Waters Institute for bestowing the Karst Award of 2015. In June 2015, Ciudadanos Del Karso also received the *France HABE Prize* awarded by the Department of Karst and the Cave Protection of the International Union of Speleology (UIS) at Postojna, Slovenia.

1 Puerto Rico's Karst Background

Karst represents 28% of Puerto Rico and it is a vital natural area for its many resources, as we normally describe Nature, i.e., biodiversity, spectacular vistas, subterranean rivers, caves, and aquifers. It contains some of the most productive aquifers of Puerto Rico, on which close to 500,000 people depend, as well as industry, commerce, and agriculture.

By the mid-twentieth century, Puerto Rico experienced almost total deforestation, due mainly to agriculture and wood harvesting for fuel and the karst regions were no exception. After mid century, the people that lived in the karst region and other agricultural regions of the island, left looking for jobs mainly in the coastal cities of Puerto Rico or in the USA. The karst region started to recover and became within Puerto Rico, the region with the heaviest forest cover, with immense value for water storage, biodiversity, tourism, and other activities not necessarily compatible with its natural values.

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To understand better what happened in Puerto Rico during the past century that impacted its natural systems, we need to provide some background on its demography. By the year 1900, the population was one million, by 1950 it was two million, and by 1975 it was three million and around 3.8 million by the year 2000, in an island of 3450 square miles. We had attained a population density of over 1100 people per square mile, almost four times the initial population in 100 years. To better understand the demography that I just described, the USA has 3.8 million square miles, which includes Alaska and Hawaii. If the USA had the population density of Puerto in 2000, the population would have been 4.2 billion instead of the 300 million for that year, more people than China and India combined. This should provide an idea of the stress that the karst and the natural systems were bearing due to the huge population density we had and still have. For the first fifty years of the last century, the per capita consumption was relatively low, but during the last fifty years, Puerto Rico developed into a consumer society which imitates the worst of the suburban lifestyle of the USA. The use of pesticides, herbicides, and other biocides and runoff from agro-industry (such as dairy farms), industry, and other nonpoint sources of pollution found their

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way to surface and groundwater. Unfortunately, this is something that is not easily seen; its effects are perceived with time in the health of living organisms. It is a sort of “invisible threat”.

Karst and other natural areas began to recover from traditional agricultural practices after the 1950s. But population growth around the cities with its need for houses, commerce, factories, schools, hospitals, roads, water, power, and many other so-called civilization needs started to take its toll on the karst region. This time, this was a visible threat. Between 1975 until the year 2000, a fast trend of urban sprawl and infrastructure development unraveled through the karst region, which imitated what was happening in other parts of the Island where the environment was not as vulnerable as the karst region. These developments threatened the natural values of the karst.

As a result, Ciudadanos Del Karso—CDK (In English, it would mean Citizens of the Karst)—was born in 1994, out of the need to protect the karst region. As a nonprofit, nongovernment organization—NGO, we undertook an effort to protect the karst. Our main objectives were research, public education, citizen’s actions to protect the karst, and purchase of land for conservation. In the first ten years after its foundation, CDK had achieved several goals. For example, four educational posters were made available free for public and private schools on karst processes and its vulnerability, its bats species, and herpetofauna. There was a 25-min video called Las Raices del Agua (the origins of our water) which was provided free of charge to the Commonwealth’s public TV station and schools. In addition, we worked with the Puerto Rico Planning Board to include the protection of the Karst in what was known as the Public Policies for Puerto Rico’s Land Use Plan, where the importance of the protection of the Karst was set as a public policy for the first time. We also helped to protect approximately 10,000 acres and stopped some projects in the karst region through the courts. Thanks to the collaboration of the US Forest Service’s International Institute of Tropical Forestry, whose headquarters are in Puerto Rico, we helped publish, in English and Spanish, The Puerto Rican Karst—A vital Resource, the most comprehensive publication on the island’s karst region to this date. Many other actions were undertaken as well, which helped citizens on the island to finally incorporate and understand the term “karst” as part of their common or daily speech. This was accomplished, especially, by publicizing our main motto: “Karst is water and life”.

Yet that was not enough. Therefore, we pursued legislation to protect the karst. I do not intend to talk about all the process that resulted in the law and the regulations that protect the karst in Puerto Rico, so I will summarize it. The law took us at least one year to get approved in the Legislature of Puerto Rico and it was approved in August of 1999, as Law 292, Law to Protect the Karst Physiography of Puerto Rico. Law 292 gave the Department of Natural and Environmental Resources—DNER, two years to prepare a study that would set aside the critical areas of the karst region that needed to be conserved based on its ecological, geological, or hydrological importance. The Planning Board was then required to use this study as the basis to delimit the region of the karst that had to be set aside for conservation through a land use plan and other regulatory means. Nothing happened within the two years that the law gave these agencies to prepare the study and adopt a land use plan. Therefore, the only recourse we had was to request a *mandamus,* or order to act, against the DNER and the PR Planning Board. In this effort, we were legally represented by the Environmental Law Clinic of the University of Puerto Rico Law School. The Commonwealth’s courts granted us our petition. However, even with the court order and supervision, it took until the year 2014 for the Commonwealth government to comply with their legal responsibility, finally establishing a specific land use framework to protect the karst. Close to 33% of the karst within Puerto Rico received the highest degree of protection possible under the law.

2 Beyond the Laws and Regulations

An article published on December 6 of this past year by a local newspaper brings to the reader’s attention a study made by Puerto Rico’s Environmental Quality Board in which it found that in several of the water reservoirs and in several rivers of the island, the agency found concentrations of antibiotics, cosmetics, steroids, insect repellents, and other contaminants. In 80% of 14 rivers sampled, they found many pharmaceutical products, hormones, and other contaminants. In this cornucopia of contaminants, there is the potential that any of them or a combination of them can cause genetic disorders, cancers, hormone disruption, reproduction problems, etc., in all forms of life.

The article explains how many of these contaminants just go through the water treatment plants that provide our drinking water. But in the story, it advises us that there is a possible technical solution: nano-filters. Who knows if this is another techno fix and at the end we have another problem as a result of trying to fix the existing one. Other example of techno fixes is the proposed technologies for scooping the excess CO_2 from the atmosphere, reducing the threat of global warming.

After such a strenuous course to get legal protection for the karst, we have to ask ourselves if we are ever going to achieve the necessary protection for nature, including the karst. It seems nonsensical but we are trying to protect nature from ourselves. We have seen some of the problems of groundwater contamination in the karst, but we are just trying to catch up with the chemical industry, agro-industry, and with many other contaminants and in the process trying to find out which are hazardous to life. So far, the agencies such as the Environmental Protection Agency or the Health Department have been reactive, that is, they act only after a chemical is found to be harmful and many lives have been lost or persons become very ill, or other life forms have been threatened.

Industry's vast financial resources, besides being used to make us consume far beyond our needs, are also used to deny claims against them or confuse the public whenever it has been denounced as affecting human health or life in general. Just as an example, how can we forget the denial of the tobacco industry that smoking had anything to do with cancer, just the same way the chemical industry did with DDT. Or the fossil fuel industry, by trying to convince us that CO_2 has anything to do with global warming. Or more recently, that fracking is not contaminating the water supply on which many communities in the USA depend.

So here we are, after several centuries of thinking that the world we live in has to be fixed, with the vision that we are the center of the world and infinite growth is possible, labeling it by the term progress. But this progress so far has been totally anthropocentric, ignoring the world's life evolution and the laws of nature that govern it. By laws of nature I mean the physical and biological world, as science has explained it through research.

My point is that this planet has approximately 4.5 billion years, and life has been present over 3.5 billion years. So we have over 3.5 billion years of continuous evolution, biochemical experiments of what works according to the conditions in the different geological eras. All life forms that can adapt and reproduce are expected to continue to live in their geologic time.

Yet most of society forgets about the evolution of life and in many cases many even deny it. Meanwhile, the pharmaceutical or agrochemical industries come up with a complete arsenal of chemicals, in order to try to control bacteria, insects, and plants. Bacteria, that is, construed harmful to a herd of animals or to humans or to plants, or insects that we have been taught that are disgusting, unhealthy or that are considered a pest for farm products, or the weeds that invade the agriculture field, are systematically trying to be controlled or exterminated.

And we are told that they are safe and nonhazardous. That they would only act on an intended purpose, which is to kill something that has life. But how, and this is something that we should always ask ourselves, can they be safe when, the basic structure of life which is DNA (i.e., double helix) is shared among all living organisms. The code or sequence of DNA (instructions for our cells) is different in different life forms. Even so, our DNA is likely more similar to plants than different. For example, we share approximately 60% of our DNA with a banana plant, birds, and insects. With other mammals, it can be between 75% to as high as 96%.

Many things have happened in these endless wars of humans against our "enemies", but I want to concentrate on two of them. One is that biological evolution shows that eventually the bacteria, insects, or weeds will evolve and become resistant to our latest invention. Trying to get rid of them, when we share part of the DNA, is a prescription to more damage to life of which we are part.

The second one is that human laws can never be above the physical or biological laws of Nature. In Nature with capital N or in the biosphere, everything is interconnected and interdependent between the abiotic and biotic. Because of our anthropocentric world view, many of the environmental and health problems that we face today are a direct result of ignoring this reality. Therefore, living organisms and humans are subject to the laws of nature, regardless that our human laws ignore this fact. And not taking into account the laws of nature is one of the reasons we have ourselves in such a detrimental environmental condition.

Human laws are a societal construction and through centuries they have changed. Slavery and serfdom were legal, colonialism was legal, denying men the right to own property or women the right to vote was legal, so as it was with apartheid for many years. In our legal system, nature is seen as a provider of resources for humans and we have come up with some environmental laws to address some of the problems we have caused. Legal systems are social constructions of those that have power, and not really a source of justice, although we have thought that *law* and order exist for the purpose of establishing *justice*.

Ignoring the laws of nature was possible, when the world population was smaller. But not any longer, with 7.4 billion and growing, with all the needs and with all the media creating consumer societies.

We have to adopt laws that are biocentric and environmentally ethical, because in the end, we can only survive as a species if we live according to nature.

Looking beyond the box: **Can we protect Nature as long as we treat it as human property?**

3 Efforts to Recognize Rights and Intrinsic Value of Nature

Nature can exist without humans, but we cannot exist without Nature, yet we ignore this at our peril. We can rest the case, on who has the upper hand in life.

The rights of nature idea acknowledges that nature, in all its life forms, has the right to exist, persist, maintain, and regenerate its vital cycles. The concept recognizes that other beings—plants, animals, fungi, entire ecosystems—have rights, just like humans. These other life forms do not just have instrumental value to humans as things to be used. They also have *intrinsic* value; they have worth in-and-of themselves.

So the time has come for us humans to understand that Nature has a right to exist, flourish, and evolve. If we have granted legal rights to corporations, which are a figure of our invention during the last centuries, we should also recognize those that belong to Nature, which has been all the way with us since we are part of it. And I wish to close my lecture with the words of the Senegalese forestry engineer Baba Dioum, who in 1968 said: "*In the end we will conserve only what we love*; *we will love only what we understand; and we will understand only what we are taught*".

Contaminant Transport in Karst Aquifers: Systematics and Mechanisms

William B. White

Abstract

Karst 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 disolutionally 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 narrow pathways instead of spreading into a plume, and 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 gradients 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.

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1 Introduction

In general, contamination threats to karst aquifers are not different from contamination threats to other aquifers. The sources of contamination are the same, but the impacts can be much more severe, particularly in the transmission pathways from contamination source to public water supply. One might say that karst aquifers have the same problems as other aquifers only more so. As a result, water quality issues in carbonate aquifers are an especially important topic that has been widely recognized (Memon and Prohic 1989; Gibert 1990; Field 1992; Green et al. 2006; Mahler and Massei 2007; Afrasiabian 2007; Lindsey et al. 2008), but there is much less information on the detailed transport mechanisms of specific contaminants. The objective of the present paper is to provide an overview of a wide range of contaminants and how these contaminants are transported, stored, and released in karst aquifers.

1.1 Unique Hydrologic Aspects of Karst Aquifers

Discussion of any aquifer begins with a consideration of its permeability, the pathways through which water may move through the aquifer. In the idealized porous media aquifer, the starting point in most textbooks, the permeability consists of the spaces between mineral grains. Thus, the permeability is dictated by the size and packing of the grains and is characterized by a single number, either the permeability (with units of area) or the hydraulic conductivity (with units of velocity). The permeability of karst aquifers is considerably more complicated. It can be described by what has been called the "triple permeability model" (Worthington et al. 2000).

(1) Primary or matrix permeability: The spaces between the mineral grains just as in the ideal porous media aquifers. Many Paleozoic limestones are dense with little matrix permeability; young limestones that have not suffered deep burial and tectonic deformation tend to have a much greater permeability.
(2) Fracture permeability: Karstic rocks tend to be fractured by tectonic forces producing pathways with apertures ranging from tens of micrometers to centimeters. The fracture permeability is highly variable but generally much larger than the matrix permeability.
(3) Conduit permeability. Conduits are disolutionally enlarged continuous pathways that behave hydraulically as pipes or open channels. Caves are fragments of conduits, but pathways too small for human exploration also may function as conduits. An aperture of about one centimeter is the practical boundary between fracture permeability and conduit permeability.

Both domestic and community water supplies in karst regions are obtained from springs and wells (Fig. 1). Karst springs draining purely fracture and matrix systems, as indicated by uniform discharge, lack of turbidity, and small chemical variation, provide reliable water supplies generally of good quality except for high hardness. Springs draining conduit systems have a highly variable discharge, sometime become turbid to muddy after storms, and are at risk from pollutants introduced through sinking streams and sinkholes. Wells drilled in carbonate aquifers only rarely intersect conduits and mostly draw their water from the fractures and in some aquifers, the matrix. Well waters may also be contaminated either directly or because of connections to the conduit system. Thus, in considering contaminant pathways from source to water supply, the interchanges between the different permeability types within the karst aquifer are important.

Aspects of karst aquifers that impact contaminant transport include the following:

Localized inputs of surface water from sinking streams and sinkhole drains with little or no filtration by the soil.
Thin soils and an epikarst that permits rapid draining through solutionally widened fractures.
Localized flow in conduits with little lateral dispersion, thus transmission over long distances with little dilution at the velocities in the range of km/day.
Large apertures and high-velocity turbulent flows in conduits allow transport of particulates and larger fragments of solid contaminants.
Rapid response to storm flows with reversed gradients between conduits and surrounding fractures and matrix.
Contaminants can be stored in the conduit system or in the conduit sediments to be flushed later during storm flows.
Backflooding from flooded surface streams can drive contaminants upstream deep into conduit systems.

1.2 Potential Contamination Sources

The movement and storage of contaminants in karst aquifers must be examined both in terms of the sources of contaminants and by the physical and chemical characteristics of the contaminants. A listing of contamination sources—which could easily be extended—includes the following:

(1) Sewage:
Septic tanks, outhouses, and other disposal systems;
Broken pipes;
Treatment plant outfalls;
Spray fields and wastewater treatment.
(2) Contaminants from agricultural practices:
Manure and other barnyard waste;

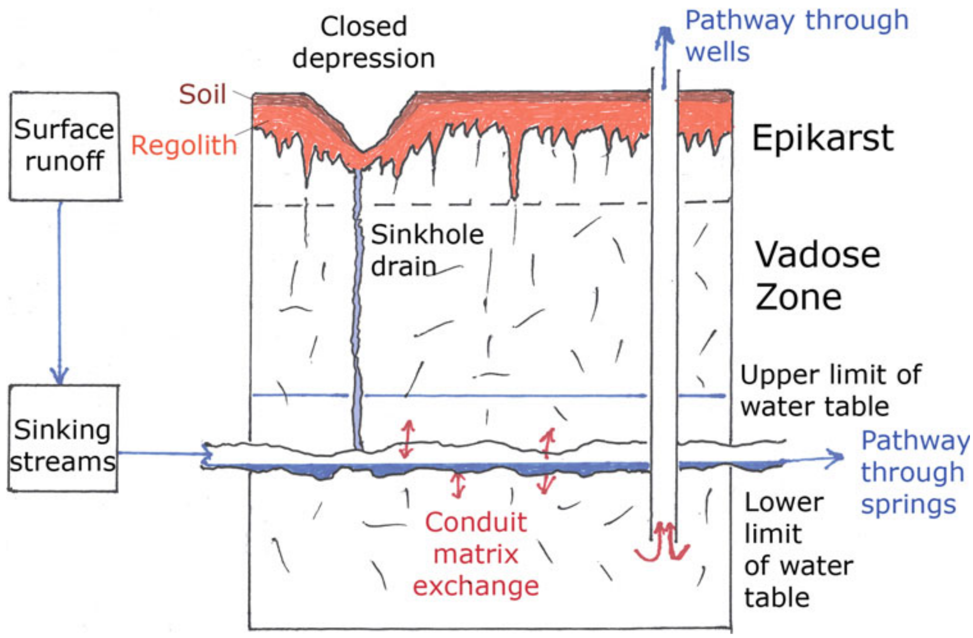


Fig. 1 Sketch showing a generic karst aquifer with its most important subsystems

Lagoons for hog lot and poultry brooder wastes;
Herbicides and pesticides spread on fields;
Discarded agricultural chemical containers.

(3) Municipal and domestic wastes:
Street and parking lot runoff;
Sinkhole dumps;
Sanitary landfills.

(4) Runoff from construction activities

(5) Contamination from highway and rail transportation:
Road salt;
Wrecked rail cars and tanker trucks.

(6) Industrial wastes
Outfalls;
Lagoons and landfills;
Injection wells.

(7) Mine tailings and related wastes
Acid mine waters;
Heavy metal contamination.

Each of these sources may contain a broad range of contaminants. Some of the sources have received extensive research. Others are obvious as possible sources, but few data may exist concerning their impacts.

How contaminants move and are stored and released in karst aquifers depends more on the chemical and physical nature of the contaminants than their sources. There are water-soluble contaminants, liquid contaminants, and particulates, the latter ranging in size from nanometers to meters (i.e., from viruses and bacteria to junk refrigerators).

2 Conceptual Models and Hydrodynamics of Karstic Aquifers

The geologic settings for karst aquifers are highly variable and, as a result, so are their hydrologic and hydrodynamic frameworks (see, e.g., Audra and Palmer 2015). These geologic and hydrologic variables determine much about the transport and storage of contaminants. The sections that follow review only a few of the essential features that impact contaminant transport. Karst hydrology is an extensively developed science, and much more detail is available in books such as White (1988), Ford and Williams (2007), Palmer (2007), and Kresic (2013). With regard to deciding whether a particular aquifer has karstic behavior that would influence contamination risk management, the cautionary tale of Quinlan et al. (1991) is well worth reading.

The subsystems that make up karst aquifers are sketched in Fig. 1. These systems provide the mechanisms as to how water enters the aquifer, how water is transmitted and stored in the aquifer, and how water is discharged from the aquifer. The varying importance and degree of development of the individual subsystems produces the great diversity of hydrologic behavior observed in karst aquifers.

2.1 Allogenic Inputs (Sinking Streams)

Drainage basins are rarely underlain entirely by carbonate rocks so that portions of the basins will be drained by surface streams. Surface storm runoff is directed to the surface streams. Some surface streams cross the karstic portion of the drainage basin with minor loss of water into the underlying aquifer while maintaining a surface channel and surface flow. In other streams, the surface channels may be dry except during periods of storm runoff. In many karstic basins, the surface streams are completely captured underground without even a surface channel downstream from the sink point.

The fraction of the overall basin area that is drained by sinking streams is a useful characterizing parameter for karst aquifers. Any surface runoff in the basin is ultimately carried into the aquifer. This is an important consideration in urban drainage basins where street runoff and storm drains may discharge into sinking streams. Sinking streams are an important source of injected contamination because the sink point is often an open cave entrance (or a debris-clogged cave entrance). Surface runoff can carry agricultural chemicals, road salt, and any trash from along the stream banks directly into the aquifer.

2.2 Closed Depressions and the Epikarst

Infiltration of CO_2-rich water into carbonate rock terrains gradually dissolves roughly bowl-shaped depressions (Fig. 2a). The term "sinkhole" is used in a very broad sense to describe closed depressions created by a variety of dissolution, collapse, and soil-piping processes. Sinkholes disrupt overland flow and act as localized catchments which inject water into the underlying aquifer, typically through a widened fracture or open drain at the bottom. Sinkholes are often soil-filled, sometimes to the level where there is little expression of the sinkhole at the land surface (Fig. 2b). Sinkholes are often considered the signature landform of karst regions, but the absence of sinkholes is not evidence for the absence of karstic transport processes in the subsurface.

Karst lands are typically covered with soil and regolith of widely varying thickness. Some regions have soil and regolith of sufficient thickness to completely mask the bedrock surface beneath. Other regions have bedrock ledges protruding through the soil (Fig. 3a). In rare situations where the soil and regolith have been removed, the underlying rock surface is found to be highly irregular with deep crevices dissolved along fractures and the intervening rock masses remaining as pinnacles (Fig. 3b). The overall relief from the bottoms of the crevices to the tops of the pinnacles is highly variable but may reach values of ten meters or more. The irregular rock surface along with its regolith in-filling is known as the epikarst (Jones et al. 2003). Some workers include the soil as part of the epikarst and some do not.

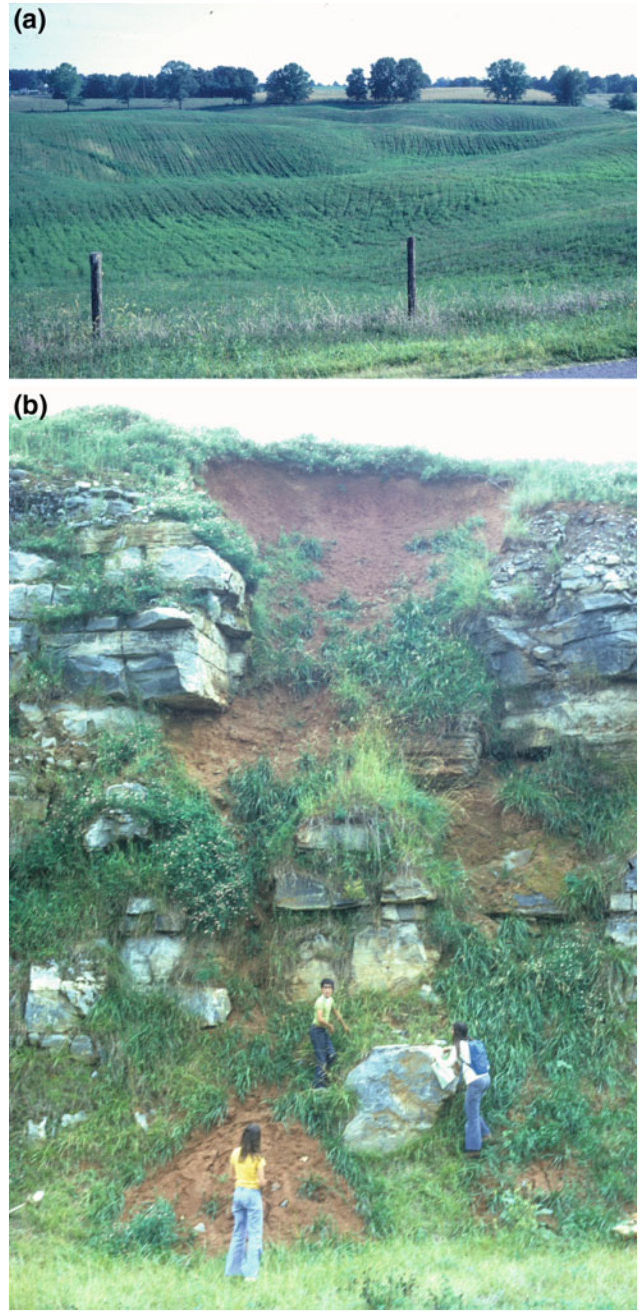


Fig. 2 **a** Closed depressions (sinkholes) on the sinkhole plain, southeast of Mammoth Cave National Park, KY. Photograph by the author. **b** Soil-filled sinkhole exposed in a road cut. Centre County, PA. Photograph by the author

Some include the closed depressions as part of the epikarst and some do not.

The epikarst is a primary recharge source for karst aquifers. Disolutionally widened fractures at the base of the epikarst provide pathways for the rapid injection of soil water and storm runoff into the underlying aquifer. Spills,

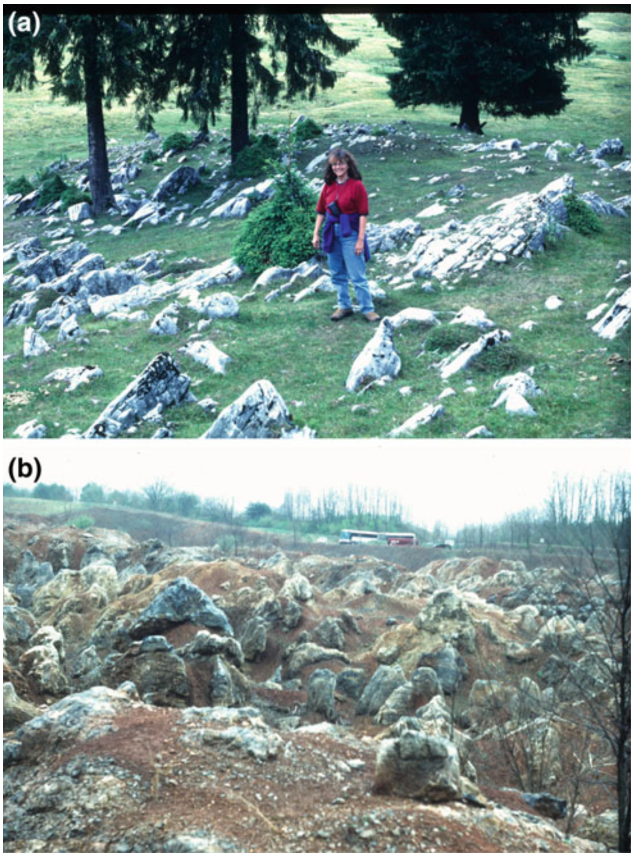


Fig. 3 **a** Projecting bedrock ledges with intermediate soil-filled trenches for the epikarst in the Pădarea Craiului Mountains, Romania. Photograph by the author. **b** The regolith has been stripped from this quarry in the Cumberland Valley near Harrisburg, PA, exposing the pinnacle topography of the underlying bedrock surface. Photograph by the author

agricultural chemicals, and other contaminants on the land surface can, depending on soil thickness, move rapidly into the aquifer. In other situations, the epikarst may serve as a storage reservoir for contaminants.

2.3 The Conduit System

Groundwater moving through soluble rocks dissolves the rock and so tends to localize itself into disolutionally widened pathways. As the pathways enlarge, their hydraulic resistances decrease and flow velocities increase often to the onset of turbulence. This is a runaway process resulting in more and more of the total flux of water being localized in the conduits.

Conduits take on a range of patterns depending on local gradients and sources of water (Fig. 4). Those with a large component of allogenic input tend to be more pipe-like, carrying the sinking stream water from the sink point to the spring. Larger and more complex branchwork systems have multiple recharge sources both from multiple sinking streams and also from closed depressions within the karst. Low gradients and multiple sources tend to produce mazes rather than single or branchwork passages. Mazes that form along bedding plane partings tend to have an anastomotic pattern, whereas those formed along vertical fractures tend to have the network pattern of the fracture system (Palmer 1991). The development of conduit systems is mainly a chemical process, and great progress has been made in computer modeling of conduit development (Dreybrodt et al. 2005).

Not all conduits are caves although most caves are fragments of conduits. However, conduits can be much smaller than caves. The size boundary between conduits and solutionally widened fractures is about 10 mm, dictated by the needed aperture for the onset of turbulence and a shift in dissolution kinetics, and lies well below the threshold for human exploration. Conduits function as pipes or channels. Some lie below regional base levels and are always water-filled. Some have been abandoned by regional base-level lowering. The larger fragments can be examined as dry caves if they happen to have a surface connection that provides an entrance. Many lie close to regional base levels and contain free-surface streams during low flow periods and are completely submerged during flood flow. This oscillation between open channel flow and pipe flow is a factor in contaminant transport.

The conduit system is a most important part of the aquifer system with respect to contaminant transport. It serves to keep injections of contaminants localized instead of spreading into a plume. High flow velocities in conduits mean that contaminants introduced by spills or other accidents will rapidly transit the aquifer and reach water supplies in a matter of hours or days. Under certain conditions, the conduit is self-flushing. Injected contaminants are swept though rapidly. Pulses of contaminants can be modeled, and the movement of dye pulses can be used to test and constrain the models (Field and Pinsky 2000).

2.4 The Primary Porosity and Fracture System

Dense, well-lithified Paleozoic and Mesozoic limestones typically have very low primary porosities. In contrast, Cenozoic limestones that have not been subject to deep burial or tectonic deformation typically have a large primary permeability with interconnected pores and vugs. These are sometimes referred to as telogenetic karst and eogenetic karst, respectively. Most limestones, especially the dense Paleozoic and Mesozoic limestones, are fractured with arrays of joints, joint swarms, bedding plane partings, and faults of various orientations. The fractures are the primary pathways for groundwater movement. Water wells in

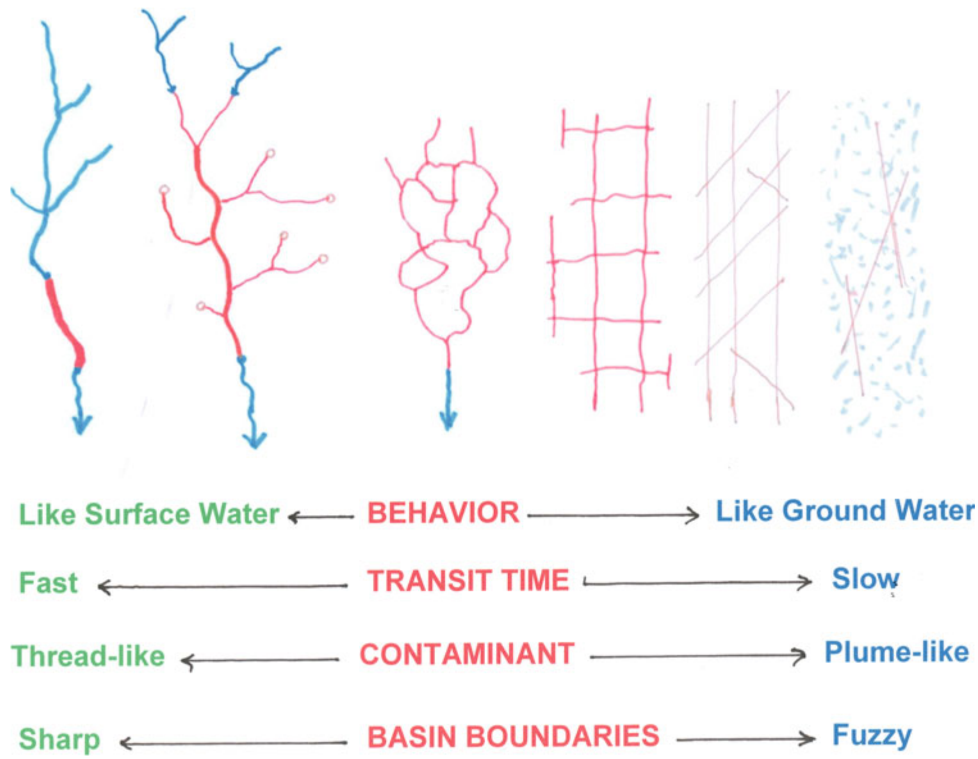


Fig. 4 Cartoon of possible conduit systems

well-compacted limestones are fed by the fractures intersected by the wells. In eogenetic limestones, the primary porosity is a more important component of the flow system. The conduit system acts as a drain, and depending on the fracture and matrix permeability and local gradients, there is a flux of water into the conduit system from the surrounding bedrock.

An examination of four diverse aquifers (Worthington 1999) showed that the matrix and fractures held more than 95% of the storage but that the conduits (called "channels" by Worthington) conducted more than 95% of the flux. Fractures become widened by dissolution so that flow velocities in fractures can be substantial. One set of actual measurements gave values of 1–33 m/day along a single fracture with values of 2–388 m/day along fracture networks (Novakowski et al. 2006). The interchange of water between the conduits and the surrounding bedrock lends itself to modeling (i.e., Bodin et al. 2007; Faulkner et al. 2009). Conduit flow is not intrinsically different from surface stream flow, except that in the case of submerged conduits, exchange of water with the fractures and matrix can take place around the entire perimeter of the conduit and not just on the channel bottom. Models for stream/groundwater exchange are also applicable (Hussein and Schwartz 2003). The difficulty with interchange modeling is the difficulty in determining accurate values for the fracture and matrix permeability and the local gradients.

2.5 Importance of Storm Flow

Storm water enters porous media aquifers by infiltration through the soil, regolith, and the pore spaces of the bedrock in the vadose zone. The pathways have a high hydraulic resistance so that the excess water from most storms appears as overland flow into surface streams and the aquifer response is subdued. Storm water enters karst aquifers from flooded sinking streams and by rapid surface runoff into closed depressions. The storm water moves rapidly through the conduit system, and the increase in velocity is often sufficient to mobilize sediment piles and other solid debris that may have been swept into the system by earlier storms. Spring discharges rise rapidly and may become turbid or muddy. Storm flows are important for mobilizing contaminants that may reside in sinking stream basins, on the land surface, or in the epikarst.

The low hydraulic resistance of the conduit system creates a trough in the water table with the gradients in the surrounding bedrock directed toward the conduit (Fig. 5). During storm flow, the conduit may flood converting an open channel flow system to a pipe flow system. The water table trough fills, the water table rises, and the gradients in the matrix may reverse with conduit water moving into the matrix. On the land surface above, a loosing stream may become a gaining stream. Closed depressions may be flooded by water moving up the drains and forming temporary ponds. Springs that drain directly into surface streams may

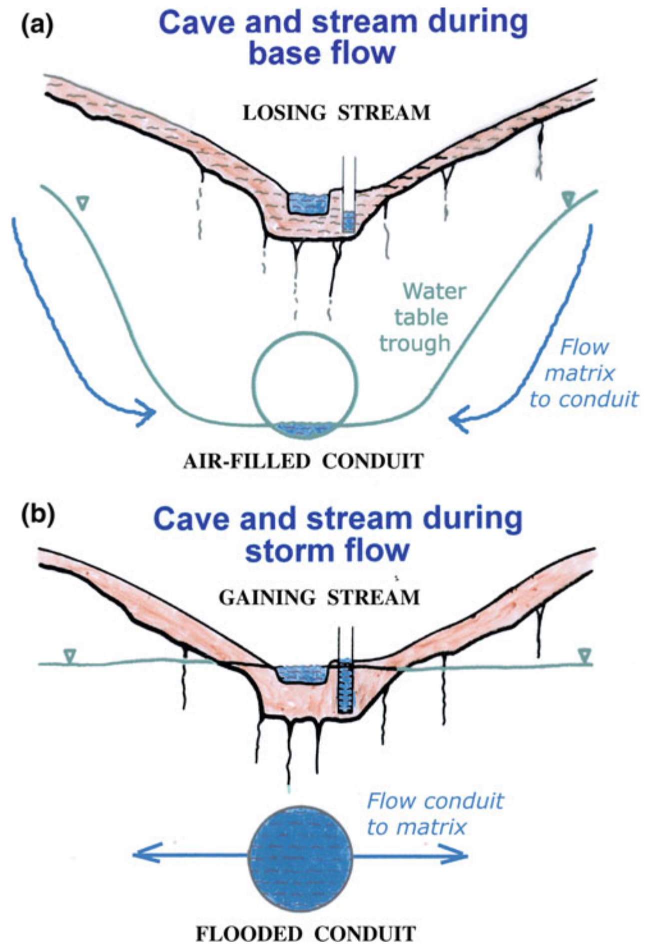


Fig. 5 Cartoon showing effects of storm flow on karst water table and on the exchange of water between conduit and the surrounding bedrock

exhibit reversed flow if the surface stream floods. Base-level backflooding can carry surface water long distances up the conduit if the overall conduit gradient is low.

2.6 Groundwater Basins

Surface waters are characterized by their drainage basins. From any chosen location (gauge point) on a surface stream, it is almost always possible to draw a boundary that follows the drainage divide to the headwaters of the stream and back down the other side to return to the chosen location. The boundary defines the divide between runoff that flows into the stream of interest and runoff that flows into some adjacent stream. In contrast, aquifers are usually characterized by their thickness but rarely by their lateral extent. In karst aquifers, the conduit system takes the place of the surface stream, and the spring where the conduit water emerges becomes the gauge point. By water tracing and by mapping the potentiometric surface, it is sometimes possible to determine specific groundwater basins for karst aquifers with well-developed conduit systems as demonstrated by the pioneering work of Jones (1973) and Quinlan and Ewers (1989).

Unlike surface water basins, karst groundwater basins may have overflow routes that are activated during storm flow. Basin boundaries have their best definition in systems with moderate to high gradients where conduit flow paths behave most like surface streams. Low gradient aquifers with network-like or poorly developed conduit systems tend to have poorly defined or fuzzy boundaries whose position shifts depending on recharge (Fig. 4). Contaminants introduced into a groundwater basin tend to remain in the basin, and their threats to water supplies can be predicted. Prediction of contaminant behavior becomes more problematic for groundwater basins with poorly defined boundaries. In both cases, storm flow could take contaminants along unexpected pathways.

2.7 Pathways to the Public

Water is utilized by the public by means of privately owned wells drilled into karst aquifers, by high-production wells drilled for public water supplies, by springs on private lands used as individual water supplies, and by large karst springs tapped for public water supplies. Small private water supplies are usually untreated except possibly a filter to remove particulates. Public water supplies receive such treatment as required by regulation but those drawing their water from springs or wells are likely to provide less treatment than water supplies drawn from rivers or surface reservoirs. The additional contamination threats to karst water supplies follow from the unique characteristics of karst hydrology as outlined above. There is the rapid injection of surface water through sinkholes and sinking streams with little filtration by the soil. There is the possibility of storm inputs flushing stored contaminants long after the initial contamination event. There is the possibility that reversed gradients during flood events will contaminate wells that are not otherwise contaminated. The details of all of these threats to the public are determined by both the characteristics of the aquifer and the specific physical and chemical characteristics of the contaminants.

3 Contaminated Recharge: Water-Soluble Contaminants

Water-soluble contaminants are materials which would be taken completely into solution at all concentrations likely to be found in the environment. Water-soluble inorganic compounds include ammonia and the nitrate ion, mostly derived from human and animal wastes and perhaps the most widespread of inorganic contaminants. Water-soluble contaminants include other inorganic ions such as chloride and sulfate as well as some highly toxic species such as cyanide ions derived from some industrial wastes. Some organic compounds are also water soluble such as alcohols, carboxylic acids, phenols, and some agricultural chemicals. There are hundreds of organic compounds produced by the chemical industry that are found in consumer products and are thus found in landfill leachates, septic tanks, and treatment plant outfalls. The human population ingests incredible quantities of biologically active compounds ranging from vitamins and pain killers to extremely potent prescription medications designed for a great variety of health issues. Portions of these compounds pass unmodified through the human body, through sewage treatment facilities, and into the environment.

3.1 Chlorides and Other Brine Constituents

The chloride ion, Cl^-, is not particularly toxic with a drinking water standard of 250 mg/L and that only because higher concentrations make the water taste salty. Chloride is a common minor component of karst waters with typical concentrations from a few to a few tens mg/L. Most chloride salts are water soluble, so Cl^- is considered a conservative ion with no possibility of precipitation within the aquifer. The two main sources of excess chloride are seawater intrusion in coastal areas and runoff from road salt.

In more northern regions, the primary source of excess chloride in aquifers is salt placed on highways for ice removal. As traffic on streets and highways has increased, safety considerations have required greater and greater applications of salt to keep highways clear of snow and ice. Winter thaw events and spring rain events dissolve the salt and carry it away. In karst areas, "away" often means drainage into sinkholes or sinking streams, thus introducing the salt into the karst aquifer. A study of the Salt Creek Basin in the greater Chicago, Illinois area (Saleem 1977) showed chloride levels in an entire fractured dolomite aquifer rising continuously over the period of record.

3.2 Seawater Invasion

Conduit systems developed in coastal carbonate aquifers during Pleistocene sea-level minima so that these conduits now lie well below sea level and often discharge from off-shore springs. Open conduits in coastal aquifers permit seawater to penetrate inland driven by tides, ocean currents, and storm surges. Saltwater mixing with freshwater from the interior can discharge to the surface again as brackish springs. Saltwater intrusion is a long-standing problem for coastal aquifers (Stringfield and LeGrand 1969) and has been widely investigated with many of the investigations focusing on the mechanisms by which saltwater can mix with freshwater moving toward the coast (Fleury et al. 2007). Investigations and modeling of how seawater can produce brackish springs as much as several kilometers from the coast have been made in Greece (Arfib and de Marsily 2004; Maramathas et al. 2006) and France (Drogue and Bidaux 1986) among many others. Density differences and the venturi effect are both functional mechanisms. A remarkable example is the Greek Island of Cephalonia where seawater sinks on the southwestern side of the island and re-emerges at a spring on the northeastern side, 15 km distant (Drogue 1989).

More important than the natural saltwater intrusions, are the saltwater intrusions caused by removing freshwater from aquifers in coastal areas. Overpumping wells lower the hydrostatic head of the freshwater lens allowing seawater to rise into the well field. South Florida which is heavily dependent on groundwater from the Biscayne Aquifer has found it necessary to move its well fields landward as increased salinity made existing wells unusable.

3.3 Nitrate, Nitrite, and Ammonia

Nitrogen is an essential component of proteins and other plant and animal compounds in which the nitrogen occurs in reduced form as amino acids. Breakdown of organic material in manure piles and other decay sites produces reduced nitrogen as ammonia, NH_3. It is this compound that gives barnyards part of their characteristic odor. Ammonia hydrolyses in water to form the mildly alkaline ammonium hydroxide which in turn dissociates to form the highly water soluble ammonium ion, $NH_4{}^+$.

$$NH_3 + H_2O \leftrightarrow NH_4OH \leftrightarrow NH_4{}^+ + OH^-$$

Ammonia and ammonium oxidize rapidly in the oxidizing surface environment through microbial-catalyzed reactions to the nitrite and ultimately the nitrate ions.

$$4\,NH_4{}^+ + 6\,O_2 \rightarrow 4\,NO_2^- + 8\,H^+ + 4\,H_2O \quad \text{[Nitrosomonas]}$$

$$4\,NO_2{}^- + 2\,O_2 \rightarrow 4\,NO_3{}^- \quad \text{[Nitrobacter]}$$

Considering the movement and interchange of nitrogen between the surface atmosphere, plants and animals, the soil, the groundwater system, and eventual discharge of nitrogen into rivers results in an extremely complex nitrogen cycle much of it involving the participation of microorganisms.

All nitrate compounds are highly soluble in water so that at the concentrations found even in highly contaminated groundwater, the nitrate ion is conservative. There are no precipitation reactions that will remove nitrate from solution although there is some evidence for denitrification in the soil (Panno et al. 2001). The concentration of nitrate ion observed at karst springs will be determined by the concentration at the source adjusted for dilution by other water sources merging in the main conduit. For this reason, nitrate concentrations have been proposed as tracers for contamination sources (Mahler and Garner 2009; He et al. 2010).

Many measurements have been made of the nitrate concentrations in karst springs including examples from Pennsylvania (Kastrinos and White 1986), Indiana (Wells and Krothe 1989), Wisconsin (Reeder and Day 1993), Illinois (Panno and Kelly 2004), Arkansas (Peterson et al. 2002; Iqbal and Krothe 1995), Texas (Mahler et al. 2008), Florida, Suwannee River Basin (Katz et al. 1999), Florida, the Woodville Karst Plain (Katz et al. 2004), and in France (Nebbache et al. 2001). The EPA-specified drinking water standard for nitrate is 45 mg/L expressed as NO_3^- and 10 mg/L expressed as nitrogen. The natural background in most karst waters is in the range of a few mg/L (Panno et al. 2006), but nitrate contamination is so widespread that few springs or streams achieve such low values. Contaminant sources typically bring the concentration up to a few tens of mg/L NO_3^-, but there are relatively few springs that actually exceed the drinking water standard.

The sources for nitrate contamination were found to be the usual suspects: (1) nitrogen-bearing fertilizers, usually ammonium nitrate; (2) manure either from barnyards or manure spread on fields; and (3) septic tanks. Of these, fertilizers, either chemical or manure, are the most important source. There is a rough correlation between nitrate levels in karst springs and the fraction of the spring basin used in agriculture (Kastrinos and White 1986). Measurement of the $^{15}N/^{14}N$ and $^{18}O/^{16}O$ ratios allows a determination of the nitrate source (Panno et al. 2001; Katz et al. 2004). Nitrate derived from manure and sewage has a higher concentration of the heavy isotope than nitrate derived from fertilizer.

Nitrate levels in conduit-fed springs tend to be highly variable because of the either flushing or dilution due to storms, whereas nitrate levels in fracture-fed springs tend to be relatively constant although the actual nitrate levels vary greatly from one spring to another. Although storm water dilution has been observed, it is actually a pulse of nitrate emerging from springs during storm flow that is frequently observed. The nitrate concentration tends to ride the hydrograph, reaching a maximum during peak flow (Fig. 6). In northern climates, frozen ground tends to hold the nitrate so that concentrations in springs are lower in the winter. This is followed by a pulse of released nitrate in the spring when the ground thaws (Reeder and Day 1993). The background concentration represents nitrate leached from the soil, whereas the storm pulse represents nitrate from the surface flushed through large pores in the soil and open fractures in the epikarst (Wells and Krothe 1989; Peterson et al. 2002). In the case of the north Florida springs, the concentration of nitrate compared with groundwater ages match changes in fertilizer use over the age record examined (Katz et al. 1999).

3.4 Agricultural Chemicals

Modern agriculture depends heavily on pesticides and fungicides to control insects and other organisms that attack crops. No-till farming also depends heavily on herbicides to control weeds and clear ground for planting. Chemicals sprayed on fields are intended to do their job of controlling pests and weeds and then degrade before infiltrating in the groundwater. In karst regions, the chemicals can be flushed through thin soils, and, once through the epikarst, they move rapidly into the groundwater system and can be detected at springs (Currens 1995). Attempts have been made to model the transport of agricultural chemicals through the soil (Roulier et al. 2006). Once in the karstic vadose zone, there is little evidence for further degradation of the chemicals.

Penn State's research farms are located on Ordovician limestones which are drained by a master conduit that discharges at Rock Spring. The spring was monitored for agricultural chemicals during 1992 (Underwood 1994). One herbicide, atrazine, used extensively for weed control in corn cultivation, exhibits a storm pulse (Fig. 7). Since both flow and contaminant concentration increase during storm flow, the actual flux of agricultural chemical discharged from the spring is the convolution of the hydrograph, $Q(t)$, and contaminant chemograph, $C(t)$, integrated over the storm pulse.

$$\text{Flux} = \int Q(t)C(t)\mathrm{d}t$$

It seems likely that agricultural chemicals remaining on the croplands in karst are flushed by storm flow before they can degrade, reach the conduit, and move rapidly through it to the spring.

3.5 Pharmaceuticals

Large quantities of vitamins, antibiotics, pain killers, and subscription medicines are consumed by humans. A substantial fraction of these compounds pass through the human body and into the waste disposal system. Even larger quantities of growth hormones and antibiotics are fed to cattle and poultry as a means of maximizing yield.

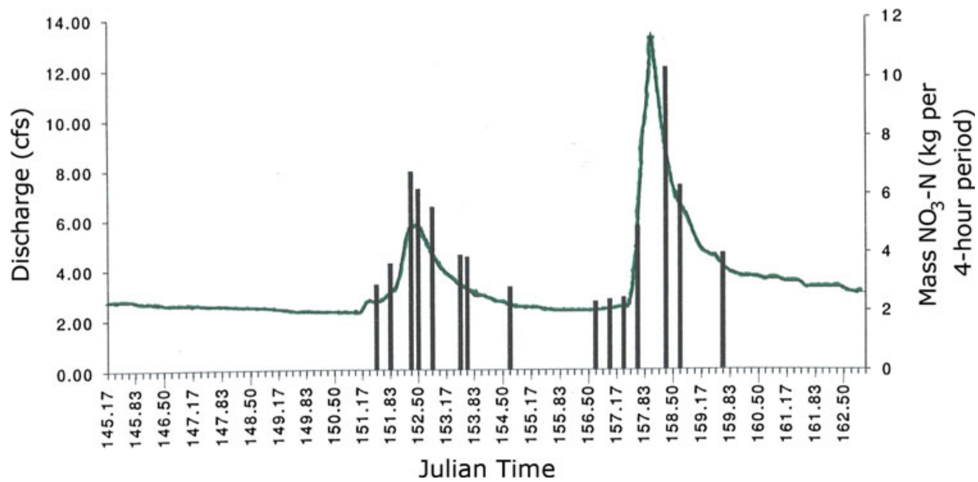


Fig. 6 Nitrate loading in kg/four-hour period calculated from nitrate analysis of spring water superimposed on the discharge hydrograph of Rock Spring, Centre County, PA. Data collected through May–June storm events in 1992. Adapted from Underwood (1994)

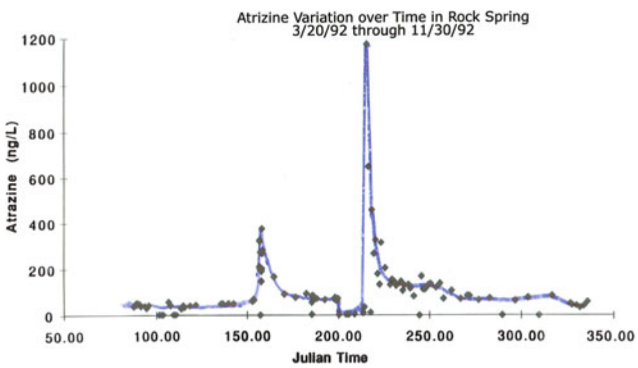


Fig. 7 Chemograph for atrazine concentration in Rock Spring, Centre County, PA, over the period March to November, 1992. Adapted from Underwood (1994)

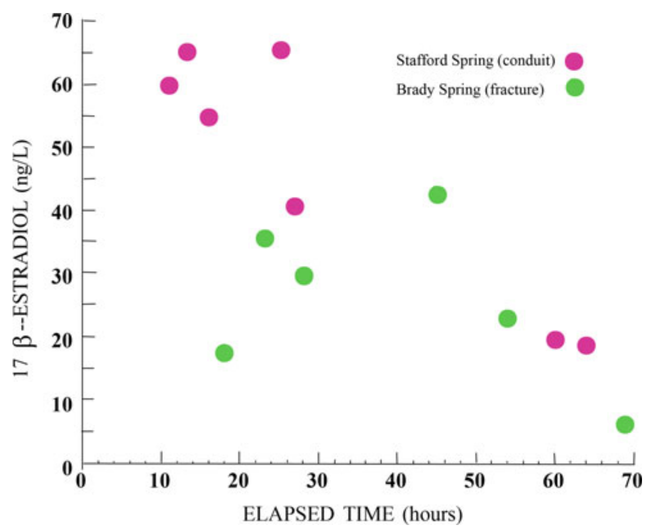


Fig. 8 Concentrations of 17 β-estradiol following a storm event in two northwest Arkansas springs. Data from Peterson et al. (2000)

A substantial fraction of these compounds also pass through the animals and are incorporated into the manure. In karst regions, human or animal waste that is injected into the karst drainage system can be swept through the system rapidly and reach springs or wells before there is time for the compounds to degrade. Biologically active compounds can have an adverse effect on aquatic organisms in cave and surface streams. The pharmaceuticals ibuprofen and diclofenac were found in the treated wastewater in southern Germany (Einsiedl et al. 2010). Both made their way to a karst spring through sinkholes and pathways through the fractured vadose zone with a total transit time of 4.6 years. Ibuprofen was found to degrade over this time period but diclofenac did not.

A pharmaceutical of considerable interest is the growth hormone 17 β-estradiol widely used in the poultry and beef industry and known to produce mutations in aquatic organisms. The hormone was found in five springs in northern Arkansas (Peterson et al. 2000). Data for two of these springs (Fig. 8) measured in response to a winter storm event show an irregular response from Brady Spring, a diffuse flow spring, and a rapid falloff from Stafford Spring, a conduit spring. Similar results were found in eight springs in southern Missouri where concentrations of 17 β-estradiol ranged from 13 to 80 ng/L (Wicks et al. 2004). The measured concentration of the hormone in the pore waters of cave sediments indicated that the compound is relatively stable in the cave environment (Peterson et al. 2005).

4 Water-Immiscible Liquids

Light, non-aqueous phase liquids (LNAPLs) are those that will float on water. Gasoline, diesel fuel, jet fuel, home heating oil, and raw petroleum are common examples. Dense, non-aqueous phase liquids (DNAPLs) will sink in water. Mostly these are chlorinated (or brominated) compounds. They include such low molecular weight, relatively volatile compounds as methylene chloride, CH_2Cl_2, trichloroethylene, C_2HCl_3 (TCE), and perchloroethylene, C_2Cl_4 (PCE), as well as higher molecular weight, relatively nonvolatile compounds such as polychlorinated biphenyls (PCB's)

Although non-aqueous phase liquids are described as immiscible and, indeed, are immiscible when present in large quantities, they are not entirely insoluble. They also have a finite and sometimes considerable vapor pressure at nominal groundwater temperatures. A few examples are given to illustrate the range of values. The main aromatic constituents of gasoline, referred to collectively as BTEX, have solubilities ranging from 1780 mg/L for benzene to 150 mg/L for ethylbenzene (Table 1). Some typical chlorinated compounds (Table 2) likewise display a wide range of solubilities and vapor pressures. The behavior of non-aqueous phase liquids in karst aquifers is guided in large part by these physical properties.

4.1 Light Non-aqueous Phase Liquids (LNAPLs)

Petroleum and its products have received much of the attention because there is so much of it. Petroleum is transported from wells to refineries through pipelines and in railroad tanker cars. Gasoline, kerosene, diesel fuel, and heating oil are transported everywhere by pipelines and tanker trucks. Accidents are inevitable, and some of them will be in karst regions. Instances are known where a wrecked tanker truck dumped its contents into a sinkhole. There are other instances where leaking pipelines or storage tanks have lost so much product that there is a lake of hydrocarbon floating on the water table. Many of the site investigations and remediation attempts address the basic spill problem (e.g., Fels 1999; Schaezler et al. 2001; Stephenson et al. 2003). The task is made difficult by the complex pathways followed by the hydrocarbons as they move through the subsurface. These pathways are described as "pseudoplumes" by Ewers et al. (2012).

LNAPL spills in karst terrain often disappear quickly, swept underground by sinking streams or draining into sinkholes. However, the spill may or may not appear rapidly at a nearby spring. Sometimes, the contaminant disappears underground and cannot be found. The conceptual model of Ewers et al. (1991) shows the possibilities. In the deep conduit scenario (Fig. 9), the conduit is completely water-filled. There are various sites for the storage of hydrocarbons that may be spilled on the land surface. Product that spills into a sinkhole (a) flows down the sinkhole drain until it reaches the water table where it remains floating. Product that enters the conduit upstream and is carried along by the stream will rise into any available ceiling channels and be trapped there (b). LNAPL spilled on the land surface or leaking from pipes or storage tanks buried in the regolith penetrate downward through the epikarst where they may be stored in the regolith itself (d), or percolate into solution cavities developed along fractures or bedding planes at the base of the epikarst (c). In situations c and d, the LNAPL remains stored in the epikarst and does not reach the water table. Of course, there will be a continued flushing of these pockets of LNAPL due to rainfall percolating through the epikarst.

The conceptual model is rather different if the master conduit lies close to the water table (Fig. 10) so that during low flow periods, water moves through sections of the conduit as a free-surface stream. LNAPL floats on the surface stream and moves down stream at the same rate as the water. Shallow conduits contain a range of obstacles—sediment banks, masses of flowstone, and breakdown. Breakdown is formed by ceiling collapse and can act as a somewhat permeable dam. Water ponds behind the breakdown, draining through openings at the bottom of the breakdown pile. The LNAPL is trapped, floating on the pond. Shallow conduits are often undulating, with reaches of free-surface stream and reaches that are always completely flooded. The final sump is also a trap for LNAPL. The LNAPL remains, floating on the ponds, until the next storm surge flushes the system, an event that may take place long after the original spill.

Conduits generally create a trough in the water table so the LNAPL contamination in the conduit tributaries and in the fracture system tends to migrate toward the master conduit. During flood flow, the trough fills and conduits with free-surface steams shift into a regime of pipe flow. Ponded LNAPL is lifted with the rising water and pressed against the ceiling. Any pockets in the ceiling will form traps for the LNAPL just as in the deep conduit model. If the ceiling is tight, the LNAPL is forced through the obstructions as piston flow. A slug of LNAPL then continues down the conduit. For this reason, spills of LNAPL do not necessarily appear at the karst springs immediately after the spill.

Table 1 Solubilities for BTEX components of gasoline (LNAPLs)

Compound	Solubility (mg/L)
Benzene	1780
Toluene	500
0-Xylene	170
Ethylbenzene	150

Data from Fetter (1999)

Table 2 Solubility and vapor pressure of some chlorinated solvents (DNAPLs)

Compound	Solubility (mg/L)	Vapor pressure (Torr at 20 °C)
Methyl chloride	20,000	349
Chloroform	8000	160
Carbon tetrachloride	800	90
Vinyl chloride	1.1	2660 (gas)
Trichloroethylene (TCE)	1100	60
Tetrachloroethylene (PCE)	150	14

Data from Fetter (1999)

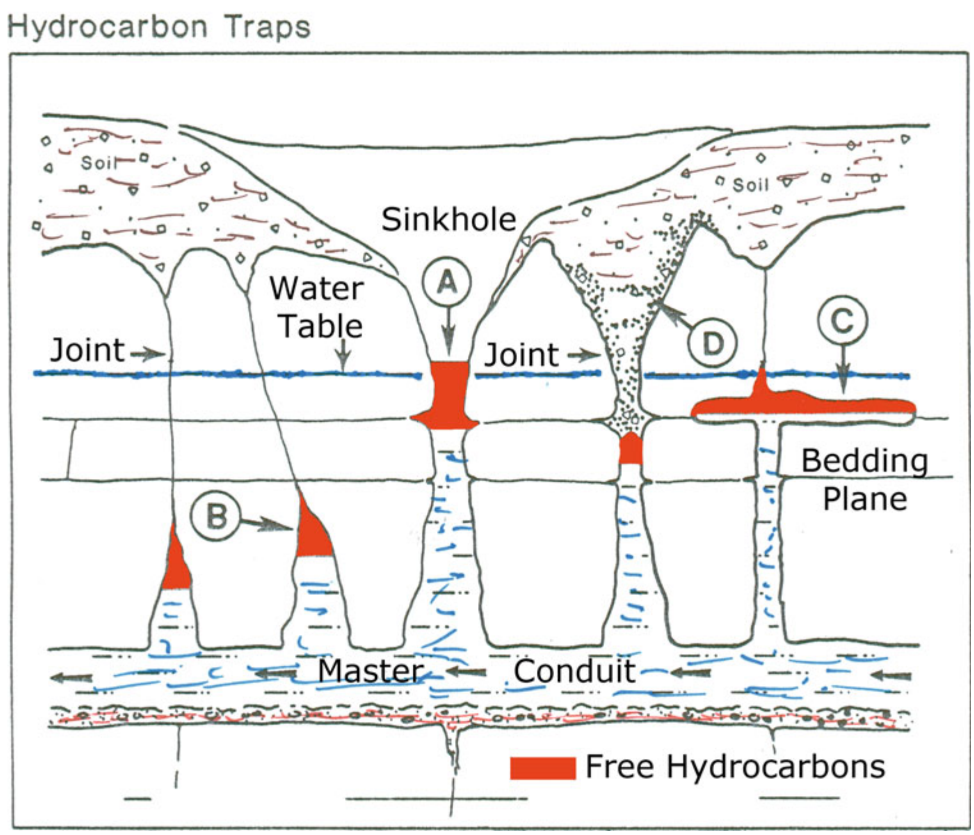


Fig. 9 Conceptual model for the injection and storage of LNAPLs into a karst aquifer with a deep, continuously pipe-full conduit. Adapted from Ewers et al. (1991)

If the ceiling is not tight, fractures permit either liquid LNAPL or fumes from the ponded LNAPLs to migrate upward to the surface. During periods of storm flow, the piston effect of the rising water pushes a higher concentration of fumes to the surface. When houses and other structures are built on the epikarst, particularly if excavations have gone down to top of rock, fumes may enter houses where they can be an explosion hazard and cause health problems for the inhabitants. Such a major health hazard was created in Bowling Green, Kentucky, where a variety of toxic chemicals were carried under the city by the stream in Lost River Cave. The health risks from toxic fumes were sufficient to produce an EPA emergency response and require fume remediation for a number of homes and schools (Crawford 1984; Stroud et al. 1986)

Many common light hydrocarbon compounds have substantial solubilities and vapor pressures. For accumulations of LNAPL ponded behind obstructions in conduits, the continuous sweep of freshwater beneath the pool will eventually dissolve and remove the pool. Differential solubility will change the composition of pools and change the mixture of compounds. Likewise, the ponded LNAPL will gradually evaporate because of the vapor pressure of the compounds. In the process, of course, the air-filled cave passages become contaminated with hydrocarbon fumes. The turnover in cave air due to barometric changes will eventually flush out the contaminants but while they are present they are a substantial hazard to cave explorers, more so in the early days of exploration with open-flame carbide lamps. Gasoline and other hydrocarbon products contain a

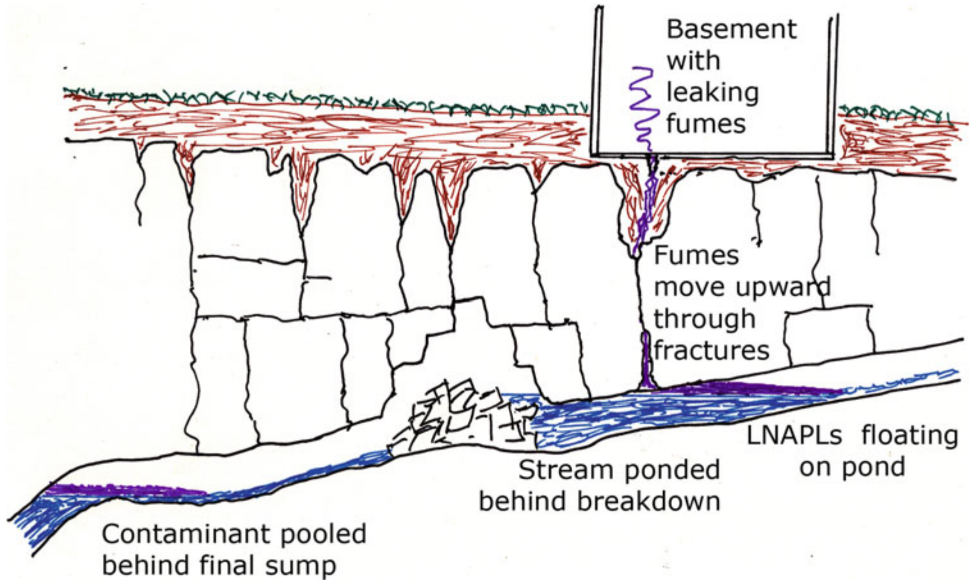


Fig. 10 Conceptual model for transport and vaporization of LNAPL in a shallow conduit with a free-surface stream subject to flooding

mix of compounds, roughly 70 compounds in the case of gasoline, and those with the higher vapor pressure will evaporate first, also changing the composition of the contaminant pool. Preferential volatilization from a petroleum spill in a glacial outwash aquifer was documented (Baedecker et al. 2011).

4.2 Dense Non-aqueous Phase Liquids (DNAPLs)

Dense non-aqueous phase liquids (DNAPLs) consist mainly of chlorinated hydrocarbons used as solvents and degreasers. Their movement through karst aquifers is poorly known. As with LNAPLs, the primary sources are leaking storage tanks and pipelines in industrial installations and from highway and rail accidents involving tanker trucks and rail cars. The initial contamination will be in the soil and the epikarst.

The pathways for heavy organic liquids migrating below the level of the epikarst will be fractures and sinkhole drains. In well-fractured limestones or in eogenetic karst with extensive primary porosity, DNAPLs can be widely distributed throughout the aquifer as has been demonstrated for the northern karst belt of Puerto Rico (Padilla et al. 2015; Yu et al. 2015). Other possible storage sites in the aquifer include cavities and dry cave passages in the vadose zone. If the aquifer contains a well-developed conduit system, DNAPL can collect in pools beneath the water surface and become incorporated into the clastic sediments that occupy the conduit. Because of the density difference, DNAPL compounds can occupy the pore spaces within the sediment pile where they can be sequestered for long periods of time.

The water table generally stands higher near the boundaries of karst groundwater basins with hydraulic gradients that point toward the conduit system. DNAPLs reaching the water table do not necessarily follow the groundwater down gradient toward the conduit but can continue to move vertically into any available storage spaces below local base level or can follow the dip of bedding planes in directions quite different from the hydraulic gradient.

The entrapment and dissolution of DNAPLs in the fractured matrix can be modeled (Yang et al. 2012). Dissolution of DNAPL depends on fracture aperture and also on the variation of the aperture widths. A larger variation in aperture means some enlargement of width where larger blobs of DNAPL can aggregate. A permeability boundary that allows the DNAPL to pool also slows down the dissolution. Differential dissolution in multicomponent DNAPL pools may change the density of the mix (Roy et al. 2002). If the light component is lost, the increased density of the remaining pool may initiate movement deeper into the aquifer. Likewise, loss of dense component may convert DNAPL into LNAPL with subsequent migration upward.

The transport of DNAPL in the conduit system has both similarities and differences to the transport of LNAPLs. Processes in common include volatilization and dissolution. Volatilization is not as effective in the case of DNAPL, because the overlying water provides a protective blanket. Either type of contaminant can degrade in the aquatic environment, but the effectiveness of this process is strongly dependent on the specific DNAPL being considered. DNAPLs have a finite solubility (Table 2) and are also gradually stripped away by the continuing flow of freshwater in the conduit. DNAPL that forms distinct pools beneath flowing streams or in low places in water-filled conduits dissolves at rates given by the exposed area of the DNAPL pool and the specific dissolution kinetics of the particular compound. DNAPL pools can also be regarded as a sort of bedload and can be dragged downstream when flow velocities exceed a necessary threshold. Higher velocities may actually entrain the DNAPL pool so that it is flushed downstream in suspension. Unlike LNAPLs floating on the water surface and thus continuously in contact with the water, DNAPL that has sunk into the sediment pile on the floor of the conduit is protected. There will be a slow percolation of water through the sediment much like any other porous media flow, but like other porous media flow, the flow velocities are very small, with only a slow turnover with the fast-moving water above. Thus, the stripping of DNAPL from the sediment pile will be much slower than the stripping of DNAPL constrained in distinct pools.

The migration of DNAPLs is very sensitive to the local geology. Because of its higher density, the migration of DNAPL is gravity-driven independent of local gradients within the groundwater flow system. It was possible to analyze a DNAPL site in the Ste. Genevieve and St. Louis Limestones in southwestern Kentucky without considering conduit flow (Chieruzzi et al. 1995). The DNAPL was found to migrate down the one-degree dip in a shallow system of vugs and bedding plane partings (Jancin and Ebaugh 2002).

A most unusual case study was a train derailment near Lewisburg, Tennessee, in 1990 (Crawford and Ulmer 1993, 1994). Ruptured tank cars spilled both styrene (an LNAPL) and chloroform (a DNAPL) into a karstic aquifer in the Ordovician Ridley Limestone (Fig. 11). The compounds were found to have pooled in the upper Ridley Limestone supported by the lower Ridley confining layer. A column of fluid was found in the recovery well with chloroform on the bottom, an intermediate layer of water, and then a layer of styrene on top. The styrene was picked up by a cave stream, flowed southeast, and appeared at a spring. The chloroform followed the dip of the bedding to the southwest where it was intercepted by another recovery well. The site illustrates the risks in drilling test or recovery wells because if these had penetrated the lower Ridley confining layer, they would have been pathways for contamination of the lower aquifer which is used as a water supply in the area.

DNAPLs and other compounds are slowly degraded by chemical reaction with the water. The actual kinetics of this process have been measured by Knauss et al. (1999) for the specific example of trichloroethylene. The degradation reaction is:

$$2\,C_2HCl_3 + 3\,O_2 + 2\,H_2O \Leftrightarrow 4\,CO_2 + 6\,H^+ + 6\,Cl^-$$

The end products of the breakdown process are CO_2 and HCl. Because the reaction is with oxygenated water which is always in excess supply, the rate equation has the simple form:

$$\frac{dC}{dt} = -kC_o^n$$

By laboratory experiments, Knauss et al. found $n = 0.85$ and $k = 5.8 \times 10^{-7}\ s^{-1}$ at 100 °C.

A conceptual model for DNAPL transport in karst aquifers was published by Wolfe et al. (1997). The rather complicated process of storage and DNAPL transport in karst aquifers has been reviewed by Loop and White (2001). Their conceptual model for DNAPL transport is given in Fig. 12.

5 Metals

The term "metal," of course, is ambiguous. About two-thirds of the elements on the periodic table are metals. Most of these do not impose environmental threats because they are rare in nature and are rarely used in commercial products. The most common heavy metal in nature, iron, is benign and essential to human health, but many other metals are toxic and a few, such as mercury and lead, are highly toxic.

Metals in karst aquifers can be divided into three categories:

(a) Alkaline earth metals derived from the carbonate rock—mainly calcium and magnesium with minor amounts of strontium and barium.
(b) Metals occurring as part of the natural background - mainly aluminum, iron, and manganese with trace amounts of many other metals.
(c) Contaminant metals introduced into aquifers through human influences.

The chemistry of the alkaline earth metals in karst groundwaters is the core of karst geochemistry but need not be further discussed here. There are extensive discussions of alkaline earth-carbonate systems in textbooks such as Langmuir (1997).

Sources that might introduce metal contamination into karst aquifers include the following:

Runoff from highways and outfalls from urban storm sewers.
Spills, leaks, and outfalls from metal processing industry
Leachate from landfills and sinkhole dumps
Leachate from mine tailing piles
Acid mine drainage.

The aqueous chemistry of individual metal-water systems is well understood (Baes and Mesmer 1976; Stumm and Morgan 1996), and thermodynamic calculations can be made to determine the limiting solubilities. In general, metals tend to be more soluble in acid solution and become less soluble as the pH increases. Variable valence metals tend to be more soluble in their lower valence states and less soluble in their more oxidized states. A few metals, such as

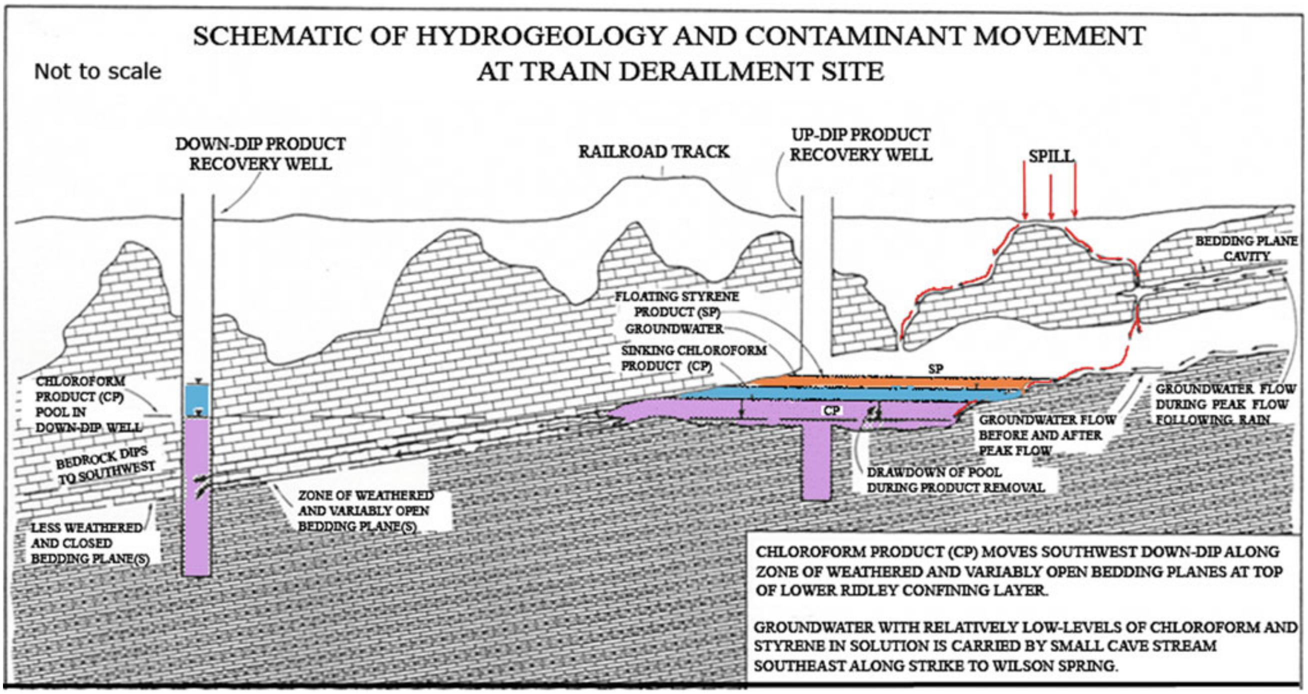
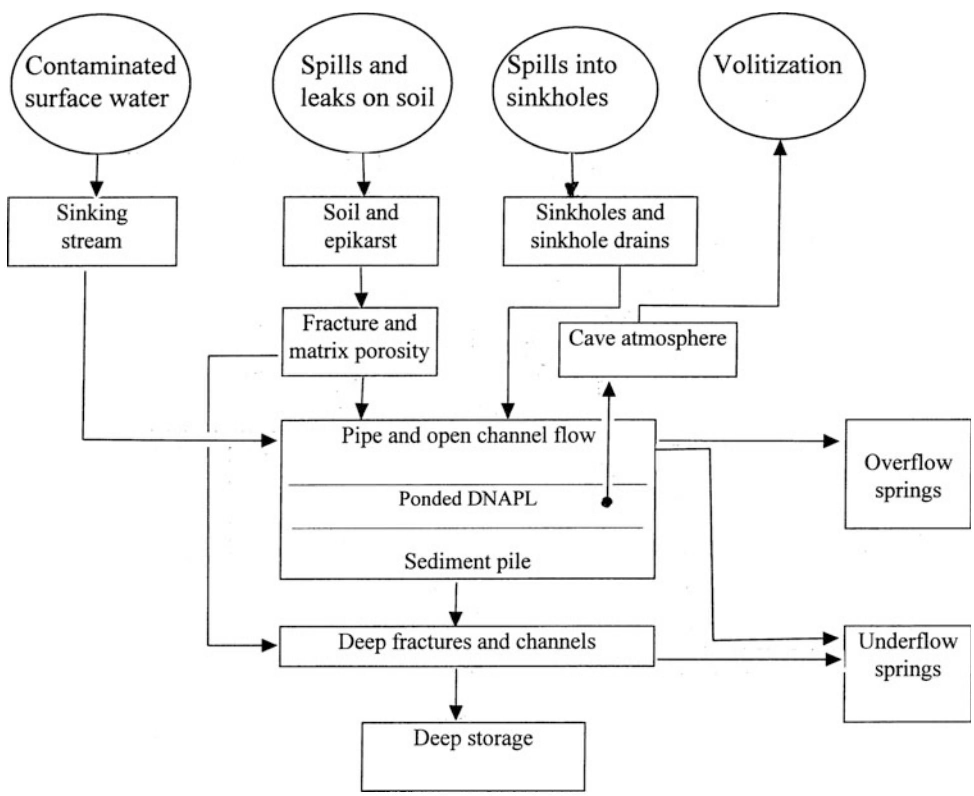


Fig. 11 Sketch of underlying geology and distribution of non-aqueous phase liquids at the Lewisburg, Tennessee, train-wreck site. Adapted from Crawford and Ulmer (1994)

Fig. 12 Conceptual model for DNAPL storage and transport in karst aquifers. From Loop and White (2001)



aluminum, are amphoteric and increase their solubility at high pH. Karst water, with its high carbonate contact, acts as a buffer constraining pH to the near-neutral regime where metals have minimum solubility. Karst waters also tend to be oxidizing. In addition, in karstic systems, the high carbon dioxide activities cause carbonates to be the limiting insoluble phase. Calculations for such systems as the Zn–O–H, Cd–O–H, and Pb–O–H systems show that in all cases, precipitation of hydroxide or carbonate phases will limit the concentration of metal ions in karstic waters to low values. However, in all cases, at the pH and P_{CO2} values of karst water, the equilibrium metal solubility could still be well above drinking water standards.

5.1 Iron and Manganese: The Ubiquitous Background Metals

Iron, in the oxidizing environment of caves and karst aquifers, is firmly locked in the Fe^{3+} state where it occurs as highly insoluble iron hydroxides and oxyhydroxides. Iron is precipitated when it is carried into the aquifer from reducing environments such as landfills. Coatings and speleothems of goethite (FeOOH) and ferrihydrite ($Fe(OH)_3$) have been found in caves.

Although manganese is a common background metal and is considered toxic, it is rarely found in karst waters. Mn^{2+} carried into karst aquifers is oxidized and precipitated onto stream sediments as black, highly insoluble Mn^{4+} oxides. The mineralogy of these coatings is variable, but birnessite ($(Na,Ca)(Mn^{4+},Mn^{3+})_4O_8{\cdot}3H_2O$) appears to be the most common phase. The mineral coatings act as extremely effective scavengers for heavy metals. Chemical analyses of manganese oxides from a selection of karst conduits reveal percentage quantities of such metals as copper, zinc, nickel, and—in one case—cobalt (White et al. 2009). The analytical data on both iron and manganese deposits illustrate a "mutual exclusion." The hydrated iron oxide deposits contain negligible concentrations of other metals including manganese, while the manganese oxide coatings are highly enriched in other transition metals but contain only relatively small amounts of iron.

5.2 Contaminant Metals

A widely distributed source for metals is storm runoff from highways and parking lots. Particulates and condensates from vehicle exhausts accumulate on the pavement surface and are removed by the first flush during storm flow. Measurements in Dade County, Florida, (Waller et al. 1984) revealed higher concentrations of lead and zinc near a highway compared to control measurements in a more remote area.

An extreme example is the city of Bowling Green, Kentucky, which uses the stream in the Lost River Cave System, which flows beneath the city, as a natural storm drain. Street, roof, and parking lot runoff are injected directly into the karst through injection wells. Analysis of waters collected at four points along the flow line (Reeder and Crawford 1989) (Fig. 13) shows high concentrations of metals but little systematic pattern from the most upstream point outside the city to the final discharge from the Lost River Rise.

5.3 Role of Small Particulates in Metal Transport

The controlling factor in metal transport appears to be adsorption onto various substrates rather than equilibrium solubility.

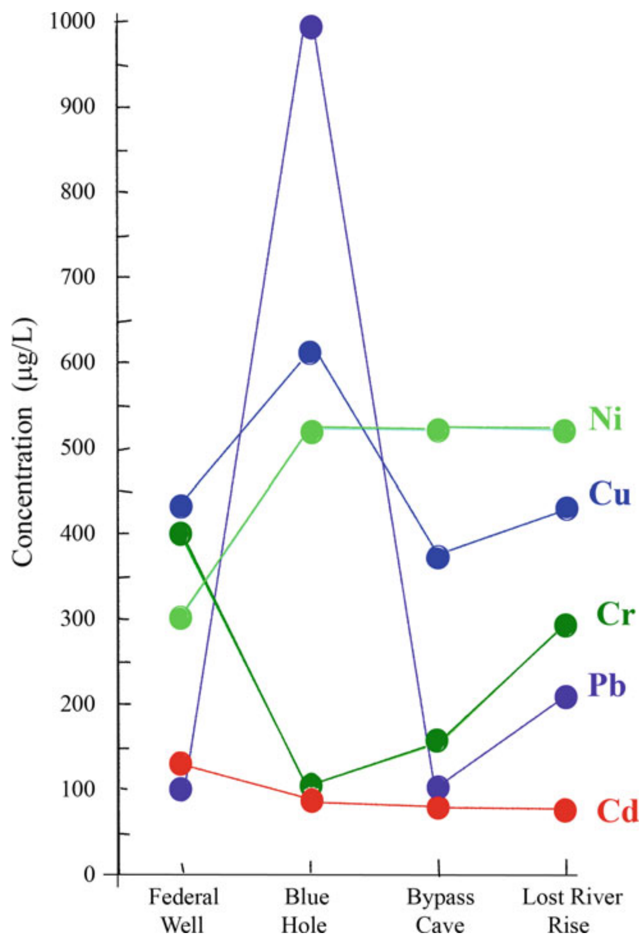


Fig. 13 Concentrations of metals in the Lost River Cave System at Bowling Green, Kentucky. Sampling points are organized in the downstream direction. Federal well is outside the city to the south. The Lost River Blue Hole is just inside the southern edge of the city. Bypass Cave is near the center of the city. The Lost River Rise is the large spring where the water emerges at the northern edge of the city. The plotted values represent the highest observed values. Data from Reeder and Crawford (1989)

Metals can adsorb onto clays and other clastic particulates, onto organic material in the water, and onto iron or manganese oxides which often form coatings on cave streams.

Shevenell and McCarthy (2002) confirmed the link between metals and solids for groundwater in the karst aquifer that underlies the Oak Ridge Reservation, Tennessee. They determined colloidal compositions via (a) the chemical difference in total and filtered water samples, (b) direct soil measurements using X-ray diffraction, scanning electron microscopy, and energy-dispersive X-ray spectroscopy, and (c) speciation modeling. In most wells, they found that aluminum, iron, manganese, and nickel were present primarily in the solid phase.

Karst springs fed by conduits often become turbid or even extremely muddy following rain storms. Such springs provide a means for testing metal transport on suspended particles. Several springs on or near the Fort Campbell Army Base in western Kentucky were sampled through the course of a storm hydrograph (Vesper and White 2003). The unfiltered, turbid, samples were evaporated, and the remaining solids digested, and analyzed for aluminum and a suite of other metals. There was a peak in the aluminum concentration coincident with the peak of the hydrograph, and there were peaks in the concentrations of the other metals coincident with the peak in the aluminum concentration (Fig. 14). These matched chemographs are good evidence that metals in karst aquifers precipitate but then adsorb onto particle surfaces, and it is these particles that are carried through the aquifer. Further analyses of the sediments themselves show the presence of adsorbed metals (Vesper and White 2004).

5.4 Aluminum—Acid Mine Drainage

Although aluminum is considered a toxic metal, it provides very little risk in the near-neutral pH environment. The solubility of aluminum near neutral pH is so low that Al is usually below detection limits in groundwater analyses. An exception is the water draining coal mining refuse and abandoned coal mines. Oxidation of pyrite produces sulfuric acid and lowers the pH. The solubility of aluminum increases with the cube of the hydrogen ion activity so that acid mine streams have both a low pH and a high concentration of aluminum and other metals. When such waters enter a karst aquifer, it would be expected that the acidity would be rapidly neutralized and the metals precipitated. The actual situation appears to be more complicated.

Crystals of calcite placed in a cave stream affected by acid mine drainage dissolved several orders of magnitude more slowly than the crystals dissolved in similar chemical conditions in the laboratory suggesting the formation of a protective layer on the surface (Wicks and Groves 1993). Drainage from abandoned coal mines on the Cumberland Plateau enters the top of the Mississippian limestone sequence and reappears as springs in the deep valleys that have been eroded into the plateau. On the East Fork of the Obey River, the Enchanted River Spring (Fig. 15) appears as an azure pool with a pH ranging from 4 to 5. Acid water has penetrated the entire thickness of the karstic limestone and remained acidic (Sasowsky and White 1993; Webb and Sasowsky 1994). The azure color of the spring is due to the flocculation of aluminum as the pH gradually increased (Fig. 16). The iron has apparently precipitated within the aquifer, perhaps forming a protective coating on the conduit walls, but the aluminum continues to the surface.

6 Small Particulates and Pathogens

6.1 Clays and Colloids

Karst aquifers carry a sediment load with an extremely wide range of particle sizes. The justification for separating small particulates from large particulates is that large particulates require high flow velocities to move them and large apertures to allow their movement. Small particulates are transported in suspension at lower velocities and can move through fractures and other pathways with small apertures.

Small particulates in natural waters consist of clay minerals, fine-grained silica (typically quartz), hydrated iron oxides, and a variety of organic materials. Atteia et al. (1998) tabulated the particle sizes from a variety of natural waters and found values ranging from 4 nm to 150 µm. Some authors also make a distinction between particles and colloids. A break in the distribution of particle sizes at about 5 µm (Atteia and Kozel 1997) suggested that the break point is a natural division between the smaller colloids and the larger particles. A more significant distinction is the density and internal structure. Colloids tend to be loosely packed, poorly crystalline, hydrated, and low-density objects with very active surfaces. Particles such as quartz or clay minerals are more dense and have a well-defined crystal structure.

Small particulates can be flushed from the epikarst, through the vadose zone, and into the main karstic drainage. The release is due to piston flow as hydraulic heads are built up in the vadose zone (Pronk et al. 2008a). The flushing of particulates tends to be concentrated on the rising limb of the storm hydrograph as uncompacted particles are lifted out as a first flush during storm events. Comparison of the movement of 1-µm spheres with fluorescent dye shows that the particles actually travel faster than the dye during low flow conditions although both travel at comparable velocities during high flow (Göppert and Goldscheider 2008). A study of agricultural chemicals and polyaromatic hydrocarbons released by snow melt (Simmleit and Herrmann 1987)

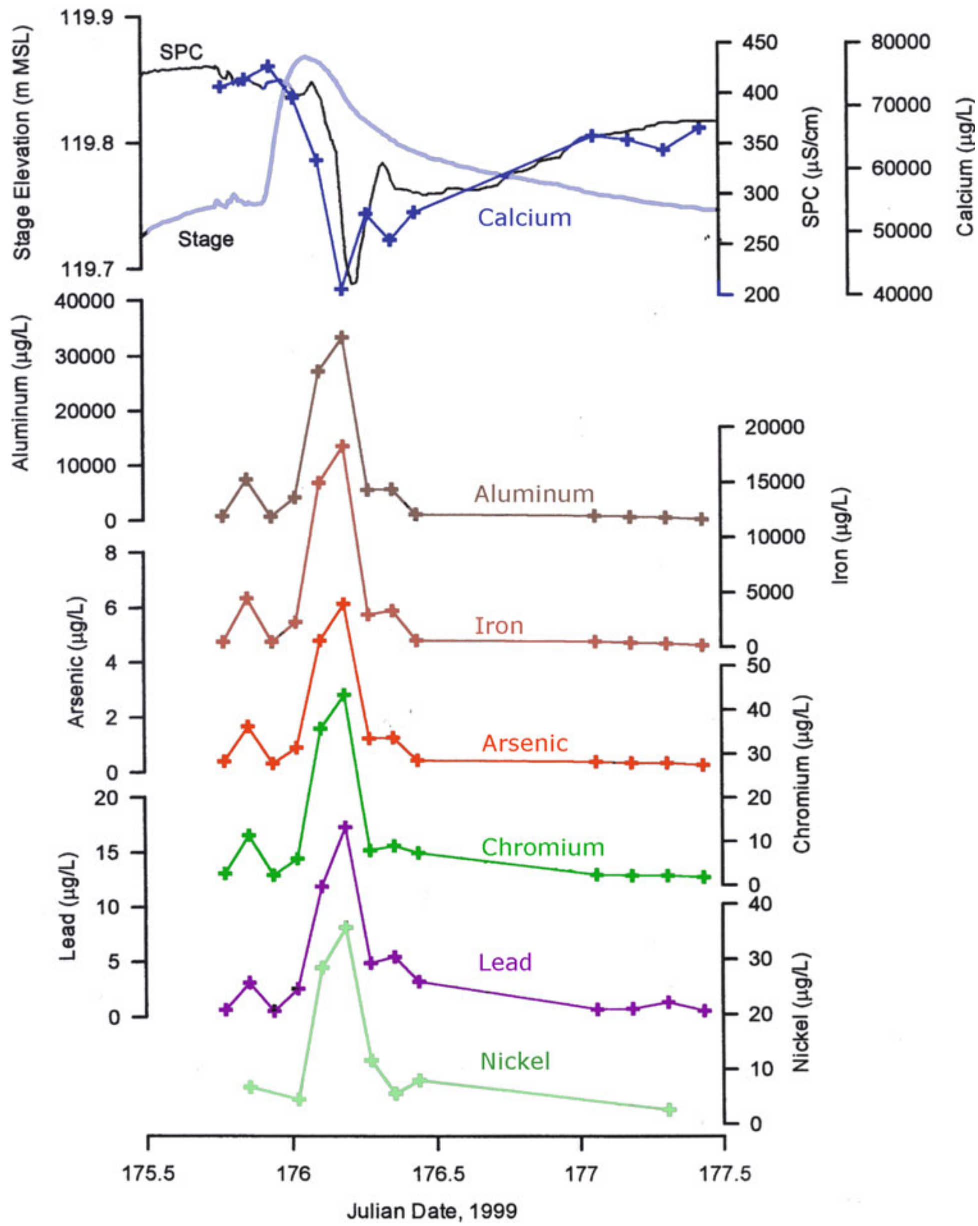


Fig. 14 Concentrations of metals in unfiltered water from Millstone Spring, western Tennessee during a storm event. From Vesper and White (2003)

demonstrated that even thin soils in karst regions trap most of these contaminants. However, small particulates released from the soil into the underlying aquifer carry the organic pollutants with them.

6.2 Pathogens

Viruses—size range 50–100 nm, bacteria—size range 1–4 µm, and protozoa such as *Gharida lamblia* and *Cryptosporidium parvum* which travel as cysts, can be considered small particulates. These organisms are easily transported into and through karst aquifers because of the absence of filtering from the soil. They can be transported in suspension in the water or as attachments to other particles of sediment or organic material.

Microorganisms can be sampled at springs, wells, and in caves. Sampling from springs and wells has been mostly for investigations of groundwater contamination, but the microbiology of caves has become a rich field of investigation in its own right (Northup and Lavoie 2001). Sulfur-oxidizing and sulfur-reducing bacteria are an important part of the mechanism for the formation of hypogenetic caves. Bacteria are involved with the deposition of black manganese oxides coatings in cave streams. Microorganisms in caves can be taken as extremophiles and as such are of interest to the field of astrobiology where investigators attempt to deduce the possibility of life-forms on other

Fig. 15 Enchanted River Spring, east fork of the Obey River, Fentress County, Tennessee. Photograph by the author

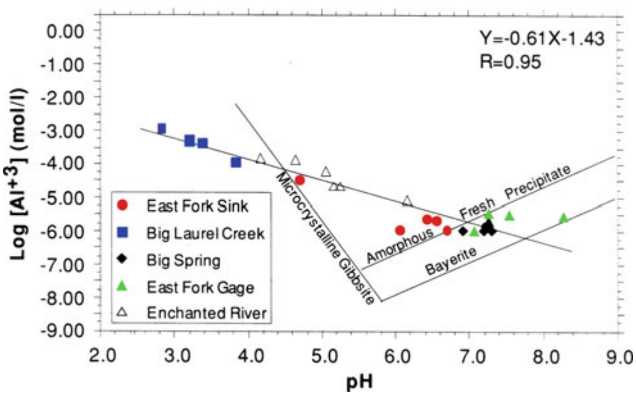


Fig. 16 Relation of aluminum concentration to pH for various water samples in the East Fork, Obey River drainage basin. From Sasowsky and White (1993)

planets (Boston et al. 2001). This review is concerned only with pathogenic organisms for which there is a summary of their occurrence in caves (Jurado et al. 2010).

Most attention has been given to the fecal coliforms, fecal streptococci, and often a particular emphasis on *Escherichia coli.* The presence of these organisms is the most common indicator of pollution from sewage or animal waste. Inventories of bacterial contamination in West Virginia (Mathes 2000), Ontario (Conboy and Goss 2000), and western Ireland (Thorn and Coxon 1992) all reveal widespread presence of fecal bacteria in carbonate wells. The West Virginia study examined the relationship of contaminated wells to the density of septic tanks and found no correlation. Because these organisms are very small, they appear to move readily through solutionally widened fractures and so are very widespread. They even appear in carbonate conglomerate aquifers (Göppert and Goldscheider 2011).

There have been many fewer studies of viruses in karst aquifers. Johnson et al. (2011) found enterovirus and reovirus in carbonate wells and springs in East Tennessee. A norovirus outbreak in a dolomite aquifer in Wisconsin was apparently traced to a faulty septic system, showing that viruses can also migrate through fractured aquifers (Borchardt et al. 2011).

The protozoa *Giarida lamblia* and *Cyptosporidium parvum* are released in a cyst form in animal feces and are present in many surface waters. The cysts are carried into karst aquifers by surface runoff and sinking streams and travel through the aquifer to be discharged at the springs. A study of Burns Cave No. 2 Spring in Greenbrier County, West Virginia, showed that while fecal colliform tended to peak with peaks in the discharge, the concentration of *Cryptosporidium* did not seem to be related to discharge (Fig. 17) (Boyer and Kuczynska 2003).

It is well established that much of the bacteria load travels through the karst adsorbed on small particulates, mostly clay particles (Mahler et al. 2000). It would then be expected that bacterial contamination of springs would be associated with events of high turbidity. However, some bacteria travel as free particles, so that the relation of bacterial contamination to turbidity is not highly accurate (Dussart-Baptista et al. 2003). Pronk et al. (2006) suggest that dissolved organic carbon is a better indicator of bacterial contamination than turbidity. The poor correlation arises in part because there are multiple sources for the turbidity particles. Some are part of the remobilization of loosely bound particles already

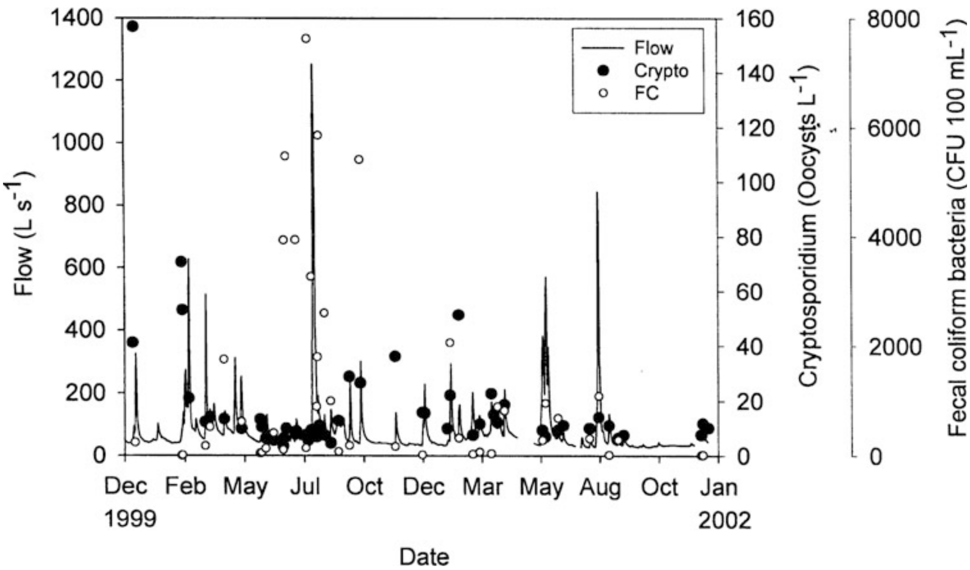


Fig. 17 Hydrograph (daily mean flow) for Burns' Cave No. 2 spring. *Solid circles* mean storm densities of *Cryptosporidium parvum*. *Open circles* mean storm densities of fecal coliform bacteria. From Boyer and Kuczynska (2003)

deposited in the conduit system. Some are fresh particles derived from surface soils or from sinking streams. The surface-derived particles tend to be more contaminated and have a smaller particle size leading to the suggestion that particle-size distribution curves might also be an indication of spring water contamination (Pronk et al. 2008b).

Bacteria appear to be compatible with limestone surfaces and readily colonized limestone test blocks to form biofilms (Personné et al. 2004). The flushing of bacteria from springs and their appearance in wells is closely associated with rainfall events. Laroche et al. (2010) examined the appearance of multiple strains of *E. coli* at a stream, its sink point, and spring, and a well and found rapid movement including antibiotic-resistant strains during rain events. Some insight into the movement of contaminants through conduit systems in response to storm events is given by a study of the Sauve Spring in France (Personné et al. 1998). The Vidaurle River receives effluent from a sewage treatment plant just upstream from a swallet that takes the entire low flow of the river (Fig. 18a). The karst drainage system re-emerges 7 km away at the Sauve Spring. Measurements at the spring following a flood pulse (Fig. 18b) show that coliform bacteria respond to the flood pulse and rise with the rising limb of the hydrograph. However, the concentration of enterococci bacteria is largely independent of the flow rate.

Understanding and predicting the behavior of bacterial contaminants in karst aquifers is an exercise in competing rate processes. These include flow rates through various pathways in the aquifer and their response to storm inputs, the episodic movement of the fine-grained sediments that act as carriers for some fraction of the bacteria, and the die-off rate of the various species and strains of bacteria. Die-off rates for *E. coli* were measured by placing inoculated chambers in a karst spring in Arkansas and observing the decay of the organisms (Fig. 19) (Davis et al. 2005). These results indicate that *E. coli* could survive in the karst environment for three to four months, a long time compared to the residence time of water in many karst aquifers. Davis et al.'s experimental results are in agreement with a study of contaminated karst springs in Israel (Magal et al. 2013) where a massive contamination event was flushed from the system in less than three months.

Microbial contamination of karst water is very common because the sources are very common. Barnyards, manure spread on fields, and septic systems are the primary sources of fecal bacteria. Spray irrigation of wastewater as a means of water conservation must be designed with great care in karst regions (Hildebrand and Oros 1987). Thin soils above the epikarst are typical in karst terrains. Rainfall events flush contaminants through the soil and the epikarst, and once in the underlying aquifer, further movement is rapid. A particular threat to wells and springs used as water supplies are sewage lagoons, either for sewage treatment or for storage of waste from hog lots and poultry brooders. If such structures are poorly lined or unlined, seepage pressure from the water column can induce soil piping and sinkhole collapse with the effect of dumping the entire contents of the lagoon into the underlying aquifer. Several such collapses have been documented (Alexander and Book 1984; Alexander et al. 1993).

7 Sediment, Coarse Particulates, and Trash

The apertures of solutionally widened fractures and conduits are sufficient to permit the passages of clays, silt, sand, and even pebbles and cobbles. Collectively known as clastic

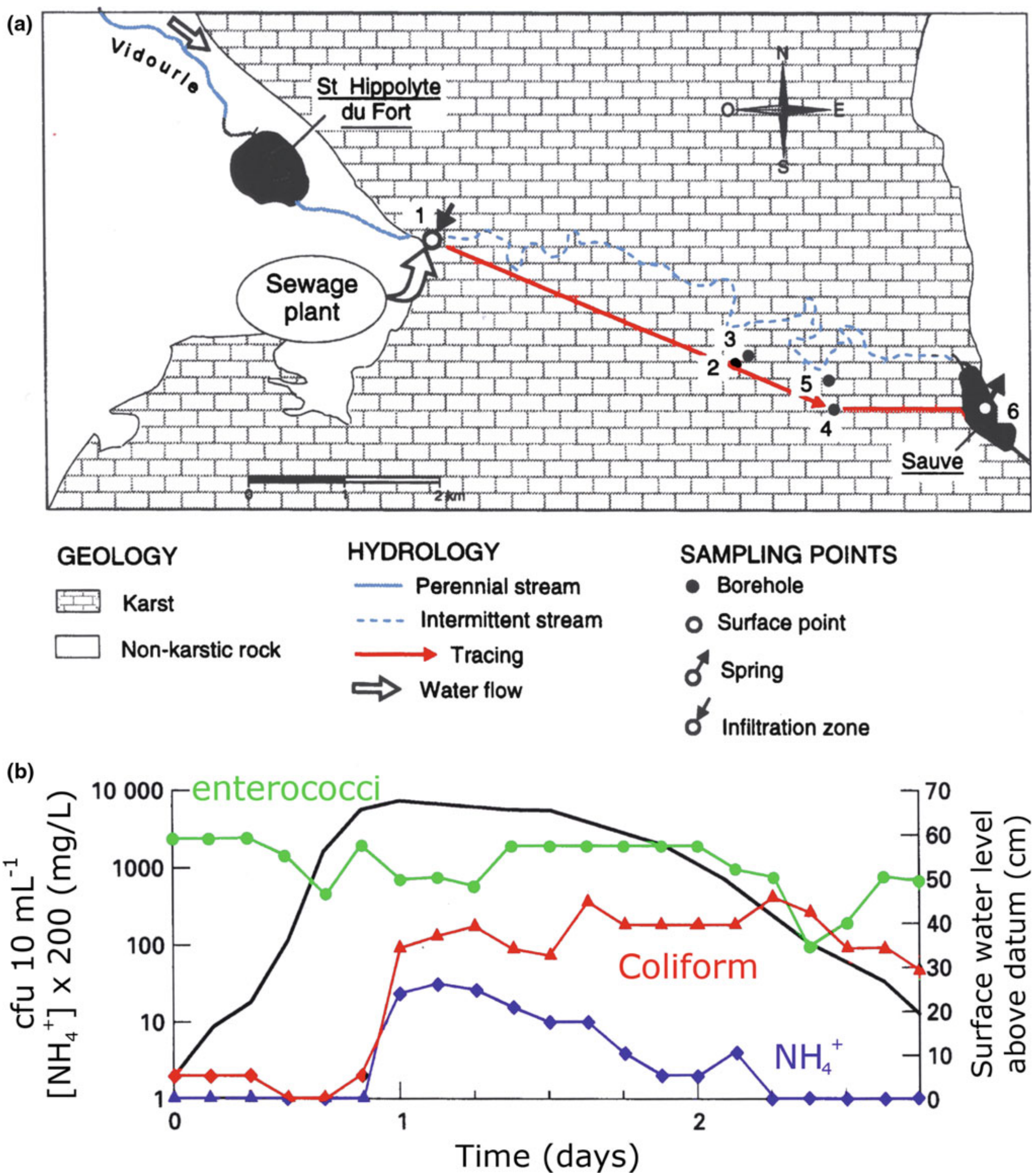


Fig. 18 **a** Geographical setting for a study of bacteria transport through a karst aquifer. Adapted from Personné et al. (1998). **b**. Concentrations of enterococci, coliforms, and ammonia following a flood event at the Sauve Spring in the south of France

sediments, a flux of these materials is an essential part of karst hydrology. In a karst region without surface streams, all insoluble weathering material must be discharged from the region by underground routes. Clastic sediments themselves can be considered as contaminants because muddy water is not usually acceptable in water supplies. Clastic sediment piles in conduits act as adsorption media for other serious contaminants such as metals and organics.

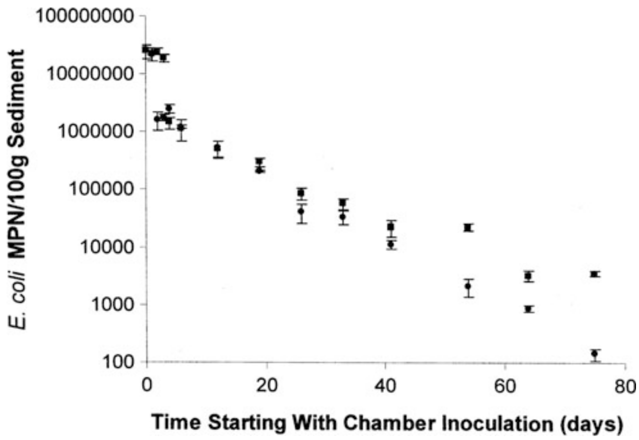


Fig. 19 Die-off of *E. coli* exposed to water from Copperhead Spring, Arkansas (*circles*) and the Illinois River (*squares*). From Davis et al. (2005)

7.1 Clastic Sediment: Transport and Storage

Clastic sediments can be sampled at springs. The spring discharge tends to represent the fine-grained end of the sediment load. Sediment piles can be sampled in caves with active streams. Cave sediments tend to represent the coarse-grained portion of the sediment load. The complex relationship of sediment sources, sediment transport processes, and sediment deposits has been reviewed by Herman et al. (2012). Sediments can be moved by being dragged along the stream bed by the shear force of water flowing over it (bedload) and by being taken into suspension by the turbulent action of the water (suspended load). Unlike the flow of water, the flow of sediments is episodic. Flow velocities must reach a certain threshold before the sediments can move as bed load or as suspended load. Sediments moving downward through fractures at the base of the epikarst or downward through sinkhole drains have a gravity assist to the action of infiltrating water.

The fine-grained suspended load is the most important vehicle for contaminant transport. The concentration of suspended particles in spring discharges tends to peak on the rising limb of storm flow hydrographs (Fig. 20) and to fall off more quickly than the recession limb of the hydrograph (Herman et al. 2008). The total load of clastic material passing through karst aquifers varies widely between aquifers depending on both available sediment sources and on the hydraulics of the conduit system. What may be an extreme example is the Massa springs in Italy which are impacted by a marble quarry and discharge up to 83 metric tons of suspended sediment during a single storm event (Drysdale et al. 2001).

7.2 Input from Surface Streams: Trash, Sediment, and Contaminants

Surface streams can impact karst aquifers from both upstream and downstream directions. Sinking surface streams can carry sediment, plant debris (leaves, brush, and even entire tree trunks), and trash directly into the conduit system. Low gradient master conduits that discharge through springs on river banks are subject to reversed flows that will carry muddy and perhaps contaminated river water deep into the aquifer when the surface river is in flood. Base-level backflooding is widely recognized in karst regions but poorly documented (Albéric 2004).

The shifting gradients and flow paths that result from the placement of storm inputs over the drainage basin control the distribution of contaminants through the aquifer. Under base flow conditions, water and possible contaminants introduced at sink points are swept through the conduit system and ultimately discharged from the spring. The gradient in the surrounding matrix is toward the conduits so that flow is toward the conduits. Water wells extracting water from the surrounding bedrock might not be impacted by any polluted water flowing down the conduit even if the conduit is nearby. Storm recharge in the drainage basin of the sinking streams can flood the conduit system, reverse the gradient so that water flows from the conduit into the fractures and matrix, and thus may contaminate nearby wells (Fig. 5). Storm recharge upstream in the surface water basin, but not in the sinking stream basins, can produce flood flow in the surface stream, reverse the gradient at the spring, and drive contaminated muddy surface water up the conduit and possibly into the surrounding matrix where it can also contaminate wells. Overall, the flow patterns are difficult to model and the contamination risks are difficult to predict.

7.3 Lined Landfills, Unlined Landfills, and Sinkhole Dumps

The modern landfill is a highly engineered structure with multiple linings, a leachate collection system, a monitoring system, and sometimes a system for capturing the methane released from the landfill. The primary threat from sanitary landfills sited on karst terrain is the possibility of liner failure. Breaching of the liner, caused by stresses induced from soil piping within the karst beneath the landfill, would allow leachate to drain directly into the underlying karst aquifer. The reason why siting landfills on karst is problematic is that potential for piping failure is extremely difficult to predict and groundwater monitoring around the landfill is difficult because of the localized flow paths within the karst. Placing

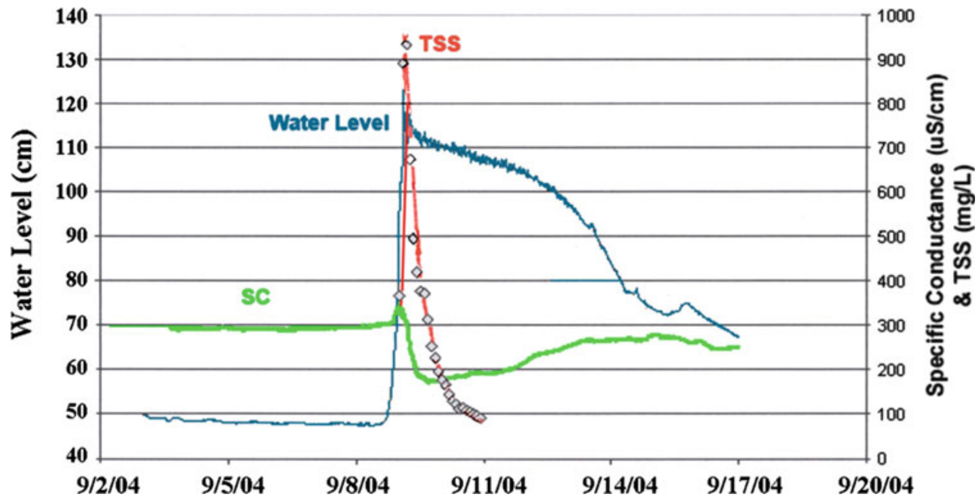


Fig. 20 Turbidograph of sediment discharge from Arch Spring, Blair County, Pennsylvania, in relation to storm hydrograph and specific conductance. From Herman et al. (2008)

Fig. 21 A sinkhole dump in central Pennsylvania containing trash and construction waste. Photograph by E.L. White. Used with permission

monitoring wells to reliably intercept escape pathways for leaking leachate is nearly impossible although monitoring springs offers some assurance.

The early sanitary landfills that replaced the city dump more than half a century ago were essentially pits dug in the ground, filled with waste, and then covered with soil. The waste decayed and compacted causing the soil cover to sag and collapse, effectively turning the waste cells into sinkholes. The decaying waste produced a highly reducing environment which in turn mobilized metals and other contaminants which could be leached into underlying aquifers. In karst regions, it was common to use sinkholes as landfills since they did not require as much excavation. In one documented case (Murray et al. 1981), the installation of a landfill near Arnold, Missouri, caused a spring, 1.5 km distant, to turn black and begin emitting hydrogen sulfide gas. Others, such as the Lemon Lane landfill near Bloomington, Indiana, have received industrial waste and are now superfund sites (Valentin 1995). It was early recognized that unlined landfills in karst are a major pollution risk, but many of the older landfills remain in place.

The most primitive form of landfill is the ubiquitous sinkhole dump. Rural residents and even entire communities have from long tradition used sinkholes as waste disposal sites. Farmers routinely use sinkholes to dispose of dead animals and also (nearly) empty containers that held their agricultural chemicals. Construction wastes and industrial waste have been dumped as trash (Fig. 21). Sinkholes act as funnels, collecting storm water runoff and channeling it into the sinkhole drain. Storm water leaches through the trash, and what enters the karst drainage system below is essentially landfill leachate. Additionally, inwash during intense storms and soil-piping failures in the underlying sinkhole sediment combines to transport solid trash into the underlying conduit system. The trash becomes a form of clastic sediment and is moved down the flow field during intense storm flow in the same manner as any other clastic sediment. Trash carried deep within the conduit system becomes a source term for continuing contamination of the groundwater and is located where cleanup is essentially impossible.

Only a few trash injections into karst systems through sinkholes have been systematically examined. A systematic survey of illegal dump sites in two counties in the Appalachian Valley of Virginia found the 23% of the illegal dump sites were in sinkholes (Slifer and Erchul 1989). A survey of sinkhole density and groundwater quality in eastern USA (Lindsey et al. 2009) showed a correlation between sinkhole density and decreased water quality.

8 Final Statement

What has been presented above is not exactly a review of the possible sources and processes of contamination in karst aquifers. It is more a catalog of contamination threats that have happened or which could happen. If anything, it is a guide to useful and important research subjects that could be undertaken. Although a great deal has been learned about specific contaminated sites, we are a long way short of being able to write a general protocol for how to deal with contamination threats to karst aquifers.

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Part III

Karst Groundwater Contaminants and Tools for Their Evaluation

Trace Metal Accumulation and Re-mobilization in Phreatic Karst Conduits

Amy L. Brown and Jonathan B. Martin

Abstract

Little is known about how trace metals accumulate and cycle in conduits within the phreatic zone. These water-filled conduits can receive floodwater 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.

1 Extended Abstract

Storm flow impacts groundwater quality in karst aquifers due to a large range in aquifer permeability, which allows both rapid transport of contaminants into the subsurface (Vesper and White 2003, 2004) as well as long-term storage in matrix porosity (Martin and Dean 2001; Wong et al. 2012). This contaminant transport and retention can be altered by changes to aquifer redox state triggered by intruding surface water, but these impacts have not been extensively studied in karst systems. Intruding storm water is initially oxidizing, but depending on the available microbes, terminal electron acceptors (TEA), and reactive organic carbon, storm water intrusion can trigger a transition to conditions more reducing than baseflow (Brown et al. 2014). Such changes from hypoxic to anoxic conditions trigger multiple shifts in water quality that include mobilizing trace metals (Jacobs et al. 1988), increasing denitrification (Green et al. 2008), inhibiting the degradation of organic contaminants (Greskowiak et al. 2006; Lapworth et al. 2012; Massmann et al. 2006), and altering the sorption of contaminants (Borch et al. 2009). These reactions could degrade (e.g., mobilize toxic metals) or remediate (e.g., denitrification) water quality through changes in aquifer redox state. Understanding these changes to aquifer redox state is particularly critical to karst system management where both rapid intrusion of surface water and long residence times occur.

The extent of aquifer redox changes can be traced through the fate and mobility of iron and manganese, which could provide key information, as well as direct impacts, on water quality. Storm flow transports iron and manganese into the subsurface as dissolved ions, bound to organic carbon, and as colloids and particles carried by turbulent flow (Atteia and Kozel 1997; Brown et al. 2014; Vesper and White 2003). Dissolved oxygen and nitrate in the intruding water may inhibit mobilization of trace metals following intrusion. Oxygen-rich water causes iron and manganese to precipitate as solid Fe oxide and Mn oxide, thereby sequestering other

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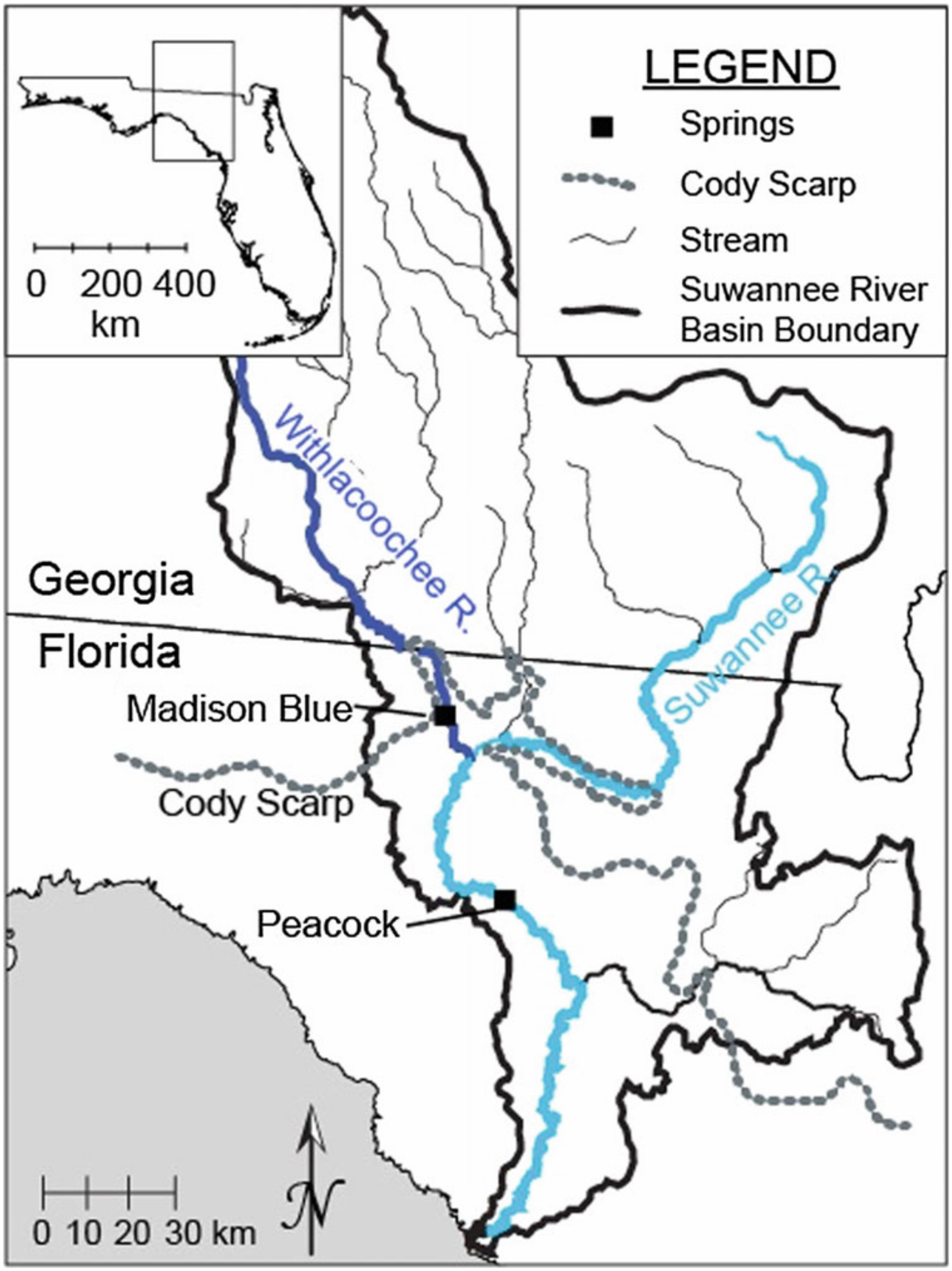

Fig. 1 Location map. Madison Blue Spring and Peacock Spring are shown adjacent to the Withlacoochee and Suwannee Rivers.

potential toxic trace metals (Frierdich et al. 2011; White et al. 2009). As available oxygen and nitrate are consumed, solid metal oxides become the preferential electron acceptor for organic carbon oxidation. These reactions cause the reductive dissolution of the Fe oxide and Mn oxide and could release co-precipitated toxic trace metals such as chromium, nickel, and lead (Frierdich et al. 2011; White et al. 2009).

Aquifer redox dynamics and trace metal mobility triggered by storm water intrusion can be readily observed at Madison Blue Spring and Peacock Spring, two submerged cave systems in the Upper Floridan aquifer adjacent to rivers in the Suwannee River Basin (Fig. 1). These observations provide the ability to evaluate timing of redox changes and relate them to the stoichiometry of redox reactions. The headwaters of the Suwannee River drain a shallow, sandy aquifer with little storage capacity because of the underlying low-permeability unit (the Hawthorn Group) that confines the karstic Floridan aquifer. Consequently, storms occurring in the headwaters trigger rapid changes in river stage. Downriver, the Hawthorn Group has eroded away, and the river flows directly over the limestone of the upper Floridan aquifer. Under normal flow conditions, this reach receives baseflow from numerous springs and seeps discharging from

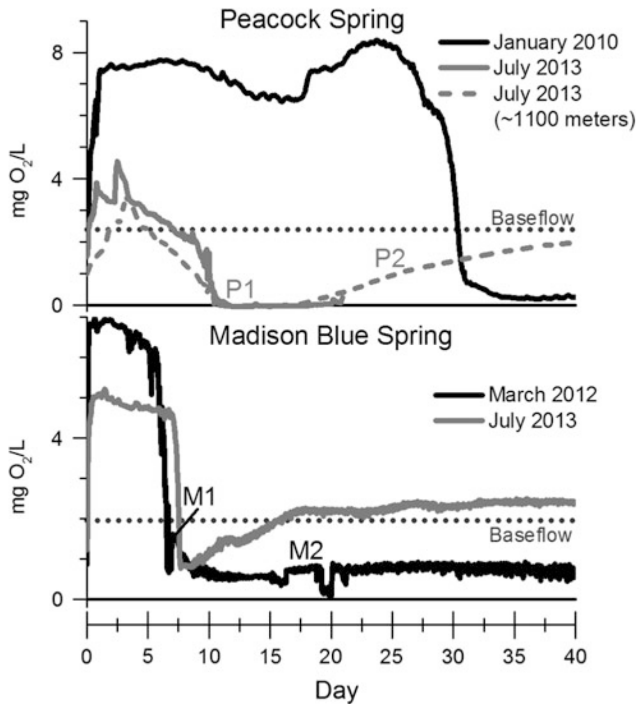

Fig. 2 Dissolved oxygen through time. Dissolved oxygen plots from four intrusion events are shown, two at Peacock Spring and two at Madison Blue Spring. Day 0 represents the initiation of river water intrusion. *Dotted line* shows baseflow oxygen concentrations measured at the spring vent. *Solid lines* show continuous data from the cave entrance. *Dashed line* at Peacock Spring shows oxygen data 1100 m into the conduit system. Time points P1, P2, M1, and M2 are shown in Fig. 4 with estimated metal mobilization.

the unconfined Upper Floridan aquifer. Following storms in the headwaters, river stage rises rapidly allowing river water to intrude into the aquifer, displacing groundwater for periods from days to months (Gulley et al. 2011).

Springs in this region discharge oxic water ($\sim$2 mg O_2/L) with elevated nitrate concentrations (1–2 mg/L NO_3 as N) that originate from anthropogenic contamination (Katz 2004). The intrusion of surface water and reactive organic carbon initially increases oxygen over baseflow levels, resulting in more oxidizing conditions than baseflow (Fig. 2). As surface intrusion slows, the redox state becomes more reducing than baseflow when organic carbon consumes available oxygen and nitrate (Brown et al. 2014). Although nitrate concentrations were not continuously tracked through any of the storm events, grab samples indicate 0.1–0.2 mg/L NO_3 as N was contained in the intruding water, or about an order of magnitude lower than baseflow conditions. With sufficiently reducing conditions, metals transported into the system with intruding storm water will be reductively dissolved. These mobilized metals could be flushed from the system as the intruded water discharges to the surface during the storm recession, but the extent of metal transport will be controlled by the persistence of reducing conditions in the conduits. Not all metals discharge during the recession as shown by solid metal oxide deposits (Fig. 3) found in these caves systems (Martin 1990). The magnitude of metal sequestration and release in the dynamic redox environment following storm water intrusion is unknown.

Mobilization of iron and manganese was modeled in siliciclastic aquifer systems using the electron trapping capacity (ETC) of the water (Kedziorek and Bourg 2009). The ETC is based on oxygen and nitrate concentrations (Eq. 1), since these compounds inhibit trace metal mobilization. This model was previously used to evaluate the redox state of water at the spring boil at Madison Blue Spring for the March 2012 event shown in Fig. 2 (Brown et al. 2014). Here, we apply the model to examine the likelihood of manganese and iron mobilization in the phreatic conduits of the aquifer over the range of oxygen and nitrate values observed during and after representative intrusion events at each cave system (Fig. 4), with specific estimates of ETC during two intrusion events. In the absence of nitrate, oxygen concentrations fall low enough to favor both iron and manganese mobilization for all of the modeled events. In July 2013, anoxia, which likely favored denitrification and low concentrations of nitrate in surface water, would result in iron and manganese mobilization (P1), followed by manganese mobilization (P1) as oxygen concentrations slowly recovered. In contrast, conditions at Madison Blue Spring were hypoxic, with a lesser extent of denitrification and higher nitrate concentrations in intruding surface waters. As a result, conditions are only sufficiently reducing

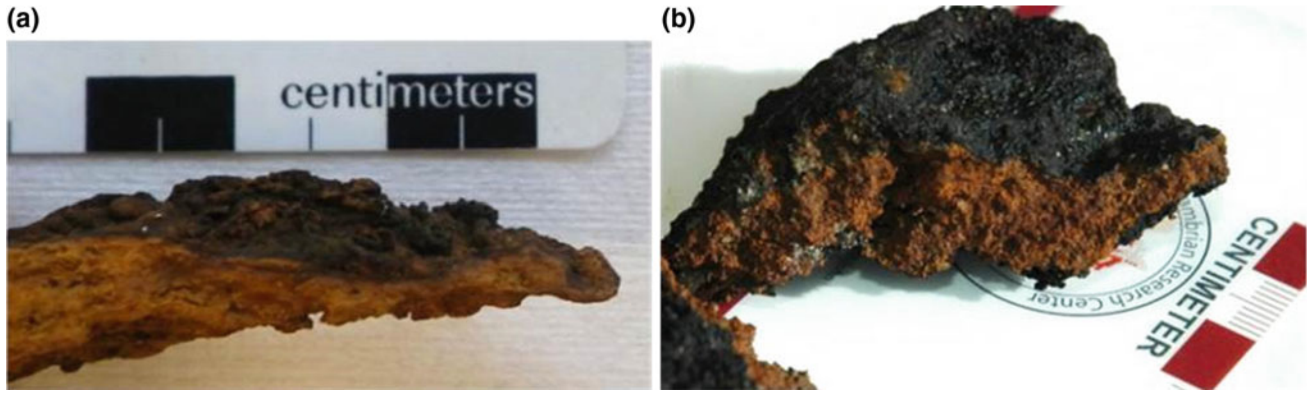

Fig. 3 Example solid metal oxides: **a** Peacock Spring. **b** Madison Blue Spring

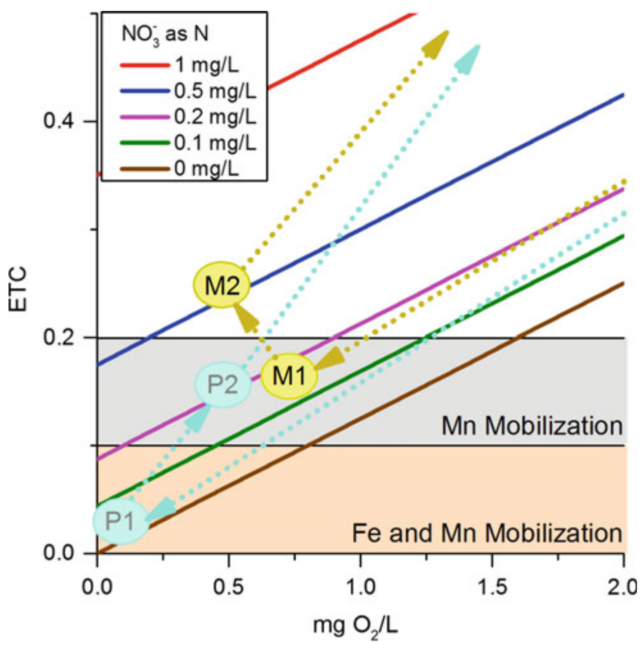

Fig. 4 Electron trapping capacity for oxygen and nitrate concentrations typical in the cave system. Baseflow nitrate ranges from 1 to 2 mg/L NO_3 as N, preventing Fe and Mn mobilization. Intruding river water has nitrate concentrations an order of magnitude lower (0.1–0.2 mg/L NO_3 as N) and transports reactive organic carbon that can further alter TEAs. *Gray box* represents zone of manganese mobilization. *Orange box* represents zone of iron and manganese mobilization. *Yellow* and *light blue dotted line* shows modeled evolution of oxygen, nitrate, and ETC for March 2012 at Madison Blue and July 2013 at Peacock from surface water intrusion through return to baseflow.

to mobilize manganese (M1) briefly, with subsequent manganese mobilization inhibited by increasing nitrate even as low dissolved oxygen levels persisted (M2).

$$\text{Electron Trapping Capacity: ETC} = 4[O_2] + 5[NO_3] \quad (1)$$

where $[O_2]$ and $[NO_3]$ are molar concentrations. ETC < 0.1 mM favors Fe and Mn mobilization. ETC < 0.2 mM favors Mn mobilization.

These results illustrate one of many controls on contaminant transport driven by changes in aquifer redox state. The oxidation of organic carbon transported into the aquifer with storm water can directly control water quality via consumption of oxygen or denitrification, but also indirectly by controlling mobilization and sequestration contaminants sorbed to iron and manganese oxides. The mobility of metal oxides depends on the combined effects of oxygen and nitrate concentrations in the water. The presence of excess anthropogenic nitrate in aquifer water could enhance retention of metal oxides, resulting in the sorption and sequestration of other contaminants. These sequestered contaminants could subsequently be released with a return to anoxic conditions. Therefore, predictive models examining the fate and transport of contamination in karst aquifers should include consideration of the aquifer redox state, especially when storm flow dramatically alters the concentration of redox-sensitive compounds in the subsurface.

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Evaluation of Spill Response System for Mammoth Cave National Park Using Quantitative Dye Tracer Studies

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Abstract

This research examines the effectiveness of check dams as containment basins using quantitative tracer studies. The focus of this study is to understand transport mechanisms from the surface into the caves and to ensure that the materials and size of the dams are sturdy enough to hold back a spill. The study included tracer studies originating from potential sources of contamination on the surface, along the water flow path and into the cave system. A known amount of Rhodamine-WT20 dye was released during storms. The flow path was monitored by portable fluorometers in the cave at different locations. The result of placing two small check dams along the surface flow path resulted in lengthening the time-of-travel from 2 hours to 16 hours. It also reduced the amount of dye entering the cave by 90%. This research will help provide options to emergency responders of spills.

1 Extended Abstract

Mammoth Cave National Park is located in south-central Kentucky (Fig. 1) and has been designated an International Biosphere Reserve since 1990. The Park is home to the world's largest cave with more than 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. Despite its vulnerability, groundwater is used as a vital resource to many communities around the world, including the USA. In fact, groundwater is used as a source of water supply by about one-half the population of the USA. Approximately, 11% of karst springs in Kentucky are used for domestic water supplies. This means over 10,000 homes rely on groundwater as their water supply source. These people have a dire need to protect the quality of the water that they are drinking. Most karst springs previously used in Kentucky for a public water supply have been abandoned because of groundwater contamination (Kentucky Geological Survey 2012).

Mammoth Cave National Park itself has a biodiversity of 43 mammals, 15 reptiles, 19 amphibians, and 3 fish which all rely on the groundwater for survival. The National Park Service controls the main part of the cave and encourages tourism while protecting the unique and fragile ecosystem in the cave. The Park is committed to the protection of its employees, visitors, and the environment during an emergency event as stated in their Emergency Action Plan. The primary objective of the managers of Mammoth Cave National Park is to protect the ecosystem and provide the tourists with a safe and sanitary cave experience by protecting their groundwater. With more than 500,000 visits per year, it is natural for accidents and spills to occur on the surface. Spills commonly come in the form of parking lot

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Fig. 1 Map of Mammoth Cave National Park by Rebel Rivers Canoe Club *Source* The Rebel River Canoe Club http://rrcc.blogspot.com/2006_11_01_archive.html

runoff due to the transport of auto diesel fuels through storm water flow and broken sewer lines. As a result, the Park is very concerned about their ability to contain high volume contaminants from spills or the wrongful release of chemicals. Therefore, it is important to develop a system that prevents the pollutants from harming the fragile cave ecosystem. Unfortunately, the same hydrogeological processes that formed the cave make the karst system vulnerable to contamination. Many of the natural storm drainage flowpaths go directly to distinct sinkholes rather than the filters that the Park has in place.

On May 27, 2014, a sewer line break occurred on Mammoth Cave Parkway near Green Ferry Road. According to the Mammoth Cave National Park After Action Report, the accident was caused by the failure of a 2-in. brass ball valve. The ball valve failed when repairs were being made to resolve a much-smaller sewer leak that resulted from an air-relief valve that failed to shut properly. The air-relief valve failure caused a small level of sewage spillage, and then the subsequent ball valve failure resulted in an initial sewage geyser that spouted approximately 20–30 ft high for a short period and then became a steady flow at ground level for over one hour before a repair was made. The Caveland Environmental Authority (CEA) employees and Park employees responded by capping the geyser and placing check dams along the flow path. According to the CEA, approximately 5000 gallons of sewage was spilled, and about 3000 gallons were recovered.

In addition, a second sewage spill occurred at the same location on April 28, 2015, when a steady flow of sewage was detected. The cause and amount of sewage released has yet to be identified, but it is assumed to have been flowing for a long period of time. The need for containment basins within the Park has increased. 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 from August 2014 to January 2015 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. Check dams are relatively small, temporary structures constructed across a swale or channel, typically constructed out of gravel, rock, sandbags, logs or treated lumber, or sediment retention fiber roll. Check dams can be temporary or permanent structures (Metropolitan Council 2000). Check dams are used to slow the velocity of concentrated water flows, a practice that helps reduce erosion. As storm water runoff flows through the structure, and the check dam catches sediment from the channel itself or from the contributing drainage area. A check dam either filters the water for sediment as it passes through the dam or retains the water, allowing the sediment to settle while the water flows over the dam. Multiple check dams, spaced at appropriate intervals, can be very effective (Tennessee Department of Environment and Conservation 2012). They are most effective when used with other storm water, erosion, and sediment control measures.

Check dams serve one or more of three functions: control water, conserve soil, and improve land (Doolittle 2010). Check dams have been built for centuries and used all around the world. Some of the earliest known check dams are located in North Africa and are thought by archeologists to date back to Roman or pre-Roman times. During Nabatean times in the Negev Desert, check dams were used to divert water from areas where it was not needed and/or toward areas where it was necessary (Evenari et al. 1982). China has been using check dams for hundreds of years. Within the last 50 years since the foundation of the People's Republic of China, they have become increasingly popular. By making use of the local geography and climate, the people of the Loess Plateau of China skillfully invented the check dam system in gullies several centuries ago, to retain sediments and to form farmland. In a small watershed, various dams can be built, such as productive dams for forming farmland, flood-control dams for preventing floodwater and intercepting sediments, and water-storage dams for irrigation. A group of such dams constitutes a check dam system. The check dams at Kanghe Gou watershed, Fen Xi County, built in Ming Dynasty 400 years ago, still operate in good condition. By 2002, about 113,500 check dams had been built, creating 3200 km^2 of farmlands with high productivity, and intercepting a total of 700 million m^3 of sediments that pour into the Yellow River. For the Loess Plateau, the check dam is the most important well-known project to conserve water and soil and the ultimate line of defense in the comprehensive control system (Xu 2004). For this study, the check dams were only used to temporarily contain spills and provide management more time remove as much of the contaminants as possible before it entered the cave.

For the tracer test, the release point chosen was the same location where the sewer break occurred: Mammoth Cave Parkway near Green Ferry Road. The surface flow channel used in this study was approximately 1500 ft in length from the tracer release point to the sinkhole. Based on availability, Rhodamine WT-20 was the dye selected for all three tests. The dye was released in conjunction with either the onset of storm runoff or as the storm was winding down. Prior to each dye release, the absence of dye was verified by monitoring waters in the cave streams a minimum of three consecutive storms before releasing the dye. The monitoring equipment was placed in the upper and lower cave passages, Cataracts and Cascade Hall area in Silliman Ave, respectively. Continuous monitoring from June, 2014, through January, 2015, was accomplished using two portable field fluorometers. The quantitative dye tracing method used follows the procedure in *Cave Geology* (Palmer 2007). Results from the test were used to determine travel time for arrival of the leading edge of the dye cloud, peak dye concentration, trailing edge, and persistence of the dye cloud at the discharge point. The amount of solute transport presented through the spectrofluorometric analysis was examined using the spreadsheet methods created by Palmer (2007) and Residence Time Distribution-Biodegradation (RTDB) method derived by Painter et al. (2012). Both have a unique way of using residence time distribution and breakthrough curves to estimate the amount of dye past a monitoring point. Using more than one method helped assure that the data are correct.

For the first test on August 31, 2014 (Fig. 2), the rainfall depth was 2.4 in. Two check dams were still in place along the surface flow routes. There was a tracer breakthrough in the cave 10 h after the dye was released. Sixteen hours after the time of the release, approximately half of the recovered dye (center of mass) had moved past the monitoring station at Cataracts. The total amount of dye accounted for was approximately 4 g out of the 180 g released, which is less than 3% of the tracer used in this study. These results indicate that the dams did a great job retaining most of the dye on the surface despite the heavy rain.

The second test (Fig. 3) was initiated on the evening of October 13, 2014, during a 2.1 in. rain event. Both check

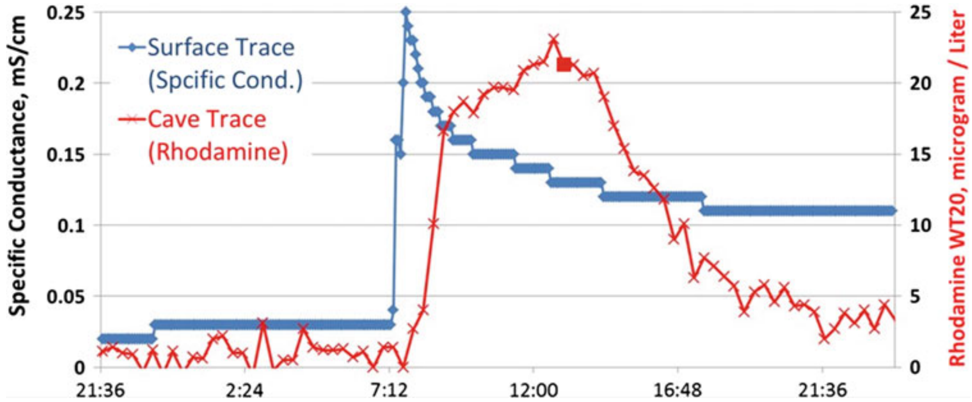

Fig. 2 Breakthrough curve for Test 1 conducted August 31, 2014

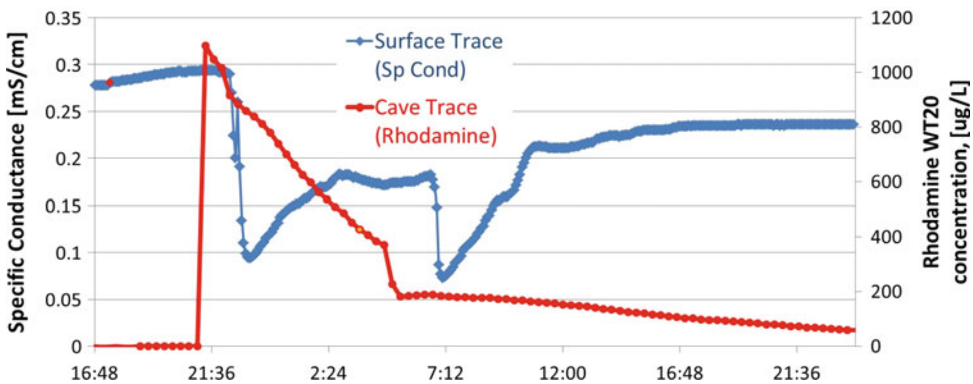

Fig. 3 Breakthrough curve for Test 2 conducted October 13, 2014

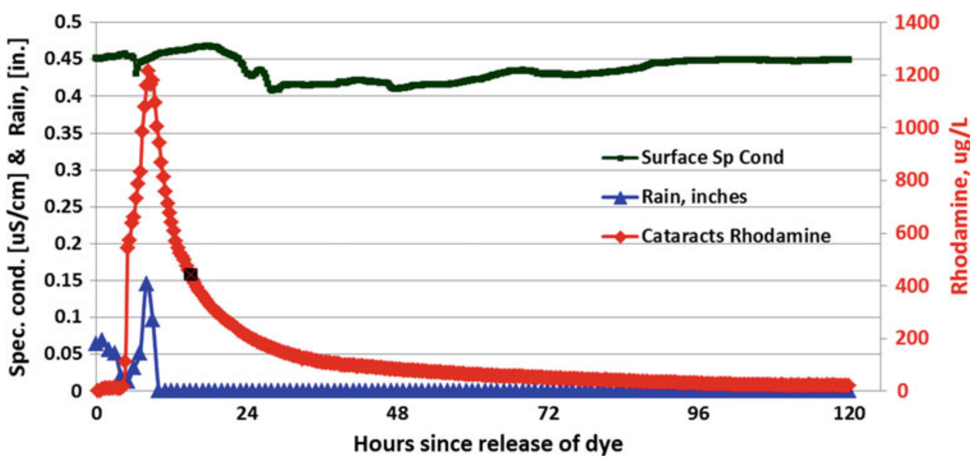

Fig. 4 Breakthrough curve for Test 3 conducted January 3, 2015

dams had been removed for this study to estimate the amount of time it would take for the dye to reach the cave with no obstacles. The breakthrough and center of mass were calculated from the results. Breakthrough in the cave occurred 4 h after the dye was released. The center of mass occurred 10 h after the release time. The total amount of dye accounted for via concentration and discharge was 262 g out of the 714 g released (43%).

During the final tracer test on January 3, 2015 (Fig. 4), the rain depth was 0.7 in. Due to timing, the release of tracer was on the tail end of the storm instead of the rising limb like the other two tracer tests. Breakthrough in the cave occurred only 50 min after the time of release. The center of mass was determined to be 15 h after the time of release. The maximum tracer amount recovered was 288 g of dye which was 48% of the total amount of dye released.

Based on these results, we can conclude that the dams increased mean residence time on the surface from approximately 0.83–16 h, 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. The dams are also esthetically neutral for tourists, seeing that they do not disturb the natural beauty of the surrounding environment. The limestone pea gravel used in the design is a natural material indigenous to the area, blending into its surroundings. More work needs to be done to identify and highlight surface to cave connections using GIS to anticipate sinkholes that are at risk of contamination. One would also need to continue to test the dams to better understand the life expectancy. In the meantime, monitoring of the site and dam maintenance should be conducted continuously to retain effectiveness.

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Bioremediation Potential in Karst Aquifers of Tennessee and Kentucky

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Abstract

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.

1 Introduction

Approximately, 40% of the USA east of the Mississippi River is underlain by various types of karst aquifers (Weary and Doctor 2014), and more than two-thirds of the state of Tennessee is underlain by carbonate rocks and can be classified as karst (Wolfe et al. 1997). Potential sources of groundwater contamination are common in karst regions; however, the fate and transport of contaminants such as chlorinated solvents or fuels in karst areas have been poorly understood and are difficult to assess because of the distinctive hydraulic characteristics of karst aquifers (Field 1993; Byl and Williams 2000). The unique and complex hydrologic conditions of karst systems can render many traditional remediation strategies ineffective. Mathematical models are being developed and adapted for karst aquifers; however, there are still limitations when applying the models to contaminants and remediation (Kuniansky 2014). From 1996 to present, the authors have been involved in studies involving bioremediation of chlorinated solvents or fuels in karst aquifers of central Tennessee and south-central Kentucky. The objective of this review article is to examine the role of bioremediation to mitigate contaminants in karst aquifers. This report presents results from previously published reports on chlorinated ethene and fuel biodegradation at karst sites in middle Tennessee and Kentucky. The report addresses microbial adaptations to karst, geochemistry, and supplements to enhance biodegradation processes within the context of karst hydrology.

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2 Microbial Adaptation to Karst Aquifers

Karst aquifers have a wide range of hydrologic conditions, from dynamic to stagnant conditions. Karst aquifers provide heterogenous hydrologic and chemical environments through the interconnection of secondary porosity, variable fracture and conduit size, changes in mineralogy and geochemistry, and variable connection with surface water and land surface. Also, karst conduits typically offer less surface areas for biofilm development per volume of water relative to granular aquifers. These conditions have led to adaptations in karst microbial communities as compared to those reported for sandy aquifers (Kölbel-Boelke et al. 1988; Barton and Northup 2007; Byl et al. 2014). Despite the lower surface area-to-volume ratio, karst aquifers support a diverse and numerous bacterial population. Bacteria were plentiful in water samples collected from clean and fuel-contaminated wells in a conduit-dominated karst aquifer in south-central Kentucky (Byl et al. 2014). Bacterial concentrations, enumerated through direct count, ranged from 500,000 to 2.7 million bacteria per mL in the clean portion of the aquifer, and 200,000–3.2 million bacteria per mL in the contaminated portion of the aquifer over a twelve month period. Bacteria from the clean well ranged in size from 0.2 to 2.5 mm, whereas bacteria from a fuel-contaminated well were generally larger, ranging in size from 0.2 to 3.9 mm. Also, bacteria collected from the clean well had a higher density relative to water and, consequently, were more inclined to sink in the water column than bacteria collected from contaminated wells (Fig. 1). The ability of bacteria to change their buoyant density and float in the presence of dissolved fuel supports the findings that free-living bacteria can contribute equally to the biodegradation of dissolved benzene and toluene in groundwater as compared to biofilms in a karst system (Painter et al. 2005). In other words, the low surface area-to-volume ratio in karst conduits does not necessarily limit biodegradation of fuels. These findings do not extend to all contaminants. In a study by Brown et al. (2014), the biodegradation rate of ammonia and quaternary ammonia compounds by karst bacteria was largely dependent upon surface area and biofilm development. Additional research is needed to understand the importance of biofilms versus free-living bacteria on the biodegradation of different contaminants in karst aquifers.

The karst aquifers of central Tennessee and south-central Kentucky tend to have a diverse microbial community (Byl and Williams 2000; Byl et al. 2014). Bacteria collected from wells in uncontaminated karst aquifers were predominantly (95%) Gram-negative and more likely to have flagella present than bacteria collected from the contaminated wells, which included a substantial fraction (30%) of Gram-positive varieties. Various bacterial types capable of biodegrading fuel (Byl et al. 2001) or chlorinated ethenes (Byl and Williams 2000) have been identified in water samples from the karst aquifers in middle Tennessee and southern Kentucky. Bacterial types identified in Tennessee and Kentucky karst aquifers include heterotrophic aerobic bacteria, ammonia-oxidizing bacteria, methanotrophic bacteria, anaerobic nitrate-reducing bacteria, iron-reducing bacteria, and sulfur-reducing bacteria. Although these bacterial types have different geochemical requirements (e.g., aerobic or anaerobic conditions), the heterogeneity of the karst aquifers allows these diverse bacteria to live in close proximity to each other (Northup and Lavoie 2001). This microbial diversity provides an inoculum of different bacterial types as aquifer geochemical conditions change, possibly in response to hydrologic changes or the encroachment of contaminants or the application of supplements.

The documented rates of contaminant biodegradation in karst aquifers varied based on the contaminant and the aquifer geochemical conditions. Aquifers contaminated with petroleum hydrocarbons tend to go anaerobic which slows down the rate of biodegradation. Anaerobic benzene and toluene biodegradation had half-lives ranging from 22 to 26 days (Byl et al. 2014), and, anaerobic crude oil biodegradation had a half-life of 1.6 years (Spear et al. 2011).

3 Supplements and Residence Time in the Karst Aquifers

The initial research concerning bioremediation in karst aquifers focused on documenting biodegradation under natural conditions. As more information about the microbial community became available, the research branched out to examine enhanced bioremediation in karst aquifers using supplements. As part of that research, methods were developed to measure residence time distribution and biodegradation in sections of the karst aquifer intersected by wells (King et al. 2005). Conservative tracers, such as salt, were injected into karst aquifer contaminated with fuel components (benzene and toluene) to calculate residence time in the test zones. The rate of contaminant disappearance was compared to the decline of the tracer concentration to determine whether benzene and toluene were being removed at a rate that exceeded nonbiological processes.

Chlorinated solvents are one of the contaminants of concern in the karst aquifers of Tennessee (Wolfe et al.

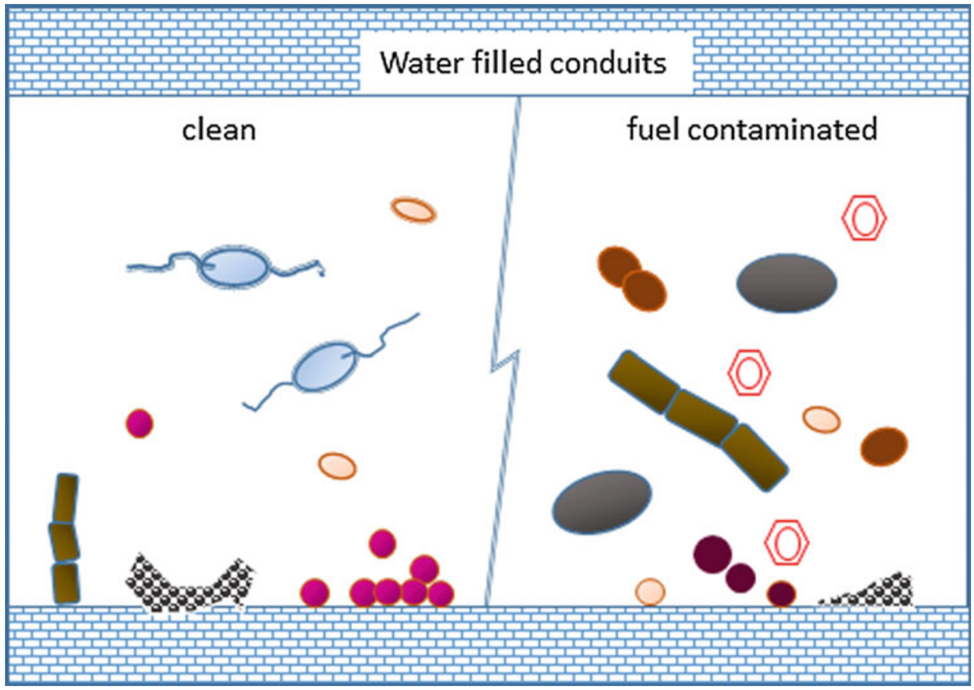

Fig. 1 Conceptual model. Aquatic bacteria in a clean and a fuel-contaminated karst conduit. In the presence of dissolved fuel, the median bacterial size is slightly larger and more buoyant

1997). In a study by Chakraborti et al. (2003), a sanitary landfill situated on a karst terrain in northern-central Tennessee had leaked chlorinated solvents, primarily trichloroethylene (TCE), into a karst aquifer. TCE has been found in water samples collected from eight wells screened in the karst bedrock aquifer. A mixture of rhodamine dye, sodium lactate, molasses, and soymilk formula was injected into seven wells to determine if the mixture would enhance biological reductive dechlorination of TCE. Electronic monitoring devices were placed in selected wells following injection to monitor changes in water levels, geochemistry (temperature, pH, dissolved oxygen, and specific conductivity). No dissolved oxygen was present in the water of any of the supplement-treated wells one week after the mixture was injected. Water samples were collected every few weeks over the following year to monitor bacteria, sulfide, nitrate, trichloroethylene (TCE) and TCE-breakdown products (cis-dichloroethylene, cDCE), and dye. After eight months, there was an 85–100% decrease in TCE concentrations in the supplement-enhanced wells, and a 65–100% decrease in cDCE concentrations in six of the wells. Two of the seven wells initially showed an increase in cDCE as TCE went through reductive dechlorination to form cDCE. Concurrent with decreases in TCE and cDCE, there was a tenfold increase in sulfur-reducing bacteria and sulfide concentrations from initial levels. The rate of TCE disappearance in the supplement-enhanced wells was approximately 2–10 times faster than the rate of tracer reduction.

4 Conclusions

The bioremediation of contaminants in unconsolidated aquifers has been well documented; however, the bioremediation of contaminants in karst aquifers is still being researched. Factors that affect bioremediation in karst are hydrology, geochemistry, and microbiology. Multiple lines of evidence are needed to evaluate potential bioremediation in karst aquifers. These lines of evidence normally include the following: (1) Geochemical data to determine if conditions are suitable for biodegradation of the contaminant, (2) laboratory or field microbiological data that indicate bacteria capable of biodegrading the contaminant are present at the site, as well as, data that show contaminant concentrations are decreasing through time, and (3) hydrologic data to assess residence time of the contaminant in the aquifer.

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Investigating and Remediating Contaminated Karst Aquifers

Malcolm S. Field

Abstract
Subsurface investigations of contaminated karst aquifers are generally regarded as extremely difficult. The difficulty not only 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.

1 Introduction

Karst aquifers are much more susceptible to contamination than are other aquifers (e.g., porous-media and fractured-rock aquifers). The susceptibility is related to the functional relationships associated with the dissolutional aspects of carbonate and sulfate rocks. For instance, if one or more resurgences are evident in a karst terrane then the existence of one or more discrete subsurface flow reaches is confirmed, at least for the discharge end of the aquifer. Similarly, if one or more sinkholes, sinking streams disappearing into swallow holes, and/or losing streams leaking through their beds are found to exist, then the existence of one or more discrete subsurface flow reaches is confirmed, at least for the recharge end of the aquifer. These discrete flow reaches are solution conduits that were formed by the dissolution of the rock along selected planes of weakness, typically bedding-plain partings and fractures.

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.

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Pollutant releases into sinkholes, sinking streams, and/or losing streams allow for relatively concentrated contaminants to rapidly infiltrate and migrate through the subsurface for discharge at the downgradient springs unless intercepted by production wells. Diffuse percolation through less defined surface openings is common as well, which tends to be ignored because of the apparent extreme situation of concentrated contaminant inflow via typical karst surface features.

Common geological structures, such as folded, fractured, and faulted terranes, also add to the complexity of karst areas. In addition, rapidly changing stratigraphic layers, overturned beds, and degrees of rock purity can also be significant in regard to water transit, fate-and-transport of contaminants, and aquifer remediation.

Although ostensibly simple and straightforward, groundwater flow and solute migration through solution conduits are extremely difficult to assess, even in flat lying relatively pure limestones (e.g., Barceloneta, P.R), because of the typical inaccessibility of the conduits, either by direct exploration or indirectly by boreholes. Figure 1 is a simplified schematic of a flat-lying karst aquifer illustrating the basic migration of water and contaminants down to the underlying aquifer, to and through the main trunk conduit, and ultimately discharged at a downstream resurgence. Unfortunately, only input and outlet locations typically may be determined along with transport velocities and some related parameters (e.g., dispersivities).

Behaviors of specific contaminants also can greatly complicate the assessment of contaminant fate-and-transport and aquifer remediation. Volatile and semi-volatile contaminants (VOCs and SVOCs, respectively) will both flow along with the subsurface waters in a karst terrane but the volatility of such contaminants, depending on the Henry's Law constant for each, will result in the vapor phases of the VOCs and SVOCs of such contaminants to migrate through the vadose zone. Concentrating the vapor phases in vadose caves and homes can become extreme and dangerous from an emergency perspective (e.g., Crawford 1984). Light nonaqueous-phase liquids (LNAPLs) will float on the surface of subsurface waters and migrate with the subsurface waters. Dense nonaqueous-phase liquids (DNAPLs) will, under the pull of gravity, displace the subsurface waters and sink as rapidly as possible down to the bottom of the aquifer and will flow as a dense mass along the bottom of the aquifer. Concurrently, the DNAPL will slowly dissolve into the water and this dissolved phase will flow along with the water according to the hydraulic gradient (Fig. 2).

Assessing actual contaminant reactivities within a karst aquifer is, in general and within solution conduits specifically for all practical purposes, impossible. However, understanding contaminant reactivities in the subsurface is essential if contaminant migration and exposures are to be understood, and if remediation approaches are to be devised.

The purpose of this paper is to present a somewhat basic overview of the efforts to understand contaminant fate-and-transport suggest a possible approach, and consider remediation in karst aquifers.

2 Recognition of Karst

Recognizing the existence of a karst terrane is sometimes quite difficult. Obvious evidence for the existence of a karst terrane is the existence of one or more sinkholes in the area; sinkholes are regarded as diagnostic of karst (Waltham et al. 2005, p. 26). However, the absence of sinkholes is not indicative that the terrane is not karstic.

Although karst has been defined many times by different people over a number of years (see, for example, Field 2002), it is important to note that there are many different degrees of karstification. The appearance of karst also varies, but much of the literature fails to adequately describe karst as it may exist at any particular location (Quinlan 1978, p. 1). Quinlan (1978, p. 25–29) developed a very comprehensive karst-classification scheme that has withstood the test of time (White 2011). According to White, Quinlan's classification scheme continues to work well for karst landforms formed by descending (top down) meteoric water (Table 1).

Recognition of the existence of a karst terrane is critical to any attempts to characterize site contamination, solute fate-and-transport in groundwater, discharge of the contaminants, exposure and risk assessments related to the contamination, and remediation of the contamination. The question of a site possibly being karstic requires that the investigator forego the typical definitions for what constitutes karst as might be found in Field (2002), and instead consider a definition more representative of environmental concerns, especially as it might be applied to groundwater quality. Consider, for example, Figs. 3, 4, and 5, which document three different examples of a karst terrane. Figure 3 is an example of a sinkhole plain in the Barceloneta, PR area. It will be noted from Fig. 3 that large solution conduits must exist in the north coast aquifer. However, Fig. 4 shows a block of limestone from the north coast of Puerto Rico illustrating the typical vuggy aspect of young tropical limestones, which would suggest that solution conduits are unnecessary for the transmission of significant quantities of water and contaminants (e.g., Vik et al. 2012), but this is an incorrect interpretation of the geology. Figure 5 is an example of very tight Paleozoic limestones in Maryland, USA, which clearly illustrates the need for solution conduits for the rapid transport of large quantities of water and contaminants.

Therefore, given the very wide range of karst terrane types, a reasonable working definition of karst with

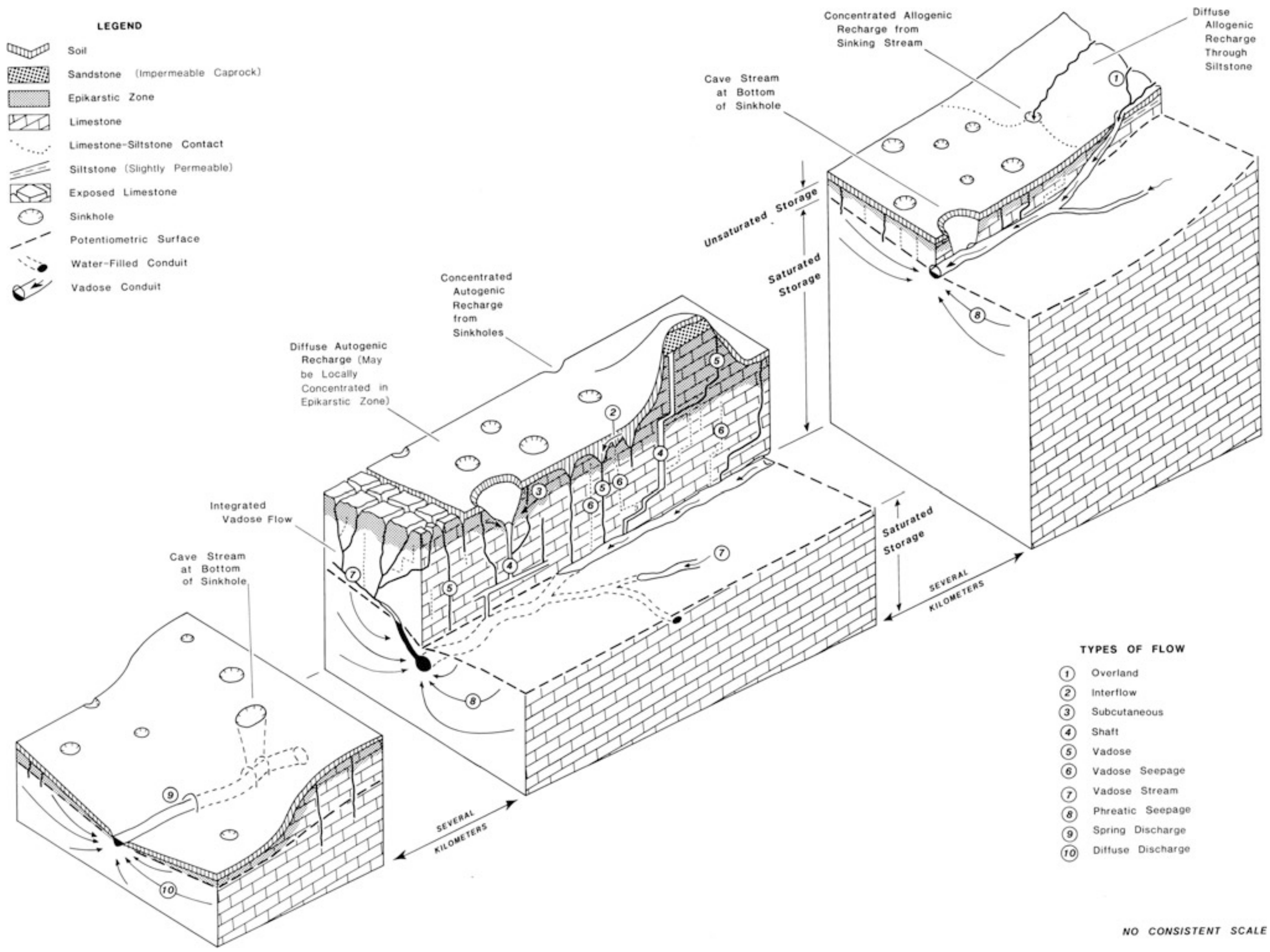

Fig. 1 Block diagram depicting the hydrological relationships that exist in a maturely karsted terrane in gently dipping rocks of a low-relief landscape. The cave is fed by *1* sinking streams, *2* vertically percolating water infiltrating through soils and sinkholes, *3* tributary cave streams, and *4* seepage through conduit walls. Contaminants will enter the aquifer through the same mechanisms that control water inflow (after Quinlan 1989)

environmental concerns would be (Quinlan et al. 1991): "As a generalization, if carbonate rocks such as limestone, marble, or dolomite are present, or if more soluble rocks such as salt or gypsum are present, assume that the water moving through these rocks is in a karst aquifer—until or unless convincingly proved otherwise." Stated more succinctly: "Any soluble rock terrane is karst unless or until proven otherwise."

2.1 Some Reasons Why Karst Is Such a Problem

In recent years, more and more karst professionals have begun recognizing the problems associated with karst aquifers, specifically the nature of groundwater flow. Unlike more commonly understood porous-media and fractured-rock aquifers (in which the rock is considered to be so highly fractured that it is said to mimic a porous-media aquifer) is that most of the flow is constrained to select solution conduits (Fig. 1).

Water and contaminants primarily enter the subsurface via discrete points such as sinking streams and sinkholes, but may also percolate through overlying materials. The contaminants then mostly migrate via the solution conduits, but exceptions do exist (e.g., Dense Nonaqueous–Phase Liquids [DNAPLs]). Contaminant transport rates can be very rapid (e.g., several meters per hour) and discharge of the contaminants typically occurs at discrete locations (e.g., springs). Long-term storage in the subsurface can still occur as well (e.g., Even et al. 1986) resulting in a long-term contaminant source.

Unlike terrestrial Paleozoic limestones, the north coast karst aquifers of Puerto Rico is riddled with vugs (Fig. 4), which has led some groundwater professionals to consider the north coast karst aquifers to resemble giant sponges and to transmit water and contaminants in the same manner as

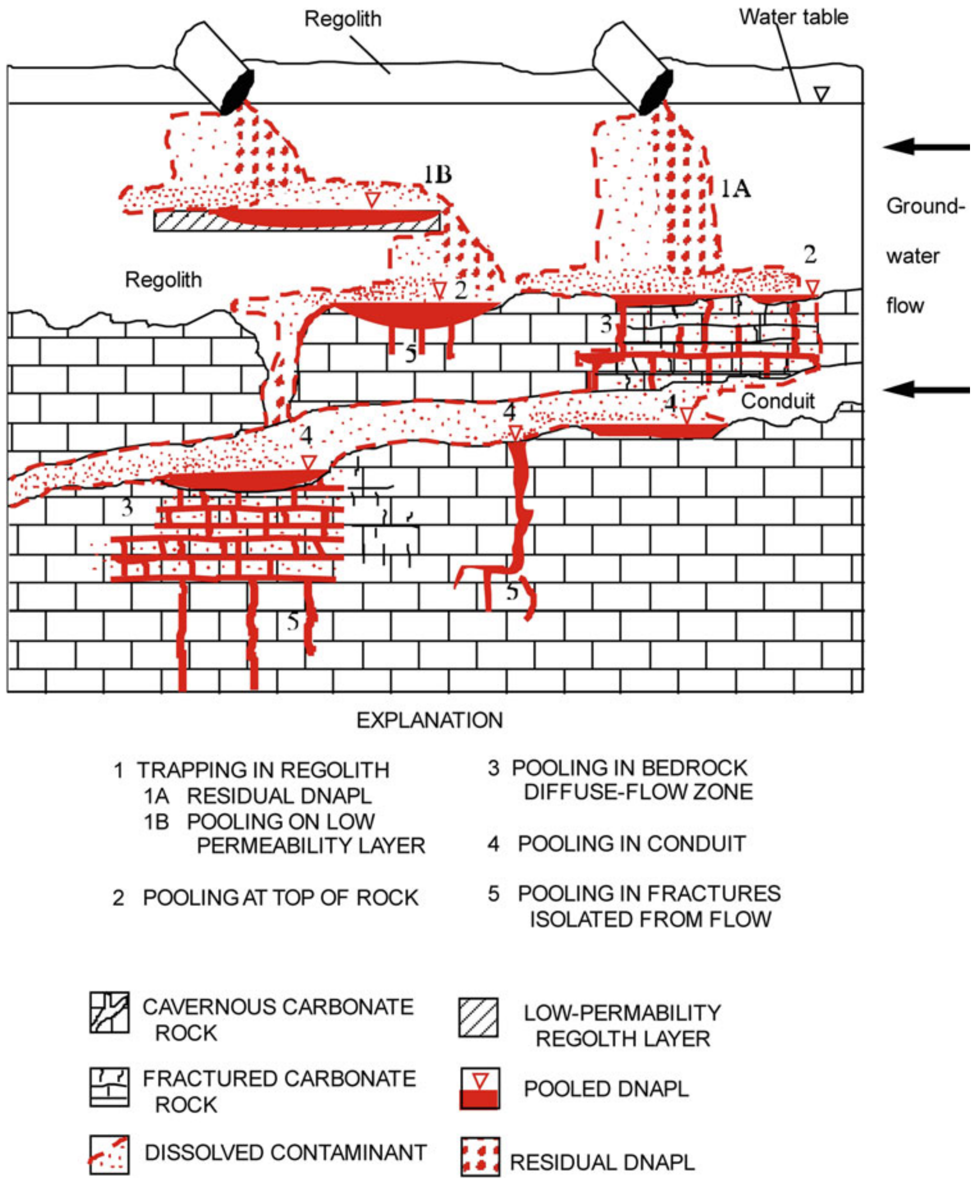

Fig. 2 Downward and lateral migration of potential DNAPL-accumulation sites in a hypothetical karst setting (after Wolf and Haugh 2001)

porous-media aquifers. This misunderstanding of the nature of water and solute migration in karst aquifers has led to serious errors in the assessment of subsurface solute transport. The fact that sinkholes (some very large—the famed Arecibo Observatory is built in a large sinkhole) and springs exist is sufficient evidence that water and solute migration occurs primarily via solution conduits. It is physically impossible for the subsurface to absorb the massive quantities of water that wash down sinkholes if the sinkholes are not connected to solution conduits and the existence of springs are clear evidence that discharge is via discrete pathways. Vuggy carbonate aquifers are incapable to receiving and absorbing large quantities of water that flow into sinkholes during large precipitation events.

3 Karst Aquifer Contamination

When the public thinks about groundwater pollution, they generally think of industrial pollution and chemical spills from pipelines, trucks, and rail cars, but many other human activities often result in aquifer contamination as well. For example, agricultural activities such as CAFOs (Concentrated Animal Feeding Operations) often result in the release of major inorganic compounds, nitrates, phosphates, heavy metals (Liu Xueping et al. 2015), steroid hormones (Lui Shan et al. 2012; Lange et al. 2002), antibiotics, other pharmaceuticals (Shore and Pruden 2009, p. 3), and microbial pathogens (Hribar 2010, pp. 8–10; Fleming et al. 1997). While the possible environmental risks posed by major

Table 1 Classification of karst types as proposed by James F. Quinlan (after Quinlan 1978)

Cover	Lithology
A. Covered karst 1. Subsoil karst 2. Mantled karst 3. Buried karst 4. Interstratal karst 5. Subaqueous karst a. Drowned karst b. Subfluvial karst c. Submarine karst 6. Sulfate-reduction karst B. Exposed karst 1. Naked karst 2. Denuded karst 3. Exhumed karst	A. Rocks 1. Carbonate a. Limestone b. Dolomite c. Chalk d. Caliche e. Phosphatic limestone f. Other sedimentary carbonates g. Other carbonate-cemented h. Marble i. Magnesite j. Carbonatite 2. Sulfate a. Gypsum, anhydrite b. Other (Epsomite) 3. Halide 4. Interbedded carbonate 5. Sulfur 6. Nitrate 7. Borate 8. Noncalcareous 9. Noncarbonate B. Unconsolidated sediment 1. Carbonate 2. Sulfate 3. Halide 4. Siliciclastic 5. Alluvium

Climate	Geologic structure	Physiography
A. Humid temperate B. Humid tropical C. Humid, arctic, and subarctic D. Arid, semi-arid E. Alpine, subalpine	A. Undeformed rocks 1. Flat-Lying 2. Homoclinal B. Deformed rocks 1. Folded 2. Faulted 3. Folded and faulted 4. Diapiric 5. Other	A. Relation of karst area 1. Allogenic streams 2. Autogenic streams B. Regional landform 1. Plain and plateau 2. Mountains and isolated massifs 3. Valley and ridge 4. Coast

Hydrology	Modification	Dominant landforms
A. Origin of water 1. Nonhydrothermal a. Meteoric b. Marine c. Water of dehydration 2. Hydrothermal a. Meteoric b. Meteoric plus magmatic B. Aquifer properties 1. Degree of confinement a. Unconfined i. Open ii. Capped b. Confined i. Artesian ii. Sandwich c. Partly confined i. Perched (a) Open (b) Capped ii. Leaky	A. No modification B. Changes in climate C. Anthropogenic changes D. Burial E. Rejuvenation F. Drowning G. Mineralization H. Glaciation I. Melting J. Abandonment	A. Doline karst B. Cone karst C. Cockpit karst D. Tower karst E. Crevice karst F. Arete and pinnacled karst G. Pavement karst

(continued)

Table 1 (continued)

Hydrology	Modification	Dominant landforms
2. Type of flow a. Diffuse b. Conduit 3. Depth of flow a. Superficial c. Deep 4. Dominant flow direction a. Near-horizontal b. Near-vertical i. Descending ii. Ascending c. Inclined 5. Thickness of aquifer a. Thin b. Moderate c. Thick 6. Number of aquifers a. One b. More than one 7. Recharge a. Type i. Diffuse ii. Concentrated b. Source i. Direct infiltration ii. Other aquifers iii. Spill-over iv. Bodies of water v. Other 8. Discharge a. Type i. Diffuse ii. Concentrated b. Destination i. Into other aquifers ii. Over impermeable beds iii. Into bodies of water		

inorganic compounds, nitrates, heavy metals, and microbial pathogens to human health are reasonably well understood, the risks posed by various pharmaceuticals to human health are only just now beginning to be recognized.

The public also tends to consider mostly organic chemicals developed in laboratories, when they think of industrial contamination, which is not necessarily incorrect, but other pollutant types are also of concern. In general, industrial chemicals may be regarded as more serious pollutant releases and in some instances more common as well. For example, the most commonly occurring chemical contaminate that may be found at Superfund sites is trichloroethylene (TCE), which is typically used for degreasing operations. Polychlorinated biphenyls (PCBs) are also ubiquitous because they are typically included in lubricating oils to help cool the oils.

Typical pollutant releases occur from any number of human activities, such as wastewater discharge (Fig. 6). Many of the releases occur as spills from shipping accidents, loading/unloading sites (Fig. 7), leaks from landfills and surface impoundments (Fig. 8), sinkhole formation beneath disposal sites (Fig. 9), leaks from underground tanks (Fig. 10), leachate from waste piles (Fig. 11), leaks from oil and gas well drilling operations, and illegal waste disposal or dumping.

3.1 Need to Understand the Contaminant Properties

Understanding basic contaminant properties and related behavior in karst aquifers is essential to the determination of contaminant transport and any possible remediation approaches. TCE, for example, is classed as a Dense Nonaqueous Phase Liquid (DNAPL) that when released initially sinks down to the water table where it initially ponds until it

Fig. 3 Sinkhole plain on the north coast in the Barceloneta area of Puerto Rico with an industrial facility in the background and surrounded by magotes (residual limestone hills). The frequent occurrence of new sinkholes in the region has routinely caused numerous problems for the industrial facilities in the area

Fig. 4 Block of vuggy limestone from the north coast karst aquifer of Puerto Rico

exceeds what is known as the organic entry pressure. Once the organic entry pressure is exceeded, TCE displaces the groundwater and sinks directly to the bottom of the aquifer unless it becomes temporarily perched on obstructions, which would be typical of karst aquifers. TCE then continues flowing down the dip of the rock or along the base of a solution conduit as a density phase while slowly dissolving; the dissolved phase will migrate with the prevailing groundwater-flow direction (Fig. 10). Lastly, TCE will also slowly degrade to vinyl chloride, will rise up into the vadose

Fig. 5 An example of the complex geology of the Stonehenge Formation at a cut in a quarry several miles to the south of Hagerstown, Md

Fig. 6 Industrial wastewater disposal into a reinforced sinkhole at the RCA del Caribe Superfund Site, Barcenoneta, P.R. The reinforced sinkhole was classed as an injection well and the wastewater disposal was operated under an approved permit

zone, migrate as a vapor phase, accumulate in open spaces (e.g., basements), and is much more toxic than was the original TCE. PCBs, on the other hand, exist as numerous congeners, has a retardation factor of about 30,000, which supposedly means that the PCBs cannot migrate from the point of release. However, PCBs tend to readily sorb onto clay particles and colloids, which in turn are transported with the flow of groundwater by a process known as facilitated transport (Huling 1989; Reimus 1995; Morales 2011). Facilitated transport may be especially prevalent in karst aquifers because the large open solution conduits typical of karst aquifers allow for the transport of large quantities of sediments.

3.2 Appropriate Sampling Methodologies

In most instances, groundwater sampling consists of the collecting grab samples from selected locations (e.g., monitoring wells and springs), which is true for karst aquifers especially if the sampling locations were shown by tracing studies to be connected to the area or specific point of

Fig. 7 Aerial view of the RCA del Caribe Superfund Site, Barcenoneta, P.R. where small and large spills from tanker trucks occurred during normal operations. Note the four liquid hazardous waste surface impoundments at the top of the photo and the sinkhole evident in the left-most surface impoundment

Fig. 8 Unlined liquid hazardous waste surface impoundment operated at the RCA del Caribe Superfund Site, Barceloneta, P.R

contaminant release. Unfortunately, simple grab sampling in karst aquifers has been shown to be almost useless because contaminant migration in karst aquifers typically occurs as inconsistent pulses. These inconsistent contaminant-discharge pulses make the detection of contaminants almost impossible to detect, because it can be nearly impossible to schedule sample collection during the same period that the contaminants are emerging.

3.2.1 Event-Driven Sampling

In an effort to resolve the problem of collecting grab samples when contaminants are actually emerging, Quinlan and Alexander (1987) proposed an event-driven sampling scheme based on precipitation occurrences. Water samples are scheduled to be collected at selected sampling station before the start of a large precipitation event is to occur and to continue at a predetermined sampling frequency

Fig. 9 Lined liquid hazardous waste surface impoundment operated at the RCA del Caribe Superfund Site, Barceloneta, P.R that was breached by a large sinkhole. All the liquid waste was rapidly flushed underground

throughout the entire storm event, possibly generating hundreds of samples over a very short timeframe.

However, planning to be at a sampling station before a large precipitation event is to occur and to be able to collect an appropriate number of samples during the rising limb of the storm-event hydrograph and somewhat lesser number of samples during the recession limb of the hydrograph can be onerous, especially if it is later determined that the storm was of insufficient size and/or duration to justify analyzing the water samples.

3.2.2 Passive Sampling

Passive sampling may be defined as any method that is based on the free flow of contaminant molecules from the sampled media to a receiving phase in a passive sampling device as a result of differences between the chemical potentials of the analyte in the two media (Górecki and Namieśnik 2000; Vrana et al. 2005). Passive-sampling methods are generally classified as either adsorptive or absorptive. Adsorptive methods take advantage of the physical or chemical retention by surfaces and rely on parameters that involve surface binding and/or surface area. Absorptive methods involve not only surface phenomena but also analyte permeation into the interceding material. This latter approach provides the possibility for compound discrimination because of the membrane's physicochemical characteristics (Kot et al. 2000). Applying a passive-sampling methodology at selected sampling stations in a karst terrane may allow for the collection of time-weighted average contaminant concentrations that will smooth out the typically spiky nature of pulse contaminant releases but will also be less likely to miss the emergence of contaminants (e.g., see Schwarz et al. 2011). However, considerable pre-analysis of the selected passive sampling device(s) is necessary prior to application. For example, use of any passive sampling device requires knowledge of the actual sampling-collection rate of the sampling device. Still, application of passive sampling devices holds great promise for the reliable collection and analysis of contaminated karst aquifers.

4 Karst Aquifer Remediation

The concept of remediating karst aquifers is a profound one because of the old adage, "it sounds much easier than it really is." A typical approach to aquifer remediation is generally termed pump-and-treat in which contaminated groundwater is pumped out of the aquifer, treated until cleansed of pollutants, and then either re-injected back into the aquifer or disposed elsewhere. This remediation approach works to varying degrees of success, but is almost useless when applied to karst aquifers because of the extreme heterogeneity and anisotropy of karst aquifers, the limited diameter and

Fig. 10 Excavated gasoline storage tank in Poolesville, Md. The *left arrow* points to a painted area of the tank where rusted small holes ($\sim$1 cm in diameter) were noted. The *right arrow* points to the lower right side of the tank where the backhoe penetrated the tank during the excavation process

length of the enclosed solution conduits, and the nature of the flow regime within the solution conduit.

Consider, for example, the installation of a pump-and-treat extraction well (a form of hydraulic control) installed in a flat-lying terrestrial karst aquifer that is expected to pump out contaminated groundwater. An immediate problem that could affect the extraction well would be the typical anisotropy of karst aquifers. Figure 12 depicts the calculated transmissivity tensor for a pumping well installed in a karstic aquifer located in Frederick, Md. It is apparent from Fig. 12 that rather than the hoped for symmetrical cone of depression created by the pumping well (envision a funnel), extreme anisotropy exists as evidenced by the elongated transmissivity tensor in the NE–SW direction.

Even more basic and significant is the near impossibility of siting the necessary extraction wells in the aquifer solution conduits. If, however, by fortuitous good luck one or more extraction wells were actually sited in one or more solution conduits in which contaminants are migrating, pumping the wells would likely be problematic. First, it is very possible that pumping the wells at a high-enough rate to be effective would cause the solution conduit to be drained because it is highly unlikely that the solution conduit would be a gigantic pipe physically similar to those explored by scuba divers in the Floridan Aquifer System. Rather, the intersected solution conduits would more likely be very small and include constricted zones throughout their length. Second, the typically large quantities of accumulated sediments in solution conduits would likely clog the extraction wells very quickly and repeatedly.

There are numerous other methodologies that fall under the category of aquifer remediation such as air sparging, in situ chemical oxidation, multiphase extraction, waterflooding, surfactant enhancement, biostimulation, natural attenuation, thermal destruction, physical barriers, and treatment barriers (USEAC 2002; Kresic and Mikszewski 2013, pp. 425–479) but they all have one thing in common, the need to target the subsurface contamination, which is

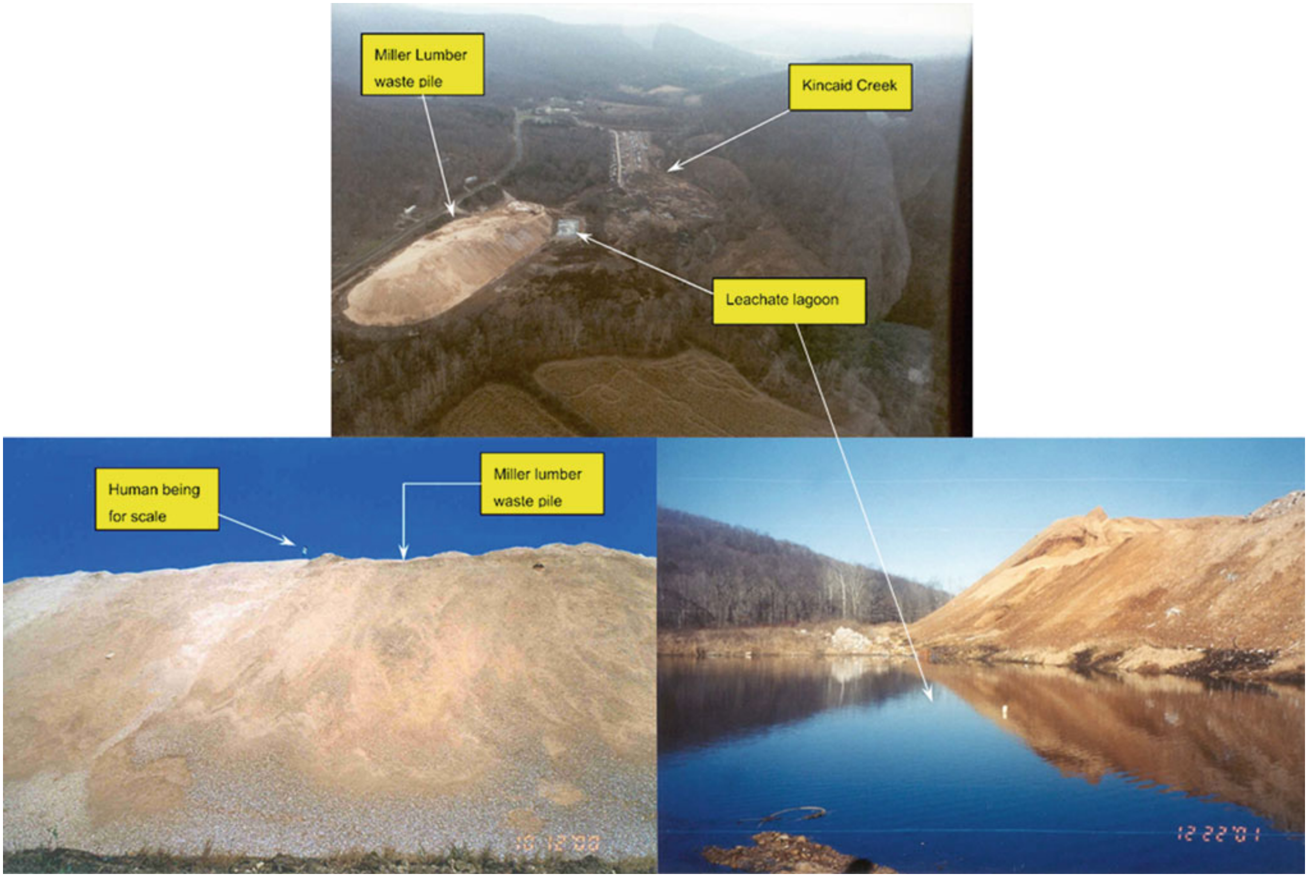

Fig. 11 Illegal Miller Lumber waste pile formed from sawdust of plywood and particle boards. Leachate from the waste pile was stored in the leachate lagoon in which ammonia concentrations commonly ranged from 2000 to 8000 mg/L. The lagoon was breached as often as every two years resulting severe surface water and groundwater contamination

almost always likely to fail when the aquifer is karstic. To that end, contaminated karst aquifers often fall under the special category of Technical Impracticability (TI) Waivers (USEPA 1993, 2011, 2012) meaning that actual remediation of the contaminated karst aquifer cannot be achieved due to the technical implausibility that an existing remediation technology could be effective, regardless of how much effort and financial resources are expended. A TI determination may be most particularly appropriate when the karst aquifer is contaminated with a DNAPL, although TI Waivers are generally considered appropriate for any type of aquifer contaminated by DNAPLs (Dawson and Golian 2001).

4.1 What Is a TI Waiver?

Technical Impracticability, or TI, refers to the realization that aquifers contaminated by DNAPLs may be impossible to remediate to expected goals (e.g., Maximum Contaminant Levels), which then require consideration of ARAR (Applicable or Relevant and Appropriate Requirement) Waivers. ARAR waivers represent alternative potentially more realistic remediation goals such as allowing for greater risk levels, interim measures, equivalent standard of performance, inconsistent application of state standards, and fund balancing (Kresic and Mikszewski 2013, p. 481). A TI Waiver does not, in general, require or even suggest that no remedial action is the expected decision to be implemented as part of an EPA Record of Decision (ROD). No remedial action may be the decision to be taken but only after determination that no other ARAR may be workable.

4.2 Why Is a TI Appropriate for Application to Contaminated Karst Aquifers?

As explained in the Introduction of this paper, the complexity of a typical flat-lying karst aquifer can be significant. If the karst aquifer is situated in an area of folded and faulted rocks such as occurs in portions of the Appalachians, the complexity multiplies. Couple this complexity with some contaminants, such as DNAPLs, and the ability to fully

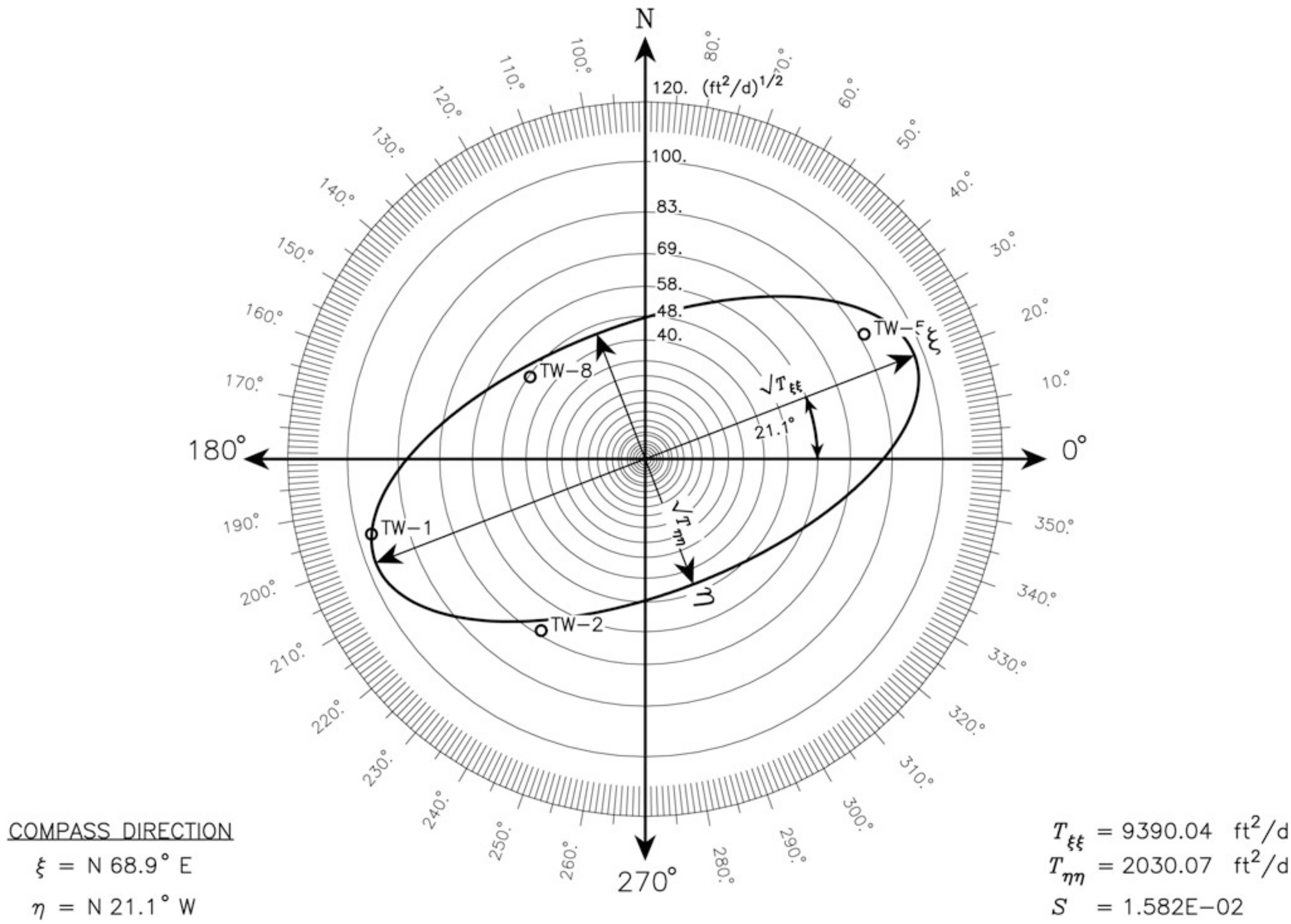

Fig. 12 Transmissivity tensor of a pumping well installed in the karst aquifer in Frederick, Md. It will be noted that the dominant transmissivity is in the NE–SW direction, which limits the withdrawal of water in the NW–SE direction. For contaminant extraction, this degree of aquifer anisotropy can be very problematic

investigate, assess, and remediate the contamination becomes overwhelmingly difficult and costly. Even when site investigation has been comprehensive and reasonable understanding of the karst aquifer and contamination have been achieved, effective remediation of the aquifer may remain elusive no matter which remedial methods are selected and no matter how much money is expended. As such, it is appropriate for TI Waiver to be considered during the period in which remedial actions are being debated.

5 Summary

Karst aquifers represent the most complex of all aquifer types. Typical aquifer investigative techniques have been known for many decades to, at times, be even worse than not investigating at all because the significant potential for misinterpreting the information gained. For example, conventional grab sampling will most often result in no detections of any contaminants because of the typical pulse-releases of the contaminants constrained to and migrating through solution conduits.

Remediating contaminated karst aquifers is even more difficult because of the difficulties in locating and accessing the sources of subsurface contaminants (e.g., DNAPLs) and the mobile phases of the contaminants (gaseous and liquid) because of our basic inability to adequately locate the solution conduits that the contaminants are traversing. Our inability to apply conventional remediation technologies thus require alternative approaches.

The most likely alternative approach to remediating a contaminated karst aquifer is the consideration of Technical Impracticability (TI) Waivers. A TI waiver allows, after thoroughly investigating the nature and extent of the contamination and the hydrogeological conditions, for the possibility of remediating the aquifer to some less stringent requirements. In extreme cases, natural attenuation may be the most appropriate remediation choice, but long-term monitoring at discharge locations will necessarily be warranted to ensure that contamination levels are in fact decreasing over time.

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Electrochemical Remediation of Contaminated Groundwater: Pilot Scale Study

Savannah Gregor, Noushin Fallahpour, Ljiljana Rajic, and Akram Alshawabkeh

Abstract

Electrochemical technologies for groundwater treatment use a low-level direct current (DC) through electrodes in wells, which enables manipulation of groundwater chemistry. There are several advantages to this approach: 1) It is sustainable and can be driven by a renewable energy source (e.g., solar power), 2) it does not require the addition of solutions or chemicals into groundwater, and 3) the rates of redox reactions can be controlled by adjusting electric current intensity. Two transformation mechanisms are evaluated within this approach depending on electrode materials used: electrochemical reduction of contaminants using iron anodes and foam cathodes, and electrochemical oxidation of contaminants by generation of reactive oxygen species (ROS) using inert electrodes. The first step in implementation of electrochemical technologies is the development of an electrolytic reactor within the aquifer. The effects of the concentration of added ferrous ions, salts, and operational conditions such as flow rates and current density have been considered to optimize the remedial system conditions.

1 Extended Abstract

Karst aquifers are highly productive and also susceptible 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 necessary. Electrochemical-based technologies are a viable option for treatment of groundwater in karst regions. One of the approaches that has been investigated is the use of solar panels to generate a low-level direct current through electrodes in wells and to enable manipulation of groundwater chemistry by in situ electrolysis leading to reduction and/or oxidation of contaminants (Yuan et al. 2013; Rajic et al. 2014; Mao et al. 2012). 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.

The electrochemical reactors are designed to be implemented in the wells and operate under groundwater circulation. They are optimized to promote electro-Fenton reaction in the presence of Pd catalyst by using the titanium-based mixed metal oxide electrodes (Fig. 1). We tested the application of electro-Fenton reaction under a current of 250 mA to treat large volumes of water (10 L) in the setup presented in Fig. 2, under different flow (20 and 500 mL min^{-1}), in the presence of different ferrous ion concentrations (5 and 10 mg L^{-1}), and in the presence of bicarbonates (413 mg L^{-1}). We measured the changes of temperature, conductivity, and pH during the treatment. We used Reactive Blue 19 dye as a model compound and measured the concentration decay at 490 nm as well as the changes in total organic carbon (TOC) during the treatment. The values of temperature (22.4 ± 0.5 °C), conductivity (1.169 ± 0.52 mV), and pH (6 ± 0.5) negligibly

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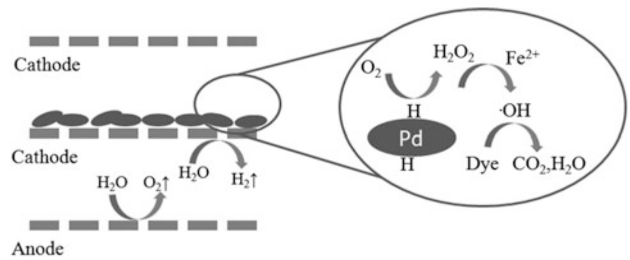

Fig. 1 The Electro-Fenton mechanism. From Yuan et al. (2013)

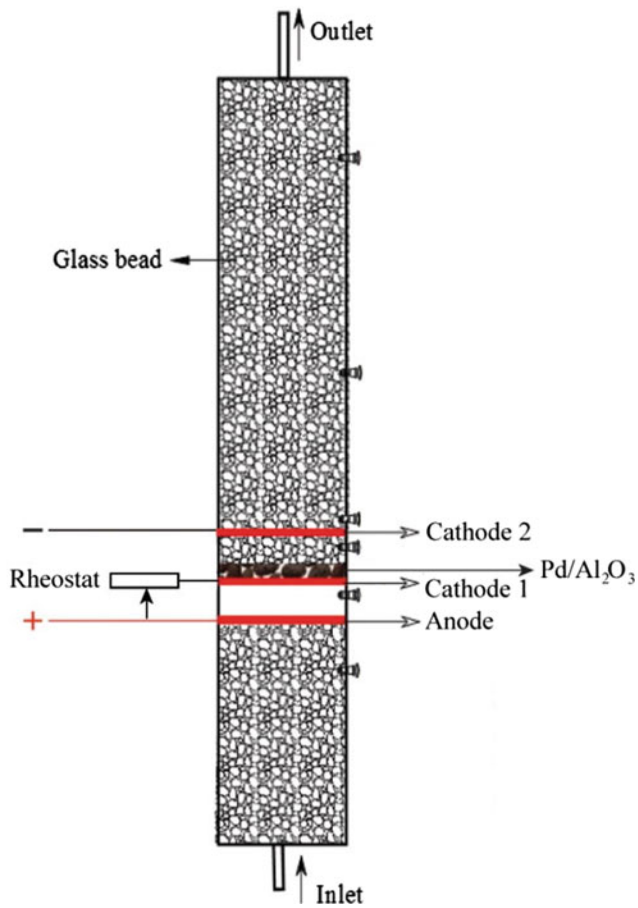

Fig. 2 The Electrochemical setup

changed in the treated water which is of great importance for real application and minimizing the influence of the treatment on the surrounding soil.

During experiments, it was found that the lower flow rates, higher concentrations of ferrous ions, and the absence of bicarbonates resulted in more effective dye removal rates according to both color decay at 490 nm and TOC changes (Fig. 3). The higher amount of ferrous iron promotes mineralization of dye via reaction with hydroxyl radicals. The presence of bicarbonates inhibits the hydroxyl radical formation because of high buffering capacity (hydrogen

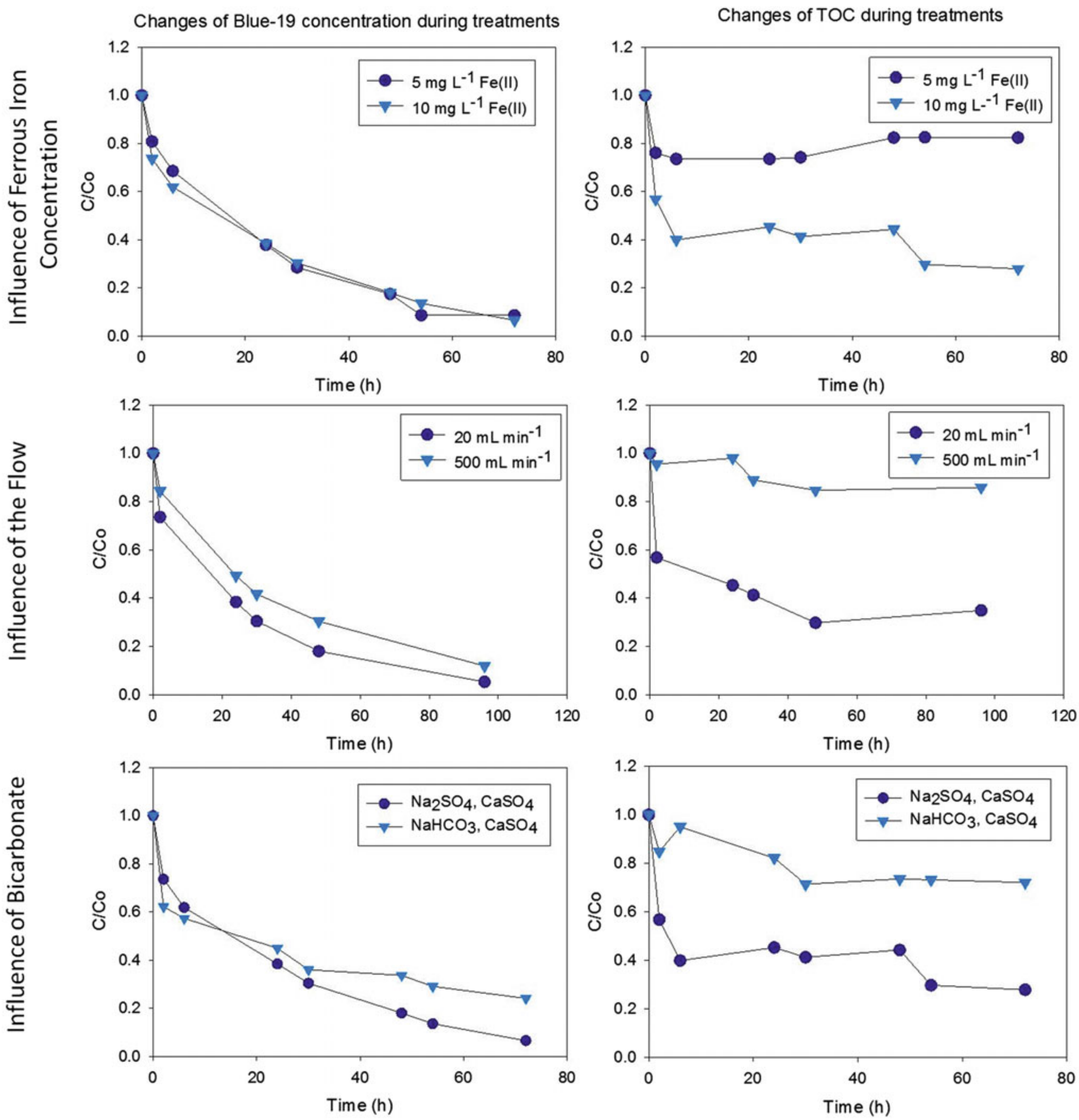

Fig. 3 Concentration decay of Reactive Blue 19 and TOC changes during the treatment

peroxide formation over Pd catalyst requires low pH) as well as by scavenging the generated radicals. The increase in the flow lowers the electro-Fenton reaction rate which adversely influences the dye removal.

Further improvements of the electrochemical setup are needed to promote reactions under high flow rates and carbonate/bicarbonate presence.

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Water Tracing Tests and Public Health in Karst Areas

William K. Jones

Abstract

Water 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 at the resurgences over time can also help predict the rate of movement of contaminants or pathogens through the aquifers. Tracer tests have been used to document the source of waterborne illnesses in karst areas since 1872.

1 Introduction

Karst is characterized by rapid recharge and flow paths that may not follow surface drainage patterns. Predicting the flow direction of groundwater in karst terrains is generally difficult using "conventional" models that assume laminar flow and a continuum of water with no consideration of discrete turbulent flow through conduits (Goldscheider and Drew 2007).

Water tracing using injected fluorescent dyes or salts is an established method to study water movement in karst aquifers (Fig. 1). These tests are economical, and the results can be determined in real time using data-logging field fluorometers. The tests determine connections between points where water sinks and reappears in springs and wells (Käss 1998; Jones 2012). Fluorescent tracers are sometimes injected or mixed with the contaminants at an active spill site because the tracers are more easily monitored than bacteria or most other chemical constituents. The tracer test results should be representative of velocities and connections under the flow levels at the time of the test. Very high flow conditions may force flow into upper-level conduits that resurge at additional points.

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Quantitative monitoring of tracer concentration over time at the resurgences can also help predict the movement of contaminants or pathogens through the aquifers. A number of salt-based tracers are available, and their recovery characteristics should mimic dissolved contaminants with similar sportive tendencies. The hydrologic connections established using dissolved dyes generally apply to the movement of suspended particulate material and NAPLS, but the travel times may be somewhat faster for particulates (Vesper et al. 2016; Bandy et al. 2016). DNAPLS in particular may move down bedding plane partings against the apparent flow direction.

2 Lausen, Switzerland

A test reported from Switzerland in 1872 used salt to show that the source of a typhoid epidemic affecting a fifth of the town's population was sewage in a stream sinking 700 m south of Lausen (Fig. 2). The tracer (9 kg of NaCl) reached the town's water supply spring within 24 h (Käss 1998).

3 Lewisburg, West Virginia, USA

Towns situated on karst, especially those far removed from surface streams, are faced with unusual obstacles in collecting and disposing of municipal sewage. The town of Lewisburg, situated on a mature karst plain with no nearby

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Fig. 1 Photograph showing the tracer dye fluorescein sodium in a sinking stream. Recovery concentrations are generally kept below the visual threshold (about 100 ppb), and the limit of detection is less than 0.1 ppb

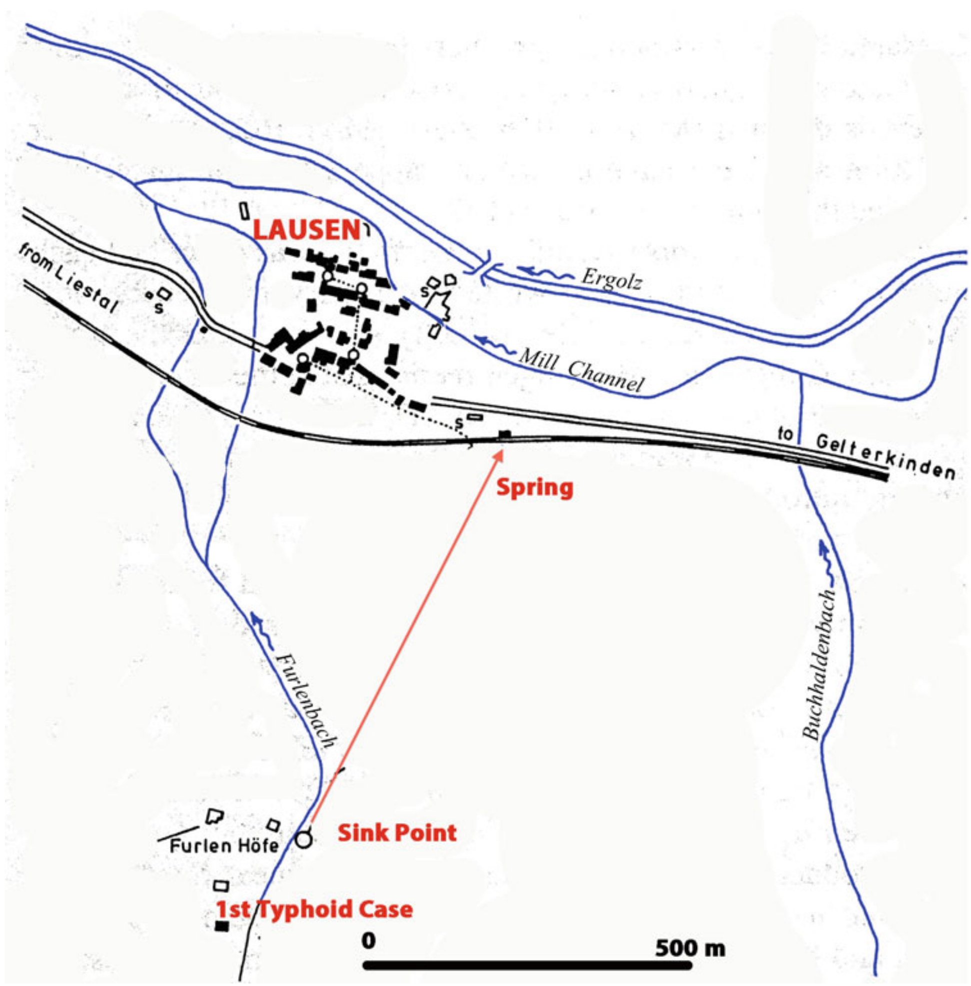

Fig. 2 Sketch showing houses with typhoid cases (*solid color squares*) and result of tracer test from the farm with the first reported case to the town spring. A few houses in town had individual wells and no typhoid cases. After Käss (1998)

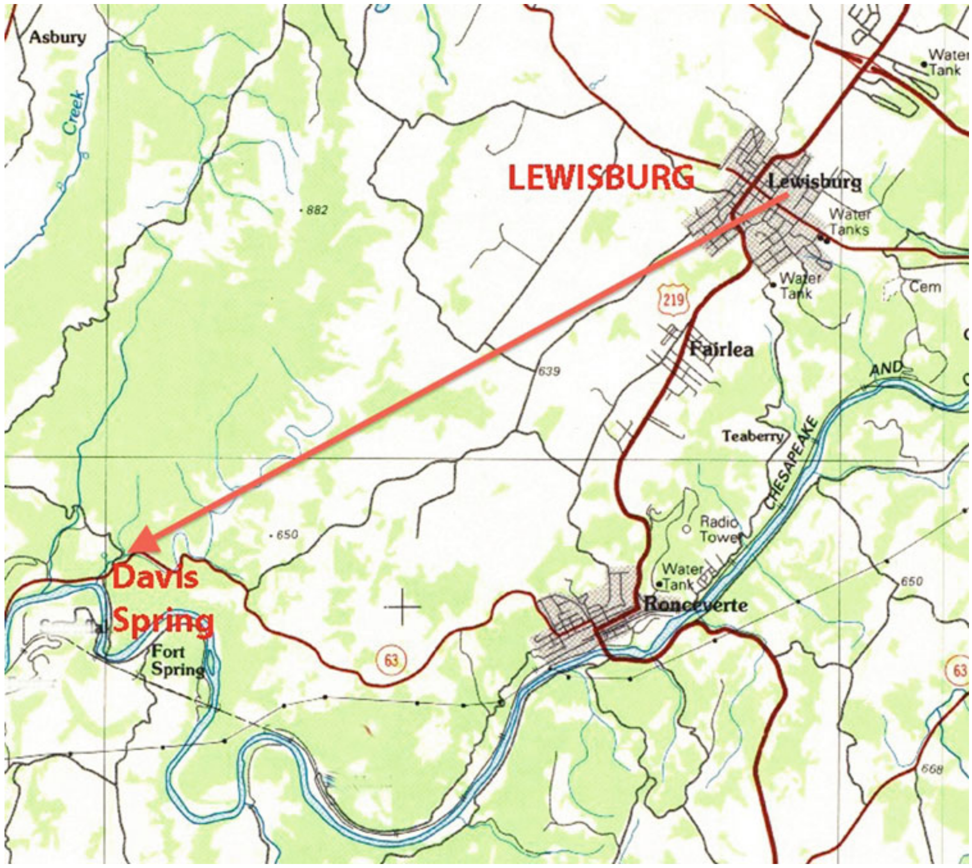

Fig. 3 Map showing result of tracer test from the Lewisburg sink to Davis Spring

surface streams, simply let all the domestic wastewater disappear into the porous epikarst without any treatment. The town had resisted installing sewer lines and treatment with the argument that the sewage disappeared into the earth and was not causing any problems. Tracer tests conducted in the 1970s determined that the sewage reappeared 10 km away at Davis Spring (Figs. 3 and 4) on the Greenbrier River with a travel time of 18 days (Jones 1997). It should be noted that bacterial sampling of the spring showed only a few cases of elevated counts following storm events and a week after the annual state fair in August of each year. The town received a grant to install collector lines and a treatment plant the following year.

4 Union, West Virginia, USA

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. The town built a sewage treatment plant on a mature karst plain a kilometer south of town (Fig. 5). Union still discharges (treated) water to a sinkhole, and this water reappears in the same spring (Jones 1997).

5 Walkerton, Canada

Walkerton (population 5000) is in Ontario and was served by three municipal wells completed in Paleozoic limestones and dolomites. In 2000, almost half of the population became ill and seven died from bacterial contamination of the water supply wells. The original hydrogeological and epidemiological investigations did not recognize this as a karst aquifer and tried to study the problem using multiple monitoring wells and numerical models of groundwater flow. These results suggested the contaminating source was very close to one of the wells with a predicted 30-day time of travel capture zone of 200–260 m and groundwater velocities of a few meters per day. Tracers injected in an observation wells at the site reached a pumping well in 5 h from one site and in 26 h from a site that was twice the 150-m 30-day distance predicted by the model. Tracer tests showed

Fig. 4 Aerial photograph of Davis Spring

Fig. 5 Aerial photograph showing the location of the new (1973) sewage treatment plant for the town of Union. The treated effluent flows into a sinkhole, and the plant is subject to flooding

an actual flow velocity of >300 m/day (Worthington et al. 2003).

6 Conclusions

The examples above demonstrate the speed and at times unpredictable nature of groundwater flow and contaminant transport in karst aquifers. Tracers are an important tool in studying flow routes and determining the source of contaminants found in wells or springs.

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Turbidity as an Indicator of Contamination in Karst Springs: A Short Review

Ferry Schiperski

Abstract

Karst aquifers are known to be prone to a variety of different types of contamination from a range of different sources. Due to the rapid recharge and high transport velocities associated with karst aquifers, karst springs usually show high discharge dynamics, and water quality often deteriorates very quickly following storm events due to the presence of contaminants such as pathogens, heavy metals, or pesticides. Turbidity has frequently been reported to vary in proportion to the concentration of contaminants in karst spring water, and its use has therefore been proposed to detect periods of contamination. A systematic relationship between such an easily measured parameter and contaminants would be useful for sustainable management of raw water resources in karst aquifers, especially in countries where water is scarce and event water cannot be easily discarded. In this study, we critically review a number of karst spring investigations in which turbidity has been shown to be an effective indicator for contamination. We conclude by identifying the conditions under which turbidity might be valid used to indicate contamination of karst spring water, and those under which this approach appears to be less effective. Our main findings are that the usefulness of turbidity as an indicator of contamination varies from one karst catchment to another and that a critical evaluation of contaminant and turbidity input and transport modes is required for each individual karst system before turbidity can be successfully used as an indicator of contamination. A conceptual model that combines different input and transport modes of turbidity and contaminants is presented.

1 Introduction

Karst aquifers are extensively used around the world as drinking water resources (Ford and Williams 2007), with water frequently being extracted from karst springs. These aquifers have considerable potential for high flow velocities through complex systems of conduits and fissures within a low-permeability matrix (as represented by dual or triple porosity models) (e.g., Liedl et al. 2003; Geyer et al. 2008). Lateral flow on the surface and subsurface to preferential recharge areas such as sinkholes result in concentrated infiltration that bypasses the soil (Pronk et al. 2006; Fournier et al. 2007). These characteristics mean that karst aquifers have low attenuation potential and high dynamics of discharge rates at karst springs, where distinct changes in the water's physicochemical parameters can consequently occur over short timescales (e.g., Mahler and Lynch 1999; Auckenthaler et al. 2002; Pronk et al. 2006; Heinz et al. 2009). While karst springs in general are known to be susceptible to different types of contamination from a variety of different sources (Vesper et al. 2003), such problems are particularly acute in karst regions where the aquifers often have inadequate natural protection and where contaminants can move unimpeded from recharge areas to the water-supply extraction point (Thorn and Coxon 1992).

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Different sources of contaminant input such as septic systems, livestock (Boyer and Pasquarell 1999; Heinz et al. 2009), agricultural runoff, urban runoff, and land-surface irrigation with primary-treated wastewater (Mahler et al. 2000; Pronk et al. 2007; Heinz et al. 2009), together with other diverse kinds of input such as from spills or leaks (Vesper et al. 2003), result in complex discharge patterns for contaminants such as pesticides (Stueber and Criss 2005; Hillebrand et al. 2014; Zirlewagen et al. 2016), pharmaceuticals (Katz et al. 2009; Reh et al. 2013), heavy metals (Vesper and White 2003), and bacteria (Pronk et al. 2007) from karst springs that are difficult to predict. Moreover, the dual porosity of karst flow systems means that both short- and long-term contaminations need to be taken into account (Einsiedl 2005; Hillebrand et al. 2014; Zirlewagen et al. 2016).

The high discharge rates of karst springs are associated with highly variable contaminant concentrations, which means that a high-frequency, flow-dependent sampling strategy is required if their dynamics are to be adequately described (Ryan and Meiman 1996; Mahler et al. 2000; Vesper and White 2003). However, analyzing contaminants such as bacteria, viruses, or organic chemicals is often time-consuming and does not therefore permit rapid adaptation of water extraction from karst springs to reduce the risk of contamination, and there are only a limited number of automated online systems available that can be used to analyze microbial parameters (Ryzinska-Paier et al. 2014; Tryland et al. 2015). A number of researchers have therefore proposed the use of easy-to-measure indicators such as the dissolved organic carbon content, spectral absorption coefficient, turbidity, or particle size distribution to identify periods of possible contamination in karst springs (Heinz et al. 2006, 2009; Pronk et al. 2006, 2007; Stadler et al. 2010).

In some karst springs, turbidity has been found to correlate well with the presence of contaminants (Ryan and Meiman 1996; Vesper and White 2003; Schwarz et al. 2011). Particle-associated transport of bacteria and other contaminants has been reported (Mahler et al. 2000; Vesper and White 2003; Schwarz et al. 2011), with higher survival rates for bacteria when adsorbed to particles (Vanloosdrecht et al. 1990; Howell et al. 1996; John and Rose 2005).

Turbidity usually involves a complex mixture of different types of particles from different sources, and distinguishing the different particle origins is not straightforward (Dussart-Baptista et al. 2003; Massei et al. 2003); it is, however, highly relevant for the detection of potential contamination (Pronk et al. 2007; Schiperski et al. 2015b, 2016). A number of investigations have consequently reported ambiguities in the relationship between the discharge of turbid water and karst spring contamination (Auckenthaler et al. 2002; Pronk et al. 2007; Heinz et al. 2009).

The following sections review a number of these investigations and provide examples of cases where the use of turbidity has been either more or less successful at detecting periods of contamination in karst spring water. The objective of this study was to evaluate the applicability and limitations of using turbidity as an indicator of different types of contamination and to determine the underlying principles behind its successful use for this purpose.

2 Case Studies

Using turbidity to indicate the presence of contaminants (in many cases bacteria) in karst spring water has been proposed by a number of authors. This parameter has sometimes been recorded simply as a basic parameter, with no intention of using it as an indicator of contamination. Most of the reviewed investigations were concerned with evaluating water quality changes and the contamination potential of karst springs, and with understanding how the transport of contaminants relates to karst spring discharge rates. Some of these investigations recorded excellent inverse correlations between turbidity and karst spring water quality. Other researchers reported ambiguities in the relationship between turbidity and contaminant concentrations, or even no systematic relationship at all. Most of these investigations were based on field programs completed during and after storm events rather than on experimental field investigations, and the boundary conditions of the investigated systems (with respect to hydrology, precipitation, and the type of contaminants) therefore usually varied considerably between different sites and between different monitoring periods.

One of the most cited investigations into the simultaneous occurrence of bacteria and turbidity was conducted by Ryan and Meiman (1996), who investigated short-term variations in water quality at a karst spring in the Mammoth Cave National Park, Kentucky, USA. The authors found a clear relationship between turbid water and bacterial counts following runoff events, with the bacteria originating from nonpoint sourced pollutants (light agriculture use). The authors also noted that neither the maximum counts of these nonpoint sourced pollutants nor the maximum turbidity coincided with maximum discharge.

Vesper and White (2003) reported a relationship between the concentrations of metals (including heavy metals) in Beaver Spring and Millstone Spring (Western Kentucky/Tennessee, USA.) and the water turbidity. They concluded that the presence of metals was associated with the discharge of allochthonous sediment from the investigated springs and that the transport of these metals was facilitated by their adsorption to mobile particles. Recharge was reported to be both diffuse (through soil infiltration) and discrete (through sinkholes), while allogenic recharge was uncommon within the catchment area.

Heinz et al. (2006) observed high concentrations of bacteria during periods with high levels of allochthonous turbidity in the Gallusquelle karst spring in southwest Germany, although the turbidity levels subsequently declined much more rapidly than the bacterial counts. However, later studies (Heinz et al. 2009) could not validate these findings. The bacteria derived from spillover of a combined sewage and rainwater tank (due to technical failure) and infiltrated rapidly through a dry valley into the groundwater. Tracer tests confirmed the aquifer beneath the dry valley to be very well connected to the spring (Heinz et al. 2009).

Fournier et al. (2007) observed a significant correlation between turbidity and phosphate that had derived from point recharge through a swallow hole during rain events in Pays de Caux (Haute-Normandie, France). In contrast, nitrate was diluted during storm discharge and was shown to have a diffuse source from the leaching of soil.

Other researchers (Schwarz et al. 2011) observed an excellent correlation between turbidity and polycyclic aromatic hydrocarbons (PAH) concentrations at the Blautopf karst spring in southwest Germany during high discharge events. They concluded that PAHs had been adsorbed on carbonaceous particles and then mobilized from the soil during high flow events; their transport was thus facilitated by these particles. Rapid recharge was estimated to make up only about 8% of the total recharge in this catchment area.

Hillebrand et al. (2014) and Schiperski et al. (2015b) investigated variations in micropollutant concentrations at the Gallusquelle karst spring in southwest Germany. Both investigations reported an association between the pesticide metazachlor and turbidity. The pesticide was thought to have originated from agricultural areas and was associated with the occurrence of allochthonous turbidity in the springwater (Schiperski et al. 2015b). Recharge within the catchment is autogenic, and rapid recharge was estimated to make up less than 10% of the total recharge (Hillebrand et al. 2014).

The studies discussed above show that in a number of cases, it was possible to use turbidity to indicate the presence of potentially harmful substances. However, in the cases discussed below, high levels of turbidity did not coincide with high counts of bacteria or other potentially harmful substances, suggesting that turbidity is not always suitable for use as an indicator of contamination in karst springs.

Ambiguities in the relationship between discharge of turbid water and bacterial counts were reported by Pronk et al. (2006, 2007) for a karst spring in Switzerland. They observed low bacterial counts during periods of high water turbidity as well as periods when turbidity and bacterial counts were well correlated. During a storm event in 2003, they found that an initial period of turbid water was associated with only a slight increase in bacterial counts while a second period during the subsequent decline in discharge (the regression phase) coincided with high concentrations of bacteria (Pronk et al. 2006). These findings were confirmed in subsequent investigations carried out in 2006 (Pronk et al. 2007). The authors concluded that the initial turbid period resulted from the remobilization of sediment from within the aquifer and that the second period was due to the infiltration of allochthonous sediment from a sinking stream that introduced large quantities of bacteria, sediment, and organic matter into the aquifer.

Stueber and Criss (2005) observed that the breakthrough of the herbicide atrazine lagged behind that of turbidity in a karst spring in southwest Illinois (USA.) following a storm event, probably due to the time required to reach the soil's field capacity and initiate surface runoff to sinkholes, or alternatively due to the atrazine source being more distant than that of the sediment contributing to the turbidity. There was no atrazine in the springwater at other times since there had been no surface applications of atrazine close to the time of sampling. They also found that some compounds (e.g., atrazine, potassium, phosphorus, and boron) moved rapidly by conduit flow to the springhead where their concentrations peaked under high flow conditions, while others (e.g., nitrate, sodium, chloride, and sulfate) percolated slowly from diffuse storage and were diluted during high flow conditions.

At the Gallusquelle karst spring, Heinz et al. (2009) observed high bacterial counts at times when turbidity levels were relatively low and similar bacterial counts at times when turbidity levels were about 50 times higher [in continuation of investigation published in Heinz et al. (2006)]. Periods of low turbidity and high bacterial counts were recorded shortly after a failure in the combined sewer and rainwater tank. The authors concluded that turbidity was not a reliable indicator for the presence of bacteria.

For the same catchment, Hillebrand et al. (2012) calculated the amount of untreated wastewater infiltrating the aquifer by rapid recharge from measurements of caffeine loads in the spring discharge. They observed large quantities of wastewater during periods of declining discharge and low turbidity as well as during periods with high levels of turbidity and concluded that turbidity is of only limited use for wastewater detection.

At the same spring, Zirlewagen et al. (2016) investigated concentration dynamics of two artificial sweeteners. They observed high counts of fecal indicator bacteria while turbidity was only slightly elevated and the discharge rate showed no response at all. Due to the simultaneous breakthrough of the artificial sweetener cyclamate and bacteria, the bacteria were traced back to another overflow from the same combined sewer and rainwater tank. The spillover was triggered by a high-intensity but short-lived storm event.

In contrast to Stueber and Criss (2005), Hillebrand et al. (2014), Schiperski et al. (2015b) and Zirlewagen et al.

(2016) all found either no correlation or a negative correlation between atrazine and water turbidity in the Gallusquelle karst spring. These authors observed a constant concentration of the pesticide under base flow conditions and dilution by freshly recharged storm water, from which they concluded that atrazine was likely to be bound to the aquifer matrix, since the use of atrazine has been prohibited in Germany since the early 1990s.

3 From a Conceptual Karst System to Natural Karst Systems

It is clear from all of the investigations listed above that turbidity cannot be used as a proxy for contamination in a classical sense, for example in the way that fecal indicator bacteria are used as proxies for pathogens (Pronk et al. 2007; Sinreich et al. 2014), or enzymatic activities for fecal pollution (Ryzinska-Paier et al. 2014). Its usefulness is rather based on the simultaneous breakthrough of turbidity and contaminants at karst springs under certain specific conditions, which can be explained and visualized using an idealized karst spring hydrograph and chemographs (Fig. 1).

Following precipitation, the spring discharge, electrical conductivity (EC), and turbidity can be used to indicate the proportions of water from different origins in the discharge on the basis of this conceptual model. The spring's reaction can be roughly divided into five phases:

1. **Pre-event state**: All parameters are stable at their base flow levels (the EC is slowly increasing while the discharge and turbidity are slowly decreasing).
2. **Piston flow phase**: Following precipitation a pressure wave moves through the aquifer as soon as storm water infiltrates the phreatic zone. "Old" water with a relatively high Ca and Mg content is expelled from the phreatic zone (e.g., Grasso and Jeannin 2002; Massei et al. 2003; Caetano Bicalho et al. 2012).
3. **Vadose phase**: Arrival of water from the vadose zone with a high Ca and Mg content, resulting in an EC peak (e.g., Williams 1983; Heinz et al. 2009).
4. **Floodwater phase**: Arrival of freshly infiltrated floodwater indicated by reduced EC and an increase in turbidity. During this stage, the relatively highly mineralized water of the phreatic zone is diluted by only slightly mineralized event water (Mahler et al. 1999; Massei et al. 2003; Caetano Bicalho et al. 2012).
5. **Recession**: All parameters gradually return to their pre-event levels (e.g., Williams 1983; Grasso and Jeannin 2002).

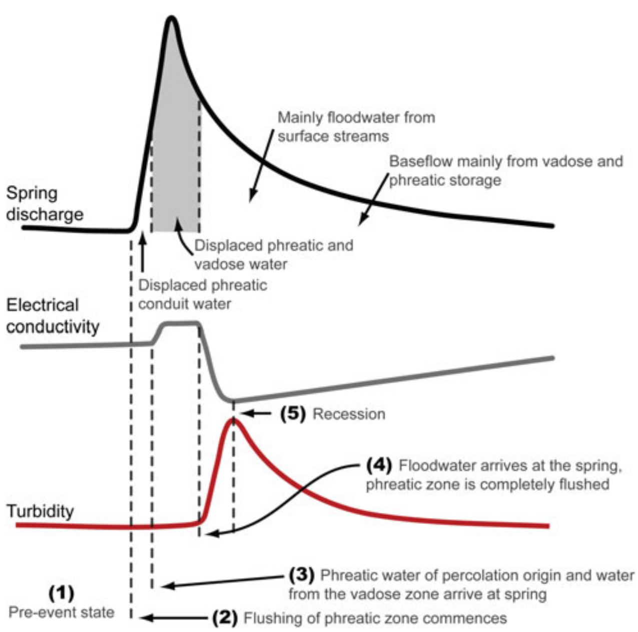


Fig. 1 Idealized spring chemographs and hydrograph showing how spring discharge, electrical conductivity, and turbidity can be used to estimate the timing of discharge waters from different locations (modified from Williams 1983)

Valdes et al. (2006) described karst systems with this type of turbidity and EC response as having short memory effects and high flow-through capacities, which means that turbidity is flushed through the aquifer with little potential for particle deposition or subsequent resuspension. However, the use of turbidity as an indicator for identifying periods of contamination is based on two underlying assumptions: (1) both turbidity and contaminants must have the same origin (e.g., the Earth's surface, which means they must have the same input location and input modes), and (2) both must have the same transport behavior. If these assumptions are satisfied, then an increase in the concentration of contaminants will coincide with a reduction in EC and an increase in turbidity.

Ryan and Meiman (1996) observed a simultaneous increase in fecal coliforms and turbidity during the discharge of storm water, which is close to the response that would be expected from the conceptual model (Fig. 2). They concluded that the delayed breakthrough of fecal coliforms and turbidity compared to already reduced EC and discharge (Fig. 2) was related to their input from distal light agricultural sub-catchment areas, i.e., due to the areal distribution of the land cover. The authors emphasized that recharge from relatively pristine input can reach karst springs at the same time as recharge from highly polluted input, as a result of highly complex hydrogeology and heterogeneous land use. A simultaneous occurrence of both pristine input and polluted input might therefore be coincidental and restricted

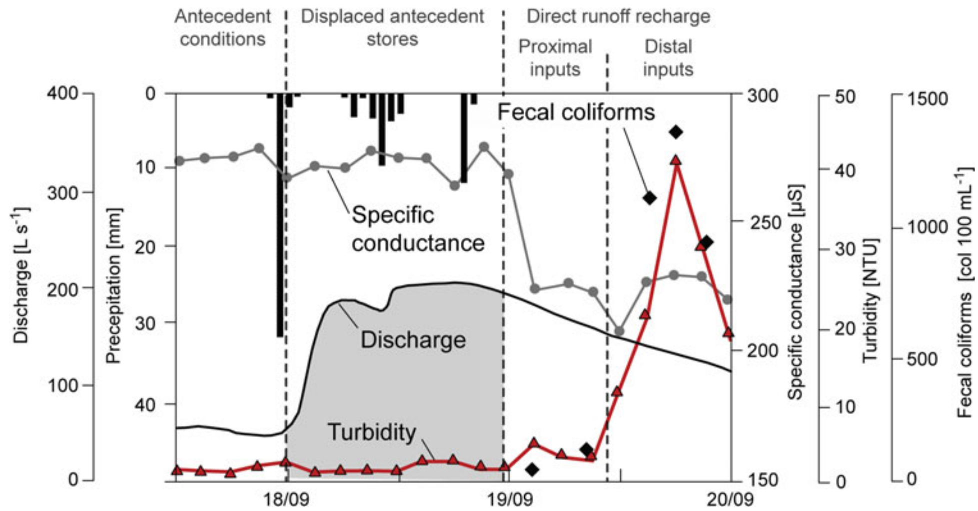


Fig. 2 Runoff event sampling data for a karst spring in the Mammoth Cave National Park, Kentucky, USA (modified from Ryan and Meiman 1996). Turbidity levels correlate well with fecal coliform counts and have a negative correlation with the specific conductance

to a certain flow regime. This puts into perspective the simultaneous occurrence of high turbidity and fecal coliform levels, and hence the applicability of turbidity as an indicator of contamination by fecal coliforms in general.

The conclusions drawn by Ryan and Meiman (1996) differ from those of both Schwarz et al. (2011) and Vesper and White (2003), who concluded that the observed correlation between turbidity and contaminants was related to the particle-facilitated transport of hydrophobic substances, for example heavy metals (Fig. 3) and polycyclic aromatic hydrocarbons (PAHs) (Fig. 4), which precludes the simultaneous breakthrough being purely coincidental. In both of these investigations, turbidity and contaminants were found to be derived from the Earth's surface and transported into the aquifer by autogenic recharge (there were no sinking streams reported within the catchments) and the turbidity and contaminant breakthroughs were closely related to the discharge state of the springs.

These investigations emphasized the significance of particle-facilitated transport of contaminants in karst aquifers. The results of both investigations provide evidence that within karst catchment areas with predominantly autogenic recharge, hydrophobicity is likely to be responsible for the excellent correlation between turbidity levels and the concentration of contaminants in karst spring water. Under these conditions, turbidity might therefore be useful for indicating periods when water quality is affected by hydrophobic substances.

4 Complex Turbidity and Contaminant Dynamics in Complex Karst Systems

Not all hydrographs and chemographs from karst springs are similar to those of the conceptual model as discharge patterns can be much more complex due, for example, to variable precipitation, a complex flow system, or different types of recharge (Bonacci and Živaljevic 1993; Ford and Williams 2007). Valdes et al. (2006) suggested that discharge, EC, and turbidity variations from the conceptual model can be ascribed to limited flow-through capacities, resulting in pronounced memory effects on the EC and discharge and indicating that deposition of suspended solids is likely to have occurred. Recharge can be either autogenic or allogenic, with the latter having the potential to recharge with sediment and contaminants that are not normally present in the autogenic recharge of a particular catchment area. It is also most important to note that both turbidity and contaminants (whether in particulate state or dissolved) can originate from different sources and be subject to different transport processes.

4.1 Origin of Turbidity and Contaminants

In contrast to the conceptual model, the turbidity in karst springs is a complex signal that is often a superposition of different types of signals from different sources (Fig. 5). Particles can, for example, be resuspended due to a pressure wave induced by percolating storm water reaching the phreatic water level (pulse-through turbidity), or they can be freshly introduced into the aquifer from the Earth's surface (flush-through turbidity) as a result of either slow percolation or more rapid point recharge such as from sinking streams (Pronk et al. 2007, 2009). The nature of turbidity also varies and is defined as either autochthonous (originating from the weathering of subsurface material) or allochthonous (originating from the Earth's surface) (Herman et al. 2012). The different origins and discharge rates of sediments in karst springs present one of the main challenges in using turbidity as a proxy for contamination since distinguishing the origin of turbidity is rarely straightforward (Dussart-Baptista et al.

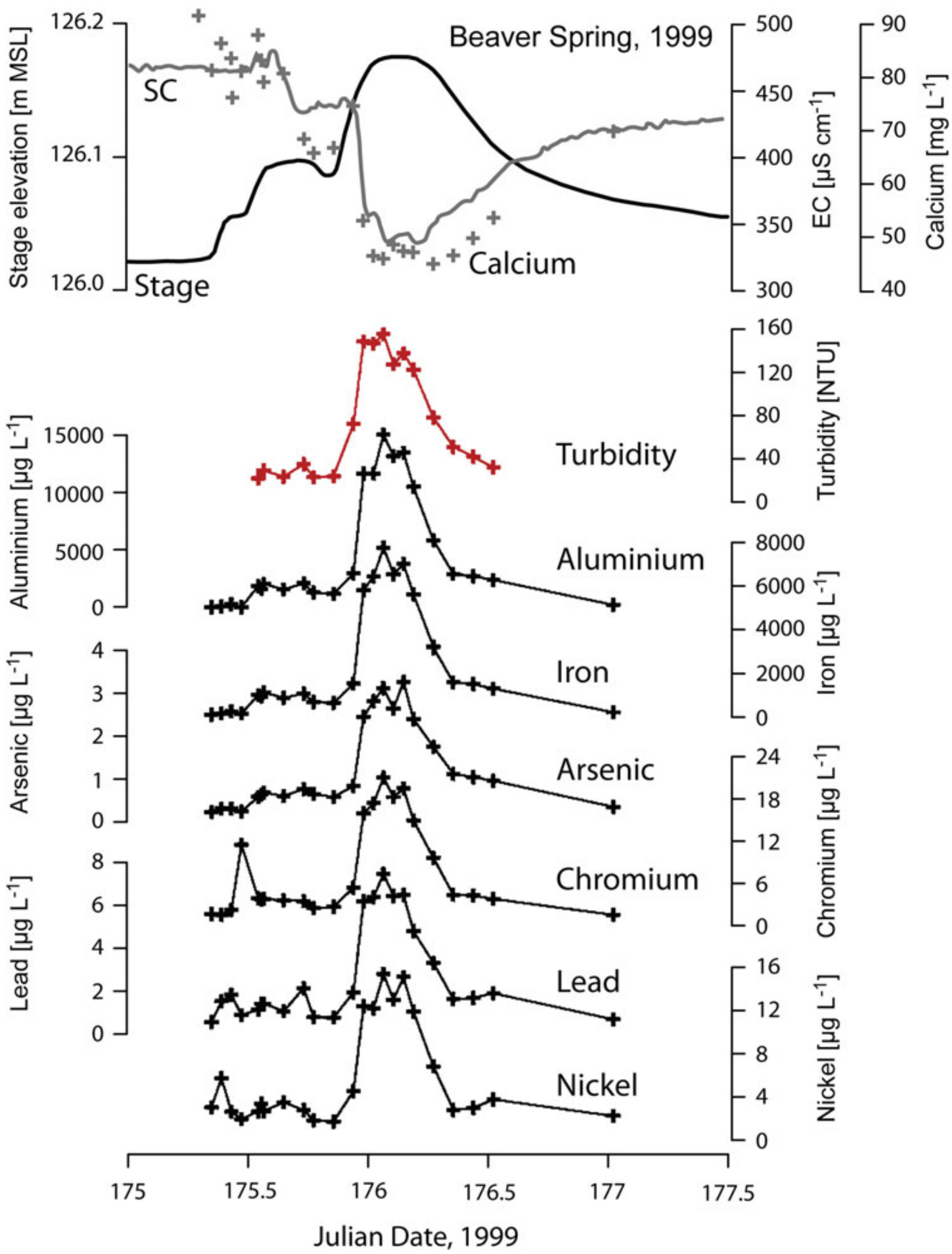


Fig. 3 Variability in the concentrations of selected elements of digested samples collected during a storm event at Beaver Spring in Western Kentucky, USA. (modified from Vesper and White 2003). Heavy metal concentrations correlate well with turbidity and both vary with the discharge rate, whereas the specific conductance shows an inverse response

2003; Massei et al. 2003), but it is highly relevant when attempting to detect any deterioration in water quality (Pronk et al. 2006, 2009). For example, the typical behavior of a first flush of particles remobilized from within an aquifer has been the subject of numerous investigations and experiments (e.g., Valdes et al. 2006; Pronk et al. 2009; Schiperski et al. 2015a). However, this remobilized turbidity is unlikely to be associated with freshly infiltrated contaminants from the Earth's surface such as bacteria or freshly applied pesticides, but rather with contaminants stored within the aquifer (Vesper and White 2004).

Different methods have been used to identify and distinguish between turbidity signals from different sources, including the use of signal decomposition (Massei et al. 2003; Schiperski et al. 2015a), particle size distributions (Pronk et al. 2007), and hydro-sedimentary process analysis (Valdes et al. 2005; Fournier et al. 2007; Schiperski et al. 2015b). The latter two methods have the advantage that they can be used for real-time evaluation. Massei et al. (2003) used signal decomposition of surface water components in a spring's discharge (proportions calculated from EC) and turbidity to distinguish between resuspended and freshly introduced sediments. They demonstrated the complex turbidity response in a karst spring to a recharge event using easy-to-measure parameters, hydrograph separation, and discharge and turbidity breakthrough curve decomposition

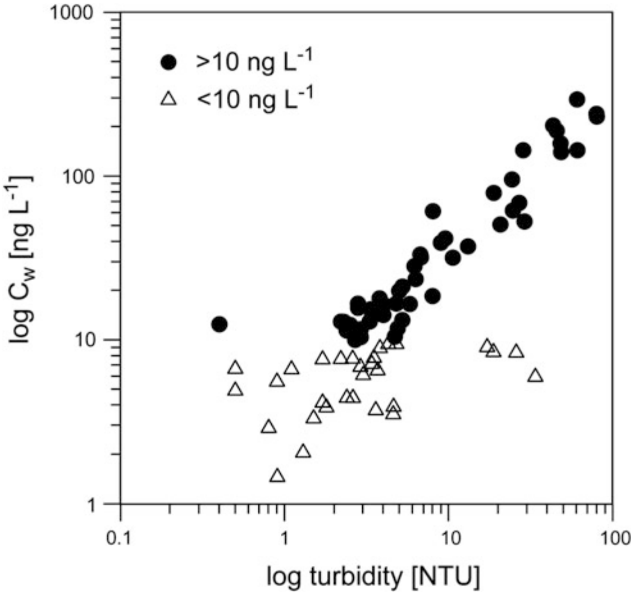


Fig. 4 Relationship between PAH concentrations and turbidity levels at the Blautopf karst spring in southwest Germany (modified from Schwarz et al. 2011)

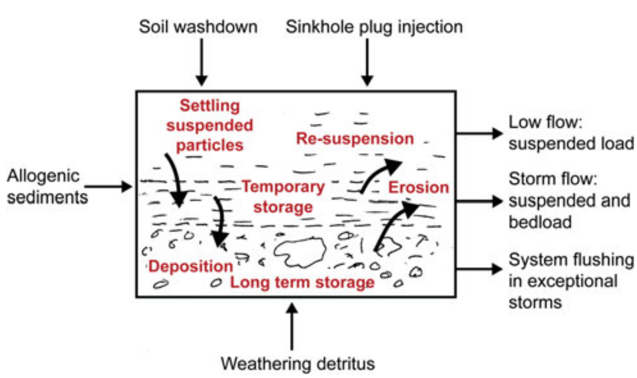


Fig. 5 Sketch showing the input and output of sediment into karst aquifers and the role of karst conduits as mixing and storage chambers (modified from Herman et al. 2012)

and recommended the use of their methods for describing karst systems in general.

Pronk et al. (2007) investigated the use of particle size distributions within a size range of 0.9–139 µm as an indicator for the contamination of karst spring water by fecal bacteria in Switzerland. The authors observed a number of effects that contradicted the idealized conceptual hydrograph model. For example, increased levels of turbidity were recorded while the EC remained at a constant pre-event level (Fig. 6), and a second period of turbidity peaks associated with *E. coli* was recorded after the discharge had already been in decline for a number of days. The EC also increased at times when the discharge was already declining. Using hydrograph and chemograph analyses, the authors concluded that the first turbidity peak(s) resulted from the mobilization of autochthonous sediment and the second peak(s) from the infiltration of allochthonous sediment. The authors attributed this exceptional discharge pattern to a distal sinking stream that contributed a large proportion of the spring's discharge water (up to 29%, depending on the discharge state; Pronk 2008), with high concentrations of suspended matter and fecal bacteria and a high EC, with a significant time delay. Relatively small particles that were introduced from the sinking stream into the aquifer could be correlated with the presence of *E. coli,* and it was therefore possible to use particle size measurements to differentiate allochthonous turbidity from autochthonous turbidity and, most importantly, as a proxy for the presence of pathogens.

Another approach to distinguish the origin of suspended matter in karst springs was proposed by Valdes et al. (2005) and further developed by Fournier et al. (2007), adapting methods previously applied to surface water (Williams 1989). The method is based on an analysis of EC and turbidity hysteresis patterns and allows a distinction to be made between hydro-sedimentary processes such as the deposition, resuspension, and direct transport of particles. This method was used by Schiperski et al. (2015b) to compare the occurrence of source-indicative organic micropollutants with periods of resuspended, directly transferred turbidity or sedimentation (Fig. 7).

At the Gallusquelle karst spring, three consecutive rainfall events led to a complex series of turbidity signals that were analyzed by Schiperski et al. (2015b) in terms of hydro-sedimentary processes. Periods of resuspension were followed by periods involving the direct transfer of particles from the Earth's surface to the spring and more or less well-defined periods of particle deposition. The authors concluded that the periods following the onset of direct transfer (flush-through turbidity) were associated with a contaminant (the pesticide metazachlor) that originated from the Earth's surface. Furthermore, following the end of periods of resuspension and with the onset of periods involving the direct transport of particles, a contaminant that originated from the matrix of the aquifer (the pesticide atrazine) was diluted by storm water. The method was, however, unable to detect the discharge of water from a sewer that was identified using the artificial sweetener cyclamate, probably because of the low levels of turbidity associated with water from this source. Similar observations were reported by Zirlewagen et al. (2016), who used two artificial sweeteners to investigate the breakthrough of untreated wastewater at the same karst spring following a short but intense rainfall event. They found that the turbidity varied around its base level and that neither it nor the discharge rate of the spring showed any response to the breakthrough of untreated wastewater containing *E. coli*.

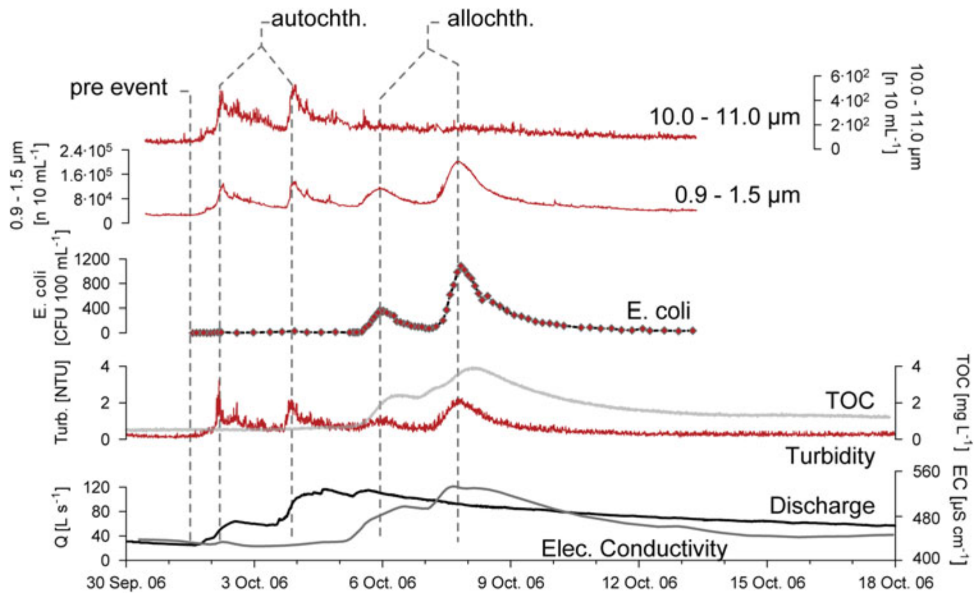


Fig. 6 Dynamics of natural parameters at the Moulinet spring in Switzerland (modified from Pronk et al. 2007). The push-through turbidity consisted of autochthonous sediment and was not associated with *E. coli* counts, whereas the flush-though turbidity involved allochthonous sediment and *E. coli* that had been introduced into the aquifer through a distal swallow hole. The concentrations of small particles (0.9–1.5 µm), the electrical conductivity, and the total organic carbon (TOC) content increased as a result of the influx of surface waters from the swallow hole

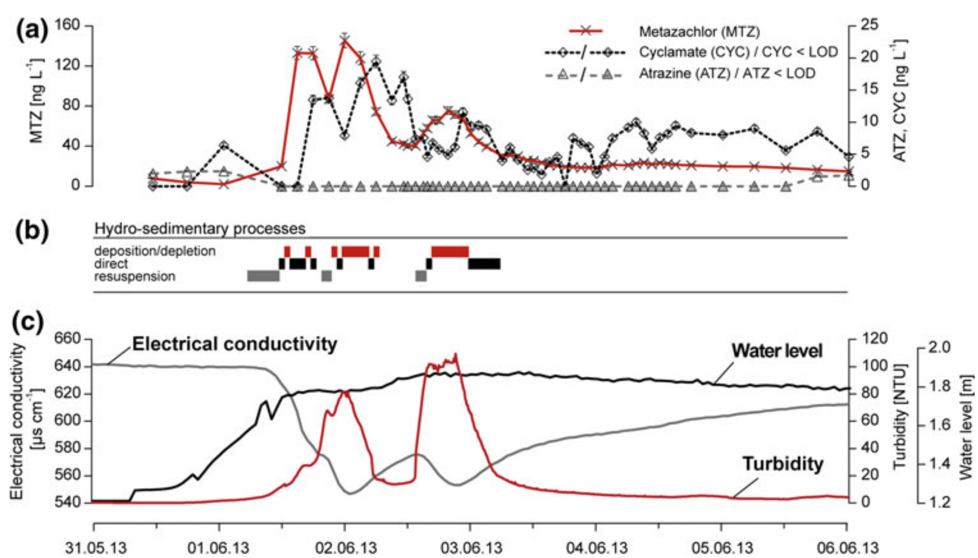


Fig. 7 Complex signals of organic micropollutants with different origins (**a**), compared with **b** hydro-sedimentary processes, and **c** electrical conductivity, water level, and turbidity in the Gallusquelle karst spring in southwest Germany during a flood event (modified from Schiperski et al. 2015b)

These investigations have shown that turbidity and contaminants can have different origins and the relationship between the two can therefore be quite complex. Contaminants that have their origin at the Earth's surface may be absent during periods when resuspended particles are discharging from karst springs but present when freshly infiltrated particles are flushed out of the aquifer. Conversely, contaminants that are located within the phreatic zone of the aquifer may be present when resuspended particles are being flushed out along with phreatic water but may later on be diluted due to the input of storm water.

4.2 Particles and Solute Transport Processes

Solute compounds are subject to transport processes such as dispersion, retardation, and elimination. Particles are also subject to processes such as size exclusion or pore exclusion. Numerous experimental studies on porous media (e.g., Jin and Flury 2002; Tufenkji and Elimelech 2005; Knappett et al. 2008; Zhuang and Jin 2008; Chrysikopoulos and Syngouna 2014) and karst aquifer field tracer tests (e.g., Göppert and Goldscheider 2008, 2011; Harvey et al. 2008; Sinreich et al. 2009; Flynn and Sinreich 2010) have reported different transport velocities for solutes and particles. The breakthrough of hydrophilic solutes and particles is therefore not generally expected to be simultaneous. The transport of hydrophilic dissolved contaminants can differ from that of particles, and inorganic particles (such as clay minerals, quartz, or calcite) are likely to be subject to different transport mechanisms from bacteria or viruses (Göppert and Goldscheider 2008; Pronk et al. 2009). Even indicator bacteria have shown transport behavior that differs from the transport behavior of other bacteria and viruses (Flynn and Sinreich 2010).

Auckenthaler et al. (2002) conducted particle tracer tests in a karst catchment in northwest Switzerland with the tracer input location about 1250 m from the karst spring. They observed an earlier breakthrough for marine bacteriophages than for uranine (Fig. 8) and a delay in turbidity and dissolved organic carbon relative to microorganisms (not shown). The authors explained these effects as being due to matrix exclusion processes. They concluded that turbidity was not a reliable proxy for bacterial contamination and suggested that the discharge rate was a more reliable alternative.

In a comparative tracer test with a clayey loam suspension and nonreactive solutes, Pronk et al. (2009) observed that mineral particles tend to travel more rapidly and have shorter overall travel times than solutes (Fig. 9). Their experiments were conducted in the vadose zone of a karst aquifer in Switzerland with a vertical extent of about 30 m. The authors concluded that effects such as pore exclusion and size exclusion, which are known from porous media experiments, were responsible for the observed differences in transport behavior.

In some cases, the experimental determination of transport processes for particles such as bacteriophages, microspheres, and especially bacteria and viruses can be hindered by legal restrictions. However, observations of karst springs following a potential input of bacteria can also be used to

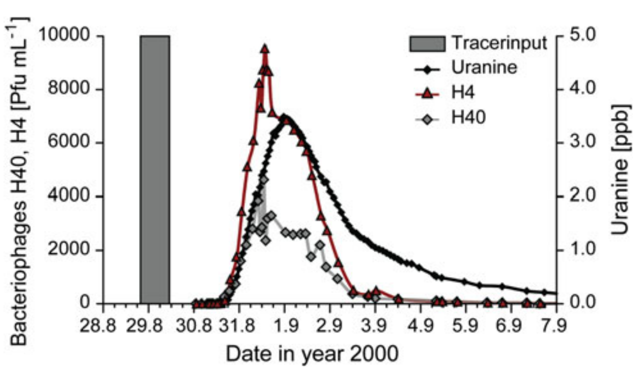


Fig. 8 Breakthrough curves for H40 and H4 marine bacteriophages and for uranine from an artificial tracer test in a karst catchment in northwest Switzerland (modified from Auckenthaler et al. 2002)

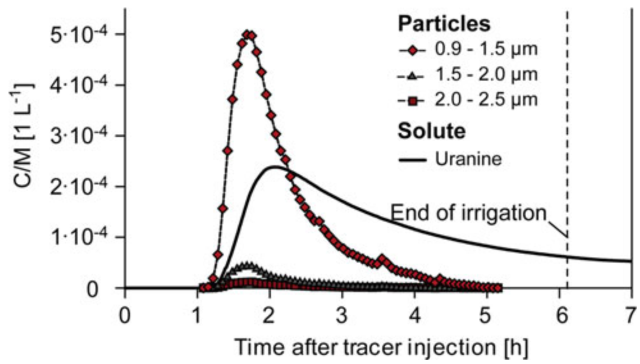


Fig. 9 Breakthrough curves for particles of different sizes (clay-loam suspension) and uranine during a steady-state flow regime, from an artificial tracer test through the vadose zone in a karst catchment in Switzerland (modified from Pronk et al. 2009). Concentrations are normalized to mass input (uranine) and particle number input (clay-loam suspension)

assess the transport behavior of particles if accompanied by investigations into source-indicative compounds such as organic micropollutants or artificial tracers. The breakthroughs of *E. coli* and a nonreactive organic trace compound (the artificial sweetener cyclamate; Hillebrand et al. 2015) were investigated by Zirlewagen et al. (2016) at the Gallusquelle spring (Fig. 10). Both *E. coli* and cyclamate came from an overflow spill of a combined sewer and rainwater tank at a distance of about 9 km from the spring, following a short but very intense rainfall event; the *E. coli* bacteria were observed to have higher travel velocities than the cyclamate.

The results of these investigations indicate that differences in the transport behavior of particles and solutes are not uncommon in karst aquifers. Some doubts remain, however, concerning the modeling of breakthrough curves of particles (Zhang et al. 2001). Particles were generally found to arrive earlier than nonreactive hydrophilic tracers. In contrast, hydrophobic compounds could be adsorbed to suspended matter and could therefore be associated with the breakthrough of turbidity (Vesper and White 2003, 2004). However, until particle transport in karst catchments is understood in greater detail, similar transport behavior must be assumed for both particles and (dissolved) contaminants when using the ideal karst spring concept (Fig. 1) to detect periods of contamination in karst springs.

5 A Modified Conceptual Model

Considering the different input functions and transport behavior of solutes and particulate matter in karst aquifers discussed above, it becomes evident that the ideal karst spring concept (Fig. 1) covers only a limited number of possible discharge scenarios. A modification and extension

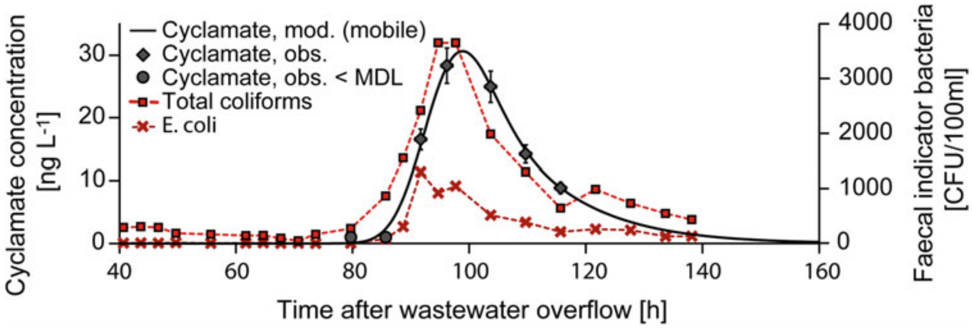
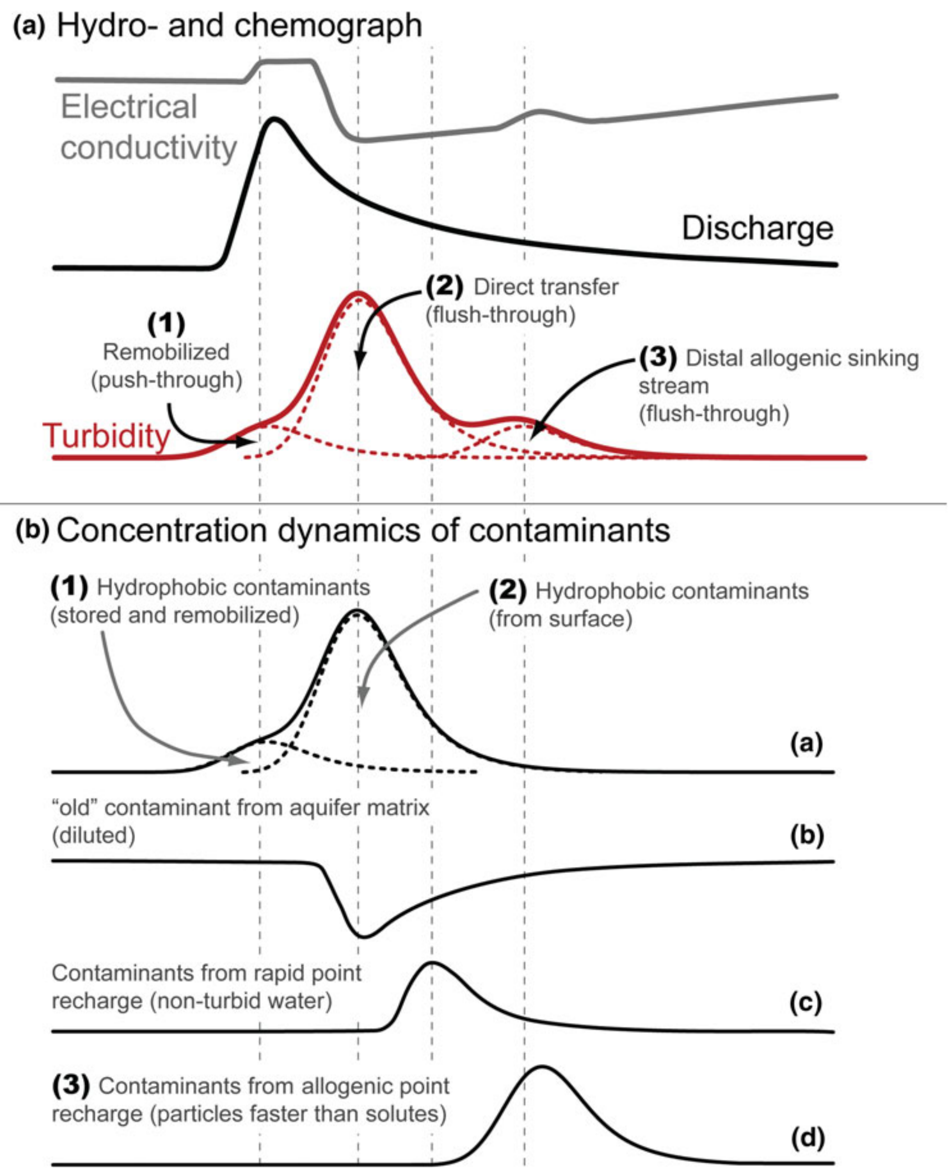


Fig. 10 Breakthrough curves for the artificial sweetener cyclamate, total coliforms, and *E. coli* from the Gallusquelle karst spring, following the overflow of a combined rainwater and sewer tank triggered by high-intensity rainfall (Zirlewagen et al. 2016)

Fig. 11 **a** Idealized spring hydrograph and chemographs showing spring discharge, electrical conductivity, and turbidity. The turbidity signal is a superposition of (*1*) remobilized turbidity (push-through turbidity), (*2*) flush-through turbidity from nearby recharge, and (*3*) flush-through turbidity from distal allogenic point recharge. **b** Variations in the concentrations of contaminants with different types of input modes. The correlation with turbidity is indicated by numbers similar to those in Fig. 11a. Contamination is due to (**a**) hydrophobic contaminants from conduit storage and the surface (e.g., Vesper and White 2003, 2004) (**b**) “old” contaminants that are stored in the aquifer matrix and diluted by freshly recharged event water (e.g., Hillebrand et al. 2014), **c** contaminants from point recharge of non-turbid water (e.g., Zirlewagen et al. 2016), and **d** contaminants from allogenic point recharge (e.g., Pronk et al. 2007), with particles traveling faster than solutes



of this concept including different input functions and transport behavior of solutes and particulate matter are more adequate to describe the diversity of discharge scenarios of these materials at karst springs (Fig. 11). The extended concept is based on an idealized spring hydrograph and chemograph showing spring discharge, electrical conductivity and a turbidity signal that is a superposition of (1) a remobilized turbidity (push-through turbidity), (2) a flush-through turbidity from nearby recharge, and (3) a flush-through turbidity from distal allogenic point recharge (Fig. 11a).

The second component of the figure describes the variation in concentrations of contaminants with different types of input functions (Fig. 11b). Hydrophobic contaminants from conduit storage and the surface are likely to be discharged together with turbid water of different origin (e.g., Vesper and White 2003, 2004). "Old" contaminants that are stored in the aquifer matrix and diluted by freshly recharged event water are unlikely to be systematically related to turbidity (e.g., Hillebrand et al. 2014). Contaminants from point recharge of non-turbid water might discharge without any signal in turbidity (e.g., Zirlewagen et al. 2016). The breakthrough of contaminants from allogenic point recharge can be slightly delayed in relation to particulate matter with the same origin (e.g., Pronk et al. 2007).

6 Conclusions

Particulate and dissolved compounds in karst aquifers are subject to complex transport processes, and both turbidity and contaminants, whether in dissolved or particulate states, can originate from different sources and have different input modes. Systematic relationships between turbidity and contaminants in karst springs are highly site-specific and need to be individually calibrated for each karst catchment. However, hydrophobic substances are an exception: if adsorbed to particulate matter, contaminants are likely to be subjected to similar recharge and transport processes (including remobilization within the aquifer) and thus exhibit the same discharge patterns as particulate matter. A conceptual model including dynamics of turbidity and a number of potential contaminants reviewed in this paper is presented in Fig. 11.

Some fundamental steps that might assist in establishing turbidity as an indicator for karst catchments would involve (1) analyzing the origin and dynamics of (push-through/flush-through) turbidity at karst springs using methods such as hydro-sedimentary process analysis or signal decomposition, (2) investigating the origin and input mode of contaminants (e.g., autogenic and diffuse from croplands, autogenic and discrete via sinkholes, or allogenic and discrete via sinking streams), and (3) establishing correlation patterns for both turbidity dynamics and contaminant dynamics at karst springs, including different recharge events and using, for example, multivariate analysis, correlation analysis, spectral analysis, and wavelet analysis to support this step.

Complex input modes of contaminants can result in unexpected contaminant and turbidity signals at karst springs. For instance, sinking streams have been found to have the potential to introduce large quantities of sediment into an aquifer, together with high concentrations of contaminants. The timing of that concentrated recharge can be very different from the timing of autogenic recharge and the monitoring of such point sources may therefore provide a way of predicting the timing of contaminant discharge at karst springs by, for example, establishing a discharge–transport velocity relationship with which to calculate contaminant travel velocities. Contributions of highly contaminated but non-turbid water from discrete recharge points can also discharge at karst springs without any turbidity signal.

Other easy-to-measure parameters such as the specific absorption coefficient (SAC), the dissolved organic carbon (DOC), and the particle size distribution (PSD), have been shown to successfully detect the occurrence of contaminants at selected karst springs, although from this review it would appear likely that their applicability is site-specific. Innovative methods such as the use of multi-tracer tests (with particles and solutes), source-indicative organic micropollutants, and microbial source tracking will in the future be able to significantly extend and improve the tools available for investigating contamination in karst aquifers.

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Using Nutrient Data and Dye Tracing to Infer Groundwater Flow Paths and Contaminant Transfer Time in Grayson-Gunnar Cave, Monticello, KY

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Abstract

The proliferation of Confined Animal Feeding Operations (CAFO) among karst terrains has been a highly controversial issue for past years. Although some studies have assessed the risk of contamination which may derive from the exposure of karst aquifers to animal wastes (Brahana et al. in Geological Survey Scientific Investigations Report 2014–5035:97–102, 2014), little study has been conducted on the impact of these operations on the quality of water in karst aquifers. We will be specifically looking at the potential loading of nutrients, including nitrogen species and reactive phosphate, during specific storm events at the Grayson-Gunnar Cave outlet in Southeastern Kentucky.

1 Extended Abstract

Epigenic karsts are characterized by surface and subsurface development features (such as sinkholes, springs, caves, and losing, sinking, underground streams) and strong hydrological connections with the surface (White 1988; Ford and Williams 2007). For decades, epigenic karst aquifers have been known to be more vulnerable to surface contaminants than non-karst aquifers. Therefore, they have raised specific concerns for water managers in terms of water quality and water resource protection (Mull et al. 1988; Brahana et al. 2014). In addition, the recent widespread of confined animal feeding operations (CAFOs) facilities on epigenic karst terranes have raised new concerns about karst aquifer's vulnerability (Brahana et al. 2014).

This study focuses on Grayson-Gunnar Cave (Fig. 1), an 11-km-long cave system in the Cumberland Plateau of Southeastern Kentucky. The regional lithology consists of Mississippian carbonates capped by Pennsylvanian clastic rocks (Fig. 2). The cave is developed in the St. Louis formation (red arrow). 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 CAFO.

This research comprises two related objectives in the study of the GGC system: (1) to assess its connectivity with potential point sources of anthropogenic contamination (septic systems and CAFOs); and (2) to determine the fate and travel time of nutrients within the cave. The results from this study will serve for a greater understanding of the critical zone, deeper groundwater, and the impact of changing land use on epigenic karst aquifers in the Cumberland Plateau.

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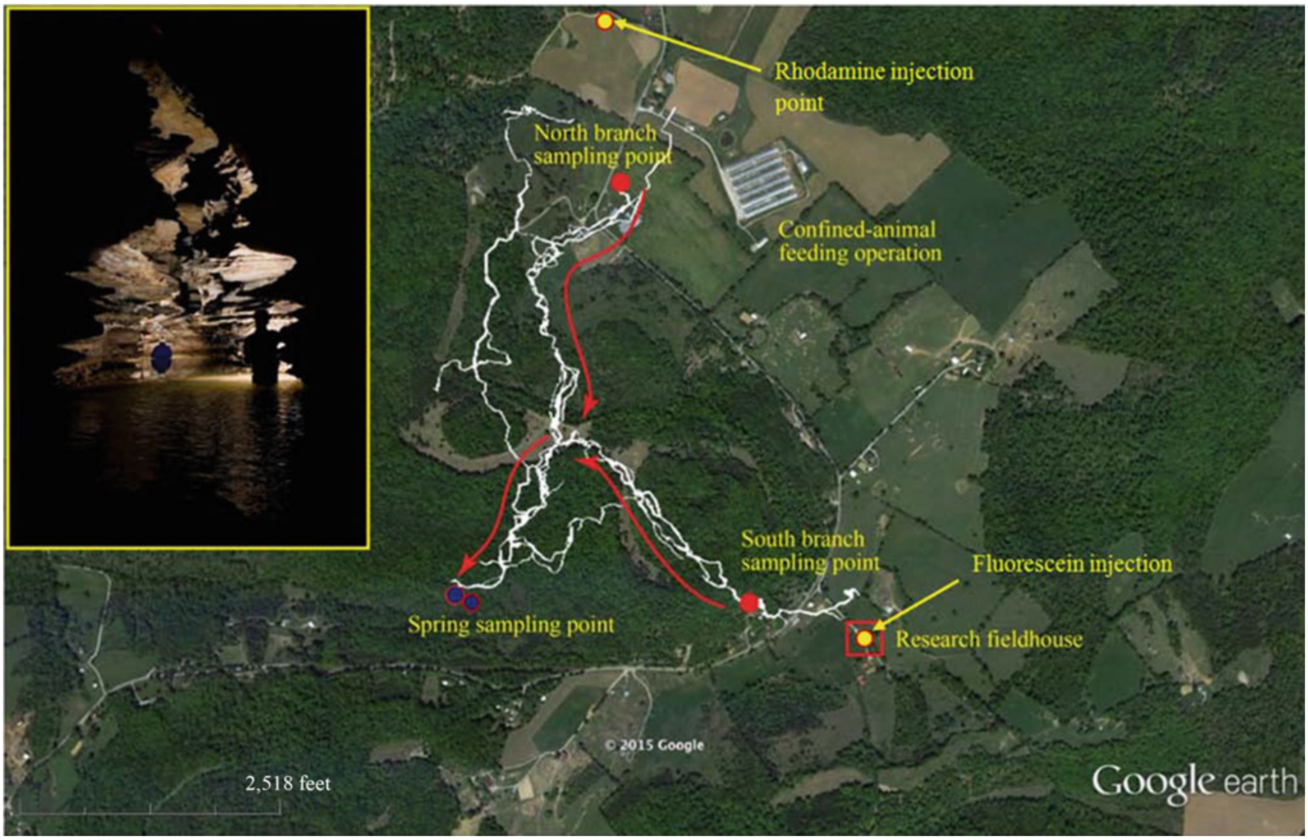

Fig. 1 Surveyed passages of Grayson-Gunnar Cave in *white*. *Yellow dots* are dye injection sites. *Red arrows* are expected dye paths. *Blue dots* are activated charcoal packets deployment sites. *Insert* shows typical passage cross section

Nitrogen and phosphate are elevated as expected (Fig. 3). Nitrate concentrations are more dilute during storm events, but phosphate levels increase due to mobilization of sediment substrates. DOC values spike during storm events and, combined with SUVA values, suggests the rapid transfer of organic matter from the land surface with limited degradation.

In contrast, neither rhodamine WT injected into a well near the CAFOs nor uranine injected into a domestic septic system, both in the headwaters of the aquifer, appeared at the spring after six weeks and multiple storm events. These results highlight the decoupling between fast flow through sinkholes and conduits and more diffuse flow in the epikarst.

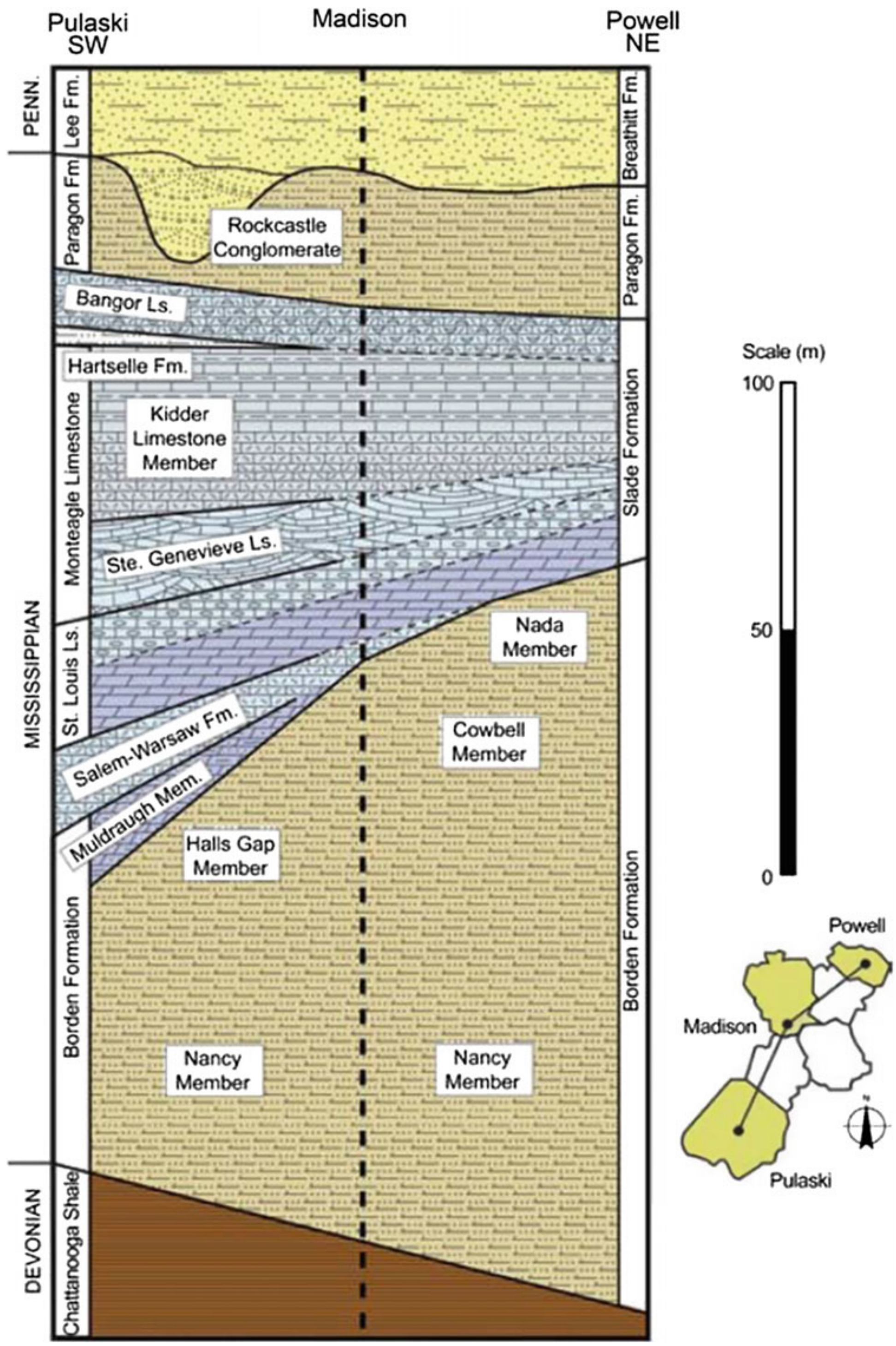

Fig. 2 SE to NW stratigraphic cross section along the Cumberland Escarpment. From Simpson and Florea (2009)

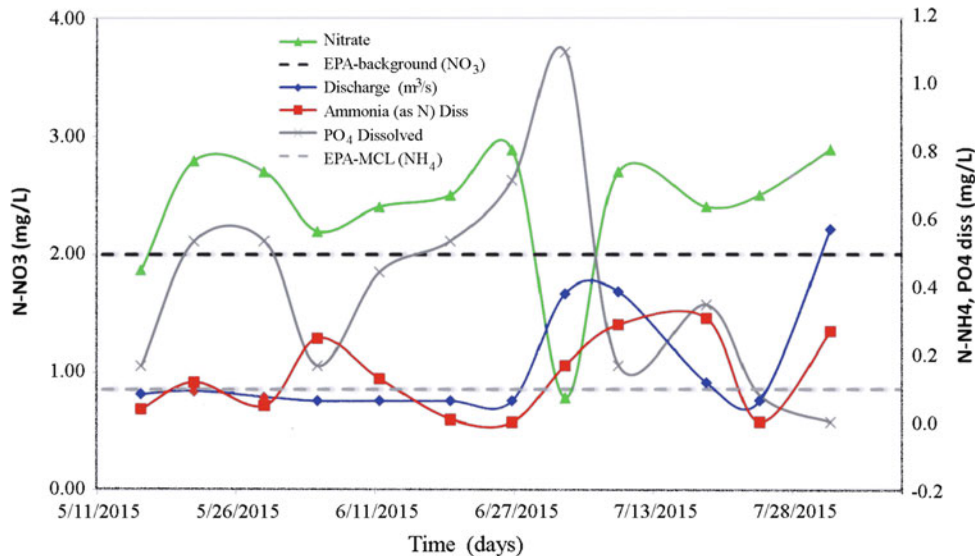

Fig. 3 Concentrations of nitrate, ammonia, and phosphate measured from weekly samples at GGC spring and plotted along with discharge. The *horizontal dashed lines* represent EPA standards for nitrate (*black*) and phosphate (*gray*)

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Development and Testing of Hydrogel Beads as Potential Floating Tracers of Contaminant Movement in Karst Aquifers

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Abstract

The transport of light non-aqueous phase liquids (LNAPLs) is not well understood in karst settings. Traditional tracers do not predict the movement of free product; therefore, this study was undertaken to develop a better tracer proxy for LNAPL. The floating hydrogel tracer beads were created using alginate polymers and adding fluorescent pigments and density-modifying additives to alter their physical characteristics. Two sets of multi-tracer field tests (beads plus a conservative solute tracer) were completed in a 60-m section of cave stream. The beads were quantified via counting for the first set of tests and using particle image velocimetry (PIV) for the second. During the 2012 tests (170 L/s discharge), the beads travelled faster than the solute tracer; however, in the 2014 tests (9.1 L/s) the results were less conclusive (the beads arrived before the solute but had a later peak time and a lower mean velocity). Most of the particle studies have reported that particles travel faster than solutes, in accordance with our 2012 studies. Although the beads are particles and thus not an ideal proxy for LNAPL contaminants, they hold promise for future experimental studies and highlight the complexity of LNAPL transport in cave systems.

1 Introduction

The fate and transport of contaminants in karst aquifers is not well known. Two critical characteristics of karst aquifers that contribute to the complexity of contamination movement, not present to the same degree in other systems, include (1) abundant sediment transport and (2) the potential existence of physical "traps" for non-aqueous phase liquids (NAPLs) (Vesper et al. 2003; Vesper 2008). The movement of NAPL through karst is not only poorly understood, but the traditional tools used to understand the movement of solutes are unlikely to predict the fate and transport of the NAPL.

Most of the information related to NAPL in karst is based on site-specific studies that highlight the challenges of tracking NAPL contaminants in karst. In 1990, near Lewisburg, Tennessee, a train carrying ca. 57,000 L of chloroform (DNAPL) and ca. 15,000 L of styrene (LNAPL) derailed, resulting in the release of these compounds into an underlying karst aquifer (Crawford and Ulmer 1994). A dye trace in the area identified Wilson Spring as the output location but during high water levels at least two other springs are connected to the basin. Chloroform and styrene were detected in Wilson Spring several months after the spill, and a well drilled in the area contained free product of both the NAPL and the DANPL. The authors interpreted the DNAPL flow path to be along dip which is upgradient potentiometrically; dissolved contaminants solubilized from the DNAPL and LNAPL were thought to travel along strike to the springs. In a subsequent study in 2000–2001, Williams and Farmer (2003) found that contaminants were still

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discharging from Wilson Spring, particularly in association with storm events.

Stephenson et al. (2003) investigated a spill of 14,000 L of diesel fuel (LNAPL) when a tanker truck crashed on Interstate 65 near Park City, Kentucky. This region is located in the upgradient portion of the Turnhole Spring groundwater basin and is known to discharge to the Mill Hole Spring. Previous dye traces from near the spill site to Mill Hole Spring took between 2 and 42 h, but no diesel product was detected at the spring. The researchers concluded that the diesel product remained localized to soils around the spill area, but the diesel could have also been trapped in the conduit leading to the spring.

Ewers et al. (1991) reviewed the movement of LNAPL contamination for two locations in Kentucky: the Fort Campbell Army Airfield and a leaky gasoline storage tank in Richmond. At Fort Campbell, dye traces confirmed a connection between the airfield and Quarles Spring; however, components of the jet fuel LNAPL at the airfield could not be detected in the spring water. At the gasoline site, dyes confirmed that water moved toward two springs but only the upper spring had detectable gasoline. Ewers et al. interpreted the lack of LNAPL transport at both locations to be the result of physical trapping and decanting structures in the karst aquifer that permitted water to flow but prohibited LNAPL transport.

A common issue identified by each of these case studies is that the movement of solute tracers did not predict if LNAPL would or could be transported. Recent multi-tracer studies that incorporate both conservative solute and non-solute tracers have confirmed that the use of traditional tracers is unlikely to predict the complexity of colloidal, sediment or NAPL transport. Multi-tracer studies that incorporate microspheres have been conducted by several researchers (e.g., Auckenthaler et al. 2002; Göppert and Goldscheider 2008; Harvey et al. 2008; Sinreich et al. 2009). Microspheres are colloid-sized (<1–5 μm) synthetic particles that are used as an analog for the movement of bacteria. Several of those multi-tracer studies have also included bacteria (Sinreich et al. 2009), oocysts (Harvey et al. 2008), and bacteriophages (Auckenthaler et al. 2002). A common outcome in these studies is that the particles and solutes are not transported in an identical fashion. In all but one of the studies, the microspheres traveled faster than the solute tracers. The enhanced transport has been attributed to particle-size exclusion where the particle moves faster because it is only able to be transported in the larger pore structures. Or, in the case of stream systems, enhanced particle transport is attributed to the lack of mixing in the water column. Göppert and Goldscheider (2008) had less conclusive results and found that microspheres travelled faster than solutes at low flow but were more similar in travel time under high-flow conditions.

The case studies and the multi-tracer tests confirm that a range of possible fate and transport outcomes exist for contamination in karst aquifers. To better understand the potential range of outcomes, particularly with regard to LNAPL transport, tracers with different physical properties (e.g., density) must be identified and tested. The purpose of this study was to develop a hydrogel bead tracer that is less dense than water; the construction, detection strategies, and field testing of the beads are reported.

2 Methods

2.1 Bead Construction

The beads are created by the dropwise addition of an alginate solution into a divalent cation curing bath. The initial solution contains 3% w/w alginate and is prepared by adding sodium alginate powder ($C_6H_8O_6Na$, Sigma Aldrich, St. Louis, MO) to deionized water and stirring overnight until all of the alginate has dissolved. Additional chemicals are then added to ~50-mL aliquots of the alginate solution: 3-M Glass Bubbles (Saint Paul, MN) are added at a 1% concentration to create low-density beads; visible florescent pigments (Risk Reactor Inc., Santa Ana, CA) are added at a 1% concentration to color the beads and make them fluorescent. The final solution is mixed on a vortex mixer until homogeneous.

The alginate mixture is placed in 60- or 120-mL syringes with 20-gauge (0.9 mm) needles and dispensed dropwise approximately 30 cm into a continuously stirred curing bath of 1 M $CaCl_2{\cdot}2H_20$ (Fisher Scientific, Pittsburgh PA) using a syringe pump (Harvard Apparatus, Holliston, MA). Beads are left in the curing solution for at least 1 min and then placed in fresh curing solution for storage. The beads are stored in a refrigerator until use. The approximate size of the beads is 5 mm (Fig. 1).

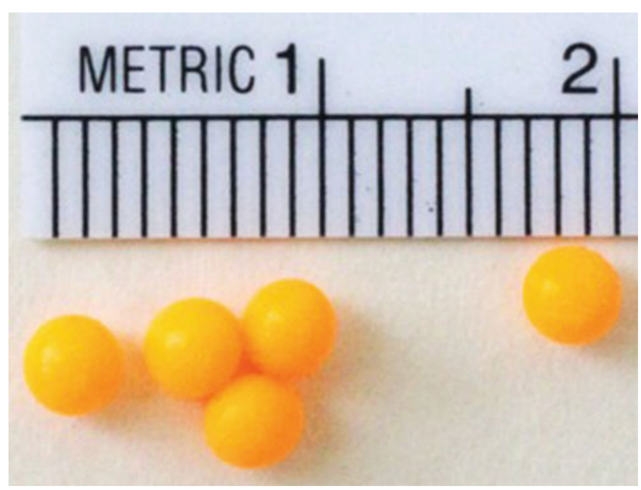

Fig. 1 Images of beads with scale

Risk Reactor pigments were used in this study to create beads that fluoresced. The adsorption and emission spectra were measured for the three colors used for the PIV detection method. A sample of each pigment was suspended in glycerol and then excited with a 395-nm wavelength UV source on a Fluorolog-3 Spectrofluorometer (Horiba Scientific, Irvine, CA) to obtain adsorption and emission spectra. The spectra were used to select the best UV-LED lights for exciting the pigments in the field tests.

As part of method optimization, beads were constructed with varying concentrations of alginate (2–4%) and dropped from different heights into the curing solution (30–100 cm). The resulting beads were viewed using a Leica Wild M3Z (Germany) with an Intralux 6000-1 Fiberoptic Illuminator (Switzerland) at a 6.5× magnification. The long and short axes' lengths were measured for at least 10 beads for each condition. The conditions yielding the most spherical beads (long axis/short axis closest to 1) were selected for the method (Table 1).

2.2 Tracer Detection and Data Analysis

For the initial field studies, the beads were collected in fish nets for 20-s time intervals. The nets were secured in the field, so no beads were lost; the beads were later quantified by manual counting in the laboratory.

In subsequent tests, bead transport was quantified using particle image velocimetry (PIV) similar to techniques employed by Muste et al. (2008) and Tauro et al. (2012b). This technique employs photographing or video-recording the bead movement and analyzing the imagery to obtain flow parameters. Tauro et al. (2012a) demonstrated the use of this method in the field using buoyant fluorescent particles (700–1200 μm). Although the buoyant particles (dry density 0.98 g/cm^2) provided a surface velocity, the authors used it to infer average stream conditions.

For tracing beads in the subsurface, the PIV approach needed to be modified to account for the lack of natural light. This was accomplished by modifying the beads to include fluorescent pigments and exciting the pigments using UV light of an appropriate wavelength (395 nm λ, Super Bright LEDs, Model NFLS-X3, St. Louis, MO). As the beads passed under a UV light strip, they fluoresced and they became readily visible for filming (Fig. 2). Images were obtained using a GoPro HERO3 + Black Edition camera (GoPro, San Mateo, CA) mounted on a bracket over the UV light strip. The camera was mounted and leveled between 30 and 45 cm above the water to account for a narrow stream (<1 m). Acquisition rates of 60–120 fps were used depending on the test, and the files were stored in mp4 format.

Image processing required four tasks completed using an image analysis algorithm in MATLAB (The Mathworks Inc., Natick MA):

1. Video images were separated into red–green–blue (RGB) color space, creating three components. Each of these three components is known as a color channel.
2. Each red and green channels was separated into a sequence of images, and the contrast was enhanced for each image. The blue channel was excluded due to lack of contrast because it detects the UV reflection on the water surface.
3. The mean pixel intensity was calculated for each frame in the red and green channels. The number of beads visible in the frame is proportional to its mean pixel intensity.
4. The mean pixel intensity data were combined with the time data from the video to obtain "concentrations" through time.

After the pixel data were obtained, several additional data processing tasks were required as follows:

5. The mean pixel concentrations were normalized to the maximum value so that comparable scales could be used for all data sets.
6. A Savitzky–Golay smoothing filter was applied to improve the signal-to-noise ratio of the normalized data. The Savitzky–Golay smoothing filter removes noise without affecting the overall shape of the curve by performing a least squares fit of a small set of consecutive data points to a polynomial and taking the calculated central point of the fitted polynomial curve as the new smoothed data point (Savitzky and Golay 1964).

Table 1 Summary of field tests completed in Buckeye Creek Cave

Date	Test	Solute	Beads released	Bead detection method	Mean discharge L/s	Mean water depth (m)
5/18/12	A	Fluorescein dye	3000	Manual counting	170	0.6
	B		3000			
7/26/14	C	NaCl solution prepared with cave water	4500 Yellow	PIV and manual counting	9.1	0.4
	D		4500 Red			

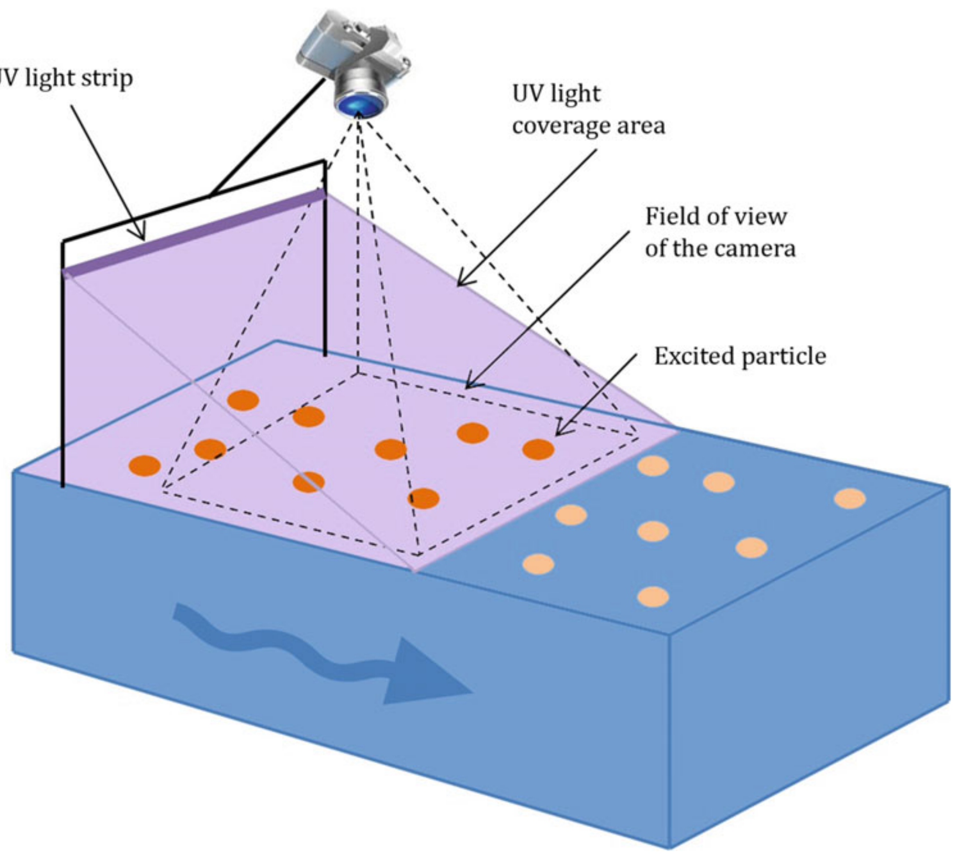

Fig. 2 Configuration of the PIV optical detection system

7. For times without data (due to camera failure), the missing values were estimated using a linear interpolation between adjacent data points.

After breakthrough curve data were generated using the mean pixel intensities, the data were entered into QTRACER2 (Field 2002) to calculate the following transport parameters: time of first detection, time of peak detection, mean velocity, maximum velocity, transit time, and longitudinal dispersal. Breakthrough curves from the solute tracers used in combination with the beads were also entered in QTRACER2 to obtain the same transport parameters.

Conservative solute tracers were released with the beads in all tests. The solute salt tracer was determined by measuring electrical conductivity (EC) in the field using a YSI 556 multimeter (YSI Inc., Yellow Springs, OH) and converting the measured values into equivalent concentrations of NaCl. A fluorescein dye tracer was determined by collecting water samples in the field and measuring their florescence in the laboratory using a Turner Designs 3100 Laboratory Fluorometer (Turner Designs Hydrocarbon Instruments, Inc., Fresno, CA) or a Varian Cary Eclipse Fluorescence Spectrophotometer (Agilent Technologies, Santa Clara, CA).

Discharge was measured using the US Geological Survey standard method described by Buchanan and Somers (1969). A Swoffer current meter (Swoffer Instruments Inc., Seattle, WA) was used to acquire velocity measurements.

2.3 Field Testing of Beads

The beads were tested in Buckeye Creek Cave in Greenbrier County, West Virginia (Fig. 3). Buckeye Creek Cave is developed in the Union limestone member of the Greenbrier Series, which is described as being a 60-m thick, gray to dark, fossiliferous to oolitic limestone, which weathers white (Dasher and Balfour 1994).

The Buckeye Creek cave system includes three caves: Buckeye Creek Cave, Rapps Cave, and Spencer Cave (Fig. 3). The cave has four levels; the lowest level—Buckeye Creek Cave—is the only active section (Dasher and Balfour 1994). Buckeye Creek and another small creek enter the cave at the southwest entrance and flow through the system until it discharges at Spencer Spring. The water flows through a near-sump: under high-flow conditions, the sump blocks access to the downstream areas of the cave. Upstream of the sump the cave is a stream passage that includes pools,

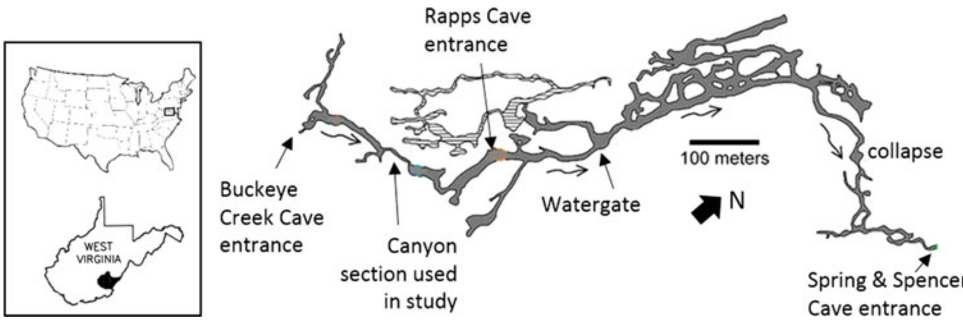

Fig. 3 Map of Buckeye Creek Cave showing the canyon section used for the study (modified from Dasher and Balfour 1994). *Insets* illustrate location of the site in the USA and its location in Greenbrier County in West Virginia

canyons, and meandering sections. The presence of large debris, often high in the cave passages, suggests that parts of the cave are flooded periodically.

The tracer tests were conducted in the canyon section of Buckeye Creek Cave (Figs. 3, 4, and 5), where the stream is about 1 m wide, and it is constrained on the sides and lined on the bottom by bedrock. The length of the traced transect was 59 m. The section of streambed had a minimal amount of sediment, the majority of which is gravel- to sand-sized. The water depth was only slightly less in the 2014 tests than in the 2012 tests, but the discharge was much less in 2014 (Table 1). In 2012, two tests (A and B) were completed using fluorescein as the soluble tracer and by collecting and manually counting the beads. In 2014, two tests (C and D) were completed using NaCl as the soluble tracer.

3 Results

3.1 Tests A and B (2012)

The duration of each field test was approximately 10 min. The average stream discharge on the day of the tests was 140 L/s.

The recoveries for the dye were 91 and 88%; the percent recoveries for the beads were 58 and 73%. Given the difficulty in collecting the beads manually during a short test, the low bead recoveries are attributed primarily to poor collection efficiency at the sampling point. The higher recovery for the second test was due to improved collection techniques. With the exception of the percent recovery, there was excellent agreement between the results of the two bead tests. The hydraulic parameters calculated in QTRACER2 agreed within 10% between Test A and Test B (Table 2; Fig. 6). The time of first detection, mean velocity, peak velocity, and mean tracer transit time agreed within 3%.

Greater discrepancy was observed between the beads and the dissolved dye. Peak time agreed within 10%, but the other parameters calculated in QTRACER2 (time of first detection, mean velocity, peak velocity, and mean transit time) varied from 8 to 17% between tests A and B (Fig. 6; Table 2).

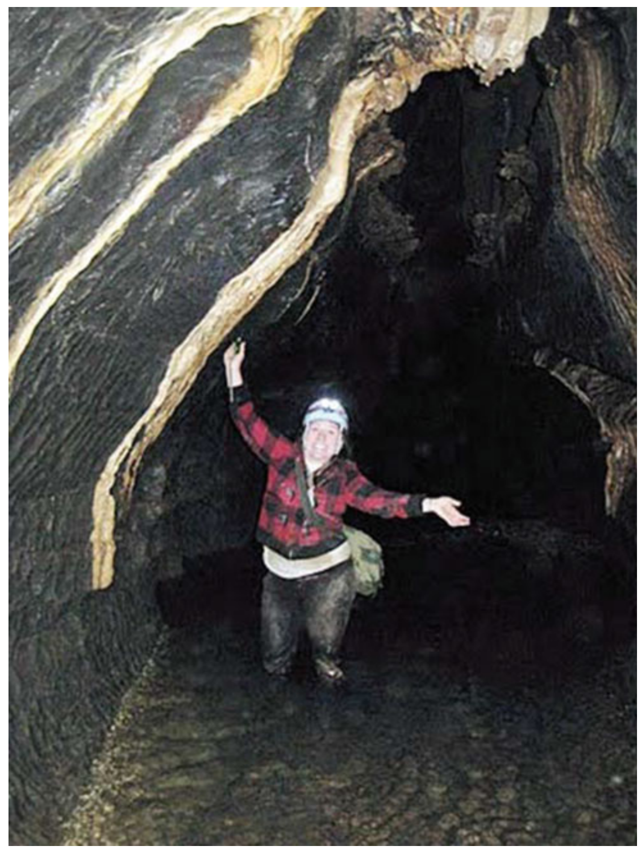

Fig. 4 Canyon section used for tracing tests in Buckeye Creek Cave

3.2 Tests C and D (2014)

Each of the two field tests in Buckeye Creek Cave lasted approximately 50 min. The average discharge in the cave stream was 9.1 L/s, which was taken to be constant throughout the day. The recoveries for the solute were 105

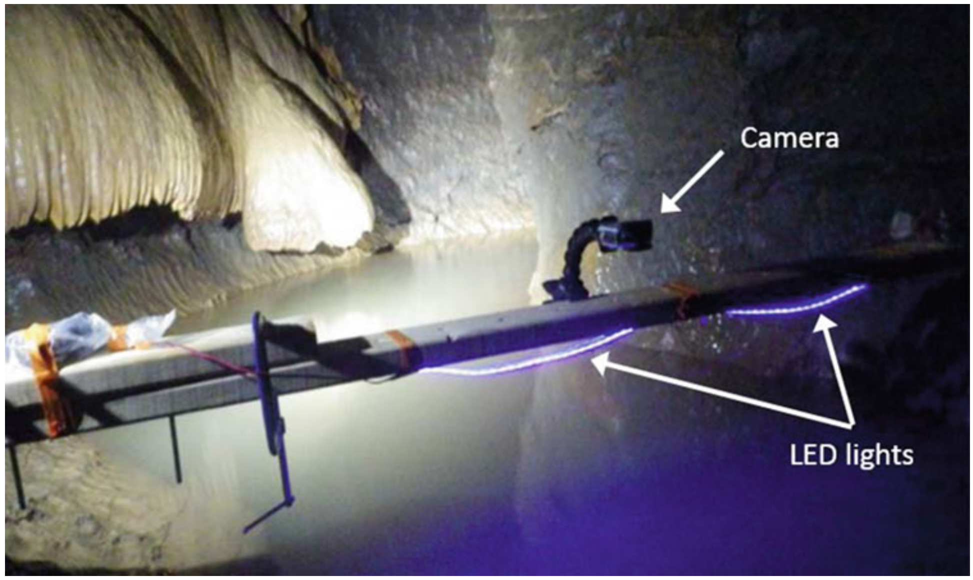

Fig. 5 PIV detection system in Buckeye Creek Cave

Table 2 Comparison of QTRACER2 results for Buckeye Creek Cave

Parameter and units	Average of tests A and B (5/18/12)			Average of tests C and D (7/26/14)		
	Solute	Beads	% Diff.	Solute	Beads	% Diff.
Time of first detection (min)	3.0	2.7	11	19.2	17.6	8.7
Peak time (min)	3.5	3.2	9.0	25.9	28.2	8.5
Mean velocity (m/h)	994	1167	16	113	106	6.4
Peak velocity (m/h)	1280	1440	12	185	202	8.8
Mean transit time (min)	3.9	3.4	14	31.4	33.5	6.5
Recovery (%)	90	66	31	109	74	38

Notes The percent difference (% Diff) was calculated as the difference of the two values divided by their average. Discharge was 140 L/s on 5/18/12 and 9.1 L/s on 7/26/14. Fluorescein was used as the solute in 2012; NaCl in 2014. The data reported for the 2014 tests are based on the PIV detection method

and 114%; the percent recoveries for the beads were 77 and 71%.

The 2014 study included both the manual method (bead collection and counting) and the PIV method to determine their relative effectiveness (Fig. 7). To compare between the two, the results of both were used to calculate the tracer parameters using QTRACER2 (Table 3). When the different methods are compared for a single test, most of the parameters agreed within 10%. In general, the parameters agreed better for Test C than for Test D, although in both cases the mean velocity and mean transit time agreed within 10%. The precision of each method was evaluated by comparing the QTRACER2 results between the two tests (Table 2). For the manual method, the parameters agreed between 12 and 84%; for the PIV method, the same parameters agreed between 3.7 and 18%. Overall, the PIV method provided more consistent results than did the manual counting method. The higher variability for the manual method is probably also sensitive to the time period used for bead collection. In Test C, the beads were collected for 1-minute intervals, but in Test D the beads were collected for 2-minute intervals. The longer interval time was used for the second test to ensure that sufficient bead-catching nets were available to complete the test.

The relative transport characteristics of the solute and beads were not consistent. The beads arrived first and had a higher peak velocity; however, the beads had a later peak time, a lower mean velocity, and a longer mean transit time (Table 2).

4 Discussion

4.1 Effectiveness of Tests

The tests conducted in Buckeye Creek Cave were intended as proof of concept for the use of the beads as an LNAPL-proxy tracer in karst systems. The manual collection

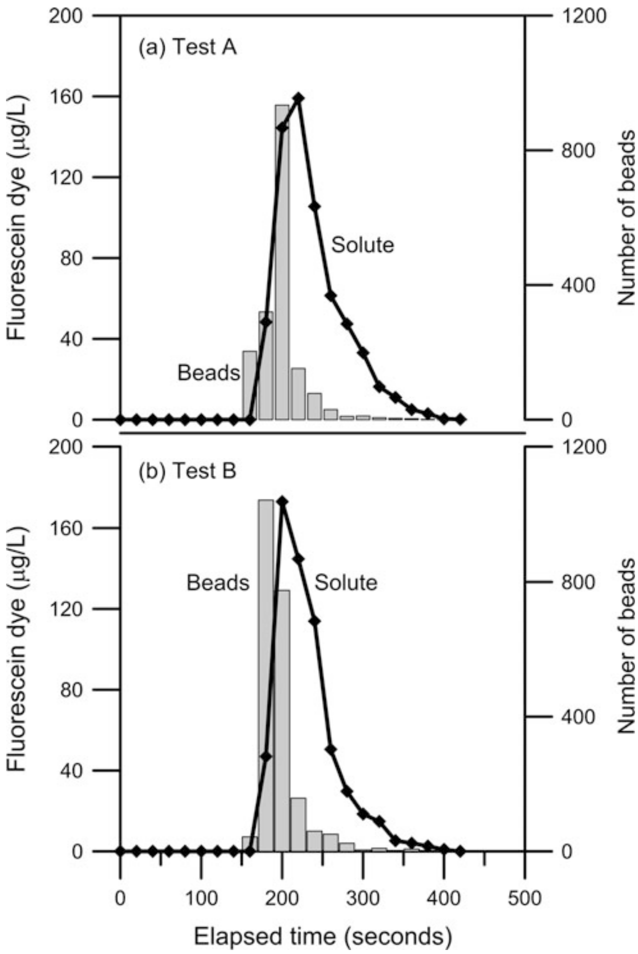

Fig. 6 Tests A and B: breakthrough curves for solute and bead tracers, 5/18/12

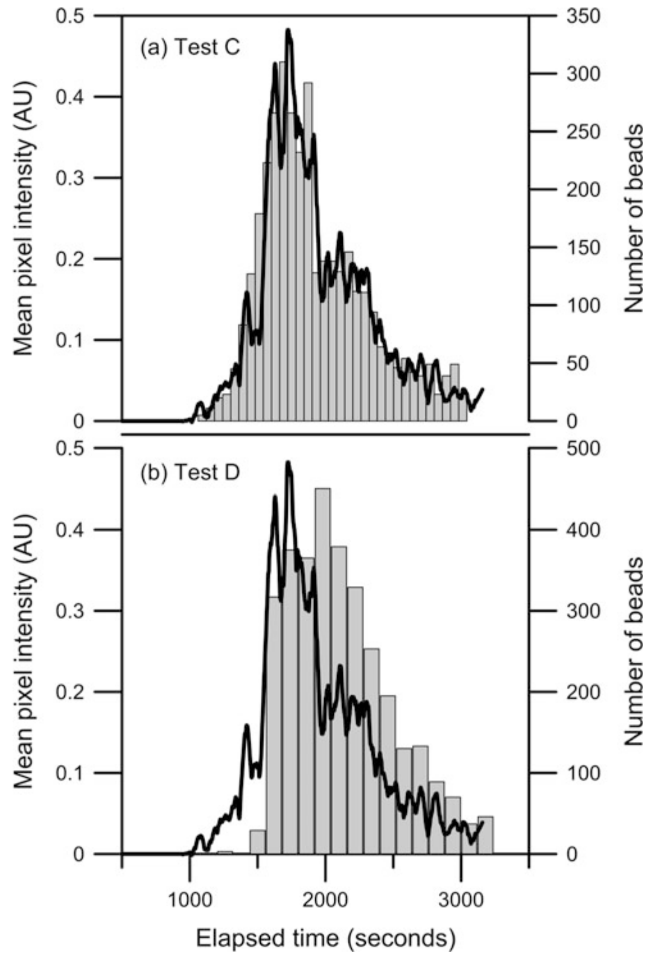

Fig. 7 Tests C and D: comparison of results from PIV method (*solid black line*) and manual counting detection (*columns*) methods

and counting of beads were effective in all tests but can only provide limited detail for flow calculations. The PIV detection method used in the 2014 tests was more automated and provided far more detail regarding the bead transport.

4.2 Results of Tests

In the 2012 Buckeye Creek Cave tests, the beads travelled faster than the solute tracers, in agreement with other multi-tracer studies that have incorporated particle tracers (Auckenthaler et al. 2002; Göppert and Goldscheider 2008; Harvey et al. 2008; Mahler et al. 1998a, b; Sinreich et al. 2009).

In contrast, in the 2014 Buckeye Creek Cave tests, the bead transport was more similar to the solute transport. The beads had an earlier first detection and higher peak velocity, but a later peak time, slower mean velocity, and longer transit time. Of the similar multi-tracer studies, the slower transport of particle tracers was only reported by Göppert and Goldscheider (2008). That study was conducted in Hölloch Cave, in the Swiss Alps, and was conducted over a 2.5-km cave-stream distance with a few sumps but mostly open-channel flow. Under low-flow conditions, with a constant discharge of ca. 20 L/s in the cave stream (ca. 170 L/s at the down-gradient Sägebach Spring), the 1-μm microspheres travelled faster than the co-injected solute dye. During a second test, under high-flow storm conditions (discharge from 582 to 1035 L/s at Sägebach Spring) the colloids and solutes arrived much closer in time.

There are some critical differences between the gel-bead tracers used in the Buckeye Creek Cave studies and the multi-tracer studies that employed microspheres: (1) the gel beads are much larger than the microspheres; (2) the beads are buoyant, while the microspheres are closer to neutral density; (3) the tests in Buckeye Creek Cave were over a shorter distance and only in open-channel flow. Although conducted above ground, the Tauro et al. (2012a, b) creek study may be more comparable to the Buckeye Creek Cave studies. The Tauro et al. study was over a fairly short reach

Table 3 Comparison of bead detection methods

Percent difference in QTRACER2 values	Manual versus. PIV methods		Test C versus. Test D	
	Test C (%)	Test D (%)	Manual method (%)	PIV method (%)
Time of first detection	8.6	12.7	14.3	10.2
Peak time	1.8	17.5	15.7	3.5
Mean velocity	1.8	2	11.3	7.5
Peak velocity	8.8	12.2	14.3	10.9
Mean transit time	2.8	2	11.4	6.6
Longitudinal dispersion	18.2	160	163	28.6

Notes The beads were collected using a 1-minute interval for Test C and a 2-minute interval for Test D

(27 m), used larger buoyant beads (ca. 1 mm), and was conducted in open-channel flow. Only two stream tests were completed by Tauro et al., but their beads travelled faster than a solute tracer in both. The average velocity in these studies was considerably higher: 1980 L/s versus 170 L/s in the high-flow Buckeye Creek Cave tests.

4.3 Limitations of This Approach

There are several limitations to the bead and PIV method for particle tracing in karst. First, the detection system needs to be modified for use over longer time periods and without having a human operator present. Power management, for the camera and LED light strings, is critical in this next step. Second, the PIV method only accounts for particles flowing on the water surface. If neutral-buoyancy or denser beads are used, then the video obtained needs to account for movement at depth as well as on the surface. Third, the transport of the beads needs to be compared with the transport of a free-phase LNAPL. The beads are discrete particles, and their use as an LNAPL proxy requires that they be tested together for comparison. The comparison study needs to be completed in an artificial setting so that LNAPLs are not released into natural settings.

4.4 Advantages of This Approach

A tremendous advantage using the hydrogel beads is that the physical characteristics can be easily altered. Additives can be adjusted to accommodate different types of detection strategies and to control the density of the beads. The relative diameter can also be altered. The bead-construction technique used in this study provides reasonably consistent sizes of beads; altering the needle diameter changes the side of the alginate drops and therefore the bead size. The beads are easier to handle and work with than are microspheres. Lastly, the beads are cost-effective to make. The estimated material cost for producing 10,000 beads was approximately $8 US.

5 Conclusions

These preliminary studies have demonstrated the potential for hydrogel tracer beads to be used as a proxy tracer for LNAPL in karst settings:

1. The beads were used to trace water flow in a cave setting. The PIV detection method was able to quantify the bead movement overtime and produce detailed breakthrough curves.
2. In a high-flow study, the beads travelled faster than solute tracers in agreement with other multi-tracer studies that included particles. At lower flow, the relative transport of beads and solutes was less clear. This suggests the importance of conducting multi-tracer tests under different flow conditions.
3. Additional studies are necessary to improve bead detection, extend the test distance and duration, and probe the possibility of LNAPL traps in karst aquifers.
4. A great advantage of the gel beads is that they are highly alterable and cost-effective. They can easily be modified for different purposes, densities, and detection methods. The potential for using gel beads in future studies is enhanced by the ease with which their physical and chemical properties can be adjusted.

Although limitations exist, hydrogel beads are a good potential tracer for controlled experiments to better understand how LNAPL moves in karst settings.

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Part IV

Contaminant Exposure and Public Health

Cave Characterization in the North Karst Belt Zone of Puerto Rico: Cave Mesofauna Diversity as an Indicator of Pathogenic and Opportunistic Species

Ángel A. Acosta-Colón

Abstract

To completely characterize a cave system, the relationship between the geological, geometrical, physicochemical, and biological properties must be described. The geological properties that provide information on the speleogenesis of the cave was found from a literature review of the region. The geometrical properties were measured to obtain the cartography of the cave in which the cave map, path, and volume were calculated using caveGEOmap. The studied physicochemical properties included the properties of bats' guano droppings that can be used to understand the mycological settings for guanophillic fungi and mesofauna. The abiotic factors such as acidity, guano-enriched soil moisture, and organic matter content were measured and analyzed. The biological properties investigated were the characterization of the bats and mesofauna of the cave by catch-and-release and traps. Total specimens, species richness, and diversity index of the mesofauna were measured for each trap. These measurements provide us with a possible indicator of regions of the cave that can have a possible health impact in humans. Although the abiotic factors measured do not show a clear relationship as a possible marker of fungi and bacteria, our study found that the mesofauna richness and diversity can be a direct indicator of pathogenic and opportunistic species that can affect the human health if their diets are known.

1 Introduction

To completely characterize a cave system, the relationship between the geological, geometrical, physicochemical, and biological properties must be elucidated. These properties can be summarized (Toomey 2009) as geometrical (cartography of the cave), chemical (soil pH, air composition, etc.), physical (climatology, geology, soil resistivity, and dielectric response, etc.), and biological (ecology, biodiversity, and microbial effects). In this study, we characterized two caves in the north karst belt zone of Puerto Rico: Ángel Matos Cave and the west section of the Efraín López Cave in the municipalities of Arecibo and Isabela, respectively. The purpose of this study was to investigate how a cave characterization methodology can help locate possible regions in caves where human health can be affected.

The flora and fauna of the caves consist of a diverse range of organisms from the microfauna (bacteria, fungi, nematodes, etc.), to the mesofauna (mites, collembola, acari, dipteras, etc.) to the macrofauna (spiders, bats spiders, etc.) (Harris 1970). Fungi and bacteria play an important role in the cave ecosystem. Caves can serve as habitat for diverse communities of fungi and bacteria that can include pathogenic and opportunistic species Nieves-Rivera 2003 and Taylor et al. 2013. The presence of these species can be a potential danger to cave visitors and scientists, especially those who are immunosuppressed, undergoing chemotherapy, or have lower defenses (Woods 2002; Jurado et al.

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2010). Multiple studies have reported infections by fungus contracted in caves. Skoulidis et al. (2004) reported the infection by *Penicillium marneffei* in a person exposed regularly to bat guano from a cave. In Puerto Rico, Nieves-Rivera et al. (2009) found multiple guanophillic fungi (guano-enriched soil fungi) in three caves in the southeast region of the country. Additional studies reported infection and documentation of *Histoplasma capsulatum* in Aguas Buenas cave for decades (Torres-Blasini et al. 1960; Torres-Blasini and Carrasco-Canales 1966a, b; Beck et al. 1976; Carvajal-Zamora 1977a, b, c). *Histoplasma capsulatum* is a fungus that can produce pulmonary histoplasmosis, a condition that frequently affects cave explorers and scientists (Nieves-Rivera et al. 2009). In a cave where bats are present, the guano produced by the bats is sufficient to create an independent and complete ecosystem (Poulson 1972) in which fungi and bacteria are food sources for arthropods (Sarbu et al. 1996). The diversity of the mesofauna (arthropods smaller than 2 mm) will vary based on the food sources and environmental conditions of the caves where the guano is located. Environmental conditions at the entrance of the cave fluctuate but are more stable in the cave zones where the bats are located. These constant conditions are characterized by the absence of light, high humidity, and constant temperature (Poulson and White 1969). The physicochemical abiotic factors of acidity, moisture, and organic matter content of the guano in the stable cave zones vary based on the type of bats (Decu 1986; Ferreira et al. 2000; Emerson and Roark 2007) that create the guano droppings.

The objective of the present study was to develop a methodology to fully characterize a cave (geological, geometrical, physicochemical, and biological properties) and evaluate the cave mesofauna diversity as an indicator of possible pathogenic and opportunistic species capable of affecting human health. Furthermore, this study aimed to verify how the abiotic factors (acidity, moisture, and organic content) influence the mesofauna diversity.

2 Methodology

To completely characterize the caves, the geological, geometrical, physicochemical, and biological properties need to be studied. The geological properties consist of the description of the cave geology. The geometrical properties of the cave involve the measurements necessary to create a digital map of the cave. This map will be used as reference for the measurements of the physicochemical and biological properties. The physicochemical properties consist of the guano-enriched soil abiotic factors (acidity, moisture, and organic matter content). The biological properties of the cave consist of the mesofauna biodiversity.

2.1 Geological Properties

To find the geological formation of the cave, we used the GPS coordinates of the caves (Fig. 1) and USGS geological maps for the Quebradillas quadrangle (Monroe 1967) and Arecibo quadrangle (Briggs 1968). After the geological formation was obtained, literature review of the formations (Monroe 1976, 1980) gave us the description needed to understand the geological properties.

2.2 Geometrical Properties

To generate 2D and 3D maps of the caves, the geometrical properties of the caves were measured. To determine the geometrical properties of the cave, reference points or stations were chosen. The stations needed to remain in a fixed position during the entire measurement period, and for that reason, some of the stalactite and stalagmites of the caves were selected. To create the cave map, we used three instruments: (i) compass, (ii) inclinometer, and (iii) distance measurer. To obtain the data for the 2D map, the compass was used to measure the angle from north (azimuth) between stations, the inclinometer measured the inclination between stations, and the distance measurer (laser) measured the distance between the two stations. To verify the measurements, they were repeated (backward and forward). Additionally, the height values such as up–down (roof and floor) and east–west distances (walls) were measured. To be able to generate the 3D map, we measured the azimuth-data and horizon-data. The azimuth-data were collected by varying the angle from the north and measuring the distance at that point (36 data points for 360°). The horizon-data were collected by varying the angle from the horizontal and measuring the distance at that point (>18 data points for >180°). Then, the maps were created by combining the 2D data points, azimuth-data and horizon-data, as inputs in cave-GEOmap (Candelaria-Soberal and Acosta-Colón, in preparation).

2.3 Physicochemical Properties

Surficial samples of bulk bat guano-enriched soil were collected for all the stations at both caves. Moisture content was determined by mass loss upon drying. The samples were dried at 105 °C for 24 h and homogenized using a mortar and pestle. The resulting homogenized guano-enriched soil was then sieved through a 0.5-mm sieve, and the fraction smaller than 0.5 mm was used for the acidity and organic matter analysis. For each sample, we measured the pH using the EPA-Method 9045-D (soil and waste pH) and Hanna HI-208 pH electrode. The organic matter content percent was

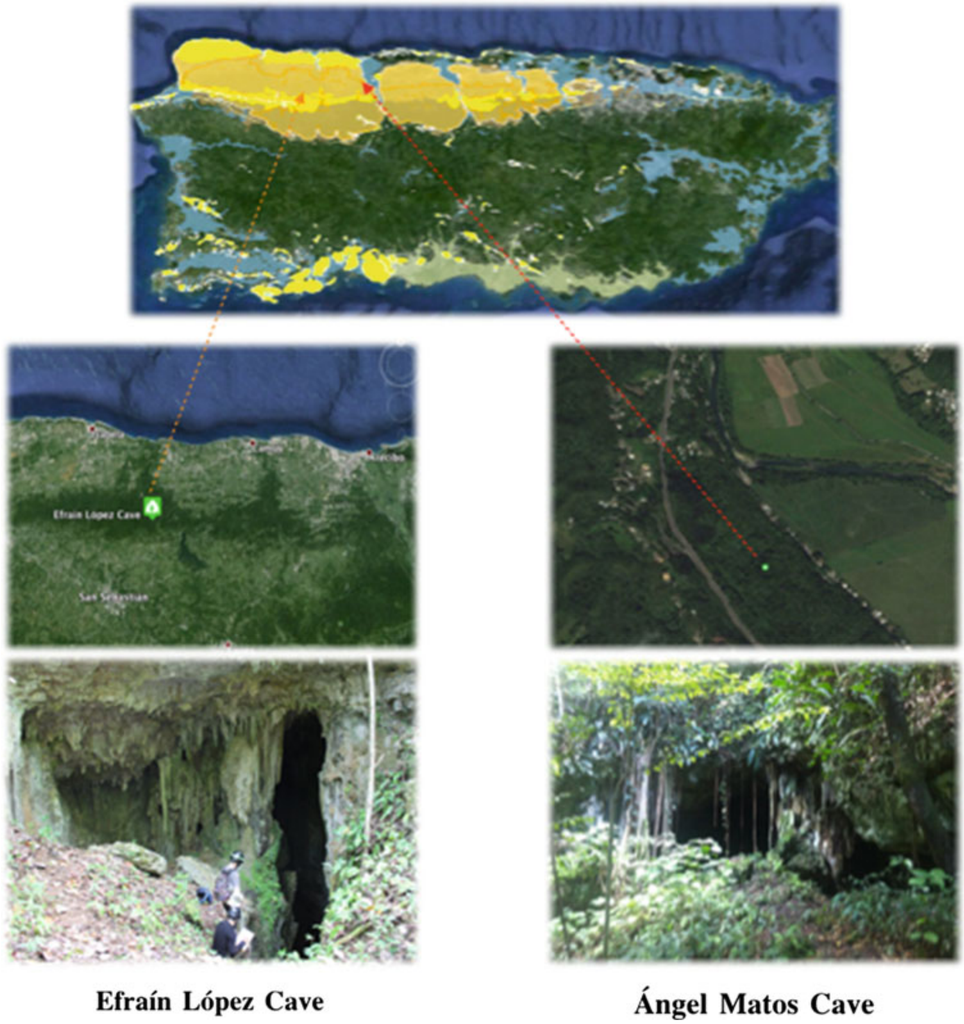

Fig. 1 Map of Puerto Rico in the Caribbean. The *yellow* section of the map is the karst region of Puerto Rico. Efraín López cave (*left*) and Ángel Matos cave (*right*) are located in the municipality of Isabela and Arecibo, respectively

determined using the loss on ignition (LOI) method. The LOI method consisted of ashing (combusting) a 1 g sample of sifted homogenized sediment in a furnace at 750 °C for 3 h and then weighing. The organic matter content percent was determined by loss in mass of the pre- and post-LOI samples.

2.4 Biological Properties

For our study, the biological characterization of the cave was carried out by classifying the bats that produce the guano and the mesofauna that lives in the ecosystem created by the guano. We identified bats, for every station, visually or by catch-and-release. We examined the bat's face, nasal region, fur (and color), uropatagium, and tail (Rodríguez-Durán and Christenson 2012). Based on these characteristics, we were able to classify the bats (and their diet) as a function of the station. The mesofauna specimens were collected by traps and identified by biological class/order per station. The collecting techniques used were as follows: (i) a cardboard trap and (ii) dead leaves trap. The traps were located near the stations used to measure the geometrical properties. After the collection of the samples, each trap was cleaned at the laboratory to collect the specimens. Excess sediment was removed from specimens, and they were closely examined using a dissection microscope to separate, identify (by biological class/order), and quantify the specimens. Then, the organisms were stored and preserved in microtubes with ethyl alcohol (70%) for further assessment. After the quantification of the specimens, the richness of species and diversity index per station was calculated. The species richness is defined as the frequency of species that were collected in the station, and the diversity of the specimens collected was calculated using the Shannon-Wiener index method. This diversity index accounts for abundance and evenness of the species at the station (Magurran 1988; Zar 2007).

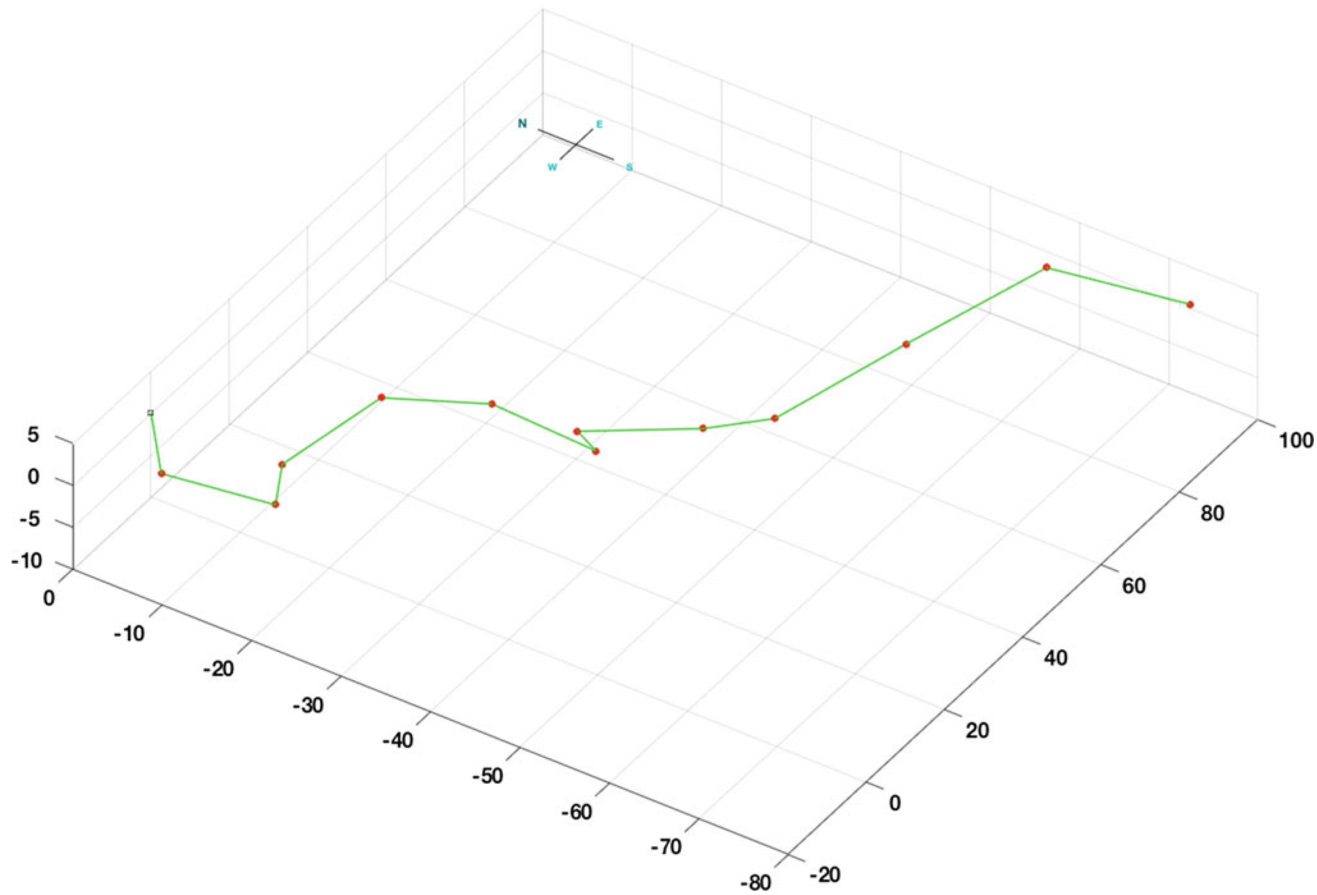

Fig. 2 Results of the cave digital cartography for the Efraín Lopéz Cave. The station path used to measure the azimuth-data and horizon-data. All axes are in meters

3 Results and Discussion

3.1 Geological Setting of the Caves

Both caves are located in the north coast karst belt zone of Puerto Rico (Fig. 1). Efraín López Cave is located in the Isabela municipality and occurs in the San Sebastian Limestone (Monroe 1967). The San Sebastian Limestone consists of red and yellow mottled clay, sandy clay, lignite beds, and carbonaceous clay (Monroe 1980). Ángel Matos Cave is located in the Arecibo municipality and occurs in the Aymamón Limestone (Briggs 1968). The Aymamón Limestone consists of very pure fossiliferous (pale orange to bright yellow) chalk limestone of large beds of oysters and other marine organisms (Monroe 1968). The two formations have similar mineral composition. The common minerals found in the both caves were carbonates (from the eroded bedrock) and nitrates (from guano deposits). Clay minerals were measured in Efrain Lopez Cave as described by Monroe (1967), and for Ángel Matos Cave, an abundance of silicate minerals was found. The mineralogical properties of the formation are important because the eroded sediments created from the rock are the mineralogical surface for the bats' guano droppings that are part of the diet of the cave mesofauna.

3.2 Digital Cartography of the Cave

A total of 832 and 850 measurements were used to create the digital maps for the Efraín López and Ángel Matos caves, respectively. Figures 2, 3, 4, 5, 6, and 7 show the results of the geometrical properties of the caves. Figures 2, 3, and 4 show the results for The Efraín López cave. The station path (Fig. 2) was measured using 13 stations (red circles) including one entrance station (black square), and the measurements for the 3D map are shown in Fig. 3. The azimuth-data are shown in black, while the horizon-data are in blue. Then, caveGEOmap used these measurements to create the 3D map of Efraín López Cave (Fig. 4). Similarly, Figs. 5, 6, and 7 show the results for Ángel Matos Cave. For this cave, we used 12 stations including one entrance station, the azimuth- and horizon-data, to create the digital map (Fig. 7). For both caves, the entrance reference station used

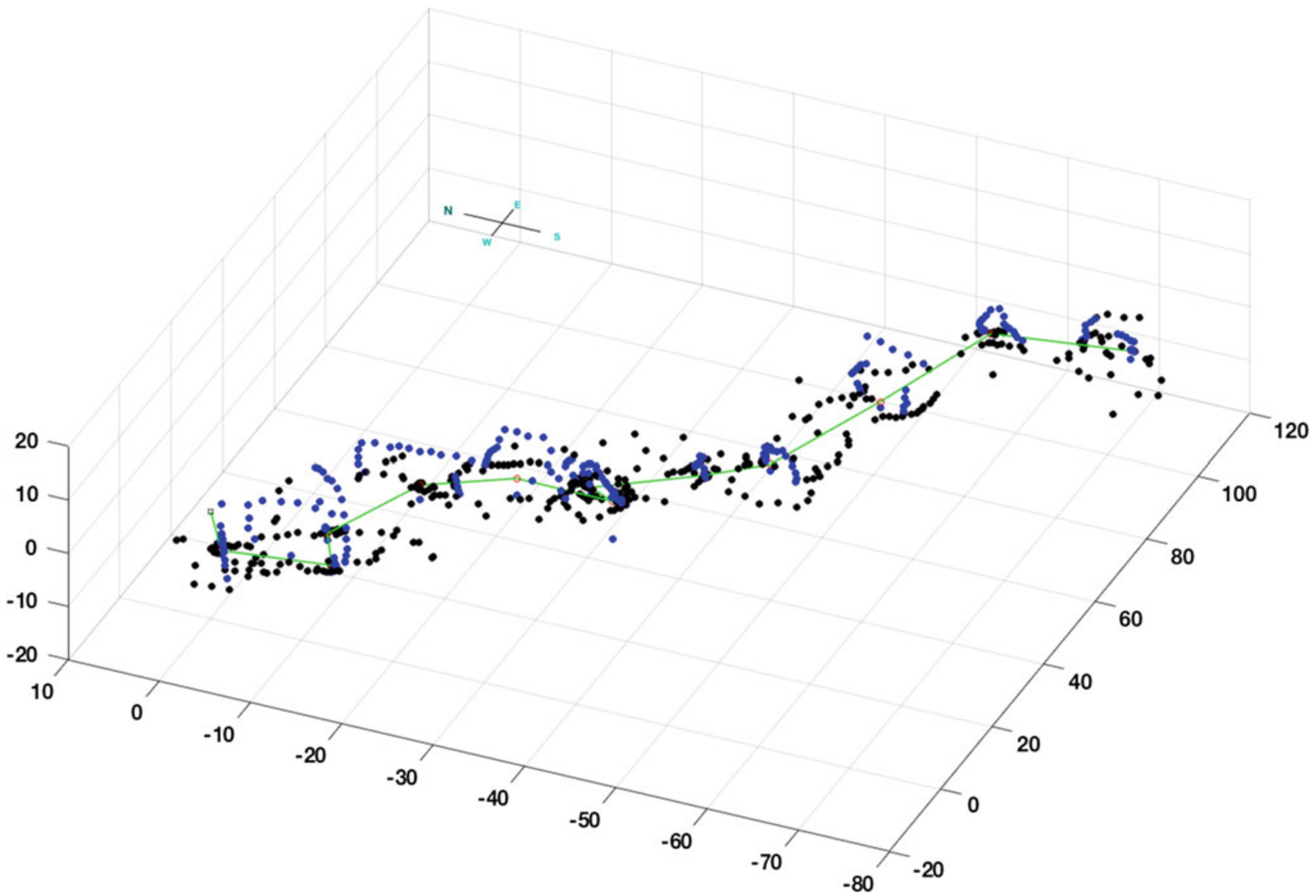

Fig. 3 Efraín López cave results for the 3D data points (azimuth-data and horizon-data). All axes are in meters

was our station zero. As we accessed the cave, the station numbers (red circles in Figs. 2 and 4) will increase as a function of the depth of the cave. The end of the cave references were station 12 and 11 for Efraín López and Ángel Matos caves, respectively.

Using the caveGEOmap results, we estimated the length and volume of the caves. Efraín López Cave has an estimated length of 135 m and volume of 3700 m^3, while Ángel Matos Cave was 244 m in length with a volume of 2000 m^3. Even though the Ángel Matos Cave is longer, the volume is smaller, and this is due to the vertical height of the cave. Nevertheless, this study did not attempt to compare the properties of the two caves. Rather, both caves were used to characterize the physicochemical and biological properties as measurements useful in elucidating independent ecosystems even though the same methodology was used in both caves.

3.3 Bat Characterization

After the visual or catch-and-release inspection of the bats in both caves, we found that Efraín López Cave only has one bat species from stations 3 through 12, the *Artibeus jamaicensis* which is a frugivorous bat. However, in Ángel Matos Cave, we detected 4 different bats species: two frugivorous species, *Brachyphylla cavernarum* and *Artibeus jamaicensis;* one nectarivorous bat type, *Erophylla bombifrons;* and one insectivorous, *Pteronotus quadridens*. Table 1 summarizes the bat types per station for both caves. The importance of the bat characterization is in knowing the diet. The bat's feeding habits can help us understand the guano properties. Multiple studies (Decu 1986; Studier et al. 1994; Ferreira et al. 2000; Shahack-Gross et al. 2004; Goveas et al. 2006; Emerson and Roark 2007) had measured acidity, organic content, nutrient mass ratios (C:N, N:P, C:P), and other guano properties. These studies have shown some dissimilarities of these properties even for the same species with same diets. These differences in elemental composition are coupled with the different needs among organisms living in the guano ecosystem, creating different community structures (Emerson and Roark 2007). For this reason, measurements of the acidity, moisture, and organic matter content were made for each station, due to changes in elemental composition even with same species with same diets.

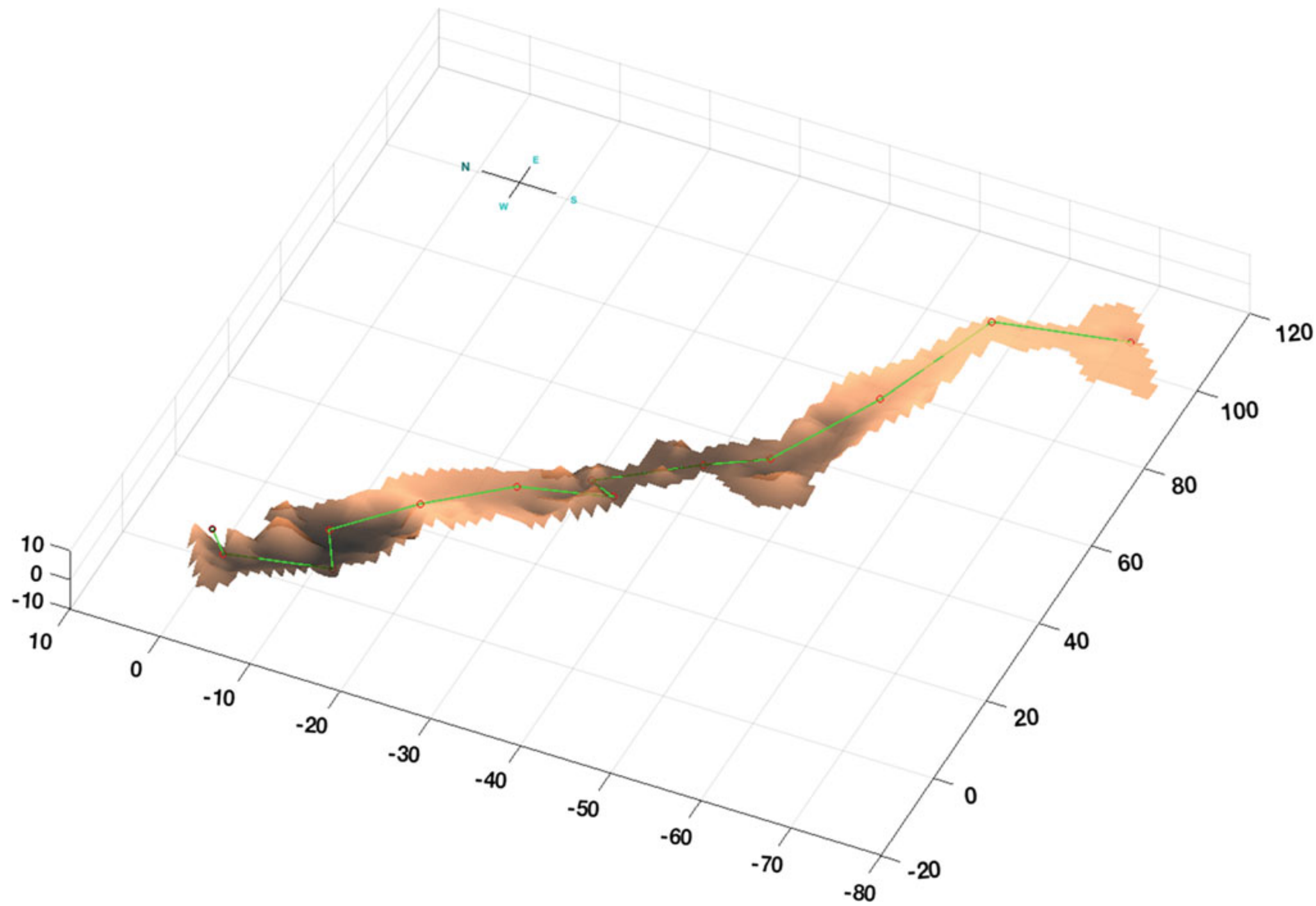

Fig. 4 The resulting caveGEOmap output cartography from the measurements on Efraín Lopéz Cave was calculated using the 3D data points and the station path. All axes are in meters

3.4 Abiotic Factors

The results of the abiotic factors such as acidity (pH), guano-enriched soil moisture (%SM), and organic matter content (%OM) are shown in Table 2. As previously mentioned, these parameters will be affected by the bat's diets. The pH values for Efraín López Cave vary slightly as a function of the depth of the cave with no recognizable pattern due to the continuity of a single bat species (*Artibeus jamaicensis)*; however, for Ángel Matos Cave, the guano-enriched soil becomes more acidic as we move from the frugivorous species into the nectarivorous and insectivorous bats. There was no demonstrable relationship between guano-enriched soil moisture variations as a function of the depth for Efraín López Cave. Nevertheless, an increase in moisture as a function of the depth of the guano-enriched soil moisture was measured in Ángel Matos Cave. This increase is due to a growth of water percolation which was visible in the cave. Additionally, a possible interpretation for some changes in the guano-enriched soil moisture can be the freshness (recently deposit) of the guano. Lastly, to interpret the organic matter content, we used the out-of-the-cave station as a baseline for the results. The percentage of organic content at the entrances was nearly 20–30% for both caves which consisted mostly of leaves and droppings from entry/exit flights of the bats. The organic matter content for Efraín López Cave was greater for the stations with bats (except station 6) than the entrance zone (stations 0–2). Station 6 was selected out of necessity relatively close to the cave wall (due to the shape of the cave in that section) which did not yield a significant quantity of bat droppings. For Ángel Matos Cave, the organic matter content shows some disparities. Although a higher organic matter content was expected for regions with bats, this was not always the case for this cave. In the regions where bats are located, the guano deposits are higher, and therefore, more organic matter content was expected.

A favorable guano-enriched soil ecosystem for the microbiological communities (bacteria and fungi) is primarily determined by favorable values of pH, moisture level, and nutritional content (Pellegrini and Ferreira 2013). In soil microbiology, these parameters are the deciding factors for

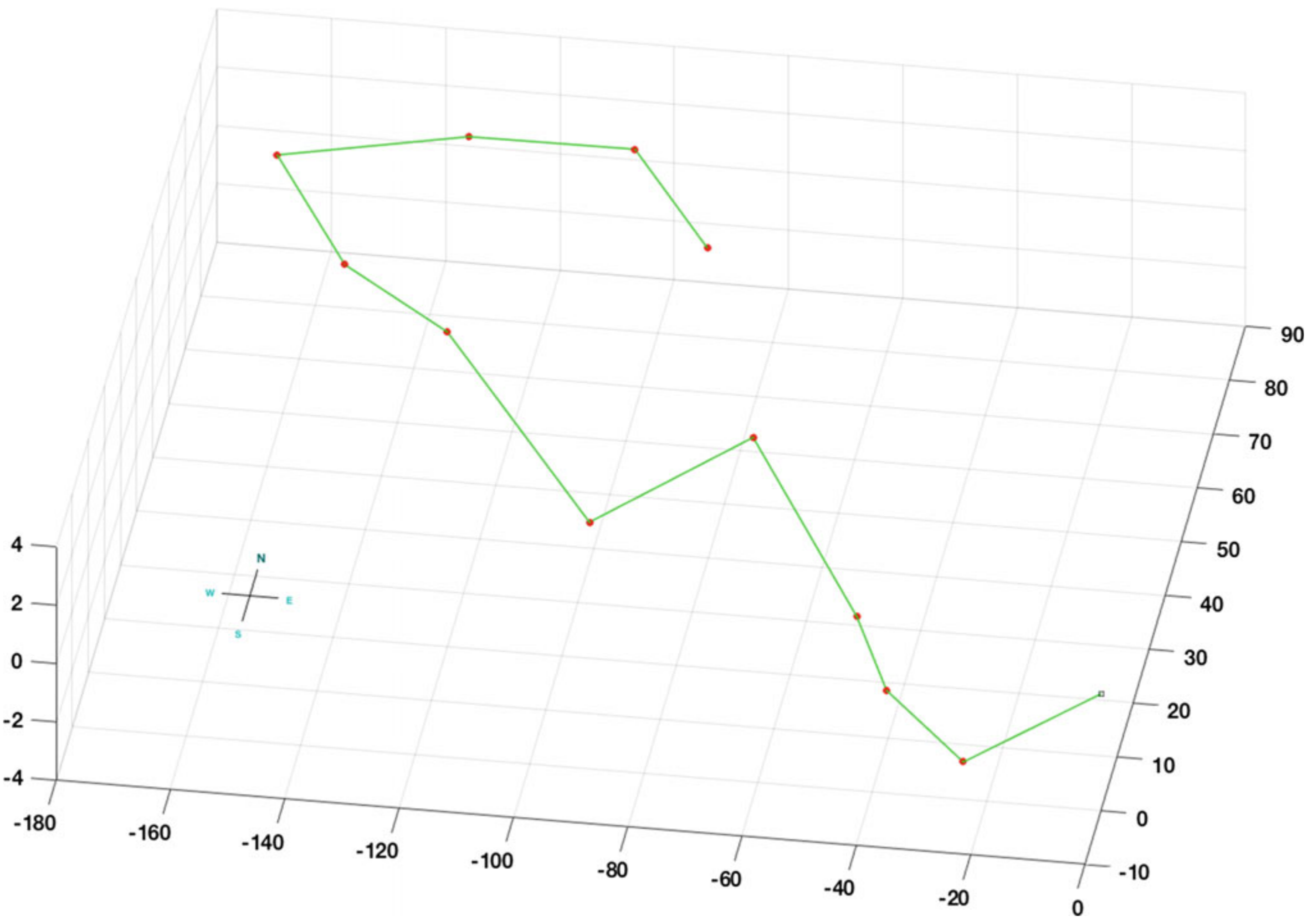

Fig. 5 Results of the cave digital cartography for the Ángel Matos cave. The station path was used to measure the azimuth-data and horizon-data. All axes are in meters

the selection of growth regions. A favorable range of pH is 4.8–7.5 (Killham 1994), but some organisms can adapt to a wider range of acidity. As the guano-enriched soil become more acidic, the fungi will be more abundant because bacteria prefer more neutral pH. Also, the guano-enriched soil moisture can be a deciding factor between fungi and bacterial selection for a region of the cave. A high moisture content will increase bacterial growth but will limit the fungi aerobic respiration. As food source for the microorganisms, the organic matter content influences the growth of bacteria and fungi. The species will select regions with satisfactory quantity (%OM) and quality (nutrient mass ratios) of organic matter. In soils, 10–40% of the total organic matter is active organisms (Bot and Benites 2005). A soil with organic matter quantity above 40% will be considered a region with sufficient food sources.

Using the favorable ranges of the pH and %OM parameters, and limiting the moisture parameter to a range from 30 to 80%, we are able to identify the possible regions in which the microbiological setting will be ideal. Based on these criteria, 80% of the stations in Efraín López Cave satisfy at least two parameters and only 46% of the stations fulfill all the parameters. In the other hand, 41% of the stations of Ángel Matos Cave satisfy at least two parameters where none of the stations achieve all the criteria.

3.5 Mesofauna Diversity

A total of 11 different biological classes/orders of mesofauna were identified in Efraín López Cave and 12 in Ángel Matos Cave. Table 3 shows their location relative to the station number. The dominant biological class/order for the guano-enriched soil for both caves was the Acari. The second foremost was Isopoda for Efraín López Cave and Hemiptera for Ángel Matos Cave. All the other species were around 1% or less of the total specimens collected. Guano-enriched soil mesofauna characterization is important because each cave arthropod has a specific selection of food sources, such as cyanobacteria, bacterial cells, organic particles, microfungal conidia, nematodes, cave microalgae, fungi, and possible pathogenic and opportunistic species.

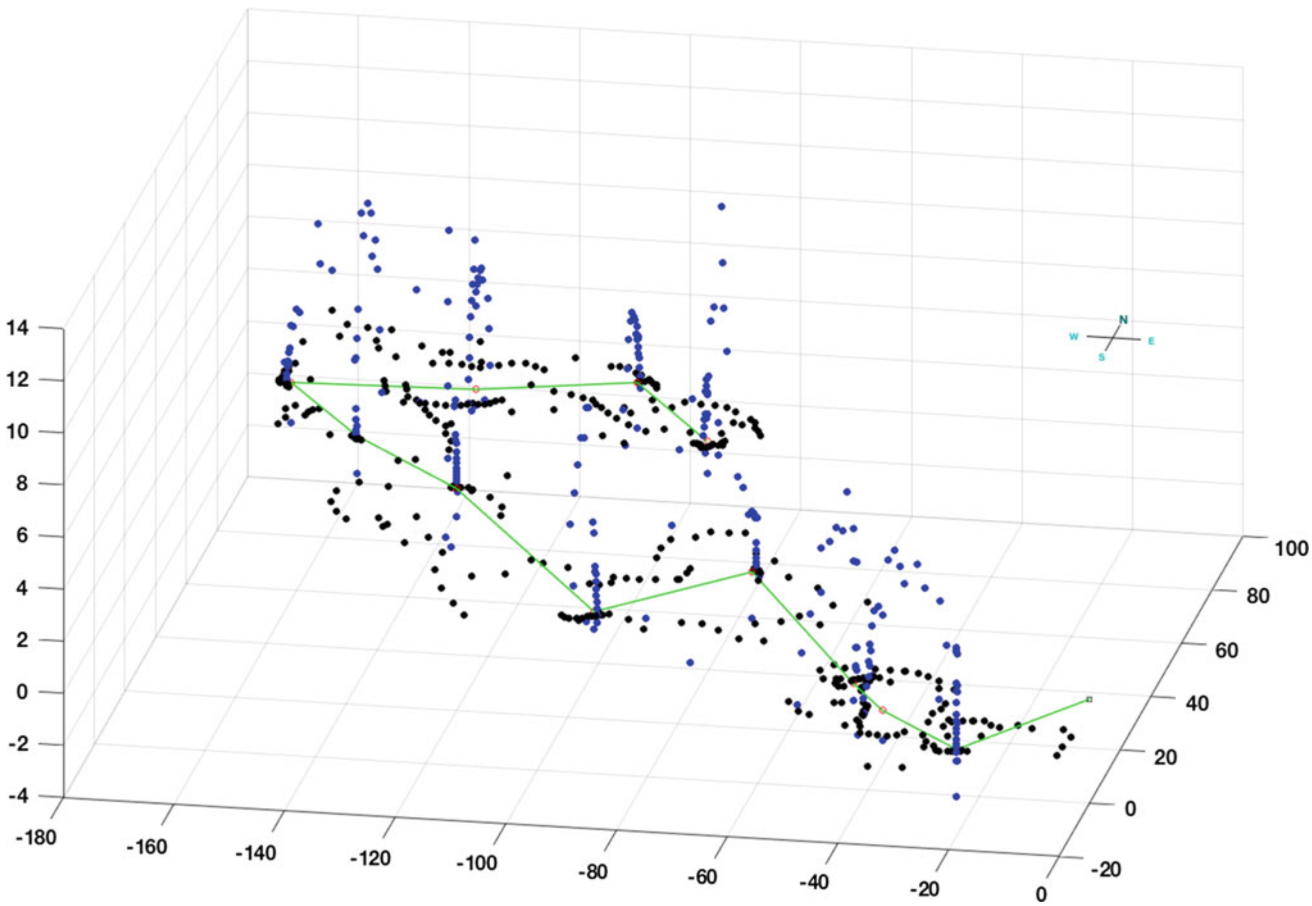

Fig. 6 Ángel Matos cave results for the 3D data points (azimuth-data and horizon-data). All axes are in meters

The relationship between the arthropods and food sources can be used to understand possible regions where the human health is at risk (i.e., an organism that use pathogens as food source can be detected and can be used as an indicator of hazardous sections of the cave).

Multiple studies describe the diets of some of the species of cave ecosystems. The most common cave arthropods such as Acari (Smrž 1989; Smrž et al. 2015) and Isopoda (Šustr et al. 2005; Nováková et al. 2005; Smrž et al. 2015) have been studied. Additionally, the diets of the Collembola (Lee and Widden 1996; Tebbe et al. 2006; Fiera 2014; Smrž et al. 2015) and Diplopoda (Smrž et al. 2015) diets have been investigated. For this study, the diet of the most common species (Acari and Isopoda) and other arthropods such as Diplopoda and Collembola have been found in the literature, but the food sources for most of the species found in this study (Table 3) need further investigations in the underground environment, specially those that have a diet that consist in pathogenic and opportunistic species that can affect the human health.

In order to calculate the total specimen quantity, species richness, and diversity index, an analysis of the collected specimens was performed (Table 4). The total specimen quantity was analyzed as an indirect measurement of abundance of nutritional content in the station however cannot be used as an indicator of heterogeneity of food sources. On the other hand, higher species richness implies more diverse food sources (microorganisms) for the guano-enriched soil ecosystem at that station. The total specimen quantity for Efraín López Cave and Ángel Matos Cave was 1842 and 1672 collected organisms, respectively. Based on the biodiversity, the expected regions with more nutritional abundance for Efraín López Cave were stations 5, 9, and 12 with 23.9, 15.3, and 14.3% of the total specimens, respectively. For Ángel Matos Cave, the stations 8, 7, and 10 had the more expected quantity of nutritional content with 26.2, 19.1, and 17.7% of the total specimens, respectively. The species richness, which can be an indicator of diverse food sources, was higher for stations 7, 11, and 6 for Efraín López Cave with 7, 6, and 6 species found on that station out of 11, respectively. For Ángel Matos Cave, the stations 7, 11, and 3 obtained the higher species richness with 7, 7, and 6 species found out of 12. The diversity index, which accounts for abundance and evenness of the species, was higher for stations 3, 0, and 6 with a index of 1.151, 1.12, and 1.109,

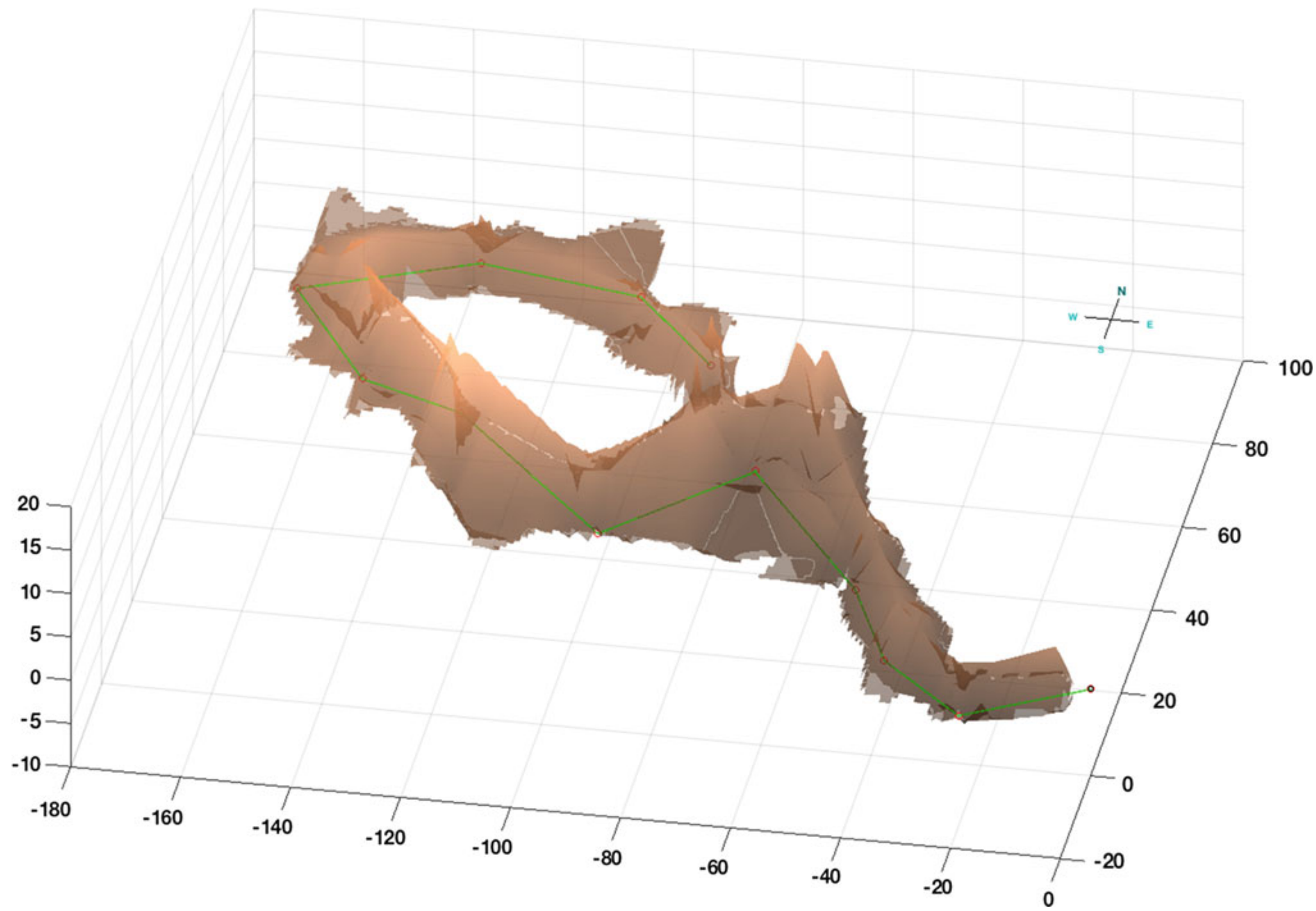

Fig. 7 The resulting caveGEOmap output cartography from the measurements on Ángel Matos cave was calculated using the 3D data points and the station path. All axes are in meters

Table 1 Bat characterization and diet obtained for Efraín López and Ángel Matos caves

Bats species	Feeding mechanism	Cave stations found	
		E. López	*A. Matos*
Brachyphylla cavernarum	Frugivorous	None	1–11
Artibeus jamaicensis	Frugivorous	3–12	2–8
Erophylla bombifrons	Nectarivorous	None	5, 9–11
Pteronotus quadridens	Insectivorous	None	9–11

respectively for Efraín López Cave. The stations with the higher index for Ángel Matos Cave were 11, 9, and 2 with 1.52, 1.24, and 1.06 diversity index, respectively.

Generally, for stations beyond the cave entrance, the total number of specimens increased because the organic matter content in the entrance is lower than the bat populated interior regions. The non-uniformity of the bat guano is the main reason for the variation patterns in richness and diversity. None of the stations in either cave displayed all the types of mesofauna species. The difference in richness and diversity is affected by the variability of food sources even though quantities of these sources are limited in the ecosystem (i.e., guanophillic fungi, as a decomposer, will prefer dry and nutritional guano-enriched soil). Decu (1986) showed that a variation in the size and diversity of the mesofauna community in guano-enriched soil will be affected more by the quality of guano rather than its quantity. Emerson and Roark (2007) suggested that the variation in nutrient ratios (quality of the guano) is due to differences in the elemental composition of bat droppings and could have a major impact in the mycological and mesofauna community. The biodiversity measurements for these two caves do not show a clear relationship with the favorable abiotic parameters. A deeper understanding of the organic matter content,

Table 2 Results of the abiotic parameters for Efraín López and Ángel Matos caves as a function of the selected stations

Stations	Efraín López cave			Ángel Matos cave		
	pH	%SM	%OM	pH	%SM	%OM
0	5.9	35.7	24.2	7.4	32.7	24.8
1	5.7	21.3	29.6	6.7	27.6	31.8
2	5.6	24.5	33.4	6.0	39.7	29.0
3	5.5	55.7	51.1	6.6	44.6	19.8
4	4.5	68.4	89.4	3.9	49.1	43.0
5	5.3	41.2	60	3.8	41.6	21.3
6	5.8	26.6	26	4.4	58.2	16.3
7	5.5	34.4	60.2	5.8	63.2	36.9
8	5.7	36.0	43.0	3.2	67.9	22.0
9	4.4	60.8	72.7	3.1	63.1	23.9
10	4.8	45.7	41.0	3.6	66.6	70.3
11	5.3	26.3	48.6	3.4	67.1	30.8
12	5.0	73.6	74.7	–	–	–

The parameters are acidity (pH), guano-enriched soil moisture percent (%SM), and the organic matter content percent (%OM)

Table 3 List of cave mesofauna arthropods identified at Efraín López and Ángel Matos caves per station

	Stations	
Biological class/order	Efraín López cave	Ángel Matos cave
Acari	All	All
Aranae	5	1–5, 7–8, 11
Blattaria	6, 8, 11	1, 4, 8–11
Collembola	3, 5–8, 11	7
Dermaptera	Not found	5
Diplopoda	3, 6, 11	Not found
Diptera	Not found	9
Gastropoda	2–3, 12	1–6, 8–9, 11
Hemiptera	0, 2–12	1, 4–5, 7, 9,11
Hymenoptera	0, 7, 9	1–9
Isopoda	0, 2–8, 10–12	1–11
Larvae	Not found	4
Lepidoptera	Not found	4, 8
Orthoptera	Not found	1–11
Polydesmida	11	Not found
Pseudoscorpion	0, 6–7	Not found

such as nutrients ratios (C:N, N:P, C:P), elemental analysis, and decomposition effects, is needed to determine whether a correlation exists between these parameters and the diversity. Nevertheless, the diversity in arthropods is an indicator of different microorganism as food sources. The diverse mesofauna, as a consumer, feeds from different types of bacteria, nematodes, and fungi, and some of them will be pathogenic and opportunistic species, such as *P. marneffei* and *H. capsulatum.*

4 Conclusions

In summary, the geological, geometrical, physicochemical, and biological properties were measured for two caves in the north karst belt zone of Puerto Rico. The relationship between the physicochemical and biological properties cannot be determined for this study. Further analyses of the organic matter content (i.e., elemental analysis, nutrient ratios, and decomposition effects) are needed to be able to study the possibility of a correlation

Table 4 Results of the analysis of the collected specimens per station for Efraín López cave and Ángel Matos cave

Stations	Efraín López cave			Ángel Matos cave		
	Total specimens	Species richness	Diversity index	Total specimens	Species richness	Diversity index
0	25	4	1.12	13	3	0.535
1	47	3	0.338	33	3	0.270
2	18	5	1.36	48	4	1.06
3	64	5	1.151	142	6	0.934
4	68	3	0.852	104	4	0.440
5	441	5	0.557	45	3	0.534
6	54	6	1.109	9	1	0
7	256	7	0.656	321	7	0.386
8	187	5	0.928	439	5	0.789
9	283	3	0.486	135	5	1.24
10	10	3	0.897	297	3	0.683
11	125	6	0.912	86	7	1.52
12	264	5	0.612	–	–	–
Total	1842	11	–	1672	12	–

The total specimens are the quantity of organisms, and the species richness is the frequency of species found at the station. The diversity index was calculated using Shannon-Wiener method

between properties. Also, this study suggests that a mesofauna diversity analysis could be a possible indicator of pathogenic and opportunistic species that can affect human health. However, after the mesofauna characterization and the identification of species, more studies are needed to understand the diet of mesofauna organisms to clearly identify species that can be used as markers for cave microbial pathogens.

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Social Determinants of Contaminant Exposure and Pregnancy in the Northern Karst of Puerto Rico

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Abstract

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 includes the study of socioeconomic and demographic variables, and the use of personal care products. 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. 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.

1 Introduction

In daily life, we are exposed to different chemicals by means of personal care products (PCPs). Parabens (p-hydroxybenzoic acid) are a class of chemicals widely used in several products such as cosmetics, lotions, sunscreen, conditioner, and many others, because of their abilities to prevent growth of bacteria and fungi and promote the shelflife for products. Recent studies (Kang et al. 2013; Calafat et al. 2010; Frederiksen et al. 2011; Ye et al. 2012; Tefre de Renzy-Martin et al. 2013; Casas et al. 2011; Engel et al. 2014; Shirai et al. 2013; Bledzka et al. 2014) have shown particular interest in these preservatives because of their potential health effects due to their estrogen mimics. In fact, observed changes in the health status of a study population from Puerto Rico were suspected to be due to exposure to endocrine disruptors including parabens (Meeker et al. 2013).

Studies (Dunn and Dyck 2000; von Rueden 2006) have shown that social determinants can impact in the quality of life of people, especially in children ("The Social Determinants of Child Health: Variations Across Health Outcomes, a Population-Based Cross-Sectional Analysis" 2010). This study provides information in terms of socio-demographic

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factors as the social determinants and their influence in selecting personal care products with contaminants.

2 Methods

Pregnant women in the northern karst zone of Puerto Rico were recruited at prenatal clinics to participate in the *Puerto Rico Testsite for Exploring Contamination Threats* (PROTECT) *Project*. Detailed methods of the PROTECT Project have been previously published (Meeker et al. 2013; Lewis et al. 2014; Cantonwine et al. 2014). While the PROTECT Project collected vast quantities of targeted and nontargeted contaminant data, pathways, and transport exposure data, and explores remediation techniques, the only information pertaining to the influence of social determinants in the selection of personal care products is reported in this paper.

2.1 Study Population

In order to be eligible to participate in the PROTECT Project, women have to be between the ages of 18 and 40, reside in a municipality within the northern karst region, not report use of oral contraceptives three months prior to pregnancy or in vitro fertilization as a method of assisted reproductive technology, and be free of known medical/obstetric complications (Meeker et al. 2013). Protect participants were recruited at approximately 14 ± 2 weeks of gestation at participant clinics throughout northern Puerto Rico during 2010–2015.

2.2 Data Collection

2.2.1 Questionnaires

Women in PROTECT are asked to complete a series of questionnaires during the 3 scheduled interviews throughout their study period. From these questionnaires, we only selected the socio-demographic variables regarding the participants (Table 1).

Table 1 Socio-demographic variables obtained from the recruitment questionnaire

Age
Employment status
Health insurance type
Household income
Marital status
Maternal education
Municipality
Residency type

Table 2 Complete sample ($n = 496$ participants) of participant's general socio-demographic characteristics. This information was reported by the participants

Characteristic	*n* (%)
Age mean	27
Gross income ($US)	
< $19,999	186 (37.5)
$20,000–$49,999	169 (34.07)
$50,000–$99,999	63 (12.70)
>$100,000	10 (2.02)
Doesn't know or	58 (11.69)
Missing	10 (2.02)
Maternal education	
High school or less	94 (18.95)
Some college	174 (35.08)
College degree	227 (45.76)
Missing	1 (0.20)
Civil status	
Single	100 (20.26)
Married	292 (58.87)
Divorced	7 (1.41)
Cohabiting	97 (19.56)
Employment status	
Has a job	307 (61.89)
Does not have a job	186 (37.5)
Missing	3 (0.60)
Residency type	
Owned or mortgage home	322 (64.92)
Rented	105 (21.17)
Occupied without rent	56 (11.29)
Other arrangement	12 (2.42)
Does not know	1 (0.20)
Health insurance	
Government insurance	173 (34.87)
Private insurance	310 (62.5)
Does not know	1 (0.20)
Missing	10 (2.02)

2.2.2 Product Use Questionnaire

Women in PROTECT are asked to complete a Product Use Questionnaire during three visits along pregnancy. The Product Use Questionnaire includes information of the products used in a period of 48 h prior and after the visits. For this study, women from PROTECT who had completed all three Product Use Questionnaires (PUQs) as of

November 2015 were selected. A total of $n = 496$ women were the sample for this study.

From the Product Use Questionnaire, we selected and evaluated two categories: (1) reported lotion used, including brand and (2) reported cosmetics used including brand. Examples of the reported lotion used by the participants included hand cream, body lotion, and body oils. As for cosmetics, brow and eyeliner, blush, foundation, concealer, eye shadow, and mascara are examples reported as used by the participants.

2.2.3 Paraben Identification in Products

A total of 57 and 46 brands were identified for lotions and cosmetics, respectively. The ingredients in these brands were obtained and compared through different cosmetic and lotion databases such as but not limited to EWG's Skin Deep Cosmetic Database and California Safe Cosmetics Program Product Database. The main ingredients for this analysis were parabens, which limited our search to p-hydroxybenzoic acids, specifically methylparaben, ethylparaben, propylparaben, and butylparaben.

2.3 Data Analysis

The first step was to conduct a descriptive analysis of the socio-demographic variables (listed in Table 1). This analysis provided important information in terms of social determinants in the population. We wanted to know whether there were differences in the response rate by municipality which encourage us to do a geographical second step. This analysis was generated using ArcGis V10. The third step was to perform two univariate analyses. The first analysis examined the number of visits in which the participant was exposed to parabens per product. The second univariate analysis described the number of participants exposed per visit. As a fourth step, we use Pearson chi-square tests for independence in contingency test tables to examine the association between demographic variables (age, employment status, marital status, maternal education, health insurance type, household income, municipality, and residency type) and lotion and cosmetic use. The statistical software for these analyses was STATA13.

3 Results and Discussion

Most participants were married, had health insurance, and had an income of less than \$20,000 a year among which 43% were below \$5000 a year (Table 2). More than half of the participants had a job during pregnancy and owned or mortgaged a home. Although most participants had college education, the highest degree obtained for around 19% of the participants was a high school diploma. The median age of the participants

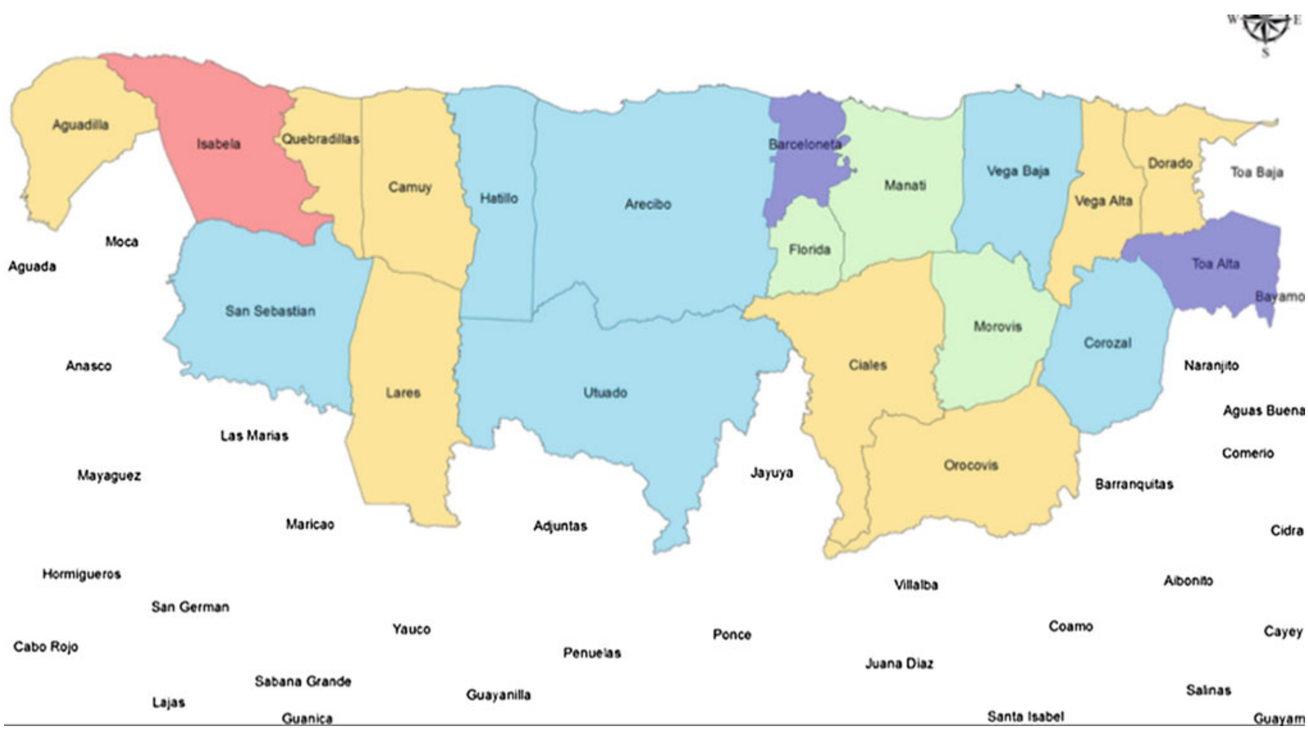

Fig. 1 Participants by municipality that completed the three questionnaires. The map includes the geographic information for the complete sample ($n = 496$ participants). The towns with more participants for this study are highlighted in *purple*. This information was generated using ArcGIS and both questionnaires

was 27 years with a range of 18–40 years. In addition to the benefits in terms of information, these characteristics also allow us to generate a basic profile of the general population that is participating in the PROTECT Project.

We had participants in the study from all towns in the karst zone in Puerto Rico. The participants from Toa Alta and Barceloneta, from the Federally Qualified Community Health Centers, were more willing to complete the "Product Use" Questionnaires resulting in higher participation, followed by the towns of Arecibo, Corozal, Hatillo, San Sebastian, and Utuado with a range between 49 and 56% of the participants (Fig. 1).

Exposure to parabens for both products was measured three times. When it comes to the lotion, 54% of the participants were exposed all three times (Fig. 2) and a total of 61% were exposed all three times thru cosmetics (Fig. 3). On average, 95% of the participants were exposed to parabens by lotion or cosmetics throughout their pregnancy (Fig. 4).

As for the analysis on product selection, Job Status suggests an association in selecting lotion and cosmetics (Table 3). Age and income also suggest association for lotion selection (Table 3). Using chi-square, we explored whether social and demographic variables play a role on selecting lotions and cosmetics. Job Status suggests an association in selecting hand or body lotion and cosmetics.

4 Conclusions

There is a need for further investigation in relation to participants' exposure due to other factors such as accessibility and awareness. The extensive contamination

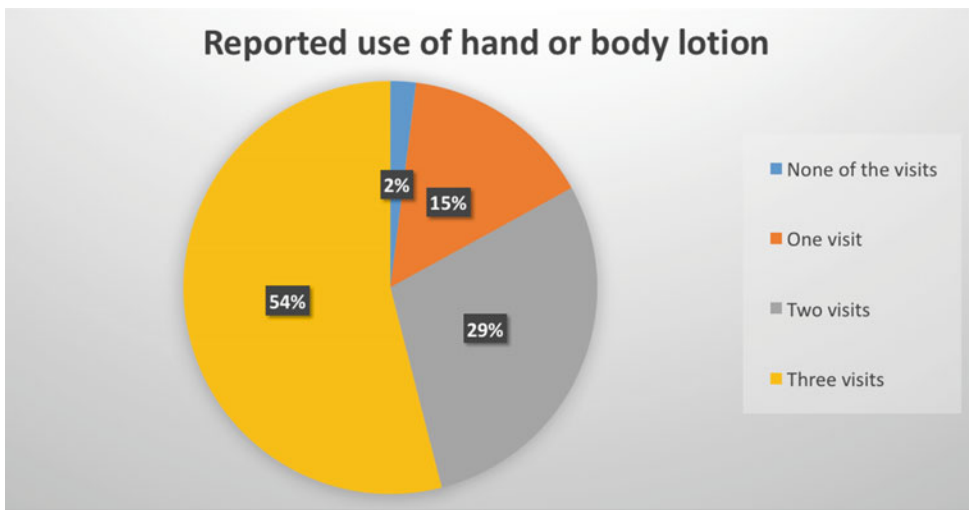

Fig. 2 Paraben exposure by reported use of lotion per visit. The sample for this analysis is n = 446 participants

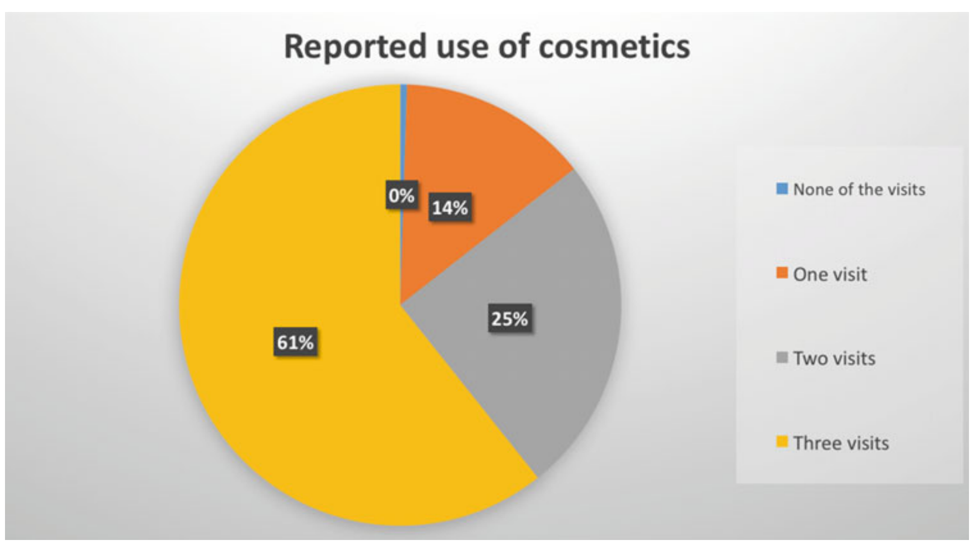

Fig. 3 Paraben exposure by the reported use of cosmetics per visit. The sample for this analysis is n = 424 participants

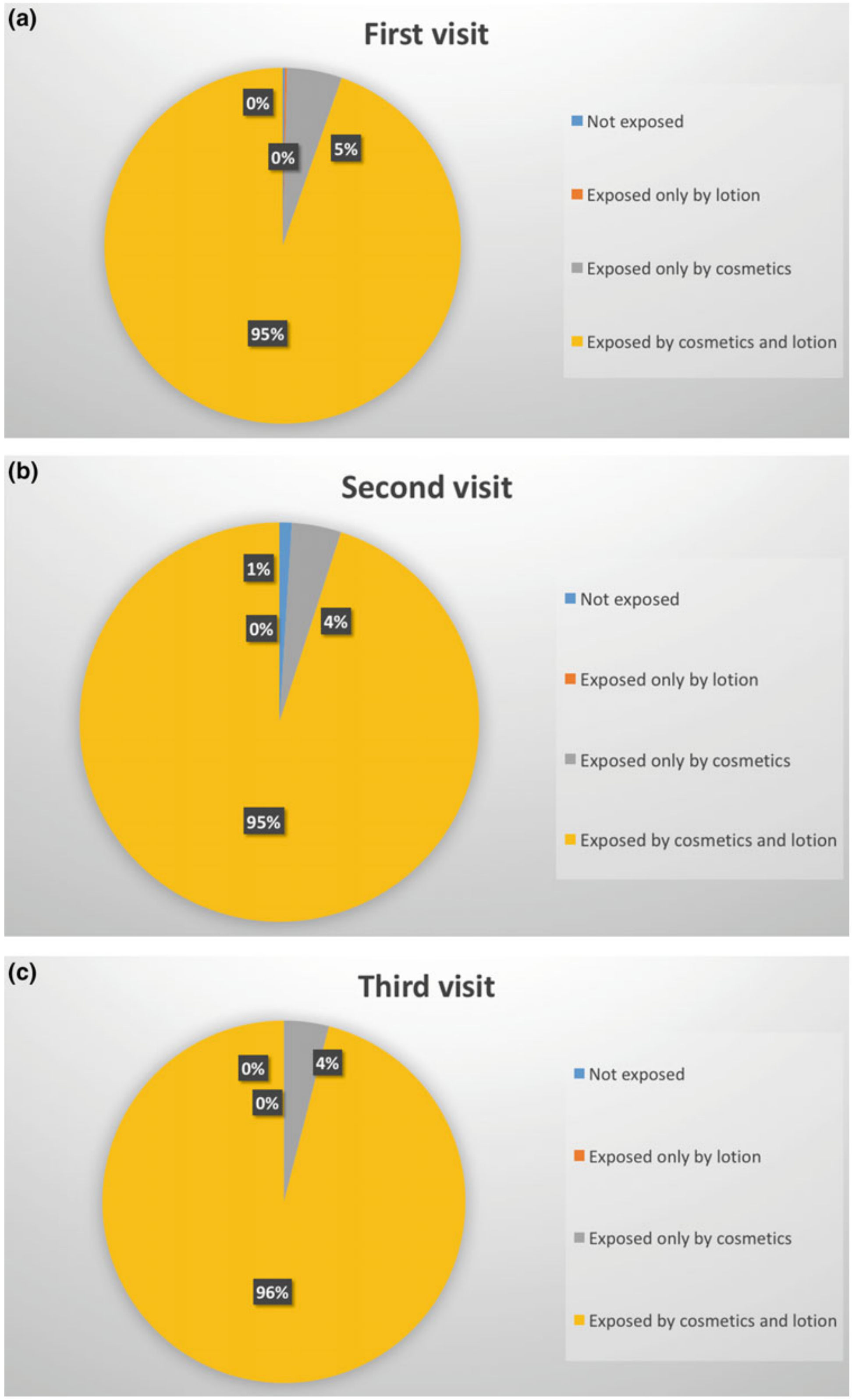

Fig. 4 Overall paraben exposure during visits along pregnancy. This graphics shows the overall paraben exposure along pregnancy during the first, second, and third visits by the use of lotions and cosmetics. **a** The sample for the first visit analysis included a total of 272 participants. **b** The sample for the second visit analysis included a total of 274 participants. **c** The sample for the third visit analysis included a total of 294 participants

Table 3 Socio-demographic influence in the product selection

	Municipality	Education	Age	Income	Job status	Residency type	Health insurance type	Marital status
Lotion	0.894	0.537	0.035*	0.001**	0.004**	0.388	0.024*	0.164
Cosmetic	0.336	0.998	0.091	0.829	0.047*	0.764	0.274	0.426

*p <0.05
**p<0.01

occurring in Puerto Rico requires research to assess its impact on the risk of mother–child health outcomes. Understanding the socioeconomic profile has provided insights on success of recruitment efforts and in the future may lead to reduced exposures that promote better health of our community and future generations. The establishment of the Community Engagement Core empowers individuals and communities in environmental health awareness and practice.

5 Limitations

This is a first overview to some of the personal care products used by participants in PROTECT. To generate a better analysis, all products containing parabens must be studied. Another limitation would be in relation to the products reported by the participants. For example, the sample for each statistical analysis in this study varied with respect to analysis. A possible explanation is that in some occasions the information reported in terms of product used could be confused with another type of product by the participant.

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Public Health Approaches to Preventing Outbreaks of Gastrointestinal Infection Linked to Karst Systems

Samuel Dorevitch

Abstract

Outbreaks of gastrointestinal illness have occurred following the contamination of karst systems used as drinking water sources. Outbreaks have been caused by the flow of fecal pollution from humans and livestock into karst aquifers and wells. These outbreaks have resulted in thousands of cases of illness and dozens of hospitalizations. Collaborations between hydrogeologists and public health specialists should be promoted in order to reduce the likelihood and severity of such outbreaks in the future. Public health agencies utilize a variety of measures designed to reduce the risk of illness among swimmers at beaches. These measures might be modified and applied to karst aquifers that are used as sources of untreated drinking water. In this chapter, the process for prioritizing beaches for water quality monitoring, the use of rapid bacterial detection methods, and public health notification processes are described. Microbial source-tracking methods used as a research tool at beaches could help identify and mitigate the human, livestock, and wildlife sources of fecal microbes that pollute karst aquifers, particularly after heavy precipitation. Other opportunities for collaboration include the participation of hydrogeologists in the investigation of disease outbreaks, the education of public health personnel about the site selection and maintenance of domestic wells, and in joint analyses of health data in relation to weather and hydrogeology data.

1 Introduction

In recent years, five large outbreaks of gastrointestinal infection linked to microbial contamination of karst systems have been described (Meusburger et al. 2007; O'Reilly et al. 2007; Dura et al. 2010; Borchardt et al. 2011). Three of these outbreaks each resulted in more than 1000 people developing illness, some of whom required hospitalization (Table 1). Pathogens responsible for gastrointestinal infections in these outbreaks included norovirus (Borchardt et al. 2011), *Campylobacter spp., Giardia spp., Cryptosporidium spp.,* and *Escherichia coli* O17:H7, a type of *E. coli* that produces a toxin capable of causing kidney failure and death (Bruce-Grey-Owen Sound Health Unit 2000). The contamination of groundwater following heavy precipitation was noted as a causative factor in three of the outbreaks. In addition to these karst-associated outbreaks that have been described in some detail, others have been reported in summaries of waterborne disease outbreaks complied by the US Centers for Disease Control and Prevention (CDC) (Hlavsa et al. 2011, 2014). A total of 172 outbreaks linked to untreated groundwater between 1971 and 2008 were recently reviewed (Wallender et al. 2014). Among those 172 outbreaks, 45 (26.2%) occurred in the context of vulnerable hydrogeologic formations. Of those 45 outbreaks, limestone features were noted in 15 (33.3%). A total of 8821 people became ill in those 45 outbreaks, with a mean (range) of 39 (5–2823) cases of illness per outbreak. Contributing factors to outbreaks that occurred in the context of vulnerable hydrogeologic formations were not specified. Among

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Table 1 Summary of epidemiologic aspect of and factors contributing to recent karst-associated outbreaks of gastrointestinal infection

	(O'Reilly et al. 2007)	(Meusburger et al. 2007)	(Dura et al. 2010)	(Borchardt et al. 2011)	(Bruce-Grey-Owen Sound Health Unit 2000)
Setting	South Bass Island, Ohio (in Lake Erie)	Rural village in Austria	Bükk Mountains, Hungary	Door County, Silurian dolomite	Walkerton, Ontario
Water source	Private and community wells	Spring	Well sunk in cave	Private well of a restaurant	Wells in area of shallow overburden
Number of people ill	1450 cases 21 hospitalized	160 cases 3 hospitalized	3673 ill 161 hospitalized	229 ill 6 hospitalized	1346 ill 65 hospitalized 6 deaths
Pathogens in stool samples	Campylobacter, Salmonella, norovirus, Giardia	Pathogenic bacteria not detected in stool samples from 14 patients	Norovirus, Campylobacter	Norovirus, Campylobacter, Salmonella	Mainly *E. coli* O157:H7; less frequent, Campylobacter
Microbes in water samples	Campylobacter, Salmonella, norovirus, adenovirus, Cryptosporidium	*E. coli* >2000 CFU/100 mL	140 *E. coli* CFU/100 mL (median of 8 samples)	Norovirus	*E. coli* 70-940 CFU/100 mL
Heavy precipitation a factor	Not noted	176.7 mm rain over a 5-day period	"Extreme precipitation" preceded outbreak	Not noted	138 mm over a 13-day period
Suspected fecal pollution sources	On-site septic systems, land application of septage, and possibly, a direct hydraulic connection with Lake Erie	Cattle, wild deer	Manure piles, pit latrines, illegal dumps	Septic leach field 188 m from well	Manure applied near the town's wells prior to the heavy rainfall

Abbreviation : *CFU* colony-forming units

the 172 outbreaks associated with untreated groundwater, the most common contributing factors were related to the location, design, and maintenance of septic systems and/or the water source. Heavy recent rainfall was thought to have contributed to 42.4% of the 45 outbreaks; the frequency of heavy rainfall as a contributing factor to outbreaks specifically in karst systems was not reported. Though recognized outbreaks such as these are uncommon, the population at risk is substantial, as an estimated 40% of groundwater used for drinking in eastern USA comes from karst aquifers. Overall, about 18% of the area of USA is karst (Weary and Doctor 2016) and worldwide, an estimated 15–20% of the population lives on and/or uses water from karst aquifers.

In the USA, public health protections are established by the Safe Drinking Water Act for community drinking water systems, including those that utilize water from aquifers. The Clean Water Act establishes protections for surface waters, including those for recreational use. Karst systems include springs that emerge from karst formations, flow as surface streams, and then "disappear" underground where they reenter aquifers. Thus, karst systems do not neatly fit into the "surface water versus groundwater" classification. Furthermore, following heavy precipitation, microbes in fecal matter from on-site sewage treatment systems ("septic systems"), agricultural animals, and wildlife can move rapidly over surfaces through the shallow soils overlying karst aquifers. If sources of microbial pathogens that pollute aquifers can be identified, methods to protect those aquifers—and people who depend on them for safe drinking water—can be developed. A variety of measures have been developed to reduce the risk of gastrointestinal illness among swimmers at inland and coastal surface waters. Those protections may be relevant in the context of reducing the risk of illness that can result from drinking contaminated waters that are part of karst systems.

The prevention of future outbreaks of disease linked to the contamination of karst aquifers would be facilitated through collaborations between geologists, hydrologists, environmental microbiologists, epidemiologists, clinicians, policymakers, and others who work in public health departments at the local, state, and federal levels. In this chapter, two public health approaches to potentially reduce the risk of waterborne infections among users of karst waters are described. The first approach includes methods—some in use and others under development—to protect swimmers in surface waters from waterborne infections. The second is a description of opportunities for collaboration between hydrogeologists and others, primarily public health professionals and researchers, that may lead to greater understanding of the connections between karst systems and health, and ultimately, to improvements in the health of the public.

2 Public Health Protections for Swimmers at Beaches

The US EPA provides funds to state, tribal, and local governments at coastal (including Great Lakes) locations in order to provide public health protections to swimmers at beaches. This funding mechanism was made possible in 2000 by the Beaches Environmental Assessment and Coastal Health Act ("BEACH Act"). Recipients of BEACH Act funding are required to satisfy the following "performance criteria" of these EPA funds: (1) evaluate and classify beaches, (2) monitor water quality, (3) notify the public and communicate risk, and (4) conduct a public evaluation of the program (USEPA 2014). These activities are described below, as are potential applications of these activities to public health protections among users of untreated karst waters for domestic consumption.

2.1 Evaluation and Classification of Beaches

Three elements of this process are as follows: (1) identify factors that indicate the potential risk to human health presented by pathogens, (2) characterize beach use, and (3) rank beaches based on risk and use. The first step in this process typically involves a sanitary survey, which includes a structured approach to characterizing sources of pollution that could impact the beach. EPA has developed sanitary survey forms, which are available at http://www.epa.gov/beach-tech/beach-sanitary-surveys. The sanitary survey includes the identification of point sources of fecal pollution, such as wastewater discharges, and non-point sources, such rain runoff from agricultural areas where manure would be present. In addition to conducting a sanitary survey, data from prior water quality testing and reports of health problems linked to use of the beach should be sought. Beach use data is combined with risk data to prioritize beaches, with heavily used beaches that are at high risk for pathogen contamination in the top tier of concern (Tier 1), while beaches that are used by few people and that have little evidence of risk of pathogen contamination are in Tier 3. Tier 2 beaches have intermediate risk and use.

2.2 Monitoring Indicator Bacteria Concentration in Water Samples

E. coli and enterococci are fecal indicator bacteria (FIB) that are widely used to evaluate potential fecal contamination health risk at surface waters. The Recreational Water Quality Criteria (RWQC) of 2012 (USEPA 2012) defines criteria values of *E. coli* and enterococci as indicators of water quality at freshwaters, while only enterococci is an indicator at marine waters. The Criteria document spells out a variety of bacteria concentrations that may be acceptable, depending on risk tolerance. Perhaps the most widely used of those are known the beach action value (BAV) of *E. coli* (235 colony-forming units [CFU]) and enterococci (36 CFU/100 mL). These BAVs are expected to limit the rate of illness attributable to swimming to 36 cases per 1000 swimmers (an alternative set of values is meant to limit the rate of illness to 32 cases/1000). While these values are considerably higher than drinking water maximum contaminant levels (less than 5% of samples should contain any detectable fecal coliforms) (https://www.epa.gov/ground-water-and-drinking-water/national-primary-drinking-water-regulations), it should be noted that swimmers typically swallow approximately 10–30 mL of water while swimming (Dufour et al. 2006; Dorevitch et al. 2011), considerably less than the hundreds of mL of tap water that might be consumed in a day. Prior to the 2012 Recreational Water Quality Criteria, surface water quality monitoring criteria were to be measured by culture methods, the results of which only become available the following day. The 2012 Criteria include an option for measuring enterococci DNA in water samples using the quantitative polymerase chain reaction (qPCR) method. (USEPA 2015) The qPCR method can generate results within 3–4 h of sample receipt in the laboratory, allowing beach managers to take action promptly if levels of enterococci DNA exceed the beach action value. Such actions might include issuing a swim advisory or swim ban, and potentially investigating potential sources of fecal contamination.

Epidemiologic research is the foundation of the Recreational Water Quality Criteria. The criteria values were developed from a large study, the National Environmental and Epidemiological Assessment of Recreational water (NEEAR), that enrolled more than 27,000 people at four Great Lakes beaches (Wade et al. 2008) and three marine beaches (Wade et al. 2010). All beaches were impacted by discharges from wastewater treatment plants. By reviewing illness rates among non-swimmers, rates among swimmers, and measures of water quality, the research team was able to describe a linear relationship between rates of gastrointestinal illness attributable to swimming and the log 10 concentration of enterococci measured by the qPCR method. That information was used in the development of beach action values and Criteria values for bacteria.

2.3 A Tiered Approach to Monitoring

EPA's Guidance document for recipients of BEACH grant funding (USEPA 2014) promotes a tiered monitoring approach, under which grant recipients apply the beach tier categories (based on beach use and risk information) to establish monitoring programs suitable for each beach tier. For example, monitoring for a Tier 1 beach that is near a laboratory that can perform same-day monitoring using the qPCR method may involve such testing 5–7 days per week. Daily FIB cultures may be appropriate if qPCR testing is not an option (for most jurisdictions it is not). A validated model that utilizes local hydrological, meteorological, and physicochemical water quality parameters to predict fecal indicator concentrations may be appropriate as a supplement or alternative to culture-based testing. A moderate use, low-risk Tier 2 beach may only need periodic (perhaps every 1–2 weeks) culture testing to confirm that FIB levels remain low as expected. Water quality monitoring may not be necessary at low-risk, low-use Tier 3 beaches. However, if available data suggest that in the past, rainfall is typically followed by high FIB levels, a "rainfall advisory" may be appropriate at such a beach.

2.4 Public Notification and Evaluation

The results of water quality testing are used to notify the public about hazards at beaches. In the past, this has often involved the use of color-coded flags or signs (such as red = swim ban or beach closure; yellow = hazard warning; green = risk not elevated). In recent years, notification through text messaging and social media has been implemented in many locales. Public input regarding beach monitoring and notification is sought through meetings and other mechanisms regarding the jurisdiction's beach monitoring and evaluation program.

2.5 Health Protections at Surface Water: In the Research Arena

Over the past 25 years, water quality monitoring methods have begun to shift from culturing the fecal indicator bacteria, to rapidly quantifying bacteria DNA using qPCR, to the use of methods that can assist in the identification of the animal hosts of bacteria found in beach water. FIB present in surface waters could have a variety of sources, including wastewater treatment plants; nearby on-site sewage treatment systems (septic systems), cross-connections between storm water and wastewater systems, agricultural animals, wildlife, and fecal matter of dogs, birds, and other animals. Additionally, FIB can persist in soil, sand, and sediment (Byappanahalli and Fujioka 2004; Byappanahalli et al. 2006). Thus, their presence in relatively high concentrations in surface waters is not always a good predictor of human health risk. By identifying sources of fecal pollution, better risk estimation may be possible, as human sources are thought to represent the greatest risk of infection by a variety of viruses. Once sources of fecal pollution are identified, pathways that link fecal sources to the surface water can be identified and appropriate protections put into place.

Many of the targets for microbial source tracking (MST) are bacteria within the order Bacteroidales and in particular, within the genus *Bacteroides*. An ideal MST marker for a given source would be a DNA sequence of a bacterium, for example, a species within the Bacteroides genus, that is unique to the host (e.g., humans) and is absent from the DNA sequence of Bacteroides (and other bacteria) found in other mammals and birds. Generally, the development of MST methods involves constructing and evaluating qPCR primers (short nucleic acid fragments used to target particular DNA sequence for identification), while being sensitive enough to detect very small quantities of those sequences in environmental samples. Recent reviews describe this process and identify promising MST methods (Harwood et al. 2014; Tran et al. 2015). Combining assays for several molecular targets specific for suspected pollutant sources ("multiplexing") could be used to identify the quantity and presence of any one of a set of wildlife, domestic animal, and human pollution sources. Multiplex assays must be tailor-made and evaluated to ensure a lack of cross-reactivity and interference among the molecular targets and primers. Chemical, rather than microbial source-tracking methods have been explored. The focus has been on the detection or quantification of chemicals found in wastewater that have exclusively human sources, such as optical brighteners (from laundry detergent), caffeine, and artificial sweeteners. Caffeine has been used as a marker of human fecal contamination in the context of karst aquifer (Hillebrand et al. 2012a, b).

2.6 Application of Recreational Water Protections to Karst Systems

Elements of the monitoring framework used to protect swimmers at beaches from waterborne infections could be applied to small surface waters that flow into the karst systems. For example, locations can be categorized into risk-based tiers based on the number people who depend upon a karst system for drinking water, historical water quality data (if available), and information about potential fecal pollution sources in the catchment area. Once such tiers are established, resources for hydrogeological investigations could be allocated accordingly. If those investigations identify the potential for significant hazards in the catchment area of the aquifer, public education and notification about increases in the risk of illness following heavy precipitation may be advisable in such locations. The use of qPCR methods to test water in domestic wells before, during, and after heavy rainfall would result in the more rapid identification of an immediate health risk (fecal pollution in an aquifer) than could be accomplished using culture methods. This, in turn, could be incorporated into notification programs that would alert the public in Tier 1 communities, perhaps through text messaging, that an aquifer has become (or is at high risk of becoming) contaminated by fecal bacteria, and that it should be boiled before consumption. As molecular targets are developed and optimized, they should become an important tool in the toolbox used by hydrogeologists to evaluate and reduce risk from fecal pollution sources.

3 Multidisciplinary Public Health Collaborations

The resource-intensive epidemiologic studies like NEEAR that had been conducted at beaches are unlikely to be undertaken to evaluate health risks associated with the use of untreated drinking water from karst aquifers. More practical approaches to characterizing those risks might involve the use of hydrogeological, precipitation, and previously collected health data. Specifically, the number of cases of gastrointestinal illness seen in emergency departments and admitted to hospitals has been analyzed in relation to heavy precipitation (Drayna et al. 2010; Wade et al. 2014, Jagai et al. 2015). This study design could be applied to karst aquifers that have many domestic wells, karst systems with community water supplies, and non-karst areas. The resulting information could be used to characterize the risks of illness associated with heavy precipitation attributable to karst hydrogeology. While a variety of privacy protections are in place in the USA to limit access to health data, epidemiologists of health departments in schools of public health have experience obtaining and analyzing previously collected emergency department and hospital discharge data. Collaborations between hydrogeologists, karst microbiologists, and epidemiologists would be a practical approach to conduct such studies.

The outbreak investigations noted above have yielded very useful information about the infectious hazards caused by precipitation in karst regions. Identifying a karst-associated outbreak—particularly if it is small and involves the family that uses a single domestic well—can be like looking for a needle in a haystack. Staff of local and state health departments have limited time and resources to investigate such outbreaks. Furthermore, health department staff typically are not experts in hydrology. The input of hydrogeologists to the investigation of a suspected waterborne disease outbreak in a region with karst geology would be extremely valuable. Such input would be much more likely to occur if ongoing collaborative relationships exist between health departments' personnel and hydrogeologists from academia or government. Environmental microbiologists at state health departments (or the CDC) may be able to provide advice about source-tracking methods and may be able to perform DNA fingerprinting to identify sources of microbes that are found in water samples and/or stool specimens.

The recognition that a waterborne disease outbreak has occurred is not assured. Consider a heavy rainfall in a region with karst geology and an aquifer that is used as a drinking water source becomes contaminated. As a result, several people who may live considerable distance from one another develop gastrointestinal illness. Health care providers who see these patients might assume that their ill patients have suffered from a foodborne illness, or person-to-person spread of a gastrointestinal infection. By educating health care providers in regions with karst geology about the possibility of outbreaks of gastrointestinal symptoms due to contaminated drinking water—particularly after heavy precipitation—such outbreaks are more likely to be recognized, reported to health departments, investigated, and prevented in the future.

Most local health departments have an environmental health specialist whose responsibilities include the permitting of private wells before they can be used. This may include reviewing the locations of on-site waste treatment systems and the results of nitrate and coliform testing. Again, the expertise of hydrogeologists would be useful in ensuring the environmental health staff at health departments have a solid understanding of the unique aspects of karst geology when advising private well owners about siting, protecting, and maintaining private domestic wells.

Health departments at state and local levels play critical roles in emergency preparedness and response. Health department personnel assess vulnerabilities of communities to health hazards of natural or man-made disasters within their jurisdiction. While not a microbial hazard, chemical releases or spills could contaminate aquifers and should result in public health responses (public notifications through broadcast and social media to not use well water until the health risks are determined to be minimal). The input of hydrogeologists would be needed in identifying such local vulnerabilities that result from karst geology. Such expertise would also be essential in evaluating strategies to test water for the chemical of concern and identifying potential approaches to remediating the hazard.

Another area of potential collaboration between karst researchers and public health departments is in the education of the public about protecting aquifers from fecal contamination in areas with karst geology. Finally, health departments may be able to ensure that any outbreak linked to karst aquifers is followed by action. It is said that "no disaster should ever be wasted." An outbreak linked to a karst aquifer should become a matter of regional concern through the news media and environmental advocacy groups. As a result, decision makers in government may become more receptive to education by health and hydrogeology experts about policies need to protect karst aquifers and public health.

4 Conclusions

Gastrointestinal disease outbreaks, some of which resulted hospitalizations and deaths, have occurred as a result of contamination of karst aquifers by human or animal fecal pollution. Prevention of future outbreaks like these will require improvements in the identification of local vulnerabilities, the protection of surface portions of karst systems, policy initiatives to ensure that land use in regions with karst systems does not result in fecal pollution entering aquifers, and the education of the public and public health professionals about the unique risks that heavy rainfall presents to karst systems. Some of the methods used to prioritize, monitor, and protect swimming beaches may be useful in this context. Undertaking these initiatives will be facilitated through the collaborations of people with expertise in hydrogeology, environmental epidemiology, environmental microbiology, emergency preparedness, health communications, and environmental policy.

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Integrated Strategy to Guide Health-Related Microbial Quality Management at Alpine Karstic Drinking Water Resources

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Abstract

Water resources from alpine and mountainous karst aquifers play an important role in the drinking water supply in many countries but require sustainable protection and management. Microbial fecal pollution is one of the most relevant contaminants in alpine karst aquifers. However, until recently, microbial fecal pollution could be detected only by traditional approaches based on individual grab sampling and time-demanding cultivation-based procedures in the laboratory. Limited information on the pollution dynamics, origin of pollution, and associated health risks of exposure is available. Due to the lack of knowledge, a joint effort between the disciplines of microbiology and hydrogeology was undertaken in the Northern Calcareous Alps in eastern Austria during the last decade. The aim was to open the "black box" of pollution microbiology by developing new techniques and strategies that will guide management of water resources and water quality in catchments of alpine karsts. These techniques and strategies will provide a sustainable framework that supports decision making at all required time scales to realise health-related water-quality targets and water safety plans according to the World Health Organization. This article provides an overview of the developed techniques and strategies. The suggested framework may also be of interest to managers of other water resources as the selected methods and strategies can be adapted to the various situations or requirements.

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1 Introduction

Water resources from alpine and mountainous karst aquifers play an important role in the water supply of many countries but require sustainable protection and management. Microbial fecal pollution is one of the most relevant contaminants in alpine karst aquifers. Until recently, microbial fecal pollution could only be detected by traditional approaches based on individual grab sampling and cultivation-based standard procedures in the laboratory.

One of the fundamental philosophies for the management of drinking water supplies is to optimize raw water quality and catchment protection with regard to microbial contaminants in order to keep the extent of necessary disinfection and treatment as low as possible. Efficient implementation of an optimized multiple-barrier approach demands sound information at the appropriate temporal resolution from all included barriers, including target-oriented catchment protection, controlled raw water abstraction, and final treatment. In the recent past, managing the microbial raw water quality of complex karst water resources was based on "black box" strategies, because technologies for advanced microbial pollution analysis were not available. Due to the lack of knowledge, a joint effort between the disciplines of microbiology and hydrogeology was undertaken in the Northern Calcareous Alps in eastern Austria during the last decade.

The aim of this article is to demonstrate how newly developed approaches and well-established methods, such as the cultivation of fecal indicators, quantitative PCR methods (qPCR), detection of genetic fecal markers, on-line surrogate measurement, and risk assessment, can be combined for state-of-the-art fecal pollution diagnostics and management of complex and nearly inaccessible alpine karstic drinking water resources. The integrated approach supports decision making at all required time scales of information, including near-real-time spring water abstraction management (within the required resolution of minutes) up to catchment protection practices (within the time frame of months to a few years). For this purpose, we followed a new strategy, the so-called "framework for integrated fecal pollution analysis and management" or, more simply spoken, "the bottom-up approach".

2 Materials and Methods

2.1 Studied Catchments

The karst catchments of the springs LKAS2 (60 km^2), LKAS6 (4 km^2) and LKAS8 (11 km^2), which are situated at different locations in the Northern Calcareous Alps, were studied over several years (2004–2013). All springs drain important karst aquifers and are situated close to the receiving creeks at altitudes between 530 and 820 m a.s.l., and their catchments reach up to 2270 m a.s.l. The mean discharges, according to the respective catchment size and different mean altitudes, range from 250 to 5100 L per second. The lithology is dominated by Triassic limestone and secondary dolomite (Mandl et al. 2002). In general, wide plateaus and steep slopes provide distinction to these areas. Alpine pastures, krummholz areas, and alpine forests are the main land-use features (Grabherr et al. 1999). In addition, tourism activities (especially during summer time), use of summer pastures by grazing animals, and wildlife potentially influence these catchments (Reischer et al. 2011).

2.2 Investigated Parameters

Due to the high dynamics of discharge and quality parameters at the limestone karst springs, hydrological data were recovered with high resolution; the measurements were recovered typically every 10–15 min. *In situ* devices with on-line connections were available within the existing measuring network as previously described (Farnleitner et al. 2010). Discharge (usually calculated via a discharge-stage relation), turbidity, spectral absorption coefficient at 254 nm (SAC254), water temperature, and electrical conductivity were selected for this investigation. The existing meteorological measuring network included stations up to 1550 m a.s.l. The data for precipitation and air temperature were measured at one-minute intervals and aggregated according to the measuring interval of the hydrological data. The microbiological sampling was performed automatically by networking via LEO-satellites (Stadler et al. 2008). Manual grab sampling was performed for evaluation purposes. Several microbiological standards including *E. coli*, enterococci, *C. perfringens,* HPC 37 °C, HPC 22 °C, and aerobic spore formers and intestinal pathogens (*Cryptosporidium parvum* and *Giardia*) were investigated (Farnleitner et al. 2010, 2011). The molecular biological parameters included ruminant-associated (BacR) and human-associated (BacH) *Bacteroidetes* genetic fecal markers quantified by qPCR that were newly developed, established and verified for the investigated areas (Reischer et al. 2008, 2011; Farnleitner et al. 2011). In addition, the applicability and usefulness of enzymatic ß-D-glucuronidase and ß-D-galactosidase measurements (Farnleitner et al. 2001, 2002) for automated application and on-line determination were evaluated (Ryzinska-Paier et al. 2014). Regular catchment surveys were performed as well in order to establish continuous information on the situation within the catchment area (i.e., condition of vegetation coverage, animal abundance on summer pastures, erosion activities, etc.), state of catchment protection measures (e.g., maintenance of sewage disposal systems) and the occurrence of potential fecal pollution sources.

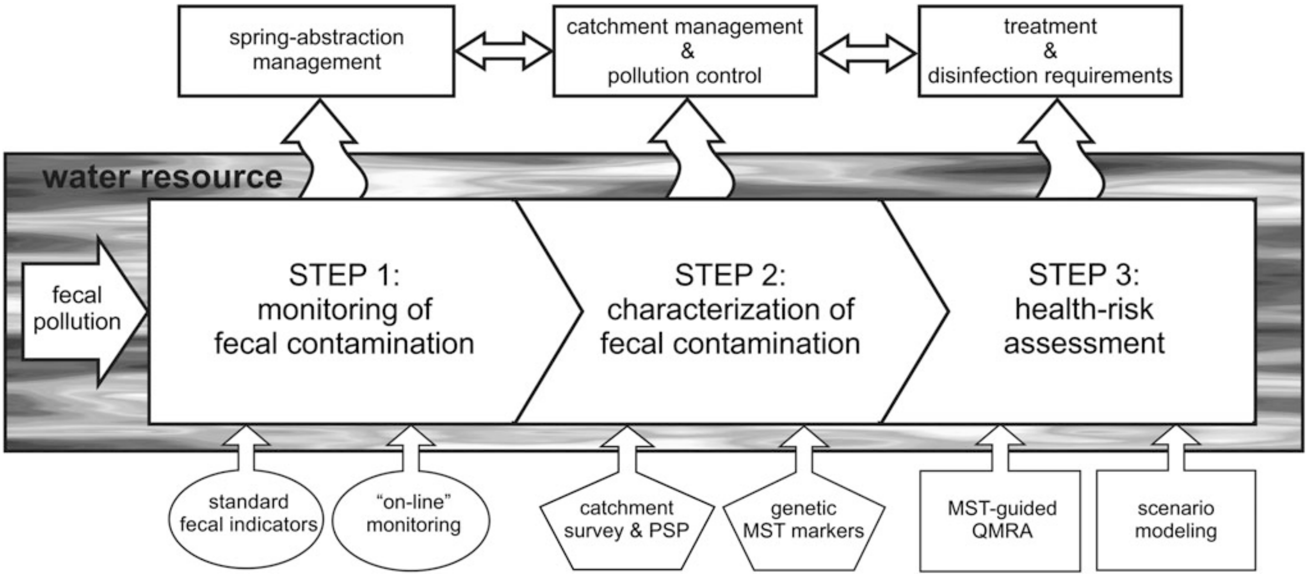

Fig. 1 The suggested framework for integrated fecal pollution analysis and management ("3-step approach"). Note that any of the 3 steps of analysis are important for catchment protection and spring water quality management (see the discussion section). The methods needed to realize the suggested "3-step approach", as shown at the *bottom* of Fig. 1, are presented in the results section. *Abbreviations PSP* pollution source profile, *MST* microbial source tracking, *QMRA* quantitative microbial risk assessment

3 Results

3.1 Conceptual Design

Three interacting levels ("three-step-approach") characterize the backbone of the concept (Fig. 1) with relevance to the following issues: (1) is there a problem with fecal pollution? (2) if yes, what is the reason for it? and (3) what is the actual health risk in relation to the fecal source(s) contributing to the observed pollution?

The suggested framework can also be referred to as a "bottom-up approach" because it starts at the most general level (i.e., general pollution monitoring, including all types of fecal pollution sources from humans, life stock and wildlife), and it becomes more specific as it proceeds to the right side of the diagram (i.e., looking for the responsible pollution source(s) and the associated health risks for the consumer of the drinking water). Each step has specific implications for the management of the water quality (cf. conclusions).

The application of the suggested approach opens the "black box" of fecal pollution and supports microbial quality management at all required time scales in regard to the World Health Organization (WHO) framework for safe drinking water supply based on health-based quality targets.

The methods and strategies required to realize the suggested framework for integrated fecal pollution analysis and management ("3-step approach" see Sect. 3.1) are briefly presented in the following sub-chapters.

3.2 Detection and Monitoring of Fecal Pollution (Step 1)

3.2.1 Standard Fecal Indicator Bacteria (SFIB) and Cultivation-Based Methods

Microbiological water quality monitoring is strongly based on the investigation of standard fecal indicator bacteria (SFIB). *Escherichia coli* (*E. coli*) and intestinal enterococci have been the most important SFIB for more than 100 years, since the introduction of the fecal indicator concept. SFIB can yield sensitive information regarding the extent of fecal contamination in water resources and are considered an essential tool for water safety management. SFIB can easily be detected by standard, cultivation-based procedures (e.g., ISO 16649-2 for *E. coli* and ISO 7899-2 for intestinal enterococci). The occurrence in high concentrations in the excreta of humans and other relevant warm-blooded animals and the inability to replicate outside of the intestinal environment are considered the most basic requirements for fecal indicators. However, the capacity of SFIB to sensitively indicate fecal pollution in water resources has been increasingly questioned by some authors recently. The reason for the debate is the report of "naturalized populations", which are thought to persist and proliferate in non-intestinal environments including sediments, soils, and algae (Ishii and Sadowsky 2008). However, evaluation studies taking comprehensive quantitative data into account are scarce.

As an essential first step, we evaluated the applicability of SFIB for the investigated alpine mountainous water resources based on enumeration by standardized ISO-techniques. We studied the occurrence of SFIB from a broad range of animal and human fecal sources, sampled from the investigated alpine mountainous catchment area (Farnleitner et al. 2010). *E. coli* proved to be distributed in all fecal source groups with remarkably balanced average concentrations (log 7.0 to log 8.3 CFU per g feces). Except for single fecal samples from cattle, the occurrence rates for intestinal enterococci were generally >87% with average concentrations of log 5.3 to log 7.7 CFU per g feces. The fecal indication capacity of SFIB at the springs was evaluated by a multi-parametric study effort that also included genetic fecal markers for microbial source tracking (Reischer et al. 2008; Farnleitner et al. 2010). The investigation showed SFIB to reliably indicate fecal pollution in the investigated alpine springs. *E. coli* was also hardly detected in pristine alpine soils. *E. coli* was a more sensitive indicator for fecal pollution than intestinal enterococci. These results provided the basic methodical foundation for the following steps.

3.2.2 Event-Based Microbial Auto-Sampling and Evaluating on-Line Proxy-Parameters for Fecal Pollution Monitoring

Four rainfall triggered summer events at alpine karst springs (2005–2008) were investigated in detail to evaluate the spectral absorption coefficient at 254 nm (SAC254) as a real-time, early-warning proxy for fecal pollution testing. All springs drain limestone aquifers of the Northern Calcareous Alps in Austria. Their mean discharge ranges from 250 to 5.500 ls^{-1}, showing discharge coefficients between 0.09 and 0.01. The observed hydraulic reaction time between spring-discharge and precipitation trigger ranged from 2 h and 45 min to 8 h and 15 min. During the events a maximum SAC254 was reached with 10.02 abs m^{-1} and turbidity with 12.06 FNU. The linear correlation coefficient (R^2) SAC254 versus *E. coli* ranged from 0.78 to 0.99 during the events. The lead time of SAC254 to *E. coli* was not at any time less than 3 h. For the investigation, Low-Earth-Orbit (LEO) satellite-based data communication between precipitation measuring stations and an automated spring-sampling device was used as developed for the investigated catchments. This method supports event-triggered microbial, chemical, and isotopic sampling and analysis and cross-evaluating to hydrological processes to elucidate the microbial pollution dynamics at the investigated spring habitats (Stadler et al. 2008). The multi-parametric data analysis included on-line event characterization (i.e., precipitation, discharge, turbidity, and SAC254) and comprehensive *E. coli* enumeration supported by Colilert field enumeration (n > 800). The results revealed that SAC254 was a useful early-warning proxy. Irrespective of the studied event situations, SAC254 always increased 3–6 h earlier (so called “lead-time”) than the onset of fecal pollution and featured different correlation phases (Stadler et al. 2010). Furthermore, it also seemed possible to use SAC254 as a real-time proxy parameter for estimating the extent of fecal pollution (Stadler et al. 2010). However, spring- and event-specific calibrations were a basic requirement for such a quantitative estimation of fecal contamination by SAC254 to take the variability on the occurrence of fecal material into consideration. It should be highlighted that for the investigated catchments, diffuse fecal pollution from wildlife and livestock runoff from the soil surface was the source responsible for triggering the SAC254 response (Stadler et al. 2010; Reischer et al. 2011).

Automated, enzymatic, on-line detection was also evaluated as a potential tool for near-real-time monitoring of fecal contamination at the investigated karst springs (Ryzinska-Paier et al. 2014). The β-D-glucuronidase (GLUC) activity was selected as a representative enzymatic model parameter for on-line determination (Farnleitner et al. 2001, 2002). Automated filtration volumes up to 5 L supported sensitive quantification of the enzymatic activities. Internet-based data transfer enabled robust enzymatic on-line monitoring during a 2-year period, using internal control parameters for verification and a dynamic determination of the limit of quantification (Ryzinska-Paier et al. 2014). A total of 5313 out of 5506 GLUC activity measurements (96.5%) could be positively verified. The enzymatic on-line measurements closely reflected the hydrological discharge dynamics and contamination patterns of the test site. However, contrary to expectations, GLUC did not qualify as a proxy-parameter for the occurrence of cultivation-detected *E. coli* contamination and warrants further detailed investigations on its indication capacity as a rapid means for fecal microbial pollution detection in such spring habitats (Ryzinska-Paier et al. 2014; Stadler et al. 2016).

3.3 Fecal Hazard Characterization (Step 2)

3.3.1 Catchment Surveys and Pollution Source Profiles: Hypothesis Generation on the Potential Relevant Fecal Sources

To determine the origin of fecal pollution in spring water, as determined by cultivation-based *E. coli* enumeration, a new strategy was proposed, combining information from the catchment and the respective spring water quality (Farnleitner et al. 2011). Within this concept, quantitative assessment of fecal pollution sources in the respective catchment—referred to as pollution source profiling (PSP)—was performed as a first step. Data from PSP facilitated the formulation of a working hypothesis on the significance of the potential fecal pollution sources for spring water contamination. It is important to note that the generation of the working hypothesis was based on the best available estimates of "fecal contamination potentials" by considering the amount of environmentally available fecal material from various animal and human sources and the estimated levels of *E. coli* cells in the catchment. A subsequent study design was then directed toward rigorous testing of the working hypothesis by a careful application of the newly developed host-associated genetic fecal marker assays for microbial source tracking (MST) and a concurrent multi-parametric characterization of the spring water quality by hydrological, physicochemical, and microbiological parameters (see next point below).

Inspection tours (catchment surveys) based on hydrogeological investigations and identification of sensitive areas using a specific questionnaire were organized to identify potential fecal pollution sources in the investigated catchment. Human sources (tourists, hikers, and alpinists), wildlife populations (red deer, chamois, and roe deer), and cattle (kept on pastures during the summer months) were identified as potentially important pollution sources. Detailed information for further quantitative characterization of the identified fecal sources was obtained from local authorities, official records, and the scientific literature (Farnleitner et al. 2011; Reischer et al. 2011). The average produced total fecal matter per source group was estimated by using information on (1) *individuals per source group* × *ratio of individuals contributing to defecation* × *amount of defecation per individual*. Because a predominant portion of the human individuals use sanitary facilities available in the catchment area (e.g., toilets at mountain lodges), the actual environmentally available fecal material in the catchments was corrected by (2) *amount of total or percentage of produced fecal material per source group* × *ratio of the respective environmental availability*. Finally, the amount of *E. coli* produced per source group was estimated by (3) *the amount of environmentally available fecal material per source group* × *source group specific average E. coli concentrations in excreta or sewage* (Farnleitner et al. 2011; Reischer et al. 2011).

Applying this concept enabled the generation of the hypotheses on the potential relevant fecal pollution sources for the investigated catchments. For example, as much as 99.9% of the daily deposited intestinal *E. coli* populations in the LKAS6 environment could be allocated to wildlife (42.4%) or livestock ruminant (57.6%) fecal excreta emissions. In contrast to ruminant animal sources, the human fecal pollution sources were estimated to be negligible within this catchment (Farnleitner et al. 2011). However, the generated hypotheses had to be reviewed directly at the considered springs by applying host-associated genetic fecal marker assays for MST (see the next point).

3.3.2 Developing and Applying Host-Associated Genetic Fecal Markers for MST

Based on intestinal *Bacteroidetes* populations, quantitative TaqMan minor-groove binder real-time PCR assays (qPCR) were successfully developed for the sensitive detection of a ruminant-associated genetic fecal marker (the BacR approach; Reischer et al. 2006) and human-associated genetic fecal marker (the BacH approach; Reischer et al. 2007). For example, the BacR genetic fecal marker assay revealed qualitative and quantitative detection limits of 6 and 20 marker copies per PCR, respectively. Furthermore, tested ruminant feces contained an average of 4.1×10^9 genetic fecal marker equivalents per g, which permitted the detection of 1.7 ng of feces per filter in fecal suspensions (Reischer et al. 2006).

The hypothesis on the potential fecal pollution sources, based on the PSP, was successfully tested by hydrological-guided spring water sampling. The study followed a "nested" sampling design to cover the hydrological and pollution dynamics of the spring and to assess effects such as differential persistence between the genetic fecal markers and SFIB (Reischer et al. 2008, 2011; Farnleitner et al. 2011). The genetic fecal markers BacR and BacH and the microbiological, hydrological, and chemo-physical parameters, as described earlier, were measured (see methods Sect. 2.2). The developed strategy allowed for the determination of relevant fecal pollution sources for the considered springs (Reischer et al. 2008, 2011; Farnleitner et al. 2011). For example, the hypothesis that ruminant animals were the dominant sources of fecal pollution in the LKAS6 catchment was clearly confirmed. In addition, *E. coli* contamination could be predicted by the concentrations of the measured BacR marker at the considered spring (Farnleitner et al. 2011).

3.4 Health Risk Assessment of Fecal Pollution (Step 3)

3.4.1 Fecal Hazard-Characterization-Guided QMRA

Improved knowledge regarding the occurrence of fecal contamination sources strongly supports quantitative microbial risk assessment (QMRA) which relies on the appropriate choice of reference pathogens (RP; Haas et al. 1999). Commonly used RP cover representative pathogens from enteric bacteria (i.e., *Campylobacter sp.*) and enteric parasites (i.e., *Cryptosporidium parvum* and/or *Giardia sp.*) to human enteric viruses (e.g., enteroviruses). However, as recently demonstrated, many more zoonotic agents can be of potential relevance in mountainous alpine catchment areas (Stalder et al. 2011a, b).

For example, the occurrence of fecal pollution from ruminants guided the QMRA towards the assessment of zoonotic pathogens in the LKAS2 area (Farnleitner et al. 2014). It is important to evaluate whether the performance criteria of the applied MST approach (i.e., fecal specificity and fecal sensitivity) supported the MST-guided QMRA. Furthermore, selection was based on multiple sources of information, i.e., including results from the performed catchment surveys and the established PSP (see Sects. 2.2 and 3.3). For the example given, only a very low prevalence of *Cryptosporidium parvum* and *Giardia sp.* could be found in investigated fecal excrements from ruminant animals in the investigated catchment area. This finding was in accordance with extremely low parasite concentrations observed during event flow situations and was below the guideline concentration of the suggested health-based quality targets from the WHO (2011) . Hence, the results of the example demonstrated that abstracted raw water resources (i.e., controlled water abstraction step before treatment) were already in line with health-based microbial quality targets (Farnleitner et al. 2014).

Based on the definition of a tolerable health-burden (e.g., a maximum of 1–10 infections per 10,000 consumers due to the consumption of un-boiled drinking water) and the application of the fecal hazard-characterization-guided QMRA methodology, it becomes possible to calculate the extent of further treatment requirements for raw spring water to provide safe drinking water according to WHO standards (2011).

As an alternative to QMRA, epidemiological investigations can also be used to evaluate and guide health-related water quality management. However, the high cost and effort of epidemiological studies and the relative low concentrations of pathogens expected in spring water make the epidemiology approach less viable for this environment.

4 Conclusions

The suggested framework for integrated fecal pollution analysis allows state-of-the-art microbial safety management of water resources. Until recently, it was not possible to open the “black box” of fecal pollution for complex alpine karstic spring water resources. With the combination of appropriate and complementary methods, it is now possible to retrieve the needed information on: (i) the extent of fecal pollution, (ii) the responsible fecal pollution sources, and iii) the associated health risks for the consumer.

In this respect, it is important to note that each step of the suggested “3-step approach” is important for water quality management (Fig. 1). In situ on-line monitoring by SAC254 probes directly at the spring water supports the use of near-real-time water abstraction management. It guides the water quality management process, i.e., whether to use raw spring water for drinking water production or not (step 1). Furthermore, determination of responsible fecal pollution sources (step 2) allows target-oriented and pro-active catchment management measures. For example, in cases where animals are the relevant fecal pollution sources, the best environmental practices should target animals (e.g., summer pasturing activities) rather than human pollution targets in the catchment. Last, step 3 directs the extent of required treatment and disinfection to supply safe drinking water according the WHO recommendations.

Finally, it should be highlighted that the suggested framework supports quality management procedures on different scales of temporal resolution ranging from minutes to years (Table 1). Because the approach yields also to a general raw water quality optimization, it also contributes to a decrease of concentrations of available organic and inorganic microbial growth substrates and

Table 1 Overview of the suggested “tools” for integrated fecal pollution analysis and management

Name of method	Principle	Parameter	Time scale
Pollution source profile	Estimating fecal production at the catchment	Standard fecal indicators	Weeks—months—years
Microbial source tracking	Fecal source determination at the spring	Host-associated genetic fecal markers	Weeks—months—years
Basic spring monitoring	Cultivation-based standard procedures	Standard fecal indicators	Weeks—months—years
Spring event analysis	Rainfall-triggered automated sampling	Standard fecal indicators, genetic markers, and intestinal pathogens	Hours—days—weeks
Online spring monitoring	In situ on-line determination of chemo-physical parameters	Fecal proxy-parameter	Seconds—minutes—hours

Note that the temporal resolution ranges over several orders of magnitude (from seconds to years). For details refer to the main text thus to decreased microbial activities (Farnleitner et al. 2005; Wilhartitz et al. 2009). This effect leads to an improved ability to distribute and store the abstracted spring water during the water supply process (i.e., increased "biostability" of the water).

The suggested approach is likely to be improved in the near future by new possibilities resulting from the rapidly developing fields of life science, biotechnology, and information technology such as improved host-associated or host-specific genetic fecal marker diagnostics (e.g., improving fecal sensitivity, fecal specificity, and the number of detectable sources), pathogen detection methods, and on-line monitoring tools.

Furthermore, linking the presented approach (as described above) also to mathematical and hydrological modeling efforts will likely be of increased importance in the future. For example, sustainable decision making should not only be based on past and current situations of fecal pollution but also needs to consider future scenarios (cf. Fig. 1., STEP 3), potentially happening in the catchment (e.g., changes of the climatic and hydrological regime, changes of the pollution sources, changes in the shedding rate of intestinal pathogen, etc.). This kind of QMRA-based scenario models are currently not yet available for alpine karstic catchments, however, they have been recently developed for alluvial water resources (Schijven et al. 2015; Derx et al. 2016). Modeling will not only support step 3 (cf. Fig. 1), but is going to improve the general understanding of the observed fecal pollution dynamics and the origin of fecal contaminants for a given karstic spring environment, in order to support sustainable and pollution-source-targeted catchment management practices. In this respect, a very promising modeling approach was recently reported by taking process-orientated hydro-geological mapping and hydrological modeling into consideration (Grayson 2000; Reszler et al. 2014).

The concept presented here is likely to be of interest for the management of other water resources because the selected parameters and methods can be adapted to the respective situation or requirements to develop robust and operable water safety plan procedures.

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Bassett's Cave, Bermuda

Maureen Handler and John Hoffelt

Abstract

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 US 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, J.P. McLendon—Ecologist and Maureen Handler—Environmental Engineer (the owner of Southern Environmental) traveled 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.

1 Introduction

Langan Engineering &Environmental Services Inc. (Langan) retained Southern Environmental Technologies, Inc. (SET) to survey Bassett's Cave on Morgan's Point, North Hamilton Parish, Bermuda. Located under a former US Naval Air Station Annex, Bassett's Cave was used as a cesspit and dumping ground from the bases' construction in the late 1940's until the base was decommissioned in 1995. After the base was decommissioned, thousands of gallons of waste oil was discovered floating on the tidal pools in the cave. SET was contracted to survey the cave, demarcate the cave on the surface, and construct a map of the cave in an attempt to estimate the extent and amount of oil in the cave. Contamination in karst regions often takes the form of contaminated groundwater but air-filled caves can also be receptacles for contaminants. Bassett's Cave is presented as an extreme example of the latter.

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2 Methods and Procedures

2.1 TimeLine

06/04/14 Southern Environmental Technology (SET) arrives in Bermuda. Survey and caving gear are staged at Langan's office trailer on-site at Morgan's Point.

06/05/14 SET performed an overland survey from the entrance of Bassett's Cave to establish the distance to Great Sound and height above mean sea level (MSL). Additionally, nearby test wells and bore holes into the cave were located and surveyed. Initial entry into Bassett's Cave for reconnaissance performed.

06/06/14 SET began survey of Bassett's Cave. Approximately 75% of the cave surveyed.

06/07/14 SET personnel reduced survey data and prepared a draft copy of the cave map.

06/09/14 SET completed the survey of Bassett's Cave. A total of 1132 ft of passage was surveyed.

06/10/14 SET collected samples from drums of white powder in entrance of cave. Samples were given

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to Langan personnel for analysis. SET marked the perimeter of the cave on the surface using pin flags.

06/11/14 SET leaves Bermuda.

2.2 Health and Safety

During the survey of Bassett's Cave, all personnel entering the cave were dressed in level D (modified) personal protective equipment (PPE). A modified level D PPE dress out includes steel toed rubber boots, a Tyvek suit, nitrile gloves, and an approved caving helmet. The modifications made to the standard level D PPE included a caving/climbing helmet instead of a construction hardhat, a Tyvek suit, and nitrile gloves. Active air monitoring was done with a MultiRAE multi-gas detector that measured carbon dioxide, hydrogen sulfide, lower explosive limit (LEL), oxygen, and a photoionization detector (PID) that measured volatile organic compounds. The MultiRAE was worn by a member of the survey team during every trip into the cave. All MultiRAE readings were 0 ppm except oxygen which consistently registered 20.9 ppm.

Workers collecting samples from the drums of unknown powder were dressed in a level C PPE. Due to the unknown nature of the white powder, along with the fact that this is an abandoned military facility, workers collecting samples were dressed in a full Tyvek suit, steel toed rubber boots, thin nitrile gloves under a set of heavy nitrile gloves, safety glasses, and a half face respirator equipped with multi-gas/particulate cartridges. The worker collecting the samples was additionally equipped with the MultiRAE/PID and a Geiger counter. Neither the MultiRAE nor Geiger counter registered any constituents of concern during the sampling.

2.3 Survey Methods

The cave was surveyed, and a map was produced from the data (Fig. 1). This was done in order to locate any borings in the cave in relation to the surface, to determine the extent of impacted oil pools, as well as to locate the approximate footprint of the cave.

A survey team consisting of three people began the survey by establishing a central, recoverable survey station in the drip line of the cave entrance (Fig. 2). This station was labeled as 0. From this station, an overland survey was performed using two hand-held Suunto tandem instruments and a 100 foot fiberglass tape. Four foot stadia rods were used to set temporary stations. Front and back sights were taken at all stations. A total of 1132 ft of cave was surveyed during the course of two trips into the cave.

After the cave survey was completed, pin flags were placed on the surface to represent the outline of the walls. This was done to assist the geotechnical crew who was on-site performing ground penetrating resistivity scanning of the site.

Data collected during the surveys were digitally managed using Compass software. The program creates a line plot of the cave which can then have the surveyed sketches of the cave passages overlain to create a map. These data were then imported into another separate cave mapping program called Therion which was used to generate the field map and the finished map. A working map of the cave and overland survey was provided during survey activities, and a final map of the survey was completed after SET returned to the USA (Fig. 1). The cave map was overlaid on Google Earth to illustrate the location and bearing of the cave in relation to topographic and man-made features in the area (Fig. 3).

Compass generates a data summary consisting of 25 data sets. Surface length is a measurement of the distance between the northernmost and southernmost survey stations. Surface width is a measurement of the distance between the easternmost and westernmost survey stations. The surface area is the surface width and length numbers multiplied together (the cave footprint). The floor area is calculated by Compass based on the LRUD (left, right, up, and down) data. Adjustments were made to the compass file to include left, right, up, down (LRUD) measurements that were not included in the initial data entry. These data were included in the data used to generate the line plot of the cave. Additionally, a splay shot was added to provide better definition of a wall section near survey station C9. After these data were included, the floor area of the cave was calculated at 36,073.9 ft^2 (3351.4 m^2).

3 Cave Description

Bassett's Cave is located on Morgan's Point in Sandy's Parish, Bermuda. Morgan's Point was developed and leased to the US Navy as a Naval Air Station Annex until 1995, when the base was closed and the American Navy withdrew from the island. During the 50 plus years that the naval base was in operation, Bassett's Cave was used as a cesspit and dump for the base's trash and sewage, additionally thousands of gallons of lubricating oil was released into the cave.

Morgan's Point is currently undergoing remediation with plans for future redevelopment. Part of these remediation activities includes addressing the floating free oil product on the tidal pools in Bassett's Cave (Figs. 4 and 5). During the initial remediation procedures, the sewage piping was removed from the entrance sinkhole. However, none of the trash, including several drums of an unidentified white powder, had been removed at the time of this investigation.

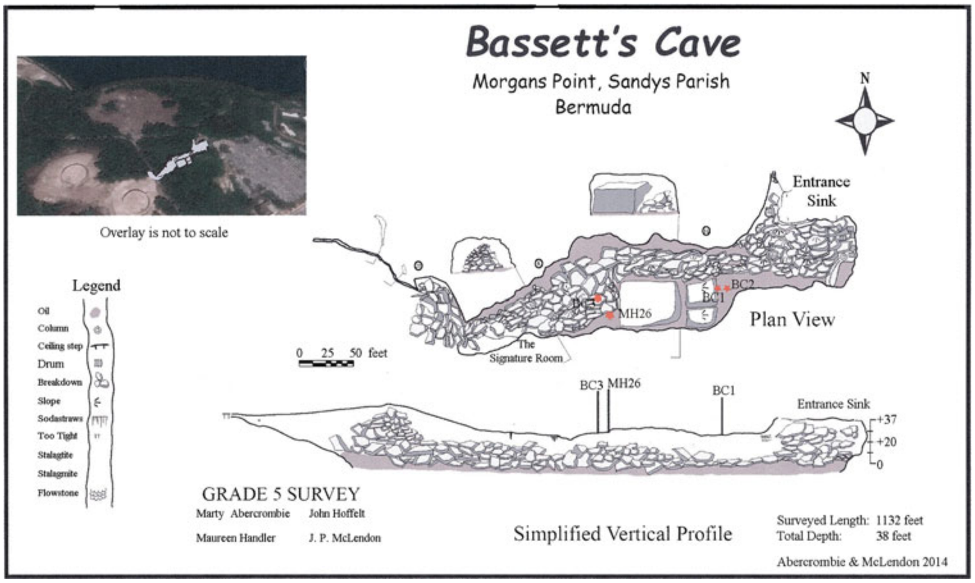

Fig. 1 Map of Bassett's Cave with plan and profile

Fig. 2 Entrance to Bassett's Cave. First entry by team in Tyvek suits

The cave exhibits characteristics indicating that development may have been more influenced by the movement of fresh, circulating groundwater (fluvial) than by brackish or tidal waters (littoral). There is undoubtedly littoral influence in development due to its proximity to Great Sound and observed tidal fluctuations in the cave. The cave has 1132 ft (345 m) of traversable passage along an east–west line with a breakdown modified profile of over 50 ft (15 m). The linear nature of the cave and cross-sectional development suggests conduit flow of water, at some period in time. These features are strikingly different from the characteristics of the caves on the eastern end of the island. The cave ends in a breakdown constriction located very near the base of the aviation fuel tank farm. A fissure type passage extends almost to the foundation of the tank farm. It is possible that the cave extended farther in a westerly direction and that the tank farm influenced breakdown in this area. The interior portion of Morgan's Point, as well as the tank farm, is situated along higher ground that may allow for additional cave development. The eastern extent of the cave is obscured by collapse associated with development of Morgan's Point.

Fig. 3 Footprint of Bassett's Cave superimposed on Google Earth image of surface topography

Fig. 4 Oil pools near the entrance

The cave is accessed by a large entrance sinkhole with three separate distinct entrances. The largest entrance is a 2 foot by 8 foot crack leading to the top of a large breakdown slope. This entrance is most likely the entrance sewage was piped into. The second entrance is located to the east of the main entrance. This entrance is a 2 foot by 4 foot hole that was used as a dumping area. There is a considerable amount of old lumber, construction debris, household trash, and several unidentified 30 and 55 gallon drums (Fig. 6). This entrance was not used to enter or exit the cave. The third entrance is a small 2 foot crack that enters the cave on the western side of the large breakdown slope. The entrance sinkhole is a chance-collapse opening due to a breakdown/collapse intersecting the surface. The entrance is not the terminus (or beginning) of the cave.

The breakdown slope leads into a large west/northwest trending passage. This passage varies from 6 to 10 ft in height and 50 plus feet wide in places. The cave floor is predominately an oil-covered pool of brackish water controlled by the tidal fluctuation of nearby Great Sound. The cave is easily traversed over breakdown which has created a bridge across the tidal pools. There are test bore holes drilled through the roof in various locations throughout this passage of the cave. The western-most end of the passage leads to a

Fig. 5 Oil pool in breakdown in the central portion of the cave

Fig. 6 Debris and drums of white powder near cave entrance

large flat room with several historic signatures ranging from the early 1700s to the 1940s (Fig. 7). The western-most portion of this room is directly under a road way, and heavy equipment could be heard driving above. The room terminates in a breakdown slope that was too unstable for exploration. A northwestern trending crack that averages 2 ft wide by 18–20 ft tall continues around and behind the breakdown for approximately 175–200 ft before pinching out in a flowstone constriction. This passage follows the trend of a gully in a hill to the west of the cave.

4 Oil Volume Calculations

Before SET entered Bassett's Cave on June 6, strings weighted with Cyalume glow sticks were lowered down three wells that were believed to be bored into the cave (Fig. 8). Each glow stick was a unique color which would allow SET personnel to identify the boring while in the cave. The glow sticks would then be used as temporary stations that would allow the survey to tie into the survey data collected during the over land survey. This would allow for

Fig. 7 Historic signatures at the west end of the cave. **a** R Bassett—1779/1781. **b** H. Wring—1781

Fig. 8 Oil pool and light stick lowered down boring at west end of the cave

Table 1 Overburden and oil thickness measurements

Bore	Overburden (ft)	Oil thickness above high tide
BC1	35.3	2 ft
BC3	33.6	No oil found on string
MH 26	38.0	4 ft

Table 2 Oil volume calculation totals

	2-ft oil thickness (Gallons)	4-ft oil thickness (Gallons)	Average oil thickness (Gallons)
Breakdown	183,000	367,000	275,000
Oil pool	81,000	162,000	121,000
Total	264,000	529,000	396,000

over burden calculations to be made as well as allowing for loop closure and controlling errors that may have existed in the survey data set. The team located and identified two of the three glow sticks lowered down the bore holes. These were later identified as BC1 and MH 26. A third string was lowered down what was believed to be BC3, but it was not observed in the cave due to the casing going below water level. No oil was on this string when it was recovered, this string was only used in overburden calculations. After the completion of the cave survey, the strings were removed. During removal, a knot was tied at the break over point at the top of the casing and the distance to the oil smear on the string was measured. The measured length was then used with the data collected during the survey to relate sea-level measurements with the elevation of the oil pools in the cave. Using the string measurement for BC-1 gave 51.2 ft from the ground surface to the oil. The data from overland survey stations showed that the oil thickness at this location is estimated to be 2 ft above sea level at high tide. Using the string measurement for MH-26 gave 51.0 ft from the ground surface to the oil. The survey data from the overland survey stations estimated the oil thickness at this location to be 4 ft above sea level at high tide.

In summary, the two calculated heights of the oil using the string measurements are 3 and 5 ft above sea level based on the tide level during the overland survey. High tide was 1 foot higher than at the time of the overland survey, yielding oil thickness of 2 ft at BC-1 and 4 ft at MH-26. The data are summarized in Table 1.

Using the estimated oil thickness, the total volume of oil present in the cave was calculated in the following way. The floor area of the surveyed cave was calculated by the survey program to be 36,073.9 ft^2. Of this area, it was established that 85% of the surface was breakdown and 15% was unobstructed pools of oil covered water. The volume (in ft^3) in the open pool areas was $0.15 \times$ floor area $\times$ pool depth. Multiplying by 7.48 gave volume of oil in gallons. The principal uncertainty in these calculations is the depth of the oil pool. Of the two measurements, one was 2 ft; the other 4 ft. The calculated volumes for both depths and their average are given in Table 2.

To determine the amount of oil pooled in the voids present between the blocks of breakdown, the square footage of the cave was multiplied by 0.85 to establish the area covered in breakdown. The area of breakdown where oil was most likely present was converted to cubic feet for oil thicknesses of 2 and 4 ft. Based on field observations, the porosity of the breakdown was estimated as 40%. The volume of the breakdown most likely impacted by oil was multiplied by 0.40 to establish the volume of space available for oil to infiltrate. The estimated volume of oil under the breakdown is then $0.85 \times$ floor area $\times 0.4 \times$ pool depth. The estimates for the open pools and the breakdown areas are given in Table 2 and added together to estimate the total volume of oil in the cave.

5 Conclusions

During the survey trips on June 05–10, 2014, Bassett's Cave was surveyed to a total length of 1456.7 ft including splay shots, with a footprint of 72,060.2 ft^2 and an open floor space of 36,073.9 ft^2. Based on the survey data, it appears that there is 2–4 ft (with and error of ± 1 foot) of oil floating on the tidal pools in the cave. These measurements are estimates based on data collected during the survey of the cave. Due to the high viscosity of the oil and physical danger presented with accessing the oil, the actual thickness of the oil could not be measured in situ.

The field data indicate a significant amount of oil in the cave. The volume of oil calculated varied between 260,000 gallons and 530,000 gallons. With the error inherent in using hand-held survey instruments, the actual volume may be as low as 132,000 gallons or as high as 661,000 gallons.

There is a considerable amount of physical debris that has been dumped into the entrances of the cave. This dumped material presents a potential physical hazard for workers entering the cave. Any workers entering the cave should be dressed in appropriate PPE and be trained/aware of both the physical hazards of the waste, as well as risks associated with working in a cave environment.

The work to remove the oil should begin as soon as practicable. The potential for oil to migrate from the cave is dependent on outside conditions such as extreme low tides, tide surges from storms, and work being performed on the surface. The limestone containing Bassett's Cave is very soft. The use of heavy equipment above the cave could cause a cave-in which could impact the remediation efforts.

Moving Beyond Case Studies: Research Examples from Mountaintop Removal Coal Mining

Michael Hendryx

Abstract

Mountaintop removal is a form of surface coal mining practiced in Central Appalachia. People who live near these mining sites express concerns about water and air quality problems caused by mining with corresponding impacts on health, but until relatively recently empirical evidence was lacking. This paper 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 poorer health conditions across multiple indicators among people living in mining versus non-mining areas. Environmental sampling documented the levels and types of air and water contaminants present in mining communities, and more recently, the first cause and effect connections have been made between environmental conditions and biological markers. 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 research on mountaintop removal provides a case study in moving from anecdotal evidence to research evidence to address an environmental health concern. Observations and recommendations are offered that may be useful in developing a research base to understand public health impacts from karst groundwater contamination.

1 Introduction

The objective of this paper is to present a "case study in developing a research line beyond case studies." The paper will review this development for the case of mountaintop removal coal mining, which is different in some ways from exposure problems that may relate to karst formations, but similar in the sense that in both cases there was a lack of research evidence in the face of plausible concerns about exposure of vulnerable populations to environmental hazards. The case study presented here is not necessarily the only or the best way to develop a research program to address this type of issue, but offers an illustration of how a research line was developed under conditions of limited resources, what the evidence shows for environmental exposures, and lessons learned that may be useful for karst scientists to consider in efforts to build an evidence base for public health problems related to karst water.

Mountaintop removal mining (MTR), sometimes called simply mountaintop mining, is a form of large scale, aggressive surface mining for coal, practiced in the steep terrain of Central Appalachia in the USA where other forms of coal mining are less practical or less profitable. MTR involves clear-cutting forests, which are often burned, and then using explosives and heavy machinery to remove up to hundreds of feet of the mountains to reach coal seams. The removed rock and soil, called overburden, is transferred to large trucks and typically carted short distances where it is dumped into the valleys between the mountains. These valley fills permanently bury headwater streams, and there is strong evidence that water emerging from the base of these fills is impaired and remains impaired for decades after

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mining at a site closes (Bernhardt et al. 2012; Bernhardt and Palmer 2011; Lindberg et al. 2011; Palmer et al. 2010). Water emerging from valley fills is characterized by elevations in conductivity and higher concentrations of selenium, sulfate, magnesium, and other inorganic chemicals (Lindberg et al. 2011; Palmer et al. 2010).

The coal itself is extracted and transported to nearby processing facilities by truck or conveyor belt. At the facilities, the coal is crushed and chemically treated to remove non-combustible material and reduce inorganics including heavy metals. The water used to process coal contains a variety of proprietary chemicals with poorly understood health risks but including organic solvents [e.g., 4-methlycyclohexane methanol [MCHM] and propylene glycol phenyl ether [PPh] that gained notoriety during the recent water spill in Charleston WV (Biello 2014)]. After use, the water is highly contaminated with the original chemicals plus the material removed from the coal. This water is either stored in unlined surface containment ponds or injected underground into abandoned mining spaces where its ultimate fate is unclear. Processed coal is then transported toward end use points using trucks, trains, and barges. Throughout the process, there is heavy use of diesel products and other chemicals in explosives, machinery and processing, impairments to surface and groundwater, and fugitive dust arising from the mining, processing, and transport activities. MTR activity stretches across a geographic area roughly equal to the size of New Hampshire and Vermont combined and has become the major driver of land use change in Appalachia (Bernhardt et al. 2012). It is estimated that by 2012, MTR will have had destroyed 2200 square miles of forest and permanently buried 2000 stream miles (Cho 2011).

Unfortunately, this mining practice occurs in close proximity to human settlements. People in Central Appalachia often live in small communities along narrow river or stream bottoms, beneath steep hillsides, and MTR activities occur in many cases above their homes. Residents of these communities expressed concerns that their health was being threatened through contaminated air and water, but empirical evidence that could be used to support or allay these concerns was unavailable. Although it was widely recognized that people in Appalachia experienced poor health outcomes relative to other areas, the assumptions appeared to be that any observed health problems in mining communities could be attributed to traditional indicators such as poverty, smoking, or obesity (Caudill 2001; Halverson and Bischak 2007). In the following section, the development of the evidence base, and the results of a set of research studies to investigate possible public health impacts of MTR, will be presented.

2 Examining the Evidence

In the beginning were the stories. The stories came from people living in the mining communities, where they had often lived for their entire lives as had the generations before them. The stories told of cancer, clustered in hamlets, and of rare form, brain, bone, and stomach cancer, sometimes affecting children. They told of other diseases and premature death. They spoke of the destruction of the mountains to reach the coal, of the loss of human labor and jobs to machines, and of the disregard of their political leaders to their plight.

The stories were not peer reviewed or published, but simply spoken. We listened to them and decided to examine the question: Was there an independent contribution to poor public health associated with coal mining? By independent, we meant poor health beyond that which could be explained by traditional indictors. And by public health, we wished to distinguish our focus from research on the occupational health hazards of coal mining.

As researchers are taught to do, we began with an investigation into the prior literature. We found a small number of studies conducted in Great Britain (Pless-Mulloli et al. 2000a, b, 2001; Temple and Sykes 1992) that generally showed poor respiratory health indicators for people, usually children, who lived near surface mining there. There were also studies conducted in India that showed elevations in air pollution around surface coal mining sites, but did not investigate human health indicators (Ghose and Banerjee 1995; Ghose and Majee 2000). We found no studies that had been published on the public health impacts of surface coal mining in the USA. More than one writer had documented accounts from residents that expressed the same concerns we heard in talking to local people (Burns 2007; Goodell 2006), but no formal health studies had been done. We decided to conduct initial studies using freely available public secondary data that could be obtained and merged from different sources at low cost.

2.1 Initial Secondary Data Analysis Studies

The secondary data included those from the US Department of Energy's Energy Information Administration (EIA) which included county-level data on the tons of coal mined over time for both surface and underground mines. We used this to identify the presence or absence of mining for each county as well as the mining quantities. We began to merge these data with age-adjusted mortality rate data provided at the county level from the Centers for Disease Control and Prevention (CDC), from CDC Behavioral Risk Factor Surveillance System (BRFSS) telephone health surveys, and from a large representative telephone health survey of West Virginia residents that had been originally conducted for other purposes. We also used data from the US Census and from the CDC on demographic, behavioral, and socioeconomic covariates.

We did not know what the results would show and thought perhaps that our colleagues would be correct that socioeconomic and behavioral disparities could account for the effects, but we found instead that these early studies confirmed the stories. That is, the results indicated that people living in Appalachia where coal mining occurred experienced poorer health outcomes compared to non-mining populations, after statistically controlling for covariates. Some of the early studies showed that people in mining communities, either in West Virginia or in Appalachia generally, had significantly higher rates of total mortality (Hendryx 2008; Hendryx and Ahern 2009), mortality from heart, lung, and kidney disease (Hendryx 2009), and mortality from total cancer (Hendryx et al. 2010) and lung cancer (Hendryx et al. 2008). They also showed higher self-reported morbidity rates for lung, kidney, and heart disease (Hendryx and Ahern 2008; Hendryx and Zullig 2009). The pattern of results indicated not only an effect related to the presence or absence of mining but a dose–response effect where the health problems became more severe as the amount of mining increased. We also demonstrated that the health problems were present for both males and females, suggesting that occupational exposure could not account for the findings, as almost all coal miners are men.

In the early studies, we had not yet identified a way to distinguish MTR from other types of surface mining. Eventually, we located satellite imagery data, once again publicly available, to designate counties in Appalachia where MTR took place. These counties are in Central Appalachia in areas of four states including Kentucky, Tennessee, Virginia, and West Virginia, although other forms of coal mining also take place in these counties. With this information, we reexamined some of the earlier studies and focused this time not on mining in general but on MTR. We found that health disparities were concentrated in areas that practice mountaintop removal, after controlling for covariates and again with an indication of a dose response–effect in that MTR counties had the worst health outcomes, and other coal mining counties had intermediate outcomes, compared to counties where coal mining was absent. In particular, we observed in these secondary data analysis studies that MTR was significantly associated with higher cancer mortality rates (Ahern and Hendryx 2012), higher cardiovascular disease mortality rates (Esch and Hendryx 2011), and higher rates of birth defects (Ahern et al. 2011a). We also observed poorer health-related quality of life (Zullig and Hendryx 2011) and higher risk for depression (Hendryx and Innes-Wimsatt 2013). CDC age-adjusted total population mortality rates are shown in Fig. 1; rates are significantly higher over time in the MTR area compared to other areas.

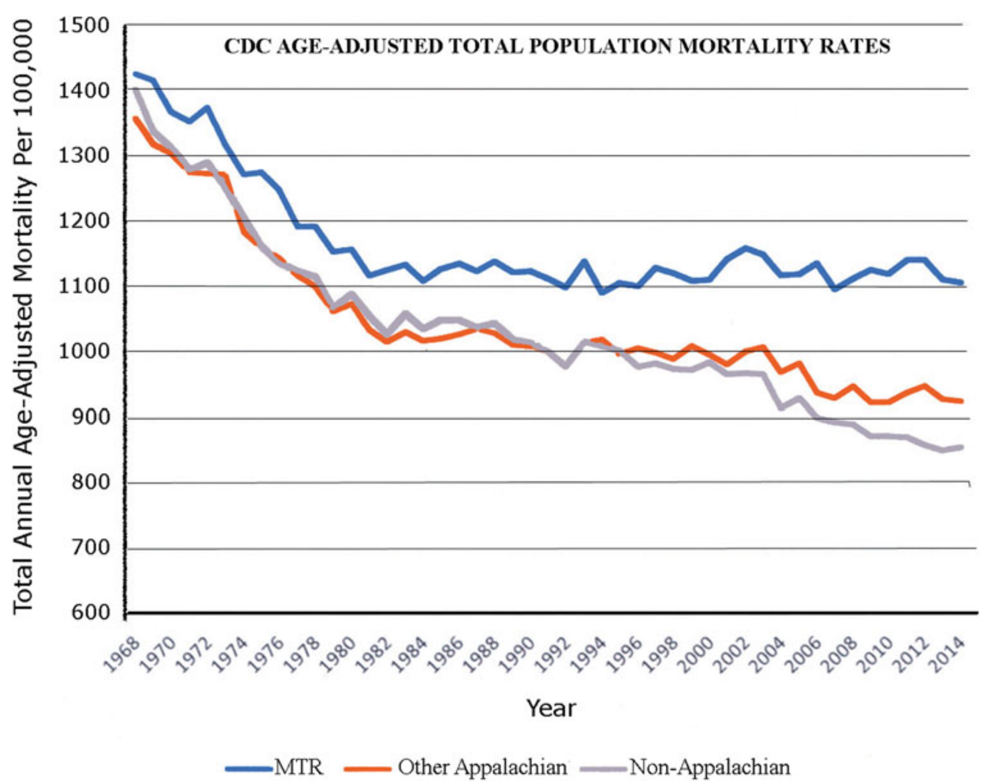

Fig. 1 Age-adjusted total mortality rates per 100,000 by MTR status in four states: KY, TN, VA, WV, 1968–2014

2.2 Community Survey Primary Data

The secondary data that we had were sometimes ecological data available at the county rather than the individual level. Exceptions included several studies with individual level data, but even then, estimates of exposure were usually limited to county-level indicators of mining activity. This limits the ability to make causal inference regarding exposure effects for individual persons. It was time to collect primary data.

Over the course of several years, we conducted a set of community health surveys in West Virginia, Virginia, and Kentucky (Hendryx 2013; Hendryx and Luo 2015; Hendryx et al. 2012). This approach allowed us to select communities within a few miles of active MTR mining, rather than relying on county-level data. In each case, it was important to identify control communities that were similar to the mining communities in other respects (i.e., rural communities in the same states with similar demographics but no mining.) The surveys were conducted at low cost using trained college students as volunteer survey data collectors. The students worked at data collection during an alternative spring break experience. Each year, over the course of several weeks in March, the students would arrive from different colleges and would canvas entire study areas to collect health surveys door to door from as many participants as possible. These surveys proved to be very useful in confirming earlier county-level studies and improving our understanding of the predominant health problems experienced by the mining community residents. We learned, for example, that respiratory problems were common for adults living near the mining sites in ways that could not be explained by smoking or other covariates (Hendryx 2013; Hendryx and Luo 2015). We also learned that health problems extended to other family members beyond those who were able to answer the surveys; households in the MTR communities were more likely to have a family member with a serious illness in the last year and more likely to have a family member who had died from cancer in the previous five years (Hendryx 2013).

At this point in the research, there was a pattern of evidence to show that public health was in fact impaired in Appalachian mining communities, especially those in MTR areas. This pattern showed dose–response effects measured by either amounts of mining, or comparing MTR to less aggressive mining forms. It showed effects for men and women, and for children's health outcomes (Ahern et al. 2011a, b; Cain and Hendryx 2010). It showed a consistent pattern of effects for mortality and morbidity data, and for primary and secondary data, emphasizing respiratory problems foremost, although cancer, heart, and kidney disease, and birth defects were also elevated. This evidence had been collected at low cost relying on available data and volunteer effort.

However, despite this strong suggestive evidence, at this point in the research program we had not yet conducted assessments of the actual environmental conditions in mining communities. There was reason to believe, based on our own findings, on anecdotal evidence, and on studies conducted by others (e.g., Lindberg et al. 2011; MSHA 2010) that water and air quality could be impaired in mining environments, but at this point, we had no direct evidence on environmental conditions in communities where people lived. The next step was to gather environmental data.

2.3 Environmental Studies

By this point, the published papers on the topic had attracted some attention, and other scientists offered to lend their environmental expertise (and resources) to the problem. We began working with environmental scientists from West Virginia University and from the US Geological Survey (USGS). These individuals provided the equipment and gave of their time to collect and analyze community air and water samples. Air samples were collected using a variety of techniques including low and high volume pumps to collect physical samples of organic and inorganic chemicals, window wipes to collect deposited samples of organics and inorganics, soil samples to study deposition, and estimates of particle size down to ultrafine (<0.1 μm) range. Sampling was conducted in residential areas where people lived, from front yards, back porches, garden and schoolyard soil, household windows, private wells, and household taps. Once again, samples were collected from rural mining communities and in other comparable rural communities where mining did not occur. Figure 2 shows examples of low-volume filters collected from mining and non-mining environments.

A number of studies have been published from these sampling efforts, and other presentations have been given at scientific conferences (Esch et al. 2011; Kolker et al. 2012; Orem et al. 2012). Results indicated that air samples from mining communities showed elevations in a variety of organic compounds especially low molecular weight polycyclic aromatic hydrocarbons (PAHs) indicative of coal itself rather than coal combustion, although other post-combustion compounds were also present (Kolker et al. 2012; Kurth et al. 2015). Inorganics from air samples showed elevations in silica and in other elements suggesting that the rock and soil overburden was the source (Knuckles et al. 2013; Kurth et al. 2015). Silica is harmful to lung tissue and is a known lung carcinogen (Guha et al. 2011). Window wipe and soil sample results were consistent with these

Fig. 2 Filters with particulate matter collected from non-mining (*middle*) and mining (*left* and *right*) residential areas

findings. Examinations of particle size distributions indicated that higher levels in mining compared to non-mining communities were most pronounced in the ultrafine range (Kurth et al. 2014). Because of their small size, ultrafine particles are of particular public health concern (Delfino et al. 2005; Oberdorster 2001; Sioutas et al. 2005).

Particulate matter samples collected from MTR communities have been used in three subsequent laboratory-based studies to date. One of these studies demonstrated that MTR dust promoted microvascular dysfunction after respiratory instillation in rats (Knuckles et al. 2013). A second study showed that MTR dust impaired the function of heart cells in rats through mitochondrial mechanisms (Nichols et al. 2015). The third showed that human lung cell lines exposed to MTR dust in vitro demonstrated several cellular changes indicative of the development and progression of lung cancer (Luanpitpong et al. 2014).

In summary, there have been a group of studies investigating environmental conditions in mining communities, which among other findings have shown that levels of ultrafines are elevated in these communities and that particular matter collected from residential mining communities contains higher levels of silica and other inorganics, and higher levels of PAHs, relative to control communities. Meanwhile, other studies showed deleterious biological effects of exposure to this MTR dust in laboratory settings. Presently, only one study has shown biological markers of effect for community residents in mining areas; this study showed higher particulate counts in both indoor and outdoor settings and showed that mining community residents had higher levels of blood inflammation measured by C-reactive protein compared to controls (Hendryx and Entwhistle 2015). There is still more to do to understand exactly what exposures are occurring and how those translate to health problems for community residents.

2.4 Evidence from Other Researchers

As the research in Appalachia proceeded, other researchers demonstrated an interest in the topic as well, in their own localities. Studies in China, Columbia, Australia, and Turkey, although not specific to MTR, have shown that surface coal mining is an air pollution concern and may pose public health risks (Higginbotham et al. 2010; Huertas et al. 2012; Leon et al. 2007; Liao et al. 2010; Yapici et al. 2006). Other researchers in Kentucky independently added to the evidence base on MTR's detrimental health impacts, presenting evidence for higher lung cancer incidence rates in eastern coal mining areas of the state where MTR occurs (Christian et al. 2011). Although the exposure routes and mechanisms of exposure are still incompletely understood, the evidence has grown to the point where the likelihood of harm far outweighs the counterargument that some unmeasured confound, or some limitations to the data, must somehow explain the results and that large-scale surface coal mining near human communities is benign. Such an argument is increasingly implausible.

3 Conclusions

A number of observations and recommendations may be offered for those who are interested in investigating whether human health risks may be present in relationship to exposures to possible water contamination from karst formations.

3.1 Using What Is Available

The research line described here was begun without extramural grants. We took advantage of publicly available secondary data from several sources that we could merge, usually at the county level, to examine associations between mining activity and health while controlling for covariates. To the extent that data sources can identify the locations or impacts of karst formations, they could perhaps be used to beneficial effect by merging with other health data using common geographic identifiers.

3.2 Partnerships

The nature of the relationship between coal mining and public health is a complicated one. Environmental exposures appear to involve a variety of possible chemicals that may operate through air or water transport routes. There is not a sole target chemical to focus on. In addition to environmental exposures, people who live in mining communities also often contend with economic hardship, so that environmental influences are difficult to disentangle from the effects of poverty, poor educational attainment, smoking, and poor diets leading to obesity. Attempting to understand these various contributions to population health is challenging. Over the course of the research, individuals who have participated include people who come from a broad range of disciplinary backgrounds in the social and physical sciences. The need for multidisciplinary teams is often touted, but perhaps nowhere better illustrated than in this case, where no one area of expertise or training could investigate this problem completely. Partnering with experts who represent different specialties, and can bring different resources to bear, is likely to be important in any situation where the causes of poor health are partially environmental but where environmental exposures occur in the context of so many other threats to health. The fact that karst formations exist in so many places around the globe and interact with so many other possible influences on health that may vary from site to site makes this challenge all the more daunting.

3.3 Funding Limitations

The first two observations noted above are closely related to this one. In the absence of large-scale funding to support this research, we relied on using available evidence and the generous donations of time and resources provided by our colleagues and by students. If larger scale studies are funded, whether they be directed to MTR or to karst, the key studies will collect data at the level of individual persons that can connect environmental conditions to personal measures of exposure, dose, and biological effect.

3.4 Political Opposition

Examinations of possible anthropogenic environmental risks to human health may threaten vested economic and political interests. The MTR research has attracted the displeasure of the mining industry and politicians who support the industry. There has even been the suggestion that political pressure was used to stop the USGS research midstream (Ward 2014), although this is not proven. It is possible that investigators pursuing research on how human-caused contamination of water in karst formations impacts health may encounter opposition as well. The only lesson here is to be aware of it and to pursue the research with this understanding.

3.5 Sticking with the Evidence

Developing an evidence base to address environmental exposures for vulnerable populations is a difficult undertaking. The research designs available are non-experimental (with the exception of the laboratory studies), and the causal inferences that one can make from any one study are necessarily limited. We have endeavored to be appropriately cautious about what the data from each study are able to say, and what the limitations are. We have gradually moved to the position that mountaintop removal mining is a risk to public health based not just on one or a few studies but on the accumulated evidence that now includes about 30 peer-reviewed studies from our group in addition to many others from other researchers. For investigators wishing to examine possible effects of karst environments on public health using non-experimental field studies, it is important to stick to the evidence in each case and to know the limitations in what any single study can say. Maybe it will be the case that water from karst formations in some cases is not a threat, where it is in other localities. Maybe threats will be widespread or limited, dramatic or subtle, or absent. In any event, the field of inquiry is wide open and contributions to move the knowledge base beyond case studies are waiting to happen.

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Using Enteric Pathogens to Assess Sources of Fecal Contamination in the Silurian Dolomite Aquifer: Preliminary Results

Maureen A. Muldoon, Mark A. Borchardt, Susan K. Spencer, Randall J. Hunt, and David Owens

Abstract

The fractured Silurian dolomite aquifer is an important, but vulnerable, source of drinking water in northeast Wisconsin (Sherrill in Geology and ground water in Door County, Wisconsin, with emphasis on contamination potential in the Silurian dolomite, 1978; Bradbury and Muldoon in Hydrogeology and groundwater monitoring of fractured dolomite in the Upper Door Priority Watershed, Door County, Wisconsin, 1992; Muldoon and Bradbury in Assessing seasonal variations in recharge and water quality in the Silurian aquifer in areas with thicker soil cover. p 45, 2010). Areas underlain by the Silurian dolomite aquifer are extremely vulnerable to groundwater contamination from various land-use activities, especially the disposal of human wastewater and dairy manure. Currently there is no consensus as to which source of wastewater generates the greater impact to the aquifer.

1 Location of Study Area

Our study area is the Town of Lincoln in Kewaunee County (town area is outlined by black box in Fig. 1). 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 [unpublished data, Kewaunee County, Land and Conservation Department]. Dairy farming and associated crop production comprise the primary land use (Fig. 1) and manure is commonly applied to crop land. Within the town, there are approximately 13,500 cattle and 334 households.

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2 Existing Water Quality

Historically, non-potable "brown-water" events have been noted in several counties underlain by the Silurian aquifer. Figure 2 illustrates purchased bottled water (right) and water (left) that was collected from a code-compliant domestic well in the Town of Lincoln during a snowmelt event in April 2008.

While brown water is an obvious indication of degraded water quality, existing data also indicate extensive contamination by nitrate-N and coliform bacteria. Figure 3 summarizes the nitrate-N and bacteria data for Kewaunee County that have been documented by the University of Wisconsin Stevens Point Center for Watershed Science (Bonness and Masarik 2014). This database of groundwater samples collected from private wells indicates that 144 of 879 samples (11.5%) for nitrate-N exceed the drinking-water standard of 10 mg/L. Of the 741 samples tested for coliform bacteria, 147 (19.8%) tested positive. The database also indicates that 23 of 144 samples tested positive for *E. coli*. Exceedances of groundwater standards are not randomly distributed but rather appear to correlate with areas where thin soils overlie the fractured dolomite aquifer. This observation is consistent with other work in the upper Midwest USA (e.g., Fig. 47A in Breen and Dumouchelle 1991).

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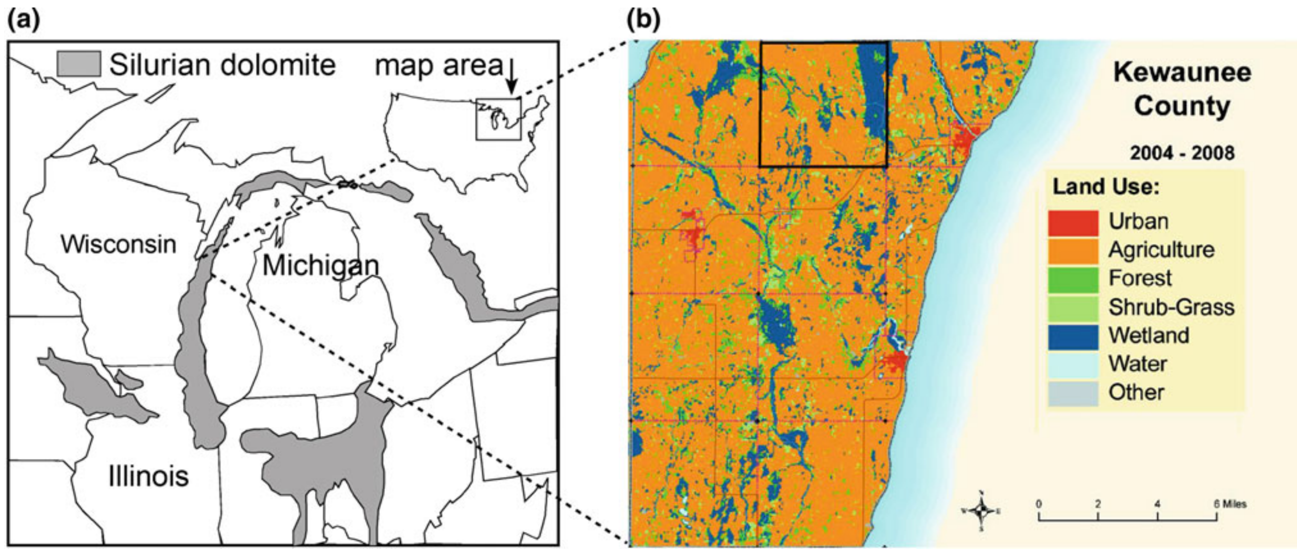

Fig. 1 Location of study area including **a** map of generalized Silurian subcrop shown as *shaded area* (modified from Shaver et al. 1978), and **b** map showing land use within Kewaunee County (*colored map*) and the location of the Town of Lincoln (*black outline*) within Kewaunee County

Fig. 2 Jars of both bottled water (purchased) and brown water produced from a domestic well. Photo courtesy of Chuck Wagner

3 Source of Contamination

As resource managers try to address these water-quality problems, there is no consensus as to whether the main source of contamination is human or bovine wastewater. In Kewaunee County, dairy farming and associated crop production comprise the primary land use and manure is commonly applied to crop land prior to spring planting or in fall after crops have been harvested. In addition, crop land receives commercial fertilizers, septic wastes, municipal sewerage sludge, as well as liquid industrial wastes (generally by-products from the cheese-making process). Fecal wastes

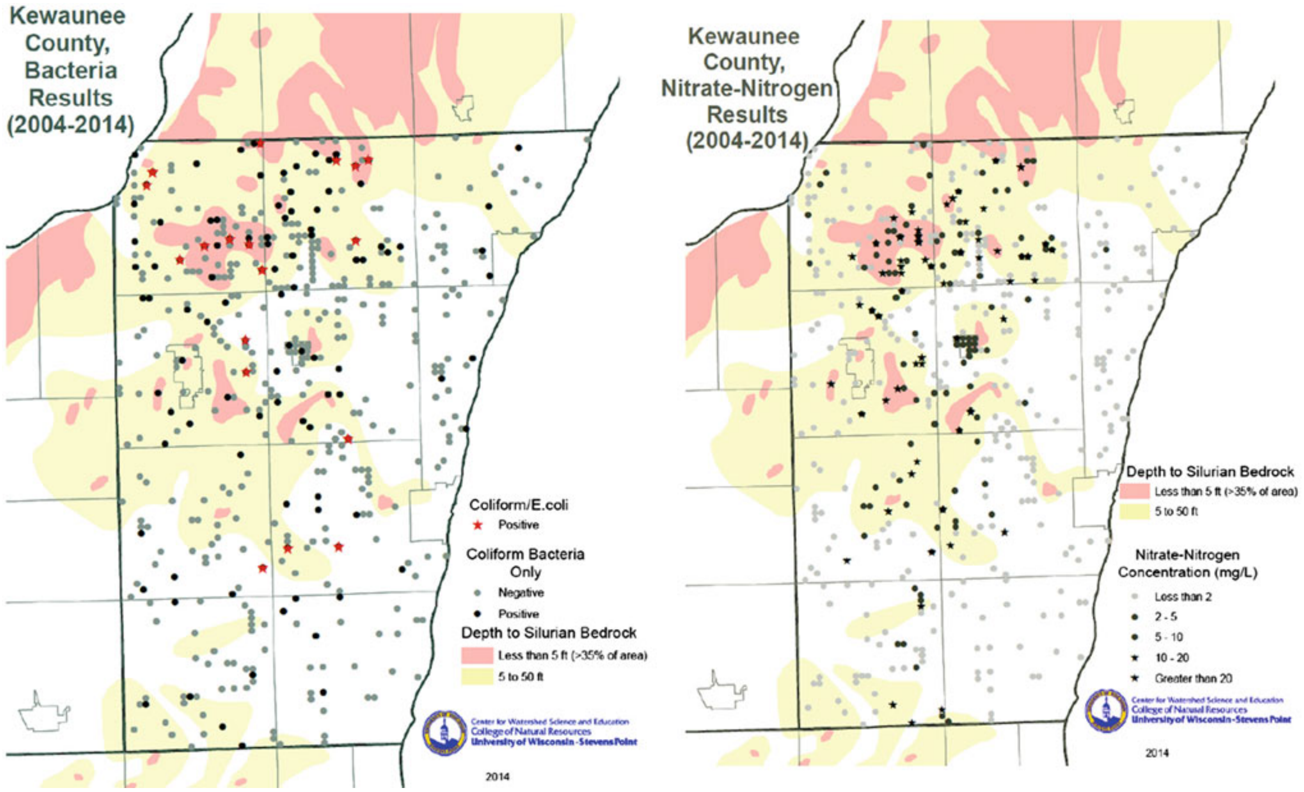

Fig. 3 Existing water-quality data for Kewaunee County (Bonness and Masarik 2014). The county is outlined in *black*; *gray lines* outline the Towns and incorporated municipalities within the county

from humans and dairy cattle serve as diffuse, long-term sources of enteric pathogens. Previous work by Borchardt (2012) has shown that pathogens from land-applied manure can survive several months after application.

4 Results of Pilot Project

We conducted a pilot project in May 2014 to assess whether sampling private wells for viruses could be an effective method of assessing sources of wastewater contaminating the groundwater. We collected water samples from private domestic water systems connected to 10 wells in northern Kewaunee County that had previously had bacteria detections or elevated nitrate values. The results indicated that seven of the ten wells were positive for fecal contamination. Two wells contained human-specific viruses, one well contained bovine-specific viruses, one well contained both virus types, and one well was positive for bovine *Bacteroides*. *Salmonella* species and *Campylobacter jejuni* were identified in four wells and one well, respectively, which is a human health concern. It should be noted that the spring of 2014 did not produce any brown-water events in northeastern Wisconsin. Our samples were also collected after the peak period of recharge due to spring snow melt. Thus, our results may represent "background" levels of contamination by enteric pathogens. An ongoing research project is using virus analyses from domestic groundwater systems collected quarterly to distinguish septic versus bovine sources of contamination.

5 Future Research

Previous work has demonstrated that recharge to the dolomite aquifer can be exceedingly rapid (e.g., Bradbury et al. 2002; Muldoon and Bradbury 2010). Muldoon and Bradbury (2010) noted that wells with up to 18 ft of surficial sediment exhibited recharge responses (changes in water level and fluid conductivity) within 24–48 h of a precipitation or melt event. Figure 4 illustrates variation in fluid temperature, electrical conductivity, and water levels for a shallow monitoring well in Kewaunee County. Recharge events, indicated by sharp rises in water level, are both rapid and episodic throughout the year. Changes in fluid conductivity in response to recharge indicate the complexities of the recharge process. The lower graph indicates a rain event in early December 2007 that led to no groundwater recharge because the ground was frozen. Then a second rain event in late December 2007, when the

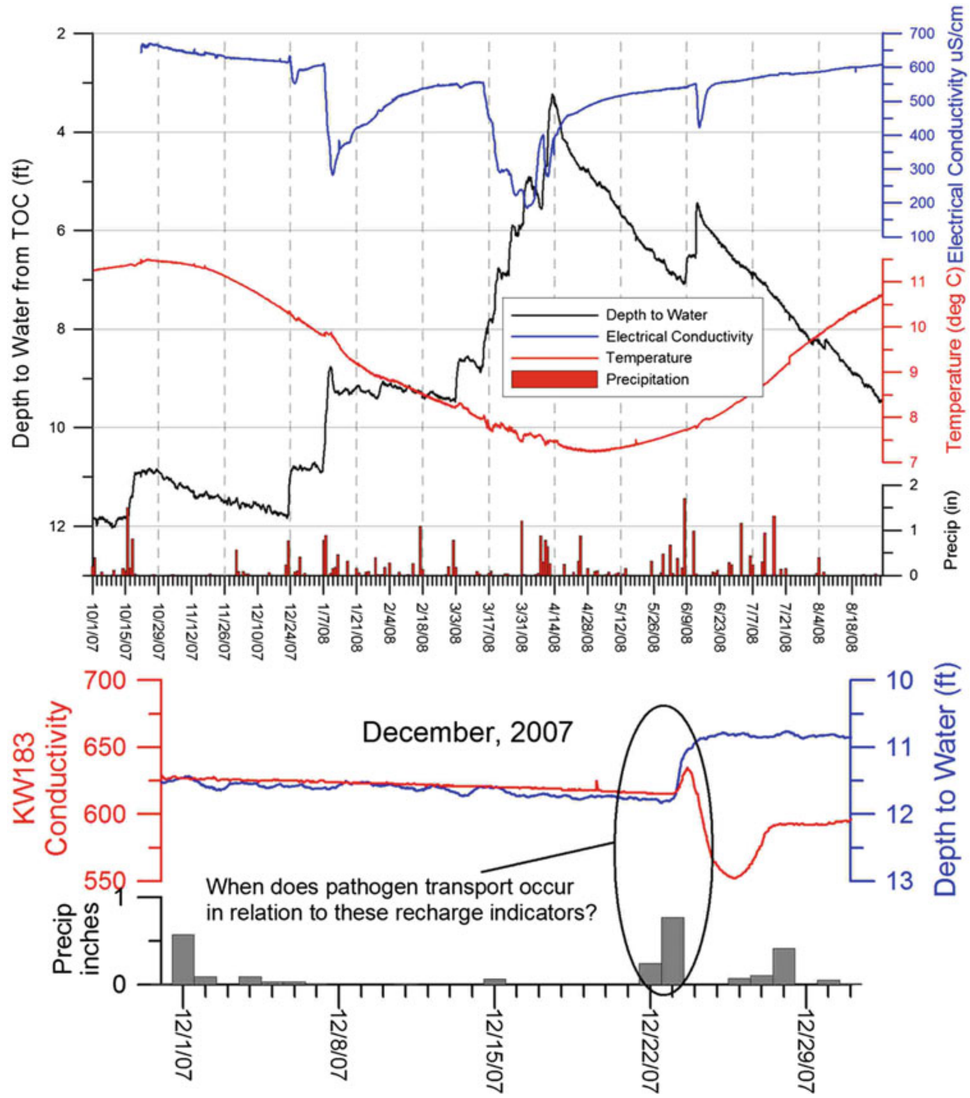

Fig. 4 *Top* Variation in water level, fluid temperature, and electrical conductivity as indicators of recharge in well KW183 along with the precipitation record (from Muldoon and Bradbury 2010). The *top graph* indicates that there were five recharge events from October 2007 through June 2008. The *lower graph* illustrates the details of the recharge event in December 2007

temperature was above freezing for several days, produced a sharp rise in conductivity (as vadose water drained) followed by a drop in conductivity as low-conductivity recharge water entered the aquifer. While these data illuminate the timing and rapidity of recharge events to the dolomite aquifer, we have very limited understanding on the delivery and transport of enteric pathogens within this aquifer.

The ongoing research project includes automated groundwater samplers installed on three domestic well systems that will be used to determine the timing of peak transport for viruses and indicator bacteria.

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Human Perceptions of Anthropogenic Impact on the Aquifer Recharge Zone in Santa Isabel, Puerto Rico

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Abstract

Santa Isabel, a small municipality in the southern part of Puerto Rico, is considered for its agricultural capital because it produces 15% of the vegetables consumed in the island. The most important factor for the sustainability of the agriculture in this area is water. All the water is obtained from the Santa Isabel aquifer that is composed of alluvial and limestone formations. In order to ascertain the perception of the socioeconomic importance of the water in the area, local farmers and residents were interviewed using a questionnaire. Educational materials will be developed for the farmers and the community based on the needs assessed in the interviews.

1 Extended Abstract

A total of 30.4% of the land surface of Puerto Rico contains important aquifers (Fig. 1). The North Coast Province of Puerto Rico contains an area of 680 mi^2 of aquifers, while the South Coast contains 230 mi^2. Both northern and southern aquifers include in their formations alluvial valleys (Gomez-Gomez 1987). The public supply of water managed by the Puerto Rico Aqueduct and Sewer Authority (PRASA) relies on these aquifers. According to Molina-Rivera (1996), during 1990 a significant amount of water was withdrawn from all aquifers in Puerto Rico for all uses at a rate of 158 Mgal/day. Of these, the public supply system withdrew an estimated amount of 80 Mgal/day from groundwater resources to serve 800,000 persons. In 1990, the North Coast Province Aquifer provided 47% of the water supplies of the public water system and the south aquifers supplied 34% (Molina-Rivera 1996). Groundwater uses for irrigation and livestock were 53 and 5 Mgal/day, respectively. Some of Puerto Rico towns use aquifer water mainly for all of their requirements. By example, Santa Isabel, a municipality mainly dedicated to agriculture and located in the semiarid region on the southern aquifer of Puerto Rico obtains all of their water from the aquifer.

The hydrogeologic formation in the area is mainly alluvial, but it also has a small part near the Rio Coamo Dam, that is limestone (Gierbolini et al. 1979). In terms of recharge, the type of formation is important since the area is mainly affected by the river flow and part of the recharge area is covered by urban sprawl. The objective of this research is to assess human perceptions of both farmers and the general public to determine: *On farmers*: (i) Changes in productivity on their farms; (ii) changes in quantity and quality of water. *On domestic users*: Changes in water quality in the area. We aim to identify water users in the area. The question to answer with this research is as follows: How do farmers and domestic users perceive agricultural and residential communities in the municipality of Santa Isabel and the socioeconomic change in land use and water quality in the aquifer recharge zone? We postulate that agricultural and residential communities of Santa Isabel are aware of the importance of the aquifer in Santa Isabel, but these communities do not implement the most efficient measures to conserve water to develop a

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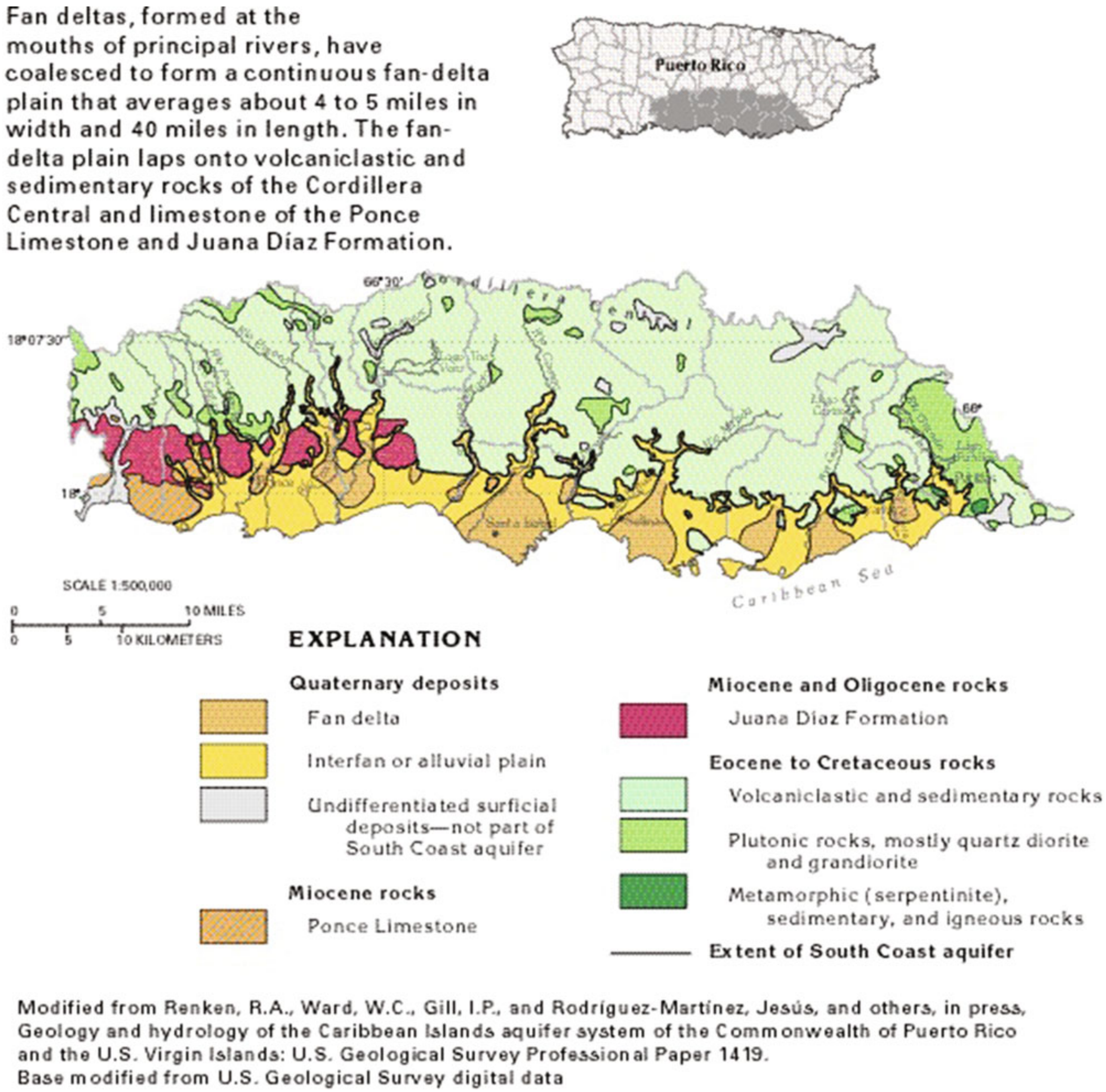

Fig. 1 Karst zones in Puerto Rico (Olcott 1999)

sustainable agriculture and residential community in the area. In the methodology, we obtained information from primary sources through interviews and secondary sources through historical documents, statistical documents, population census, and agricultural related agencies, among others (Lucca Irizarry and Berríos Rivera 2009). The questions in the questionnaire were unstructured because our study is descriptive and is intended to inquire into the history of the struggles that the past landowners had related to water issues. With the interviews, we looked for their decisions on changing from flood to drip irrigation and a description of existing structures to move water through the farms, their current condition, and whether they are in use. In addition, we looked for perceptions about the use of various retention ponds, infiltration, and any other water storage facilities. We inquired about the knowledge among farmers and domestic users of the water problem in Santa Isabel in socioeconomic terms, and the impact on quality and supply of water in the area.

We interviewed experienced farmers in the area on how they have been impacted by the deterioration of the water quality in the aquifer. Also, we interviewed residents with more than 40 years in the area. The sources of historical information included *Worker in the cane* by Sidney Mintz, and the book, *La Historia del Valle del Cemi* and a blog from Melvin Rivera. The last two contain data and photographs on the history of the sugarcane in Puerto Rico and in the Santa Isabel area before the establishment of the municipality. These resources allowed us to locate all the history of water issues in the study area and their relation with agriculture. The interview protocol consisted of an exploratory analysis before the interviews we conducted. We interviewed a farmer and a citizen to explore possible flaws and to validate the instrument. The questionnaire had semi-closed questions and provided space for additional answers if needed (Lucca Irizarry and Berríos Rivera 2009). There were questions to explore the relationship between climate change and the quality and quantity of water from the aquifer, from the point of view of the predictions of a prolonged drought, increases in sea level, and the possibility of more intense hurricanes. We computed the statistical average of each numerical answer obtained per category through the questionnaire and the semi-structured interview. Each question had three to five possible answers from which the person could choose more than one answer, but also had open questions. A frequency analysis designed for quantitative analysis was performed using SPSS software. The data were graphed and classified by percentages, and then the average of the data obtained was tabulated.

As a result of the survey, we want to develop dissemination material to educate the community about the importance of the resource and the repercussions that the depletion of groundwater would have for this region.

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Factors Influencing the Occurrence and the Fate of *E. coli* Population in Karst Hydrosystems

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Abstract

The persistence of *Escherichia coli*, a bacterial indicator of water quality, is relevant to assess the health risk associated with aquifer use for drinking water supplies. In order to investigate the fate of *E. coli* in a karst aquifer, populations of both viable and culturable *E. coli* were monitored, according to their settling velocities, for contrasting hydrological conditions. Solid-phase cytometry was carried out to quantify the viable *E. coli*, and both the genetic diversity and the resistance to antibiotics of *E. coli* were investigated. This study shows that: (i) at the sinkhole, the structure of the *E. coli* population varied with the hydrological conditions and land use; (ii) the input of *E. coli* strains resistant to antibiotics was linked to contamination of human origin during rainfall events; (iii) irrespective of the hydrological conditions, the karst system is a permanent reservoir of viable but non-culturable *E. coli* even when culturable *E. coli* became undetectable at the well; and (iv) following a rainfall event or during a dry period, both populations of culturable and viable but non-culturable *E. coli* are mainly associated with non-settleable particles, corresponding to organic or organo-mineral microflocs.

1 Introduction

Assessment of the microbial quality of the water environment, including the spread of antibiotic-resistant faecal bacteria and their corresponding genes, will be one of the major challenges of the next decades. Such assessment is vital to cope with the expected increase of human population and the related agricultural activities (Bartram and Cairncross 2010; Hales and Corvalan 2006). Among aquatic environments, karst aquifers represent one of the most important freshwater resources: water supplies originating from karst are used by 25% of the global population. In France, this resource supplies water for up to 33% of the population. Karst hydrosystems are complex and original aquifers: they are fissured aquifers, mainly in carbonate rocks, limestone, or dolomite, where surface water disappears in a conical depression named the sink, then flows until it emerges at a natural resurgence (the spring). Usually, drinking water is pumped out at the well through an artificial opening connected directly to the aquifer (Bakalowicz 2005). In the phreatic zone, there is a hydraulic connection through the karst aquifer between the surface water and the groundwater.

Consequently, owing to farming practices or the human use of karst watersheds, karst aquifers are particularly vulnerable to microbial contamination, mainly during rainfall events, which are frequently associated with an increase of turbidity (Bakalowicz 2005; Dussart-Baptista et al. 2003; Fournier et al. 2007; Nnane et al. 2011; Sinclair et al. 2009; Viau et al. 2011). Faecal bacteria such as *Escherichia coli* (*E. coli*), originating from septic tank systems, wild animals or livestock, can be introduced into groundwater by both surface water run-off and soil leaching (Mahler et al. 2000; Muirhead et al. 2006; Page et al. 2012; Pronk et al. 2007). Although *E. coli* is currently considered as a commensal

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bacteria from the intestinal tracts of humans and vertebrate animals (host-associated habitats), water and sediment are now recognised as secondary habitats (open or non-host-associated habitats), to which some strains could have become naturalised (Bergholz et al. 2011; Ishii and Sadowsky 2008; Vital et al. 2008). On the basis of epidemiological studies to link the abundance of *E. coli* to the risk of waterborne outbreaks of gastroenteritis, *E. coli* has been identified as one of the two bacterial indicators of faecal contamination used to monitor the microbiological quality of water, according to the World Health Organisation and European regulation (2006/7/EC). High genetic and phenotypic diversities were observed within the *E. coli* population, which could be divided into seven major phylogroups, to which *Escherichia* clades have been added (Tenaillon et al. 2010; Gordon 2010; Walk et al. 2009). While *E. coli* was the most abundant heterotrophic culturable bacteria in microbiota gut of human and animals, some *E. coli* strains were also important human pathogens (Kaper et al. 2004).

In groundwater, the fate of *E. coli* is mainly dependent on (i) grazing by protozoans, viral lysis, and competition with autochthonous microbial communities and (ii) their ability to overcome environmental stresses such as low temperature under oligotrophic conditions (Rozen and Belkin 2001; Van Elsas et al. 2011). Furthermore, in such environments, some bacteria can survive (viable bacteria including culturable bacteria) although some of them fail to grow on laboratory media (non-culturable bacteria); these bacteria have been designated as viable but non-culturable (VNC) bacteria (Oliver 2010; Trevors 2011). In this physiological state, the VNC bacteria, sometimes designated as latent or dormant cells, could be considered as an adaptive response in order to survive under hostile conditions, and their presence could lead to an underestimation of the pathogens in a water environment (Oliver 2010; Trevors 2011). Today, while the issue of the resuscitation of VNC *E. coli* in the environment, mainly the virulent strains, is still highly debated (Arana et al. 2007; Keep et al. 2006; Özkanca et al. 2009), detecting and counting the total quantity of viable *E. coli* mainly by a cytometry-based method has been to be an appropriate way to follow the presence of these bacteria at very low cell concentrations in water (Vital et al. 2012). However, in drinking water supplies, the monitoring of the total quantity of viable *E. coli*, including putative VNC cells, could be particularly relevant to estimate the return time—i.e. the time required for this aquifer to regain its original level of microbiological quality—following a rainy event.

There is a little understanding of the persistence of viable *E. coli* in karstic aquifers. The survival of *E. coli* in water environments, that is, the time during which bacteria maintain their viability—with or without culturability—has been shown to be greatly influenced by their association with particles (Garcia-Armisen and Servais 2009; Pachepsky and Shelton 2011; Trevors 2011). The percentage values of particle-attached bacteria reported in the literature are highly variable, ranging between 18 and 55% in estuary or river water and reaching 100% in karst aquifers after a storm event (Characklis et al. 2005; Garcia-Armisen and Servais 2009; Krometis et al. 2007; Mahler et al. 2000; Pronk et al. 2007). However, to date, water quality models have been developed on the assumption that 20–44% of *E. coli* are associated with particles in rivers (Jamieson et al. 2005). Indeed, while turbidity has proven to be a valuable proxy for microbial quality of water (Nnane et al. 2011; Viau et al. 2011), estimation of the relative contributions of particle-associated versus free-living *E. coli* still remains a significant parameter for assessing the main processes that govern the transport and fate of these bacteria in aquifers. In karstic aquifers, considering their hydrological properties, the fate of *E. coli* must take account the two main processes which control the particle transfer in this hydrosystem: (i) the direct transfer of particles from the inlet to the outlet of the karstic system (surface origin), and (ii) the re-suspension of previously deposited particles, i.e. mainly the adherent bacteria that settle with larger particles within surface bed sediments (karstic origin) (Dussart-Baptista et al. 2003; Fournier et al. 2007; Massei et al. 2003; Pronk et al. 2007).

The aim of the present study is to identify the main factors influencing the occurrence and the fate of *E. coli* population in a karst hydrosystem. 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^2) which comprises a surficial watershed on the chalk plateau drained by a permanent creek (the Bébec creek). The creek is swallowed by 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 from the spring. The abundance of viable or culturable *E. coli,* depending on their settling velocities, was monitored on the surficial watershed (i.e. the upstream part of the system) and at the spring downstream for contrasting hydrological conditions (dry and wet). In addition, both the genetic diversity—i.e. phylogroups distribution—and the resistance to antibiotics of the *E. coli* population were investigated.

2 Materials and Methods

2.1 Study Site

This study was carried out on a karstic test site of particular importance as a source of drinking water, which was included in an INSU/CNRS (National Institute for Earth Sciences and Astronomy/National Center for Scientific Research, http://www.insu.cnrs.fr/node/3973) national observatory network on karst hydrological systems. The study site is a chalky karst aquifer located in Haute Normandie (France), a rainy Atlantic temperate climate located on the north side of the Seine estuary (Fig. 1). This small rural karst hydrosystem has been extensively studied and its geographical limits and hydraulic connections are well known (Fournier et al. 2007; Massei et al. 2002, 2003). With a production capacity of 4000 m^3 d^{-1}, this aquifer provides drinking water for 2400 inhabitants, after treatment by chlorination. This karstic system is composed of a sink (surface water), a spring and a well (groundwater). The sink is a point of infiltration of Bébec Creek, draining a small watershed of about 10 km^2 of which 95% is classified as agricultural land. The land-use patterns are as follows: approximately 55% cropland, 30% pasture (42 beef cattle, 130 dairy cattle), 10% forest, and the remaining 5% has several other allocations. There were 213 households in the watershed (639 equivalent inhabitants), relying on on-site septic systems. Only 49 septic tanks (147 equivalent inhabitants) were located between 500 and 600 m from the creek. These could contaminate the water by soil leaching only during rainfall events. Moreover, untreated sewage of human origin (four equivalent inhabitants) was located 400 m away from the sampling point and contaminated the creek water by run-off. The elevation of the plateau is about 100 m. Soils on the plateau, consisting of silts approximately 10 m thick, are highly susceptible to crusting, compaction and erosion, particularly during autumn and winter sowing. Discharge in Bébec Creek is variable, from 3 L s^{-1} in summer dry periods to 15 L s^{-1} in winter, and close to 500 L s^{-1} in response to major winter storms, when turbidity can exceed 1000 NTU as a result of soil erosion (Massei et al. 2002). Water from the creek recharges the chalk aquifer via a swallow hole. When the discharge exceeds the infiltration capacity of the swallow hole (saturation), the creek water overflows its banks and floods the valley.

The spring discharging from the foot of a karstified chalk cliff is an overflow of the aquifer resulting from the fine semi-permeable alluvial deposits that cover the chalk in the Seine valley (Fig. 1). The spring is the major outlet for the waters introduced in the swallow hole, with a transit time of

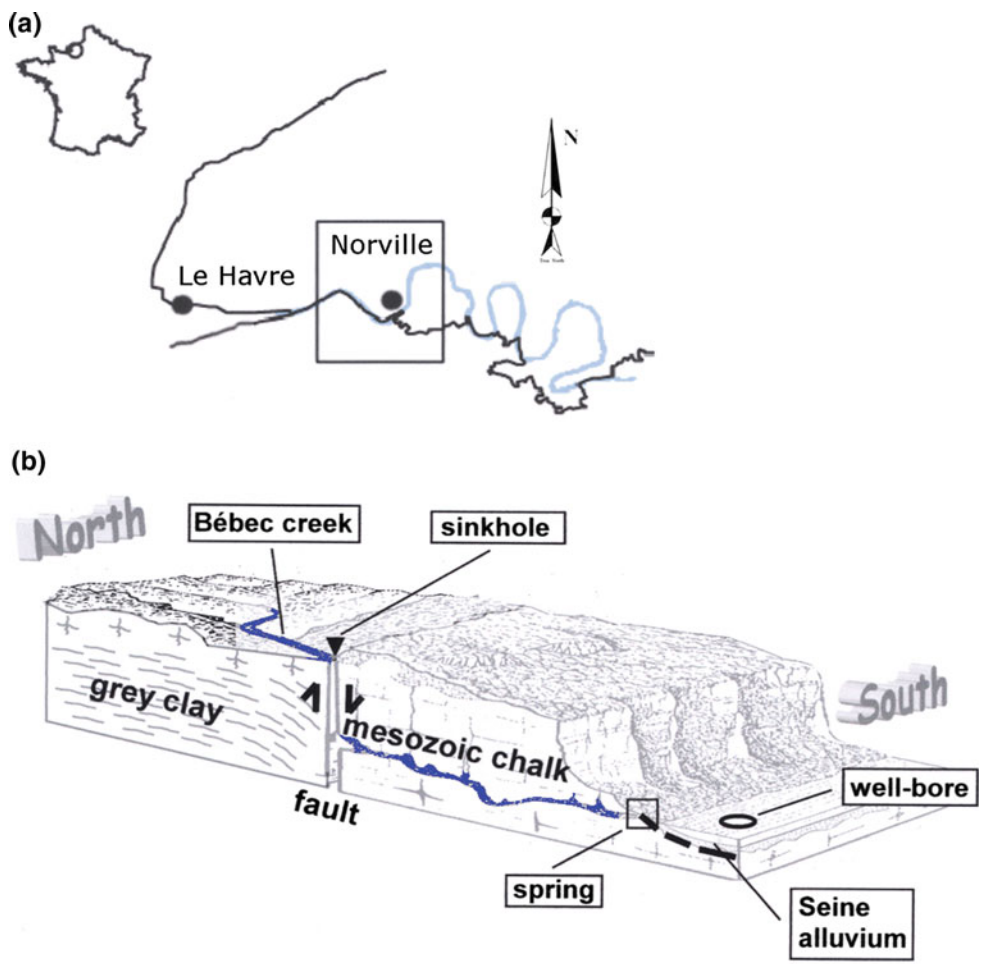

Fig. 1 **a** Location of study site, **b** sampling points on a 3D geomorphologic diagram of the Norville karst/alluvial system

less than a day (Massei et al. 2003). The spring water is, therefore, a mixture of surface water and groundwater. After storms, the turbidity of the water discharging from the spring can exceed 600 NTU, and this water consists of around 60% surface water. Because of the low microbial quality of the water according to the European standards, use of the spring as a drinking water supply was ceased in 1994 in favour of a well located 130 m away in the alluvial plain. The well (located 130 m from the spring) passes through the overlying alluvium and is screened to where it intercepts the chalk (Fig. 1b). During rainfall events, the well water can include as much as 10% rapidly infiltrated surface water, and the turbidity can reach 15 NTU (Fournier et al. 2007). The connections between the well and the spring are more complex than those between the spring and the swallow hole (Massei et al. 2002).

2.2 Materials and Sampling Method

Three sites were sampled, i.e. the sinkhole, the spring, and the well prior to chlorination (Fig. 1), with autosamplers (ISCO 6700) for five contrasting hydrological periods and land use: three campaigns during dry periods: (i) with pasture (May 2007), (ii) without pasture (February 2012) and (iii) in response to a heavy rainfall event (July 2007); and two campaigns during wet periods: (iv) without pasture (February 2007) or (v) following a rainfall event with pasture (March 2008). The sampling strategy at the spring and the well was defined on the basis of the transit time between the inlet (sinkhole) and the outlets (spring and well). Based on previous studies, the delays in spring and well response after recharge at the sinkhole were estimated at +30 h (dry periods) and 15 h (wet periods) at the spring, and +40 h (dry periods) and 20 h (wet periods) at the well, respectively (Fournier et al. 2007). During each sampling period (Table 1), about 1 L of water was collected every hour for 24 h, and about 300 mL of the hourly samples were mixed together in order to obtain a daily averaged sample. Water samples (100 mL) were filtered through pre-weighed Millipore filters (0.45 µm) to determine suspended matter concentrations. All samples were kept at 4 °C until the microbiological analyses were carried out, which occurred within 4 h.

2.3 Particle Settling

A water sample of 600 mL was placed in a separation funnel at room temperature to separate large particles from smaller ones on the basis of settling velocity. The sample was partitioned into three fractions collected through a tap positioned at the bottom of the funnel without sample perturbation. The fraction unable to settle within the 30-min experimentation time, referred to as "non-settleable" in this study, corresponded to the top water of the settling experiment and was mainly composed of particles with settling velocities ranging between 10^{-5} and 10^{-2} mm s^{-1}, with a dominant particle population of 8 µm size. The bottom fraction, referred to as "quickly settleable" in this study, was enriched with the larger particles with settling velocities ranging from 10^{-1} to 1 mm s^{-1}. This fraction was composed of two dominant particulate populations, with peaks in size distribution at 8 and 40 µm.

2.4 Microscopy

The filtered particulate material of each settling fraction was identified by electron microscopy (Au-Pd coating, secondary

Table 1 Hydrological characteristics and land use of the karst watershed for the sampling campaigns

Sampling period	Date	Turbidity NTU		SPM g L^{-1}		Flow rate m^3 s^1		Human input[a]	Head of cattle 172 ± 10 (40 ± 10)[b]	Pluviometry mm	
		Sinkhole	Spring	Sinkhole	Spring	Sinkhole	Spring			Day 1[c]	Day 5[d]
Dry period	03/05/2007	4	NA	0.011	NA	0.005	0.05	+	+ (+)	0	3.8
	16–17/02/2012	21	15	0.025	0.017	0.01	0.06	+	–	0	3.7
Heavy rainfall after a dry period	11/07/2007	33	16.5	0.075	0.025	0.025	0.065	+	+ (+)	50	8.4
Wet period	21/02/2007	15	NA	0.023	NA	0.02	0.075	+	–	2	27.8
Rainfall event during wet period	01/03/2008	105	NA	0.55	NA	0.02	0.045	+	+ (+)	14	17.4

[a]On the watershed (10 km^2) 639 inhabitants, 172 septic tanks for which there was one malfunctioning septic tank located 400 m from the sampling point; [b]for which cattle located at the vicinity of the sampling; [c]pluviometry on day of sampling, [d]cumulated rain 5 days before sampling; *SPM* suspended particulate matter; *NA* not analysed

electron-based method, voltage of 20 kV), and more than two hundred particles were observed. The proportions of particles were estimated by counting organic and mineral particles for 15 different microscopic fields for each particle class.

2.5 Bacterial Dissociation

The enumeration of culturable and viable bacteria and bacterial dissociation of particles were performed on 20 mL of each fraction by sonication for 30 s at 4 °C with an ultrasonic probe (20 kHz, 20 W). These values were obtained from a specific protocol which had been previously designed based on the counts of viable and culturable *E. coli* (see Sects. 2.6 and 2.7) according to the time of the ultrasonic treatment. The analysis of two distinct water samples—the bulk water sample and the corresponding settling fractions (see Sect. 2.3)—was carried out in triplicate for two contrasted water samples: (i) treated effluent from a waste water treatment plant (MES 1.94 mg L^{-1}, mainly organic flocs) and (ii) river water (MES: 16 mg L^{-1}). A control experiment was carried out on an exponential-phase culture of *E. coli* (2.2×10^8 CFU mL^{-1}). This treatment enabled the recovery of 80% of culturable *E. coli*, of which the membranes were undamaged.

2.6 Enumeration of Culturable *E. coli*

Escherichia coli were enumerated in duplicate using membrane filtration methods (0.45 µm HA047 Millipore, Bedford, MA, USA). *E. coli* strains were directly isolated from previously treated water samples with a selective chromogenic medium specific for *E. coli*, with the addition of a selective supplement for water samples (RAPID'*E. coli* 2 Medium and Supplement; Bio-Rad, CA, USA) and incubated for 24 h at 37 °C. To obtain a number of colonies ranging from 5 to 35 with a filter, 10 to 100 mL of water was filtered depending on the hydrological conditions. The threshold value for the enumeration of *E. coli* in water was 5 CFUs 100 mL^{-1}.

2.7 Enumeration of Viable *E. coli*

Water samples were filtered through a 25-mm-diameter 0.4-µm Cycloblack™-coated polyester membrane filter (AES Chemunex). Labelling of viable *E. coli* cells was prepared following the manufacturer's instructions (*E. coli* drinking water AES/Chemunex). *E. coli* cells were labelled with β-D-glucuronide substrate linked with fluorescein, and viable cells were enumerated by solid-phase cytometry (Chem*Scan*® RDI, AES Chemunex, Ivry-sur-Seine, France) as previously described (Lemarchand et al. 2001). The solid-phase cytometer consisted of a laser-scanning unit equipped with a 488-nm argon laser that scans a 25-mm-diameter membrane filter in 3 min. Each fluorescent event was confirmed by using an epifluorescent microscope (Nikon 50I Tokyo, Japan), equipped with an FITC filter block (500-nm dichroic mirror, a 450–490-nm band-pass excitation and a 515-nm cut-off emission filter). Enumeration of viable *E. coli* was performed in duplicate for each sample, VNC *E. coli* was evaluated by calculating the difference between the number of viable *E. coli* and the number of culturable *E. coli* growing on the selective media described above, which was then expressed as a percentage.

2.8 Determination of the *E. coli* Phylogroups

The phylogenetic group to which the *E. coli* isolates belonged was determined by the PCR-based method as proposed by Clermont et al. (2011). The identification of Escherichia clade strains, which are phenotypically undistinguishable from the *E. coli* sensu stricto strains, were performed by PCR as described in Clermont et al. (2011).

2.9 Antibiotic Resistance Testing of *E. coli*

E. coli antibiotic resistances to antibiotics were tested by the agar diffusion method according to the recommendations of the Comité de l'Antibiogramme de la Société Française de Microbiologie (CA-SFM). *E. coli* CIP 7624 (ATCC 25922) was used as a control. The tested antibiotics (17) included the most commonly used in France for the treatments of *E. coli* infections in human and veterinary medicine: amoxicillin (AMX, 25 µg), amoxicillin + clavulanic acid (AMC, 20 + 10 µg), ticarcillin (TIC, 25 µg), ticarcillin + clavulanic acid (TIM, 75 + 10 µg), imipenem (IPM, 30 µg), cefoxitin (CEF, 30 µg), ceftazidime (CAZ, 30 µg), cefotaxime (CTX, 30 µg), gentamycin (GEN, 15 µg), kanamycin (KAN, 30 ui), streptomycin (STR, 10 µg), chloramphenicol (CHL, 30 µg), tetracycline (TET, 30 µg), trimethoprim–sulfamethoxazole (SXT, 23.75 + 1.25 µg), nalidixic acid (NAL, 30 µg), ciprofloxacin (CIP, 30 µg), and chloramphenicol (C, 30 µg).

2.10 Statistical Analysis and Data Transformation

Statistical analyses were performed using R software. The Pearson test was performed to determine whether the numbers of *E. coli* associated with each class of settling particles were significantly different along the karstic aquifer, from the sinkhole to the well.

3 Results and Discussion

3.1 Vulnerability of a Karstic Aquifer to Contamination by *E. coli*

Before the infiltration of surface water into the karst aquifer (Fig. 1b), the Bébec Creek water drained a small, well-known watershed characterised by human pressure combined with pasture. Five campaigns were carried out for contrasting hydrological conditions and land use (Table 1). In order to monitor the occurrence of *E. coli* in the karst aquifer following a rainfall event, the sampling at the sinkhole, the spring and the well takes into account the time of transfer of the water body.

In the karst aquifer, a continual level of contamination by *E. coli* ranging from $(1 \pm 0.5) \text{ x } 10^2$ to $(4 \pm 0.3) \text{ x } 10^4$ was observed. Maximal values were observed following a heavy rainfall event during a dry period with pasture on the watershed. The lowest contamination was observed during dry period in the absence of cattle. In such dry period, it has been demonstrated that more persistent *E. coli* strains better adapted to the water circulate in karst aquifer (Berthe et al. 2013). 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 (Table 2). Once in the karst, as expected, the rapid mixing between ground and surface waters was the main explanation for the decrease in culturable *E. coli* densities previously introduced at the sinkhole, in addition to the disappearance of cells by die-off or grazing (Dussart-Baptista et al. 2003; Rozen and Belkin 2001; Van Elsas et al. 2011). However, no significant decrease of *E. coli* densities was observed from the sinkhole to the spring in the absence of cattle grazing.

Based on the proportion of the B1 phylogroup within the *E. coli* population, a change of the genetic diversity was observed, with the maximal ratio of *E. coli* belonging to the B1 phylogroup in water during dry period and pasture. Nevertheless, no significant change of the proportion of the B1 phylogroup within *E. coli* population occurred from the sinkhole to the spring for the five sampling campaigns. A greater proportion B1 phylogroups was detected here, suggesting the main faecal contamination was of bovine origin. Indeed, it has been demonstrated that the *E. coli* population structure of humans significantly differs from that observed in herbivorous animals such as cows, the B1 phylogroup being more prevalent in the gut microbiota of cows (Carlos et al. 2010). The percentages of *E. coli* isolates

Table 2 Contamination of karst water by *E. coli* for contrasting hydrological conditions and land use[a]

Sampling campaigns		*E. coli*	Sinkhole	Spring	Well
Dry period	With pasture 03/05/07	Culturable CFU 100 mL^{-1}	$(6.2 \pm 0.3) \times 10^2$	$(5.5 \pm 1.1) \times 10^1$	<5
		Antibiotic resistance % (*n*/*N*)[b]	0 (0/45)	5.7 (2/35)	$X < 10$
		Phylogroups B1 (%)	86.7%	77.1%	NA
	Without pasture 16–17/02/2012	Culturable CFU 100 mL^{-1}	$(9.8 \pm 2.2) \times 10^1$	$(5.6 \pm 0.9) \times 10^1$	<5
		Antibiotic resistance % (*n*/*N*)[b]	NA	NA	NA
		Phylogroups B1	7.4%	4.8%	NA
	Heavy rainfall event with pasture 11/07/2007	Culturable CFU 100 mL^{-1}	$(4.0 \pm 0.3) \times 10^4$	$(2.5 \pm 1.1) \times 10^3$	$(9.6 \pm 3.3) \times 10^1$
		Antibiotic resistance % (*n*/*N*)[b]	55.8 (18/34)	35.7 (5/14)	44.8 (13/29)
		Phylogroups B1 %	44%	28.6%	NA
Wet period	Without pasture 21/02/2007	Culturable CFU 100 mL^{-1}	10^2	10^2	<5
		Antibiotic resistance % (*n*/*N*)[b]	0 (0/44)	0 (0/39)	0 (0/28)
		Phylogroups B1 %	39%	41.1%	NA
	Rainfall event[c] with pasture 01/03/2008	Culturable CFU 100 mL^{-1}	$6 \pm 0.3 \times 10^2$	10^2	<5
		Antibiotic resistance % (*n*/*N*)[b]	54% (14/26)	41% (11/27)	30 (7/23)
		Phylogroups B1 %	15%	NA	NA

[a]According to Ratajczak et al. (2010) and Laroche et al. (2010), [b]*N* total number of *E. coli* isolates, *n* number of strain resistant to at least one antibiotic; [c]+6 h after the rain event

resistant to at least one antibiotic were the highest after a rainfall event, with no significant change along the karst aquifer. However, based on microcosm experiments it has been shown that some culturable *E. coli* enabled to persist in water less than two days, and are resistant to most antibiotics (Berthe et al. 2013).

3.2 Change of Structure of *E. coli* Population During a Rainfall Event

To have a better understanding of the variation of the structure of the *E. coli* population in water, Ratajczak et al. (2010) studied in detail the kinetics of the water contamination during a rainfall event after a wet period (March 2008) (Fig. 2). During this rainfall event, the turbidity increased, as the number of *E. coli* did. Thus, before the rainfall event, the level of contamination by *E. coli* was low. Six hours after the rainfall, the *E. coli* density increased up to a maximum value of 720 CFU 100 mL^{-1} and then decreased to a value close to that initially observed (+19 h) (280 CFU 100 mL^{-1}) (Fig. 2). In the most highly contaminated water (+6 h), there was an input of the *E. coli* phylogroup A0 (23%), phylogroups E/D (23%) and *Escherichia* clades (28%), showing a structure of the *E. coli* population that was significantly different from that observed in the less contaminated water 19 h after the rainfall event (χ^2 test $P < 0.001$). Six hours after the rainfall event, the resistance level to one or more antibiotics was significantly highest in the *E. coli* population isolated at the peak of high flow event (Laroche et al. 2010; Ratajczak et al. 2010). Some of these bacteria exhibited resistances to more than three classes of antibiotics, suggesting faecal contamination of human origin resulting from septic tank overflow. These strains were thus

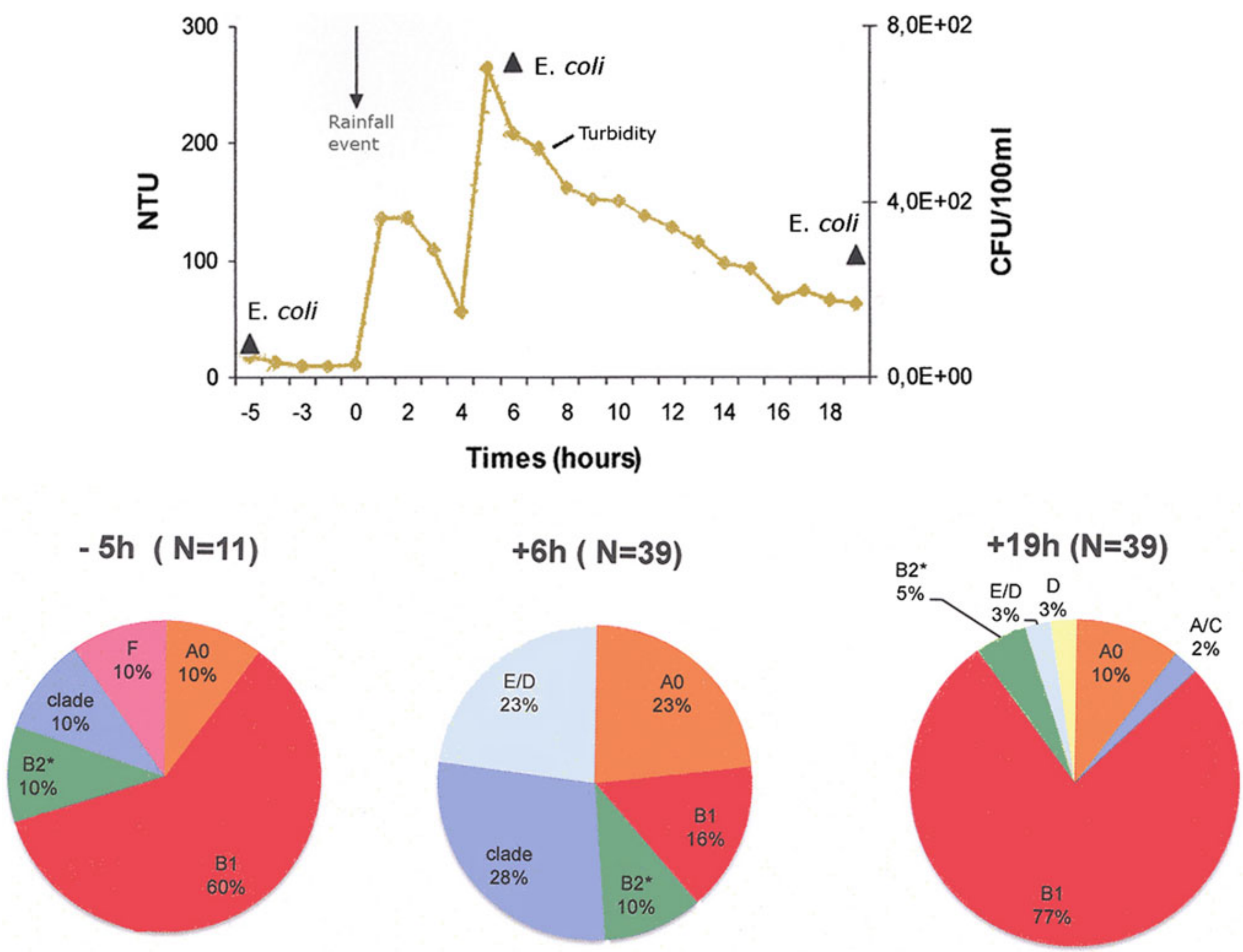

Fig. 2 Change of turbidity (*filled diamond*), density (*filled triangle*) and diversity of *E. coli* population at the sinkhole during a rainfall event following a wet period. The *arrow* indicates the beginning of 14-mm rain event. Diversity assessment of *E. coli* population has been carried out by estimation of the phylogroups distribution according to Clermont et al. (2013)

considered as multiple-resistant strains as defined by Magiorakos et al. (2012).

In contrast, in the less contaminated water (+19 h), *E. coli* B1 strains (77%) became the main *E. coli* phylogroup again. These isolates are mainly *hly* positive (72%), and antibioresistant (AR index = 5%) (amoxicillin, tetracycline, chloramphenicol and ciprofloxacin), suggesting a distant input of *E. coli* of bovine origin resulting from run-off and/or a leaching of the soil. These results showed that during the storm event, an increase in the contamination was accompanied by a change of the structure of the *E. coli* population, reflecting the faecal contamination of the watershed with a high percentage of phylogroup B1 in water contaminated by run-off of pasture land.

3.3 Transport of Culturable and "Viable but Non-culturable" *E. coli* in the Karst Aquifer

Interestingly, irrespective of the hydrological conditions, the prevalence of a population of viable *E. coli* greater than that of the culturable one was always observed, indicating that a population of VNC *E. coli* was always resident in this karst aquifer. Following a rainfall event (sampling campaign 11/07/07), in addition to the high input of culturable *E. coli*, a large proportion of VNC *E. coli* was introduced into the karst. From the sinkhole to the spring, the two sub-populations of viable *E. coli*, culturable and VNC *E. coli* populations, decreased (Fig. 3a). In the dry period (sampling campaign

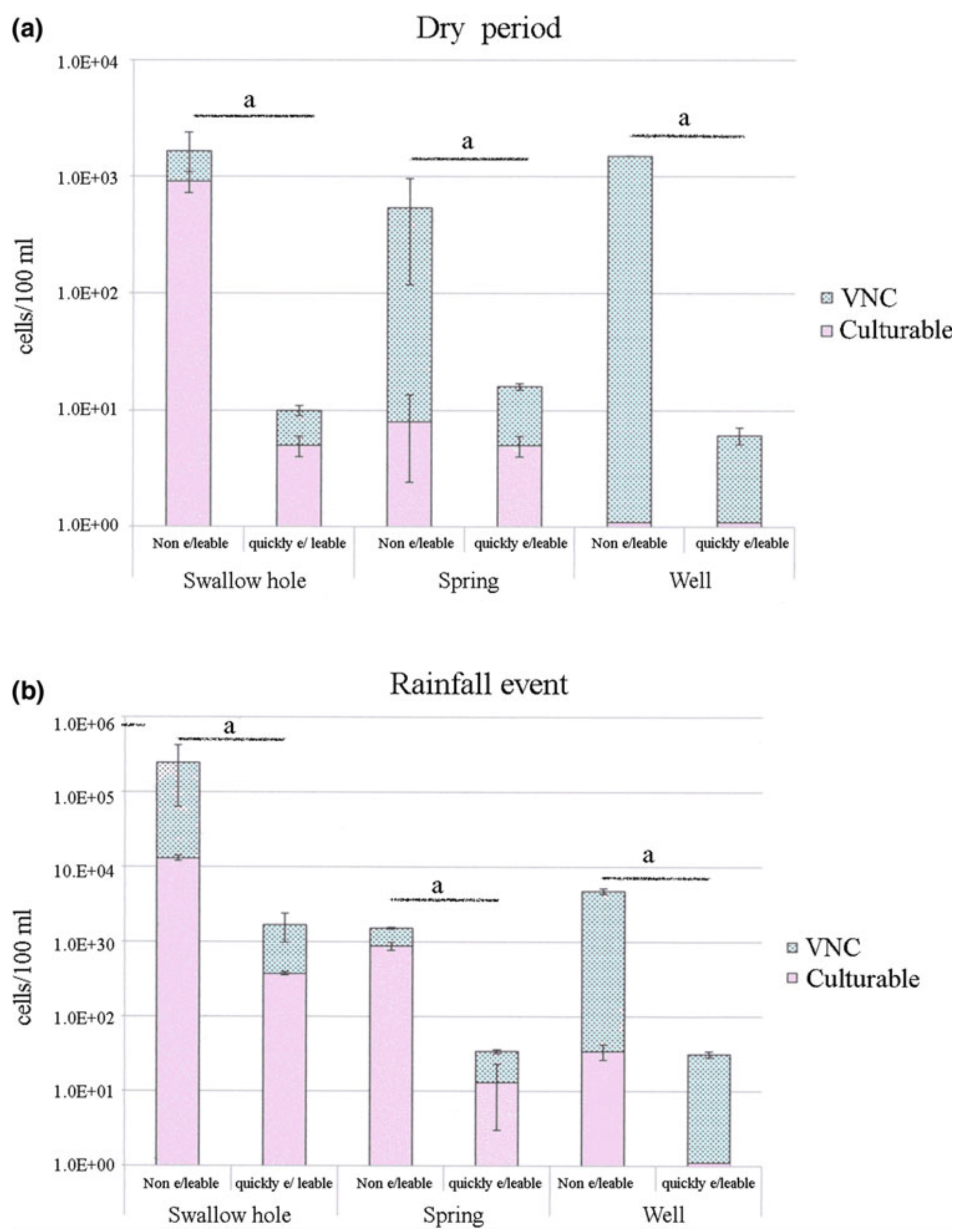

Fig. 3 Transport of culturable and viable but non-culturable *E. coli* related to their settling velocities **a** during dry period and **b** following a rainfall event. **a** *P* value < 0.01 compares VNC *E. coli* associated with non-settleable particles to quickly settleable particles; **b** *P* value < 0.01 compares culturable *E. coli* associated with non-settleable particles to quickly settleable particles

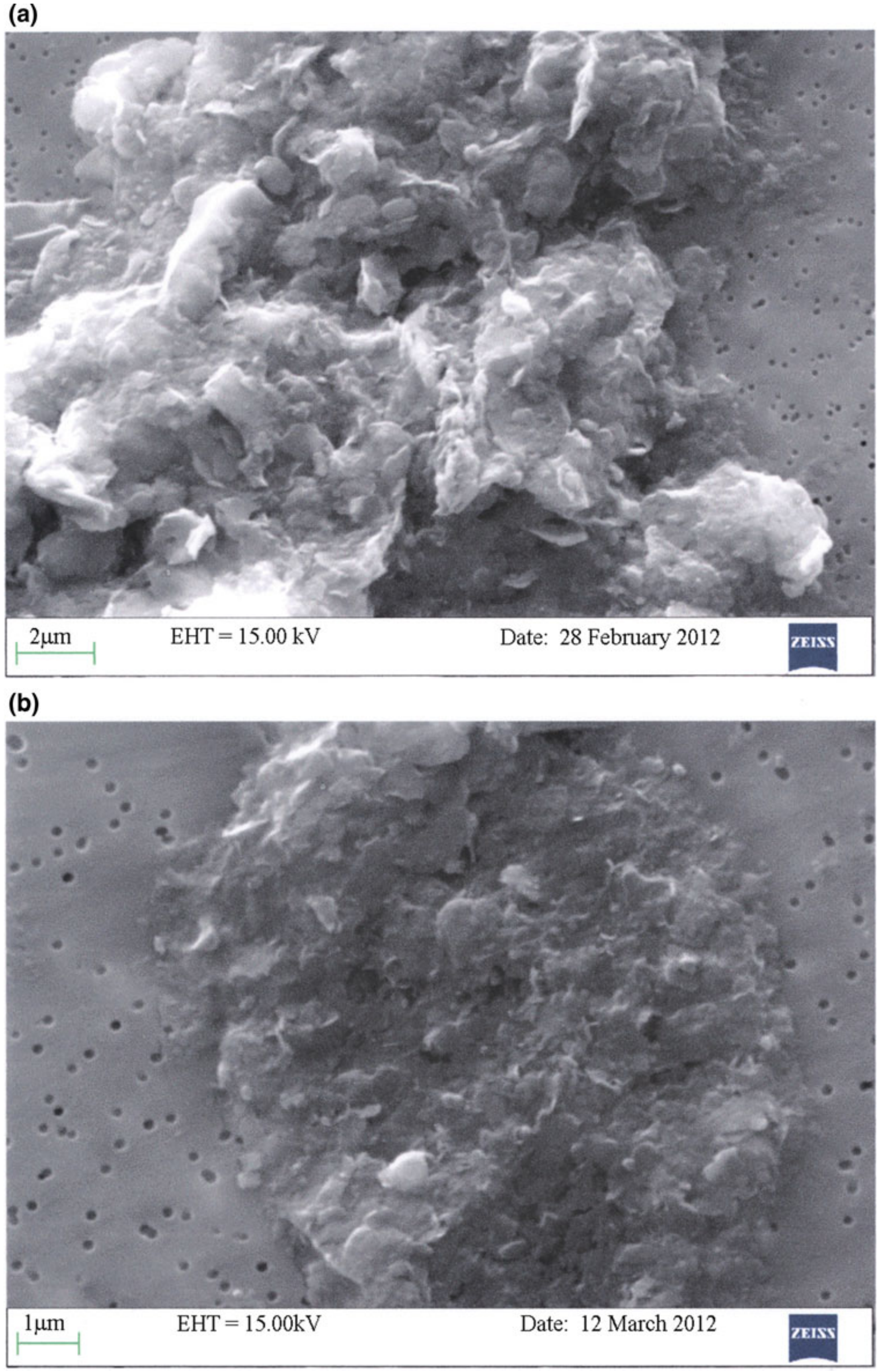

Fig. 4 Scanning electron micrographs of particles of organo-mineral microfloc from "non-settleable particles" fraction with settling velocities between 10^{-5} and 10^{-2} mm s^{-1} (**a**); and of floc dominated by mineral particles from the "quickly settleable particles" with settling velocities between 10^{-1} and 1 mm s^{-1} (**b**)

03/05/07), without an event of contamination by faecal bacteria, the density of culturable *E. coli* decreased in the karst aquifer, until they were not detectable at the well, while the proportion of VNC strains among total viable *E. coli* increased from the sinkhole to the spring. Irrespective of the sampling campaign, when water was pumped out at the well, the VNC *E. coli* were predominant among the viable *E. coli* population (Fig. 3b). As previously described, the occurrence of *E. coli* in the VNC physiological state—corresponding here to bacteria unable to grow on the selective medium used for the enumeration of this bacteria in water—suggests that viable bacteria persist more longer than culturable ones in karst (Rozen and Belkin 2001; Van Elsas et al. 2011). Even if some of these bacteria could correspond to injured cells, here we show that the karst aquifer could be a reservoir of viable *E. coli* even outside a rainfall event.

The monitoring of viable, culturable and VNC *E. coli* was carried out according to their settling velocities *i.e.* according to their association with particles (Fig. 3). For each sample of water, a 30-minute settling experiment in a settling funnel led us to define two classes of particle-associated *E. coli*. Each class was characterised on the basis of its settling velocity combined microscopic analysis (Fig. 4). Following a rainfall event or during a dry period, both populations of culturable and viable but non-culturable *E. coli* are mainly associated with non-settleable particles, corresponding to organic or organo-mineral microflocs (Kruskal–Wallis $P < 0.05$, and with Bonferroni correction $P \leq 0.01$). At the well, in dry period, viable and non-culturable *E. coli* were also mainly associated with “non-settleable” particles. Culturable *E. coli* could not be detected at the well, while an increase of VNC *E. coli* associated with both “non-settleable” and “quickly settleable” fractions was observed, suggesting that when water was pumped out, an input of VNC bacteria associated with each class of settling particles occurred. These results are consistent with those previously described by estimating the fraction of free-phase and particle-associated organisms using filtration techniques, which demonstrated that a substantial fraction of bacteria are associated with particles circulating in the karst hydrosystem (Mahler et al. 2000). As previously reported in a similar aquifer by Pronk et al. (2006), this *E. coli* population, associated with the “non-settleable” particles corresponds to organic or organo-mineral microflocs, probably originated from the leaching of bacteria by surface run-off associated with aggregates or colloids originating from cowpats (Muirhead et al. 2006; Soupir et al. 2010).

4 Conclusions

- The abundance of culturable *E. coli* in the studied 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 (pasture).
- 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.
- At the sinkhole, the structure of the *E. coli* population in water—i.e. the distribution of phylogroups—varied with the hydrological conditions and the land use, with a higher proportion of B1 phylogroup of bovine origin during pasture.
- The input of *E. coli* strain resistant to more than three classes of antibiotics (i.e. a multiple antibiotic-resistant strain) was linked to contamination of human origin during a rainfall event.
- Irrespective of the hydrological conditions, the karst system is 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 periods.
- Following a rainfall event or during a dry period, both populations of culturable and viable but non-culturable *E. coli* are mainly associated with non-settleable particles, corresponding to organic or organo-mineral microflocs.

In 2015, the main conclusions drawn regarding the karst aquifer and rivers were reported to the stakeholders and to the French ministry of health, to enable assessment of the microbiological risk due to the spread of antibiotic-resistant bacteria, according to the DPSIR (Driving forces—Pressure-State-Impact-Response) concept.

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Spatiotemporal Assessment of CVOC Contamination in Karst Groundwater Sources and Exposure at Tap Water Point of Use

Vilda L. Rivera, Ingrid Y. Padilla, and Norma I. Torres

Abstract

Extensive historical contamination poses a potential threat to karst aquifer systems. Karst terrains are characterized by well-developed conduit porosity and highly transmissive zones. These characteristics make the karst aquifers highly productive but also highly vulnerable to contamination. As an important freshwater resource, groundwater systems in karst areas pose significant risk for exposure and lead to potential public health impacts. Of particular concern is the pollution with chlorinated volatile organic compounds (CVOCs) because they are ubiquitous in the environment and have been identified as potential precursors of preterm birth complications. The study aims at determining the link between contamination at karst groundwater source and pollution at the tap water point of use. GIS technology and statistical methods are used 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 the presence of CVOC in groundwater and tap water. 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 tendency in tap water. Spatiotemporal analysis suggests the pollution comes from multiple sources and extends beyond the demarked sites. Future work will assess additional sources of tap water contamination.

1 Extended Abstract

Well-developed conduit porosity and highly transmissive zones characterize karst terrains. These characteristics make karst aquifers highly productive but also highly vulnerable to contamination (Göppert and Goldscheider 2008; Green et al. 2006). This is indeed the case for the karst aquifer system of northern Puerto Rico. This system has been subjected to a long history of toxic spills, chemical waste and industrial solvent release into the subsurface (Hunter and Arbona 1995; Padilla et al. 2011; Padilla et al. 2015; Yu et al. 2015) that have caused the inclusion of 12 superfund sites and several Resource Conservation and Recovery Act Corrective Actions (RCRA CA) since 1984 (Fig. 1).

As an important freshwater resource, groundwater systems in karst areas pose significant risk for exposure. It is often assumed that the chemical contamination of groundwater resources used for drinking water purposes translates to similar levels of chemical contaminant exposure at the tap water point of use. Of particular concern is the pollution with chlorinated volatile organic compounds (CVOCs) because of their ubiquitous presence in the environment and the potential health impacts. CVOCs are commonly used as solvents, degreasing agents and a variety of commercial

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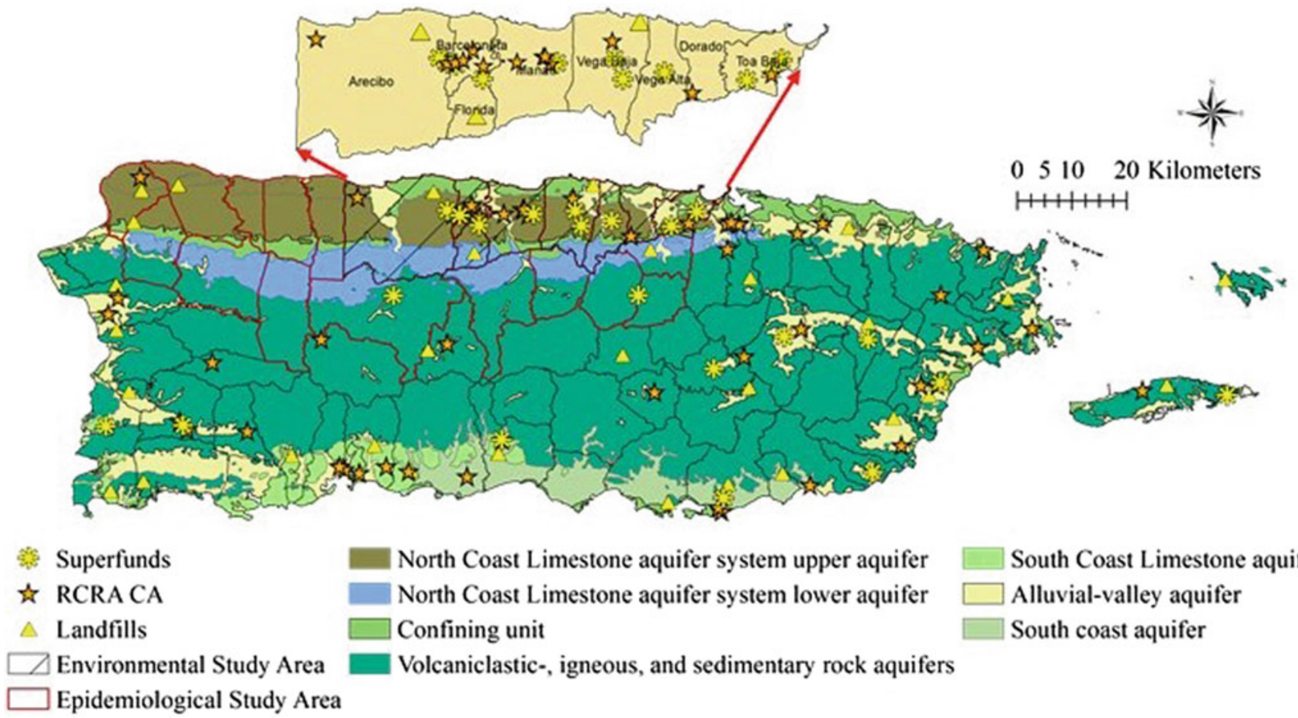

Fig. 1 Hydrogeology, landfills, superfunds and RCRA CA sites in the study area within the northern karst region of Puerto Rico

Fig. 2 Total CVOC detection frequency for: **a** groundwater and **b** tap water samples

products (Huang et al. 2014). They enter the environment through accidental spills and poor disposal practices. Toxicological studies suggest potential associations with cancer (Huang et al. 2014) and adverse reproductive outcomes (Meeker et al. 2009; Nieuwenhuijsen et al. 2000).

This study assesses potential associations between CVOC contamination of groundwater in the aquifers of the northern karst system of Puerto Rico and that at the tap water point of use. The northern karst region contains two of the most extensive and productive aquifers in Puerto Rico (Lugo et al. 2001). The karst system contains three major hydrogeological units (Fig. 1): the upper aquifer, which is mainly composed of the Aymamon and Aguada Limestone Members; the lower aquifer that consists of the Montebello Limestone and the Lares Formation; and the confining unit, the Cibao Formation, that separates the upper and the lower aquifers. The upper aquifer is unconfined and linked to the surface throughout most of its outcrop area. The lower aquifer is confined towards the coastal region and is recharged through its outcrop to the south of the shallow aquifer, and the confining unit separates the aquifers (Renken et al. 2002). The aquifers have higher vulnerability to contamination through the outcrop areas where they are directly exposed to the surface.

GIS technology and statistical methods are applied to perform spatiotemporal analysis of the collected data. The analysis incorporates historical data gathered from water quality reports in regulatory agencies, and current groundwater and tap water samples collected from residential homes. Current groundwater data are collected from springs and industrial, residential, agricultural and public supply wells two to three times a year. The collection of groundwater samples follows a modified USGS sampling method (Koterba et al. 1995). The tap water data are collected throughout the year from the homes of pregnant human cohort participants in the PROTECT Centre (Cordero et al. 2012). Coordination and collection of tap water samples follows Institutional Review Board (IRB) protocols. The preparation and collection of samples follow a modified method from the Illinois Environmental Protection Agency (IEPA 2009). CVOC extraction and analysis follow a modified EPA 55101 Method (Cotto 2015; Munch and Hautman 1995).

Results show extensive presence of CVOC in groundwater and tap water (Fig. 2). Several CVOCs, including carbon tetrachloride (CCl_4), tetrachloroethene (PCE) and trichloroethene (TCE), are found at higher frequencies and

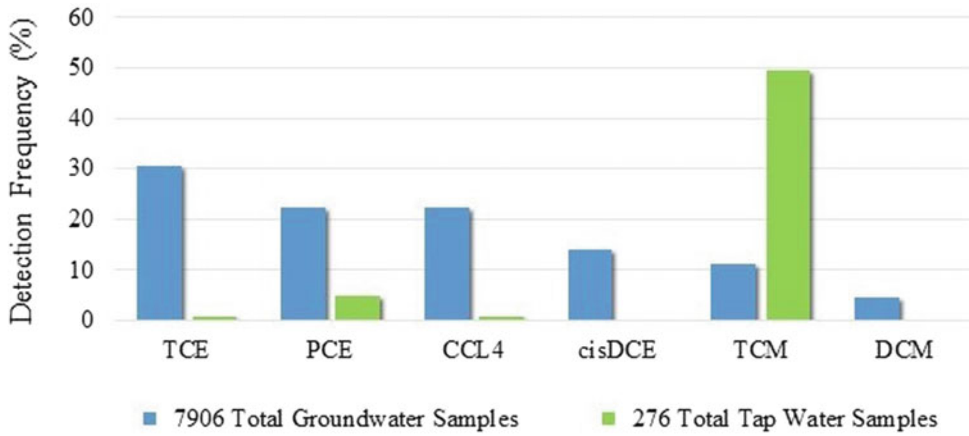

Fig. 3 Detection frequency per contaminant for groundwater and tap water samples

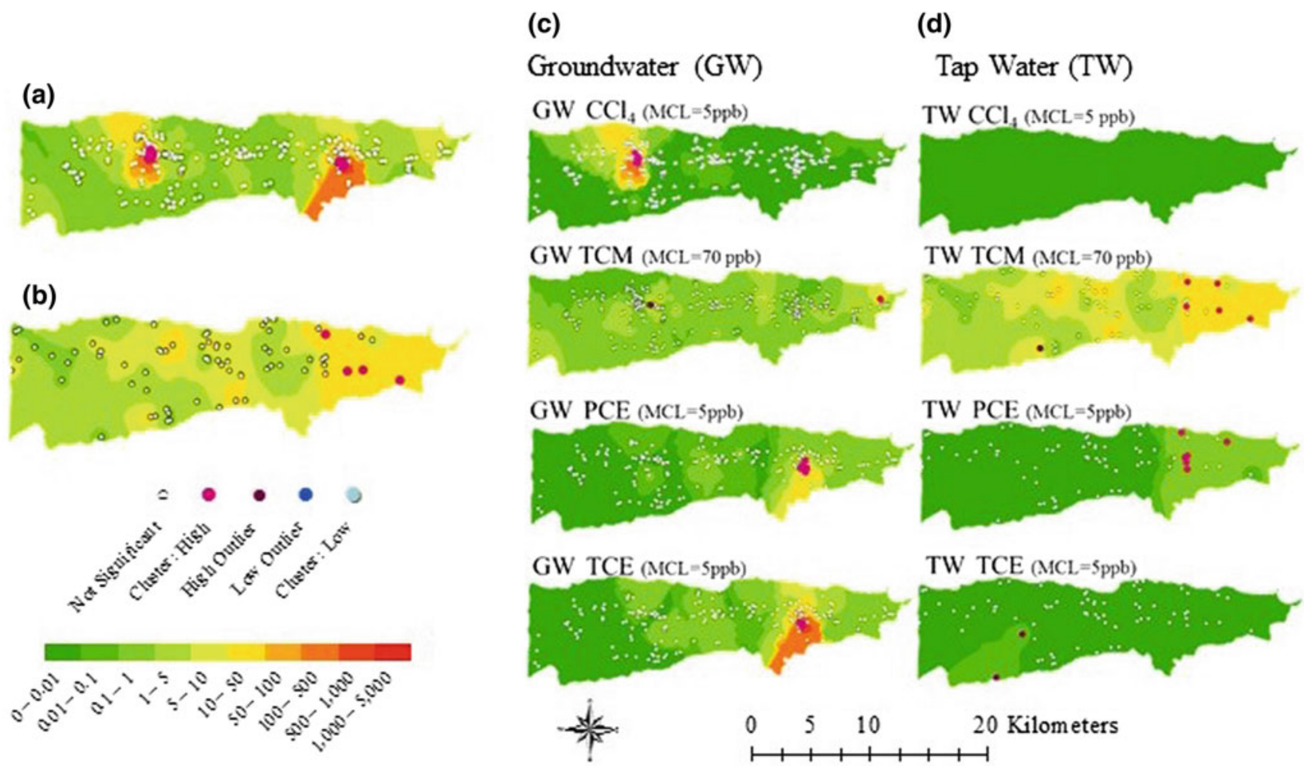

Fig. 4 Spatial distribution of average concentrations for: **a** total CVOC in groundwater, **b** total CVOC in tap water, **c** principal CVOC contaminants in groundwater and **d** principal CVOC contaminants in tap water

concentrations in groundwater than tap water (Fig. 3). Trichloromethane (TCM) is, however, found at higher frequencies and concentrations in tap water than groundwater (Fig. 3). Spatially, contamination is found throughout the study area, with some hot spot clusters in certain regions (Fig. 4). Temporal analysis shows a decreasing concentration trend for CVOC in groundwater (Fig. 5a). TCM temporal distribution shows an increasing concentration trend in

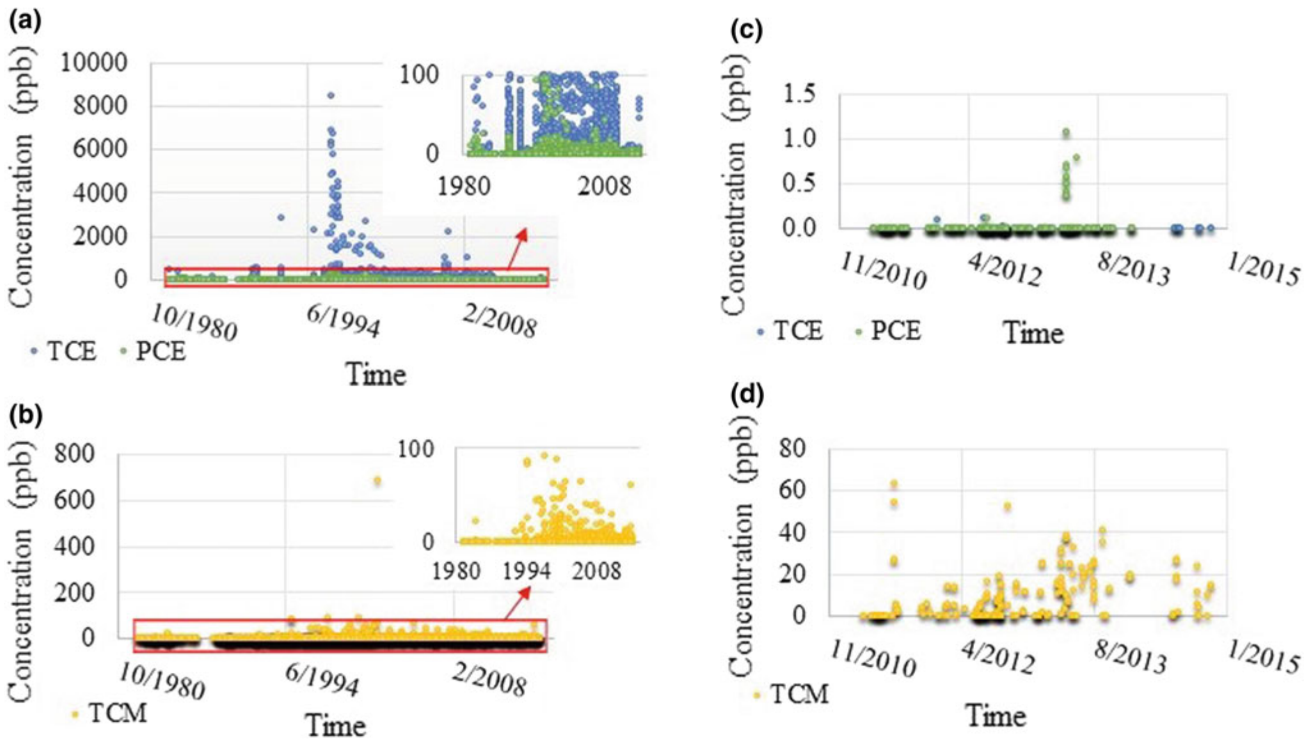

Fig. 5 Temporal distribution of **a** TCE and PCE in groundwater, **b** TCM in groundwater, **c** TCE and PCE in tap water and **d** TCM in tap water

both groundwater (Fig. 5b) and tap water (Fig. 5d) samples. 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.

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Potential Exposure of Emerging Contaminants in Tap water from Karst Groundwater Sources

Norma I. Torres, Ingrid Y. Padilla, and Vilda L. Rivera

Abstract

Karst aquifers are the most productive groundwater supplies on Earth, providing 20–25% of the global population water needs. In Puerto Rico, groundwater provides a significant source of drinking water (52%). The northern karst system of Puerto Rico is very susceptible to contamination, serving as route of exposure to human and wildlife in the region. Previous studies of groundwater in that region have shown significant distribution of different contaminants beyond demarked sources of contamination, some of them related to long-lasting health problems. This work develops a spatio-temporal distribution of phthalate contamination in groundwater and tap water in the northern karst region of Puerto Rico and determines the statistical correlation between different factors and phthalate contamination. Geographic Information System (GIS) technologies and statistical models are applied to attain these objectives. Results show that there is an extensive contamination with phthalates in tap water and groundwater samples. Phthalates were detected in 53% of the tap water samples and 6.84% of the groundwater samples. They were detected as mixture components in areas of high urban and industrial development. Results from the statistical models show that the presence of phthalates in groundwater is significantly related to hydraulic conductivity of the aquifers and time. The analysis suggests that land use could be an additional source of contamination to tap water. The extensive spatio-temporal contamination of groundwater suggests that contaminants can persist in the environment for long periods of time and that hydrogeological factors are important factors contributing to the presence of phthalates in karst systems.

1 Extended Abstract

Karst aquifers represent about 20% of the planet's dry, ice-free land (Ford and Williams 2007). They are characterized by conduit porosity and high permeability (Bakalowicz 2005), rapid hydraulic responses, and fast groundwater flow and transport in conduits (Green et al. 2006). Those characteristics make karst aquifers highly productive, providing 20–25% of the global population water needs. In the USA, karst aquifers underlie 20% of the continent and provide over 40% of the groundwater used for drinking water purposes (Veni et al. 2001). The same features that make karst groundwater highly productive also make it highly vulnerable to contamination (Göppert and Goldscheider 2008). These systems impart an enormous capacity to store and convey contaminants from sources to potential exposure zones and can serve as an important route for contaminant exposure to human and wildlife (Padilla et al. 2011).

The Northern Karst Aquifer System (NKAS) of Puerto Rico (Fig. 1) contains the most extensive and productive aquifers, comprising 19% of the island (Lugo et al. 2001; Veve and Taggart 1996). This aquifer system provides important freshwater resources for industrial, domestic, and agricultural purposes (Molina-Rivera 2009) and contributes

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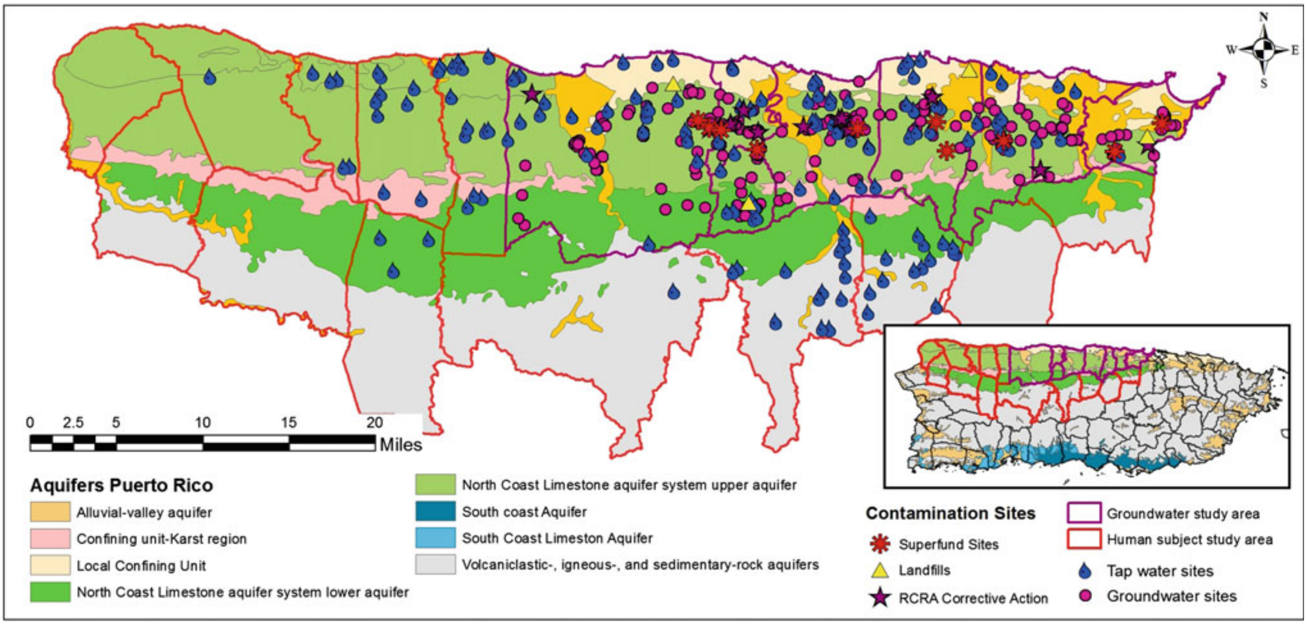

Fig. 1 Location of the study area in the NKAS, including potential sources of contamination, groundwater and tap water sites

to the ecological integrity of the region (Padilla et al. 2011). Strong connections between surface and subsurface features associated with sinkholes, sinking streams, caves, conduits, and springs allows for easy entry of pollutants into the aquifers, making them highly susceptible to contamination. Industrial, population, and urban development in the region has resulted in a long history of toxic spills, chemical waste, and industrial solvent release into the subsurface (US EPA 2011; Hunter and Arbona 1995; Zack et al. 1987). Significant contaminant releases have caused the inclusion of 12 Superfund Sites and 13 RCRA Corrective Action Sites in the area (Fig. 1). Previous studies in the karst region of northern Puerto Rico have shown significant presence of phthalates and other contaminants in groundwater beyond the sources of contamination for long periods of time (Padilla et al. 2011; Irizarry 2014).

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. Phthalates are contained in commonly used products, including plastics, food packaging, home furnishings, paints, clothing, medical devices, cosmetic products, perfumes, building materials, adhesives, and children's toys (NIH 2006; Zeman et al. 2013). Many of these contaminants are known endocrine disruptors and have been recently associated with decreased gestation length (Latini et al. 2003; Meeker et al. 2009), reproductive and neurological damage, and other adverse reproductive outcomes (CERHR 2006). Potential environmental exposure by inhalation (perfumes), dermal adsorption (cosmetic products), or ingestion (fatty foods and tap water) (Heudorf et al. 2007) occurs when phthalates are released from products.

This work develops the spatio-temporal distribution of phthalate contaminants in groundwater and tap water in the NKAS region, and assesses potential correlations between hydrogeological and anthropogenic factors and phthalate contamination. The study is conducted within two areas: the groundwater contamination assessment (GCA) and the epidemiologic study areas (Fig. 1). The GCA study area comprises a smaller subset of the epidemiological study area, where the tap water assessment is conducted. The methodology includes the collection of water quality data of DEP, DBP, and DEHP from historical records and a current groundwater and tap water sampling campaign conducted under the PROTECT Center (Cordero et al. 2012), and spatial, temporal, and statistical analysis of the results. The historical groundwater data include records from different agencies (Irizarry 2014) from 1981 to 2013. The current sampling campaign includes groundwater samples collected 2 or 3 times per year since 2011. Tap water samples are collected from houses of PROTECT recruited participants, following IRB protocols. Groundwater and tap water samples are extracted and analyzed following US EPA methods 3510C and 8270D (Cotto 2015).

Spatial analyses of the data are performed using Geographic Information System technologies and include development and application of spatial distributions of phthalate detections and concentrations, land use, and hydrogeological analysis, among others. Land use maps were obtained from

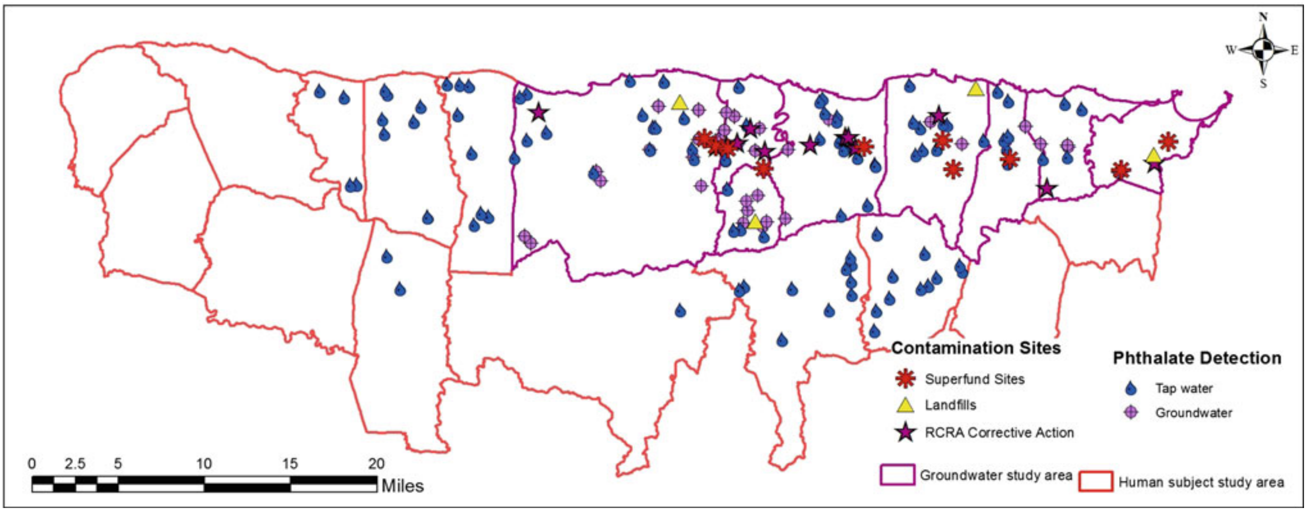

Fig. 2 Phthalates detection in tap water and groundwater samples in the study area

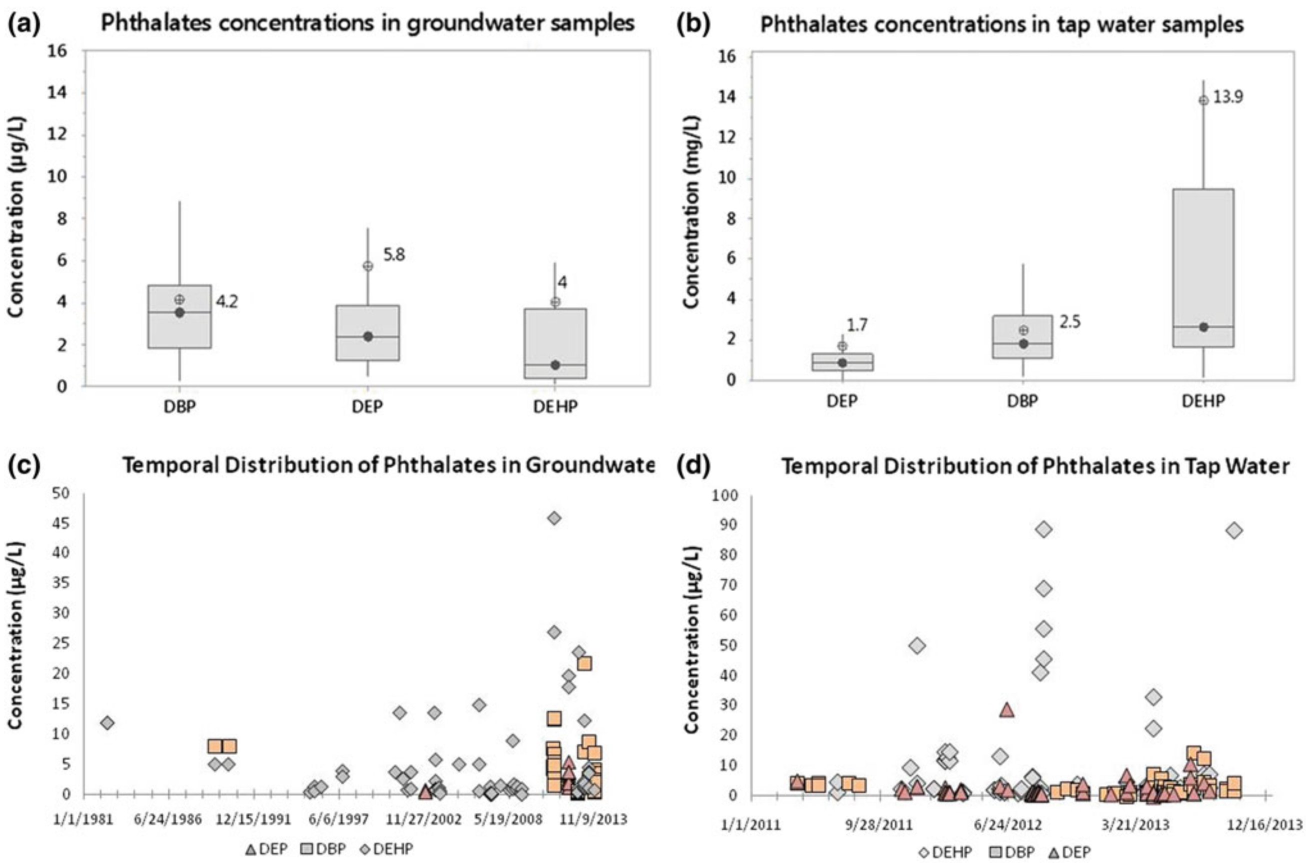

Fig. 3 Box plot of phthalate concentrations in groundwater (**a**) and tap water (**b**) samples. Temporal distribution of groundwater (**c**) and tap water (**d**) phthalate concentrations

the Graduate School of Planning of the UPR (EGP 2014). Hydrogeological data used for the analysis include hydraulic conductivities (obtained from Renken et al. 2002) and sinkhole density (obtained from Giusti 1978). Statistical analyses of the data applied detection frequencies, simple descriptive statistics, and logistic regression models to assess

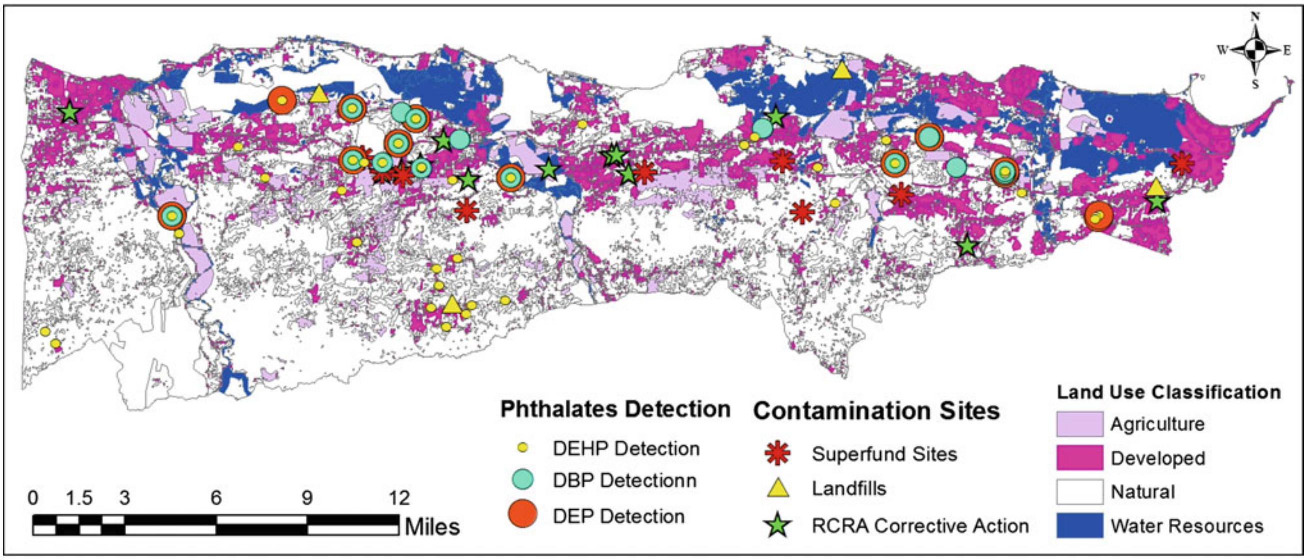

Fig. 4 Detection of phthalates in groundwater and land use in the study area

the potential correlation between phthalate contamination and hydrogeological and anthropogenic factors.

Results show extensive phthalate contamination in groundwater and tap water samples that vary in space and time (Fig. 2). Overall, phthalates are detected in 7% (n = 2004) and 53% (n = 331) of the groundwater and tap water sites, respectively. DEHP is the most detected phthalate and is present in 4% of the groundwater samples and 26% of the tap water samples. Box plots of phthalate concentrations in groundwater and tap water samples (Fig. 3) show that concentrations for DBP and DEP tend to be higher in groundwater, but concentrations for DEHP are higher for tap water sources. Although groundwater serves as a route of contamination to tap water sources, higher detection of phthalates in tap water (53%) than groundwater (7%) indicates additional sources of contamination in the water distribution system that may be related to land use. The temporal assessment shows a slight increase of DEHP concentrations with time in groundwater and tap water (Fig. 3c and d).

Spatial analysis indicates that phthalates in groundwater are detected as a mixture of components in areas of high urban and industrial development (61% of the sites) (Fig. 4). Statistical models suggest that time and high hydraulic conductivities were statistically significant variables in the detection of phthalates. The analysis also suggests that phthalates persist for long periods of time and that hydrogeological factors significantly contribute to their presence in karst systems than anthropogenic factors. The large temporal and spatial distribution of phthalates in groundwater and tap water sources in karst regions, thus, poses significant risk of exposure to humans and wildlife in the area.

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Part V

Risk Assessment and Regulatory Issues

On the Implementation of Environmental Indices in Karst

Marianna Mazzei and Mario Parise

Abstract

Peculiarity of karst environment, related to a number of specific geologic and hydrologic features, makes it a unique setting on Earth, characterized by high fragility and vulnerability 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 contributes to highlight to stakeholders, land managers, and people living in karst the fragility of such environment, and the need to safeguard it and the natural resources therein contained, first and foremost the groundwater. In this chapter, 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.

1 Extended Abstract

A peculiarity 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 (Gutierrez et al. 2014; Parise 2015) and to a variety of anthropogenic disturbances. Even though such features have been well recognized for a long time, only in recent years efforts have been produced to develop approaches and methods specifically dedicated to karst. Using these approaches represents a mandatory step in the management of karst terranes, contributing to highlight to stakeholders, land managers, and people living therein the fragility of this environment and the need to safeguard the natural resources it contains. The main features of karst are as follows: lack or scarce presence of surface water; presence of an underground world (caves); and no correspondence between topographic divides at the surface and hydrogeological watersheds. Without taking into account such elements, knowledge of karst is bound to be incomplete, and wrong approaches and methods are likely to be applied, with high possibility of obtaining wrong and erroneous results.

The methods so far proposed, dedicated to karst environments, can be broadly ranked into different groups, based upon the scale of application: national, regional, local, and site (cave)-specific.

At the national scale, the Karst Disturbance Index (KDI), introduced by van Beynen and Townsend in 2005 to assess the disturbance produced by man to the natural karst environment, was one of the first approaches dedicated to karst. It analyzes disturbance by means of an evaluation of the negative effects caused by anthropogenic changes, taking into account a number of indicators, subdivided into five categories. KDI shows that knowledge of the main features of karst, encompassing many different fields and disciplines of interest, is fundamental for a proper understanding of the changes occurring and for linking such changes to specific

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actions by man or to variability of other factors, including climate change. The initial proposal was slightly revised by North et al. (2009), and a quite high number of applications in different karst areas worldwide have been implemented so far (Calò and Parise 2006; van Beynen et al. 2007; De Waele 2009; Day et al. 2011; van Beynen and Bialkowska-Jelinska 2012; Kovarik and van Beynen 2015).

The Karst Sustainability Index (van Beynen et al. 2012) is a standardized metric of sustainable development practices, introducing for the first time in karst the concept of environmental sustainability. The domains taken into account are social equity, environmental values, and economic development. Each possesses a subset of indicators and target levels that determine progress toward sustainability. Benchmarking the current state of karst environments allows the comparison of sustainability practices temporally and spatially to highlight areas where remedial policies or actions are needed.

Some approaches (as that by Angulo et al. 2013) are aimed at emphasizing the value of the karst landscape in protected areas and at analyzing their current state of degradation or conservation. Identifying sectors in the territory with different levels of disturbance and significance may help to facilitate plans for land use and management and to guide research programs. The method uses a zonal differentiation of the land which permits to compare its results with the Land Use Maps established in the Master Plans of karst-protected areas, to reveal different areas particularly disturbed or significant, and therefore with different management needs. The interest in evaluation of karst-protected areas is also shown by further works, covering such issues in different karst areas of the world (Day 2011; Day et al. 2011).

Moving at a local scale, as that of the single cave, more detailed analyses need to be performed. A Cave Conservation Index (CCI) has been proposed by Ramos Donato et al. (2014) and applied for evaluating a set of caves in Sergipe State, Brazil. The method (divided into the stages of environmental impact and pressure analysis, vulnerability analysis of the cave, and comparison of results) is an attempt to put together parameters inside the cave with those of the surrounding environment, aimed at providing suggestions for developing environmental management plans at the municipality level.

Show caves are natural heritage features, for a long time exploited as sites opened to the public and in many cases becoming a significant source of income for the local economy (Parise and Valdes Suarez 2005; Parise 2011; Šebela and Turk 2014; Ravbar and Sebela 2015). They were the first to be the object of attempts in defining the impact of tourists on the environment, and the possible damage, or disturbance they caused (Cigna and Forti 1988). A first evaluation was obtained through the definition of the visitor capacity, defined as “that flow of visitors into a defined cave that confines the changes in its main environmental parameters within the natural ranges of their fluctuation” (Cigna 1993). Pani and Cigna (2013) defined the Cave Disturbance Index to evaluate the level of disturbance of an already existing or potentially developable show cave, aimed at providing organizations and communities with an opportunity to holistically analyze their caves in a systematic and standardized manner, thus forcing them to consider threats that they may have not previously taken into account.

This brief summary of the main approaches proposed for karst environments highlights that karst requires specific approaches and dedicated efforts. In this direction, definition and implementation of indices in karst represent important initial steps. However, there are many difficulties related to availability and/or collection of data, as well as problems with data quality, and when comparing data from different sources and at different times. Typically, when applying an index, a snapshot of the situation in that specific moment can be drawn, but it would be much more useful to follow the evolution of the index through time and to link its changes to natural and/or anthropogenic activities. Beside improving our understanding about karst, further efforts are eventually needed to transfer our knowledge to stakeholders, land managers, authorities, and the local population, to create a social awareness of the environment where they live. As a matter of fact, the social and environmental consequences of disasters are strongly increasing and cause high costs to society. Involvement of stakeholders and population in strategies to manage the impacts, aimed at protecting karst aquifers and the remarkable and valuable character of biodiversity in karst, have therefore become mandatory.

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Fitting Regulatory Square Pegs into Round Holes: Local Land Use Regulation in Karst Terrain

Jesse J. Richardson Jr.

Abstract

The variability of conditions that characterize karst terrain presents unique regulatory issues for local governments in the USA. Under our federalist system of governance, states hold the lion's share of authority to regulate. However, states have not generally regulated karst, leaving the local governments to address karst issues through land use regulation. The standard land use tools fail to properly address the variability of karst conditions, however. Properly regulating karst likely entails a case-by-case approach, frowned upon by the law. Local governments rely mainly on buffer areas, performance standards, and required geophysical investigations to regulate karst areas. While buffer areas form a familiar type of regulation that will be upheld by the courts, the tool fails to take into the reality of karst. Performance standards meet legal requirements and can properly conserve karst areas but are difficult to draft. While required geophysical investigations respect the science of karst and effectively provide protection, the tool will likely fail legal challenges. Non-regulatory approaches can complement regulations or replace regulations in some areas. Conservation easements, purchase of development rights programs, low impact development, and conservation subdivision design are major non-regulatory approaches to address karst concerns. All of these tools can be effectively employed in karst, but their voluntary nature limits the scope of implementation. By combining modified land use tools and non-regulatory approaches, local governments can better address karst issues, but new models will need to be created to fully address karst concerns. For the present, local governments can use overlay zones, conditional use permits, and performance standards to address karst concerns. Ideally, however, state governments must step in, utilizing their broad regulatory authority to protect karst resources. Puerto Rico's statutory protections provide a good example for other states, but more resources are required to implement the provisions in Puerto Rico and across the country. Education of key stakeholders can build support for karst protection and encourage more resources for implementation.

1 Introduction

Human interactions with karst landscapes pose unique risks that do not appear with other types of landscapes. Most prominently, development on karst may cause subsidence (Kemmerly 1981; Newton 1984), groundwater contamination (Smith and Vance 1997; Panno et al. 1997), and flooding (Smith and Vance 1997). Regulation of non-karst landscapes, although far from simple, has evolved into a fairly consistent system of controls in the USA. Importantly, these standard forms of regulation have passed the test of legal challenges. These land use controls are fairly uniform across the nation.

Regulation of karst landscapes, on the other hand, fails to conform to the norms of existing land use regulations. Each karst parcel proves to be very different. The uniqueness of each karst parcel calls for a parcel-by-parcel approach that

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tailors regulation to each situation. However, legal regimes for land use regulation consist of uniform approaches that apply generally.

This disconnection between the uniformity demanded by legal restraints and the flexibility demanded by the hydrogeologic realities of karst raises complex questions of how to develop land use regulation for karst terrain that both meets the legal requirement of a general framework and adequately protects the fragile ecosystems that exist in karst. This paper explores these questions and proposes regulatory and non-regulatory solutions, while failing to find a panacea.

Section 2 describes the allocation of regulatory authority in the federalist system of governance in the USA and the standard land use regulatory approaches in non-karst terrains. Section 3 explains why these approaches fail to adequately address the unique issues present in karst areas. Section 4 proposes regulatory approaches that better address these issues, while Sect. 5 explores a handful of non-regulatory tools that offer promising approaches. Finally, Sect. 6 summarizes and concludes the discussion.

2 Land Use Regulations in the USA

2.1 The Federalist System of Governance in the USA

The USA uses a federalist system of shared governance where the federal, state, and local governments each assume different roles. The first allocation of authority addresses the federal and state governments. The Tenth Amendment of *United States Constitution* provides, in part, that "[t]he powers not delegated to the United States by the Constitution, nor prohibited by it to the States, are reserved to the States respectively, or to the people." This provision limits the federal government to authority granted under the *United States Constitution*, granting all other authority to the state governments.

State governments, in turn, delegate authority to local governments. Local governments have no authority except that given by the state government through the state constitution, local government charters, and state legislation (Richardson 2005). Most state courts use "Dillon's Rule," a rule of thumb for courts that narrowly construes grants of authority from the states to local governments. Namely, Dillon's Rule assumes that local governments lack authority unless specifically granted by the state, or absolutely necessary to conduct local affairs or to carry out the expressly granted authority (Richardson 2005).

Under this framework, the federal government holds limited authority to address karst concerns. The main avenues for the federal government include incentives (usually financial incentives) and management of federally owned land. The Cave Resources Act (16 U.S.C.A. §§141, et. seq.) protects caves on federal lands. The formation of several national parks also indirectly protects karst resources, as does the Endangered Species Act (16 U.S.C.A. §§1531, et. seq.) and miscellaneous other federal actions.

States hold the lion's share of authority under our federalist system. However, states fail to regulate the issues associated with karst in any meaningful way (Richardson 2005). Aside from miscellaneous provisions in some states addressing the siting of landfills or storage of hazardous waste on karst terrain, only Puerto Rico has passed significant legislation (12 L.P.R.A. §§ 1143, et. seq. (Protection and Preservation of Caves, Caverns and Sinkholes); 12 L.P.R.A. §§ 1151, et. seq. (Protection and Preservation of Puerto Rico's Karst Region)). The legislation contains fairly comprehensive provisions that address karst concerns, and applies to public and private lands. However, by all reports, the legislation is not being enforced.

Given this state of affairs, local governments must regulate karst in the USA if karst is to be regulated at all. The most logical tools to address karst fall under the category of land use regulation. The regulatory tools include zoning and subdivision ordinance. Section 2.2 discusses these tools in general.

2.2 Land Use Regulation in the USA

2.2.1 Zoning

The comprehensive plan provides a vision of a community's future and provides the centerpiece of land use regulation. The plan guides the local government on issues regarding land use, economic development, and housing (Richardson et al. 2001). Local governments may use a variety of tools to implement the comprehensive plan, with zoning and subdivision ordinances among the most common.

Zoning consists of "division of a municipality's entire territory into districts, and the imposition of restrictions upon the use of land within these districts" (Salkin 2016, Sect. 118). The restrictions generally address the height and size of buildings and other structures, lot coverage, minimum lot sizes, setbacks, and density (United States Department of Commerce 1926).[1]

The Standard State Zoning Enabling Act provides for two types of exceptions to zoning. First, the special exception, more commonly referred to as a special use permit or a conditional use permit, refers to a use allowed in a particular

[1]The US Department of Commerce formulated the Standard State Zoning Enabling Act in 1926 to give state legislatures a model to develop enabling authority for localities. Most states adopted variations of the Act, and state statutes today generally retain many aspects of the Act.

zoning classification, but only in certain locations and under certain conditions. Second, the administrative body may grant a variance, allowing the landowner to engage in a use that is not allowed under the zoning ordinance, or to deviate from area requirements such as setbacks. However, variances should only rarely be granted, and only where the hardships are severe to the landowner.

2.2.2 Subdivision Ordinances

In contrast to zoning, subdivision regulations address the design of new developments, focusing on infrastructure (Salkin 2016, Sect. 120). These regulations commonly impose standards that, for example, require new streets be efficiently constructed and logically related to the existing street system (Ibid). Subdivision ordinances also commonly address stormwater management, curbs, gutters, and sidewalks, among other infrastructure issues.

3 The Problem of Regulating Karst

3.1 Generally

The law views local government decisions differently, depending upon the nature of the local government decision. Legislative decisions receive the most deference, while decisions that resemble judicial proceedings receive less deference. The law also classifies some actions as administrative, meaning that the local governments hold very little discretion to deny the application or request changes. If the developer meets the requirements of the law, the developer must be allowed to proceed.

To escape scrutiny and to avoid arbitrary decisions, local governments should promulgate detailed standards that apply to all landowners equally. However, karst terrain presents conditions that vary considerably from parcel to parcel. This variability requires regulation that provides flexibility and allows case-by-case decision making. Therefore, local governments must balance the uniformity required by law with the flexibility necessitated by the nature of karst.

Local government attempts to address land use regulation of karst most often take the form of (1) buffer areas around karst features; (2) performance standards; or, (3) development allowances based on geotechnical investigations (Richardson 2003). Each of these tools will be addressed in the sections that follow.

3.2 Legislative V. Quasi-Judicial Actions

Local government actions with respect to zoning may be classified as legislative, quasi-judicial or administrative. Administrative actions are ministerial functions performed by staff or administrative bodies.

Legislative acts establish policy impacting the entire community or large portions of the community. (Rathkopf et al. 2016, Sect. 40:21) Quasi-judicial actions are characterized by the facts that:

1. The decision directly impacts a limited number of persons or property owners, with relatively little impact on the community at large;
2. The action seeks to arrive at a fact-based decision, choosing between two or more alternatives; and,
3. The decision involves applying policy to specific facts. (Rathkopf et al. 2016, Sect. 40:21)

Decisions on subdivision requests amount to administrative decisions and local governments hold very little discretion in reviewing applications for subdivision approval. According to the West Virginia Supreme Court, "[w]hen an applicant meets all requirements, plat approval is a ministerial act and a planning commission has no discretion in approving the submitted application" (*Kaufman v. Planning & Zoning Commission of City of Fairmont* 1982). Consequently, including factors within a subdivision ordinance that conditions subdivision approval on discretionary judgments invalidate that portion of the ordinance.

Zoning ordinances present more complex issues of classification. The enactment of the original zoning ordinance clearly amounts to a legislative act. Broad amendments to the zoning ordinance also qualify as legislative. However, state courts view changes in zoning applying to one or just a few parcels differently, with some courts viewing such amendments as legislative, and others viewing the small-scale changes as quasi-judicial. Legislative actions are accorded a presumption of validity. Quasi-judicial actions cause the parties to be accorded greater procedural rights, direct judicial review, and closer scrutiny by the courts of the action (Rathkopf et al. 2016, Sect. 40:22).

The distinction between legislative and quasi-judicial actions "[b]asically … involves the determination of whether action produces a general rule or policy which is applicable to an open class of individuals, interest or situations, or whether it entails the application of a general rule or policy to specific individuals, interests, or situations. If the former determination is satisfied, there is legislative action; if the latter is satisfied, the action is judicial." (Holman 1972).

> The great deference given true legislative action stems from its high visibility and widely felt impact, on the theory that appropriate remedy can be had at the polls. … This rationale is inapposite when applied to a local zoning body's decision as to the fate of an individual's application for rezone. Most voters are unaware or unconcerned that fair dealing and consistent treatment may have been sacrificed in the procedural informality

> which accompanies action deemed legislative. Only by recognizing the adjudicative nature of these proceedings and by establishing standards for their conduct can the rights of the parties directly affected, whether proponents or opponents of the application, be given protection… To allow the discretion of local zoning bodies to remain virtually unlimited in the determination of individual rights is to condone government by men rather than government by law. *Cooper v. Board of County Com'rs of Ada County*, 101 Idaho 407, 614 P.2d 947, 950–951 (1980).

Courts express concerns about the potential arbitrariness of quasi-judicial decisions made by local governments. "To place [quasi-judicial decisions] in the hands of legislative bodies, whose acts as such are not judicially reviewable, is to open the door completely to arbitrary government" *Ward v. Village of Skokie*, 26 Ill. 2d 415, 186 N.E.2d 529,533 (1962).

In conclusion, zoning ordinance decisions may receive increased scrutiny from the courts where the application involves individualized decisions. Given the nature of karst, this scrutiny may directly implicate regulation of karst.

4 Regulatory Solutions

Local governments in the USA use three primary strategies to specially regulate karst today: buffer areas, performance standards, and required geophysical investigations and plans for each development site (Richardson 2003). Buffer areas or setbacks refer to established zones around karst features (rock outcroppings, sinkholes, or cave entrances, for example) within which development or agricultural activity is prohibited or restricted (Richardson 2003). Buffer areas form a common part of zoning ordinances, so should be upheld so long as uniformly applied. However, scientists and hydrogeologists uniformly dismiss set buffer areas as arbitrary when applied to karst. Effective buffers must be set on a case-by-case basis to address each individual circumstance.

Performance standards regulate activity by setting criteria for external impacts such as peak stormwater discharge, noise, or pollutants, as opposed to regulating allowed uses (Rathkopf 2016, Sect. 1:32; Blackwell 1989). Courts accept performance standards as zoning, and so long as the standards are uniformly applied, the standards should be upheld. With respect to karst, a local government may, for example, provide for karst protection by providing that peak stormwater discharges and overall stormwater discharge from a developed site may not exceed predevelopment quantities. Drafting performance standards, however, often proves difficult.

Finally, geophysical investigations and plans require landowners, at their expense, to study the geology and hydrology of a site and propose a development plan, prior to initiating development (Richardson 2003). The plan must be approved by the local government (Ibid). Although geotechnical investigations best mirror the complex science and hydrogeology of karst, this tool contradicts many basic legal principles.

Most state enabling authority fails to give authority to local governments to engage in such a case-by-case analysis of karst sites. Without very detailed guidelines (which would be extremely difficult to draft), this approach is prone to arbitrary decisions. Therefore, required geophysical investigations would likely fail court challenges.

Conditional use permits most closely resemble a geophysical investigation requirement. However, detailed guidelines are required to lawfully implement conditional use permits in karst terrain. The author is aware of no local government with a sufficiently detailed framework for conditional use permits in karst.

These and other zoning regulations in karst are often implemented through the use of overlay zones. Overlay zones "[refer] to a mapped district superimposed on one or more established zoning districts" (Rathkopf 2016, Sect. 1:31). This tool allows local governments "to impose supplemental restrictions on uses in these districts, permit uses otherwise disallowed, or implement some form of density bonus or incentive zoning program" (Rathkopf 2016 Sect. 1:31). Overlay zones present great promise for application in karst. In practice, however, overlay zones often inappropriately include subdivision regulations and other provisions not appropriate to a zoning ordinance. Karst regulations most appropriately are included in all local governments regulations in a comprehensive fashion.[2]

5 Non-regulatory Solutions

5.1 Introduction

Several factors limit the effectiveness of regulatory approaches to controlling land use in karst terrain. First, in some areas, particularly rural areas, the citizens oppose traditional regulatory approaches (Richardson and Brown 2005). Second, traditional regulatory approaches often fail to address indirect consequences of development in karst areas, such as over-pumping of karst aquifers and the increased risk of chemical spills (Ibid). Finally as discussed in Sect. 3.0, legal constraints on local government regulatory authority may limit the effectiveness of regulatory (Ibid).

Public outreach and education prove vital to any effort to protect karst, either regulatory or non-regulatory. Voluntary

[2]See. e.g., *DeCoals, INc. v. Board of Zoning Appeals of City of Westover*, 284 S.E.2d 856 (1981).

incentives may also provide effective alternatives. This section discusses non-regulatory land use tools that may serve to protect karst resources, without the stigma that accompanies regulatory approaches.

5.2 Conservation Easements

A conservation easement extinguishes all or a portion of the development rights on a portion of the property. State statutes create this device and provide rules to create the document. In addition the Internal Revenue Service has created a complex set of rules to qualify a donation of development rights, either in part or in full, to a "qualified organization" as a charitable contribution, deductible, with limitations, for federal income tax purposes (Internal Revenue Code Sect. 170(h)). The Internal Revenue Code rules have become the overriding considerations in many conservation easements, and most conservation easements are donated to take advantage of Internal Revenue Service rules.

5.3 Purchase of Development Rights (PDR) Programs

Purchase of Development Rights (PDR) Programs involve the purchase of a conservation easement. Local, state, and federal government agencies may purchase development rights to protect property. Although these purchased development rights may be less than permanent, perpetuity remains the overwhelming standard. PDR programs offer the benefit of increased targeting of special properties, but the cost of purchasing development rights forms a barrier (Richardson and Brown 2005).

5.4 Transfer of Development Rights (TDR) Programs

A relatively recent innovation in zoning and other land use regulatory programs is the treatment of "development rights" attributable under a zoning ordinance to a particular parcel of land as severable from that tract or zoning lot and transferable to another tract or zoning lot. This type of transfer of development rights program allows permitted density or floor area attributable to a particular parcel of land (the granting site) to be transferred to and utilized on another parcel of land (the receiving site). Various forms and methods of implementing transfer development rights (TDR) programs have been discussed in the growing body of literature devoted to this topic.

While the details of the various programs vary considerably, transfer of development rights schemes generally are utilized by the creation of eligible granting sites or zones (upon which the development rights to be transferred are calculated) and the creation of eligible receiving sites or zones (upon which the aforementioned development rights may be transferred and utilized). Parcels of land designated as sending or granting sites are usually, but not always, subject to stringent land development restrictions. Owners of these sending sites may utilize the development rights eligible for transfer from such sites on other eligible receiving sites that they own or they may be able to sell the development rights to another party or possibly even to a development bank created for the purpose of buying and selling these development rights (Rathkopf 2016, Sect. 59:2).

TDR programs may be used to transfer development rights from karst areas to areas more appropriate for development. Although TDR programs offer quick protection, the programs are complex (Richardson and Brown 2005).

5.5 Low Impact Development

Low Impact Development (LID) involves a decentralized approach to stormwater management that attempts to natural hydrology (Coffman 2003). The techniques seek to protect natural areas such as karst terrain and offer promise in that respect.

5.6 Conservation Subdivision Design

Conservation subdivision design incorporates natural features, such as karst, into the design of a development, eschewing conventional subdivision design (Ohm 2000). Lots are generally clustered in areas that are less environmentally sensitive (Haines 2002). This tool offers creative ways to accommodate development and cave conservation in karst. The Texas Cave Conservancy has pioneered use of Conservation Subdivision Design in karst. The Discovery Well Preserve in Williamson County, Texas serves as an interesting example.[3]

5.7 Conclusions

Non-regulatory approaches may complement regulatory approaches to karst conservation or, in some cases, offer a more palatable alternative to regulation. Similar to regulatory approaches, these tools must be based on science to be effective. Public education as well as education of regulators and legislators also proves vital.

[3] See http://texascaves.org/preserves_2.

6 Conclusions

The unique nature and variability of karst terrains present both scientific and regulatory struggles. The law prefers uniform approaches to regulation to prevent arbitrary decision making and to promote fairness. Karst features make a uniform approach difficult.

At present, local governments, by default, hold the most regulatory responsibility with respect to karst terrains in the USA. Local governments often lack the technical expertise, resources, and legal authority to effectively regulate karst. However, several tools are available to local governments. Most importantly, local governments can use performance standards and conditional use permits to respect scientific and legal principles. Drafting the legal instruments to implement these principles is extremely difficult and few, if any, good examples exist.

Ideally, state governments, which hold broad authority to regulate karst, should assume more responsibility for karst protection. States can implement broad regulations that protect karst. Puerto Rico's regulations provide a model for state regulation, but these regulations are not enforced. Like many other regulations in states across the country, resources are required to enforce the regulations. Education for the public, legislators, regulators, and others may encourage communities to support regulatory protection of karst resources. In the meantime, non-regulatory measures may fill some of the gaps.

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Recommended Strategies for the Response to Hazardous Materials Releases in Karst

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Abstract

The US Environmental Protection Agency has identified karst aquifers as one of the most vulnerable aquifer types to contamination. Many karst aquifers have a direct connection to the surface through sinkholes, sinking streams, fractures and faults, and cave entrances. Thin soils or soils containing root zones, desiccation cracks, and animal burrows provide little filtration or retention of contaminants. Karst aquifers are noted for rapid recharge, high groundwater velocities, 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, surface, and groundwater ecological systems and threaten public and private water supplies. Most industrialized and urbanized communities have well-developed hazardous materials (Hazmat) response teams to contain and mitigate hazards. However, Hazmat teams may not understand some of the unique aspects of karst terrains, and remediation measures to prevent direct exposure to a release. This may result in unforeseen contamination of groundwater resources. This paper is intended to identify potential strategies to mitigate potential impacts from the release of hazardous materials in karst terrains. This includes preplanning with hazardous materials response professionals, hydrogeologic research, techniques to investigate potential receptors, and on-site remediation and monitoring recommendations that include special considerations in karst.

1 Introduction

The US Environmental Protection Agency has identified karst aquifers as one of the most vulnerable aquifer types to contamination (Federal Registry 2000). Karst is noted for rapid recharge though sinkholes, sinking streams, caves, enlarged fractures, and bedding plane partings. Water is transmitted though the subsurface via interconnected preferential flow paths ranging in diameter from centimeters to meters. Groundwater velocities in karst have been measured using tracer testing and other techniques and range from tens to thousands of meters per day. Depending upon local conditions, contaminants may be retained in the soil and/or epikarst or may be transmitted directly into the aquifer with little attenuation.

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Hazardous materials are placed into nine classes commonly referred to as “Dangerous Goods” as follows: explosives, gases, flammable liquids, flammable solids, oxidizing substances, toxic and infectious substances, radioactive materials, and corrosives. The manufacture, transport, storage, and disposal of hazardous materials are well regulated; however, releases of hazardous materials can occur during any of these activities. Many industries and municipalities have well-developed hazardous materials response teams to address releases that occur in their area. States have hazardous materials response contractors that are under contract to respond to spills that occur outside of local response areas or exceed the capability of local resources. The release of hazardous materials in karst terrains has resulted in the contamination of public water supplies, the occurrence of explosive fumes in buildings, and deterioration of groundwater and surface water resources.

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This paper identifies some of the sources of hazardous materials releases and recommendations regarding a response strategy including preplanning with hazardous materials response professionals, techniques to investigate potential receptors, and on-site remediation and monitoring recommendations to include special considerations in karst. Contamination has occurred in rural, industrial, suburban, and urban environments and along transportation corridors. Contamination sources may be grouped as nonpoint or point sources.

2 Types of Releases

2.1 Nonpoint Source Pollution

Generally, nonpoint source pollution is not considered a hazardous materials release. However, some nonpoint sources, such as nitrate from fertilizer, can exceed drinking water standards. Nonpoint pollutants originate from a wide variety of sources rather than from a single source such as a pipe discharge (Boyer 2004). Nonpoint source pollution is regulated in the USA under the Clean Water Act. In rural settings, the application of fertilizers, herbicides, and pesticides and dispersed animal production areas has resulted in degradation of water quality. In suburban and urban settings, nonpoint source pollution can occur from storm water runoff, on-site sanitary systems, and the application of herbicides and pesticides such as lawn care products. Industrial settings may also result in impacts to groundwater resources from storm water runoff and fallout from air emissions, etc.

Agricultural and urban nonpoint pollution sources such as row crops and grazing land, as well as on-site sanitary systems, leaking sewer lines, and storm water runoff, are signification sources of contamination to groundwater in karst. Sediment is also considered a major nonpoint source contaminant and has resulted in degrading and plugging of recharge features resulting in flooding in some areas such as along sinking streams and sinkholes.

Many nonpoint sources of contamination are relatively continuous and can result in an increase in the “background” concentration of contaminants of susceptible aquifers over large areas over time. In some cases, contamination can exceed maximum contaminant limits for drinking water or in-stream aquatic standards.

2.2 Point Source Pollutants

Point source pollution is contamination that originates from any discernable or discrete source such as a pipe, ditch, channel, well, container, concentrated animal feed operation, landfill, or industrial storage area (Schindel and Hoyt 2004). In the USA, point source contaminants have a long history of regulation through a number of federal and state programs, including the Clean Water Act, Underground Injection Control Act, Safe Drinking Water Act, Resource Conservation and Recovery Act (RCRA), and the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA or Superfund). Point sources may also be a continuous discharge from a permitted industrial or municipal source to a lake or river.

Industrial and municipal point sources are closely regulated through the National Pollution Discharge Elimination System (NPDES) permitting process at the federal level or at the state level for those states having primacy. Generally, point sources are regulated through the NPDES system and are issued permits that limit the concentration of pollutants and their impacts on surface water bodies. However, depending upon the constituent toxicity and volume and rate of release, a point source may create a chronic degradation of groundwater or surface water quality. Mechanical, maintenance, or operational errors may create an “acute” release that rapidly degrades water quality or creates a public or ecological health threat. For example, some publically owned treatment works (POTW’s) result in the bypass of untreated sewage due to infiltration of large volumes of storm water during rain events.

2.3 Hazardous Materials Releases

The handling, transport, storage, and inadvertent disposal of hazardous materials over karst aquifers have resulted in many releases and commensurate contamination of groundwater and surface water systems (Ewers 2016). An accidental hazardous materials release would be considered a point source. Some examples of common contamination sources include pathogens associated with concentrated animal feeding operations (CAFO) and lagoon failures; releases from breaks in sanitary sewer lines; overflow of sewer lift stations; transportation and storage accidents involving industrial chemicals, gasoline, diesel fuel, and related petroleum products; releases of organic compounds such as PCBs, solvents and degreasing agents such as PCE and TCE; herbicide and pesticide releases from formulators; and industrial sources of heavy metals such as zinc, lead, and mercury.

Depending upon the physical and chemical properties of the constituents of concern, as well as the volume and exposure pathways, releases can present a number of hazards to both public health and the environment. Exposures to contaminants can create both an acute and chronic impact on public health through public water supply contamination, to biologic communities that rely on groundwater and surface water resources, and damage to property and civil infrastructure though fire and explosions. The US Federal Motor

Carrier Safety Administration classes hazardous materials into nine classes (1) explosives, (2) gases, (3) flammable liquid and combustible liquid, (4) flammable solid, spontaneously combustible and dangerous when wet, (5) oxidizer and organic peroxide, (6) poison (toxic) and poison inhalation hazard, (7) radioactive, (8) corrosive, and (9) miscellaneous. The US Department of Transportation closely regulates all aspects of hazardous materials transport including requirements that all trucks and rail cars must meet placarding standards indicating the class and material being transported.

A transportation accident involving a gasoline tanker truck is a good example of a release that may create an acute threat to public health and infrastructure by causing a fire or explosion hazard and/or may contaminate a public water supply system requiring interruption of service, expensive treatment systems, or abandonment.

In the USA, a number of federal agencies regulate hazardous waste operations and emergency response including the US Coast Guard, the US Environmental Protection Agency (EPA), and the Occupational Safety and Health Administration (OSHA). Federal agencies develop standards and regulations for responses and may respond to large incidents that exceed the resource base for local and state agencies. Incident response is commonly delegated to state and local agencies that perform the physical emergency response. Reponses are directed toward protecting human health and the environment including personal and community property with an emphasis placed on migrating risks as safely and quickly as possible. Each response requires a balance between public and environmental health and safety, timeliness in the response, and cost.

Most urban communities have well-established hazardous materials response teams that address releases. Industry may also have specialized Hazmat teams and equipment that address on-site incidents and unique compounds. They commonly have mutual aid agreements with surrounding communities. Hazmat teams are focused on the immediate protection of public health and the environment and commonly have to make difficult choices and compromises related to response strategies. For example, there are many options to address a hazardous materials release such as containment and removal, neutralization/treatment, evaporation, combustion, and dilution. Each of these options has a consequence that must be balanced with public health and environmental concerns including time restraints and economic costs. Groundwater, as an unseen resource, may not be considered as a high priority for protection in regard to acute threats to public health and property. However, failure to consider the rapid movement of groundwater and the poor attenuation of contaminants in karst terrains can have unforeseen and detrimental consequences to water resources and public health.

2.4 Why Releases Happen

Most releases are accidental and are the result of failure of containment systems or transportation accidents. Severe weather commonly plays a role in transportation accidents, but other releases are a result of human error, aging infrastructure, poor maintenance, vandalism, and occasionally, willful intent. The US EPA has established minimum reportable quantities for most regulated substances. A release that exceeds the reportable quantity must be reported to the state or community environmental agency. Releases may range from less than 100 L of gasoline or diesel fuel in a truck fuel storage tank to millions of liters from a sewage or petroleum pipeline failure or industrial or sewage lagoon failure.

2.5 Unique Aspects of Karst

The description of groundwater movement in karst is well documented in the literature (Worthington 1999). Karst terrains are noted for rapid groundwater velocities and little attenuation of contaminants. Karst land surfaces may be mantled with thick soil covers or expressed as bare limestone pavements or any combination. The movement of contaminants is dependent upon soil type, permeability, thickness, and saturation as well as the presence and frequency of conduits in the bedrock connected to the local and regional flow system. Many conduits that transmit water also have free air surfaces which may allow for the volatilization of liquids to a gasses phase. Cave ceilings may also act as a "strainer" for light non-aqueous phase liquids (Crawford 1988). Gasses may migrate to the surface though conduits and, in some cases, have resulted in explosive levels in buildings. Depressions in the floor of conduits may act as traps for dense non-aqueous phase liquids making detection and remediation extremely difficult.

3 Strategies for Addressing Hazardous Materials Releases

A hazardous materials release in karst presents some unique problems in protecting public health and the environment. However, before a release can be adequately addressed, the presence of karst must be recognized and understood by professionals responsible for responding to hazardous materials incidents. A regional strategy to address hazardous materials releases in karst includes education of responsible parties; defining and identifying karst resources; development of land use planning goals and objectives; prerelease planning and organization; hydrologic data collection and research; and incorporation of findings into emergency response actions. Unless the area of interest has had significant environmental issues related to karst, there may be difficulty in convincing responsible parties that there is a significant karst issue. Especially if there is little existing scientific research or a poorly defined conceptual model of groundwater occurrence and movement in the area of concern.

3.1 Education of Responsible Parties

Proper response to hazardous materials releases must include the education of responsible parties regarding the unique challenges of living and working in karst terrains. Responsible parties include state and local officials and politicians, city planners, environmental and public health regulators, hazardous materials response teams, business owners, and the public. Education should be based on scientific research and data and a well-developed conceptual model discussing possible receptors and case histories of previous incidents, possible sources and impacts, and response scenarios. Most responsible parties have limited knowledge and experience dealing with karst issues which creates a challenge to focus their attention and allocation of resources on a relatively uncommon but potentially high impact problem. It is not uncommon that little is done until a large incident has occurred and results in the allocation of sufficient resources to address the karst related hazardous materials spills. Education may also be required of non-karst groundwater professionals as many do not have specific training or experience working in karst (Ewers 2006).

3.2 Identification of Karst Resources

The identification and characterization of karst are usually performed by a hydrogeologist with specialized knowledge, training, skills, and experience in karst. There are a limited number of colleges and universities that have faculty or programs where karst is a focus of study and fewer private sector practitioners that specialize in working in karst terrains. The identification of karst on a state, regional, and local level may range from high-quality geologic and hydrologic data, and a high degree of understanding of karst processes, to those areas that are poorly defined and studied and even misidentified. This wide degree of understanding or misunderstanding of karst processes and resources may occur within the local geologic community and is practitioner dependent.

After some period of study, a karst hydrologist can commonly provide a site conceptual model on the local and regional behavior of karst. The conceptual model is commonly based on a review of the literature, an examination of the regional and local geologic structure and stratigraphy, evaluation of well logs and water levels, a spring inventory and flow measurement, collection and analysis of water quality samples, previous investigations and findings from hazardous materials releases, and, most importantly, existing tracer test data. Based on the available data, they may be able to identify potential vulnerable receptors, areas of high risk for releases that may impact groundwater, ranges of expected groundwater velocities and flow direction, potential dilution or attenuation of contaminants, and make recommendations for land use planning and facility sighting. They may work with other professionals to identify sensitive ecological concerns such as endangered species. The karst hydrogeologist plays a critical and central role in helping to define all other strategies and actions in dealing with a hazardous materials release and identifying data gaps.

3.3 Hydrogeologic Research

Understanding the occurrence and nature of the karst environment is critical to developing proper spill response strategies (Quinlan and Ewers 1986; Quinlan 1989; and Ewers 2006). A well-developed research and data collection program should include the following:

Detailed hydrostratigraphic mapping and tracer testing program.
Identification of vulnerable community assets such as private and public water supply wells, springs, and sensitive ecological areas.
Location of caves, sinkholes, and sinking or losing streams for inclusion in monitoring and tracer testing programs, and evaluation for contaminant impacts.
Creation of groundwater flow path maps and time-of-travel data from multiple tracer tests at a range of hydrologic conditions.
Groundwater potentiometric surface maps based on synoptic water level events over a range of hydrologic conditions.
Location of transportation routes (major roadways, pipelines, and railroads).
Location maps of potential contaminant sources.
Background water quality data from wells and springs.

The data can be utilized to develop an aquifer conceptual model and compile and made available resources to support a Hazmat emergency response.

3.4 Land Use Planning

Once a karst terrain has been identified and characterized, this knowledge can be used to help identify sensitive areas for protection. Land use planning can be used to control development over sensitive areas and encourage development of less sensitive areas. Restrictions on growth and development may take the form of zoning controls or local or state regulations. Land use planners may consider placing restrictions on the location, density, and type of residential, commercial, and industrial development. In some communities in karst, the percentage of impervious cover may trigger regulations that require low impact development (LID) methods such as storm water retention structures, and vegetative strips. Communities have also regulated or banned certain activities on sensitive areas (aquifer recharge zones) such as bulk hazardous materials storage and distribution. For example, retail businesses that sell gasoline and diesel fuel may be banned from certain locations or be required to have additional spill prevention measures in place. Other businesses that utilize solvents or heavy metals such as dry cleaning, painting, metal plating, and degreasing operations may also be banned or highly restricted. Some states place restrictions on light and heavy industry and on solid and liquid waste containment or disposal businesses in karst.

Land use planning may also define hazardous materials transportation routes to control the location and areas used as transportation corridors for rail, pipeline, and roads. Land use planning may also be used to identify sensitive areas for inclusion in development of natural areas, parks, greenways, and purchase of conservation easements or development rights. Land use planning should not only include the aquifer recharge area but may also include areas that contribute to the recharge area from runoff from less permeable geologic units (Schindel et al. 1996).

3.5 Regional Spill Response Planning Team

A regional spill response planning team can develop a coordinated program to address hazardous materials releases in karst. The team should be used to define the roles of various agencies; identify and develop communication channels, decision makers, and technical advisors; and the need for special services, laboratories, and contractors. Team members should include representatives from environmental and health department programs, political bodies, karst hydrogeologists, fire department and Hazmat representatives, local land use planners, industry and environmental non-governmental organizations, and the public.

Some of the responsibilities for the Strategic Spill Response Planning Team include the following:

Recommend land use planning goals and regulations to protect sensitive karst lands including controls on the type of development over sensitive areas, identify low impact development requirements, define limitations on types and volumes of hazardous materials in sensitive areas, outline best management practices, and assess hazardous materials transportation routes.

Identify possible contamination sources and release scenarios and recommended response strategies.

Define the role and responsibilities of each agency during a hazardous materials release.

Develop communication between agencies and develop resource lists of technical experts and remediation teams.

Identify critical public infrastructure that may be impacted by a release such as public water supply wells and springs and develop contingency plans for remediation or replacement.

The planning teams should meet frequently to evaluate plans and also evaluate after action reports to improve responses.

3.6 Hazardous Materials Response Team

Hazardous materials response (Hazmat) teams should train and be well versed in the types of potential spills in karst areas and the best strategies to protect public health and the environment. Considering that very low levels of contamination may require expensive treatment or abandonment of a public water supply, all efforts should be made to prevent and minimize the release of hazardous materials into the subsurface. The application of large volumes of water in an attempt to dilute a spill should be avoided to minimize the production of leachate and runoff from a release site. Large volumes of water may also create a piston action and propel contamination from the soil, epikarst, and the groundwater flow system directly into private or public water supplies and springs. As little as a few thousand gallons of water is commonly sufficient to reach the active subsurface flow system in karst. Contaminated material is much easier to contain and remove on the surface than it is from the subsurface where flow paths and travel times may be uncertain.

3.7 Monitoring Program

Once the initial response has occurred and imminent danger to public health and the environment has been mitigated, potential receptors such as private and public water supplies, springs, and caves should be identified and monitored for possible contamination and contingency plans should be made for replacement or treatment of private and public water supplies as necessary. Laboratories should be placed on standby for quick turnaround of samples for constituents of concern.

Considering the cost, time, and difficulty in analyzing for many contaminants, a surrogate for contamination in the form of fluorescent dyes may be useful to identify flow paths, travel times, and impact to private and public water supplies. This does require significant preplanning and experience in the analysis of dyes which may be provided by a karst hydrologist. Dyes are cheaper, easier, and quicker to analyze than for many other contaminants, and some of the instrumentation is relatively portable and easy to use. However, tracer testing requires the expertise of a karst hydrologist and should only be performed under their direct supervision and guidance. For example, only specific dyes should be selected for tracer testing based on toxicity, solubility in water, detection, cost, availability, etc. (Note, some dyes may be toxic or have other properties that are not suitable for tracer testing.)

Based on the results of tracer testing and analysis, in consultation with a karst hydrologist, proper remediation methods may be designed and implemented to mitigate a release.

4 Conclusion

The release of hazardous materials into a karst terrain can result in a direct and rapid impact to groundwater resources, surface water ecological systems, and public health. Communities that have prepared and trained to deal with hazardous materials releases specifically related to karst terrains have the best opportunities to minimize impacts. Preplanning, communication, identification of resources and responsibilities, and characterization of karst resources are critical to protect public health and the environment.

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Investigating Groundwater Vulnerability of a Karst Aquifer in Tampa Bay, Florida

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Abstract

The Floridan aquifer system (FAS) is known to be one of the most productive aquifer systems in the USA. With the FAS being a karst aquifer, it presents unique challenges to land-use planners because of inherent vulnerabilities to contamination through direct connections between the aquifer and the surface. In this study, a new geographic information systems (GISs)-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 major differences between the two models with SI suggesting greater vulnerability for the study area than KAVI. Validation of these two models found that KAVI vulnerability levels best reproduced spatially varying concentrations of nitrate, orthophosphate, and arsenic in the aquifer. Sensitivity analysis, the application of a variation index, and measuring the effective weights for each parameter included in KAVI confirmed the importance of epikarst 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.

1 Introduction

Karst aquifers are resources of growing importance throughout the world. Approximately 25% of the world's population gets its water from these aquifers, particularly in Asia, the Mediterranean, and the USA (van Brahana 2008). Growing populations will stress these aquifers through the need for increasing withdrawals. The accompanying urban and industrial expansion that accompanies population growth increases the risk of groundwater contamination from chemical spills, dumping of pollutants, and land-use changes. Karst aquifers are particularly vulnerable to such risk because of rapid water infiltration through the epikarst or sinkholes which often provide direct connections between the surface and aquifer (Ravbar and Goldscheider 2009).

The inherent vulnerability of all aquifers to groundwater contamination has lead to the creation of groundwater vulnerability models (GVMs) whose aim is to quantify an aquifer's level of intrinsic or specific vulnerability. COST Action 620 (Zwahlen 2004) defines intrinsic vulnerability as "…vulnerability of groundwater to contaminants, takes into account the geological, hydrological, and hydrogeological characteristics of an area, but is independent of the nature of the contaminants and the contamination scenario." By

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contrast, specific vulnerability refers to "the potential impacts of specific land uses and contaminants" (Stigter et al. 2006). In simpler terms, intrinsic vulnerability refers to vulnerabilities brought upon by the natural, hydrogeological factors of an aquifer and specific vulnerability refers to vulnerabilities due to both natural hydrogeological parameters and human activities. One of the most widely used intrinsic vulnerability models is DRASTIC, a generic model that incorporates various physical components of both aquifer and overlying substrate (Aller et al. 1985). More recently, researchers in Europe have attempted to create their own GVMs that include GOD (Foster 1987), AVI (van Stempvoort et al. 1993), EPIK (Doerfliger et al. 1999), and PI (Goldscheider et al. 2000). In Florida, the Department of Environmental Protection (DEP) commissioned a new model (FAVA) that measures vulnerability specifically for the three aquifers in Florida (Arthur et al. 2007). Most recently, Guo et al. (2007) adapted DRASTIC to create DRARCH for assessing arsenic contamination in a Chinese aquifer. All of these models have two common threads: They all concentrate on only physical parameters and use geographic information systems (GISs).

The approach taken in this paper is to combine physical parameters used in most of these GVMs with the anthropogenic contribution to groundwater vulnerability, the compilation of which we define as a specific vulnerability model. Specific vulnerability models, as stated above, take into account human activities on the surface that can lead to greater vulnerability of the aquifer system. For example, an industrial–chemical complex bordering on a concentration of sinkholes would pose a substantially threat to the aquifer than land designated as a national park. The new specific vulnerability model proposed here, the Karst Aquifer Vulnerability Index (KAVI), incorporates both physical (including a karst specific parameter) and human components. KAVI will then be compared to another specific vulnerability model adapted from DRASTIC and developed by Ribeiro (2000) called the Susceptibility Index (SI), in order to determine which approach better represents the measured concentration of nitrate in the Upper Floridan aquifer. We expect that the incorporation of the epikarst layer into KAVI will allow it to outperform SI in the validation process due the fact that our study area is a karst landscape. Hence, SI is used here as a control for the experiment.

2 Study Area

The study area encompasses a small section of the Floridan aquifer system (FAS) within Hillsborough County, Florida, where there is a variety of human land uses above the aquifer and the physical parameters are well constrained. This area was selected because the FAS was not overlain by the surficial aquifer system (SAS) or intermediate aquifer system (IAS), or any substantial confining layers. In addition, it is the area with the second highest withdrawal rates in the State of Florida. Hillsborough County is located on the west coast of central Florida (Fig. 1). In 2015, the county had a population of ~ 1.2 million with urban areas covering approximately 45% of the land area of the county, the rest being predominately rural (Hillsborough County 2005). Since the 1950s, the county has undergone rapid development resulting in significant urban sprawl.

As a physical landscape, this region lies within the Gulf Coastal Lowlands physiographic unit (Randazzo and Jones 1997), with low relief, and a mantle of sandy clay interspersed with some calcareous rock (Hawthorn Group) which overlies the Suwannee and Ocala Limestone units. The Hillsborough River dissects the county as it meanders on a NE–SW trending course and a high density of sinkholes puncture the land surface in center and western portion of the study area. Below, the conduits characteristic of Floridian karst are permanently flooded by the upper portion of the FAS.

The FAS is contained within the highly permeable carbonate rocks of Paleocene to Miocene age (Miller 1986). Beds of impermeable anhydrite provide the bottom confining layer while the upper portion of our study is unconfined but covered by Miocene to Holocene clastic deposits (Swancar and Hutchinson 1992). South of the study area the FAS is overlain by the intermediate and surficial aquifers. Due to this added complexity, we have decided to concentrate only on the upper half of the county (Fig. 1) where the FAS is not covered by any other aquifer.

3 Methods

The aim of creating KAVI is to incorporate both anthropogenic and geophysical parameters into determining groundwater vulnerability using GIS. The dominant anthropogenic parameter that affects vulnerability is land cover, which encompasses all of the various human land uses above the aquifer including agriculture, parks, residential, industry, and mining. However, major highways are a major contamination risk due to substantial truck traffic, so they were added to land cover to form a combined anthropogenic GIS layer.

Hydrogeologic parameters that are most common in other models are soil permeability, aquifer hydraulic conductivity (derived from wells), epikarst (which is best represented in our study area as closed topographic depressions), and depth to water table (as measured by wells). The data for each of the GIS layers of the four parameters were extracted from either DRASTIC, FAVA, or Megamodel which had been previously applied to our study area (Swancar and

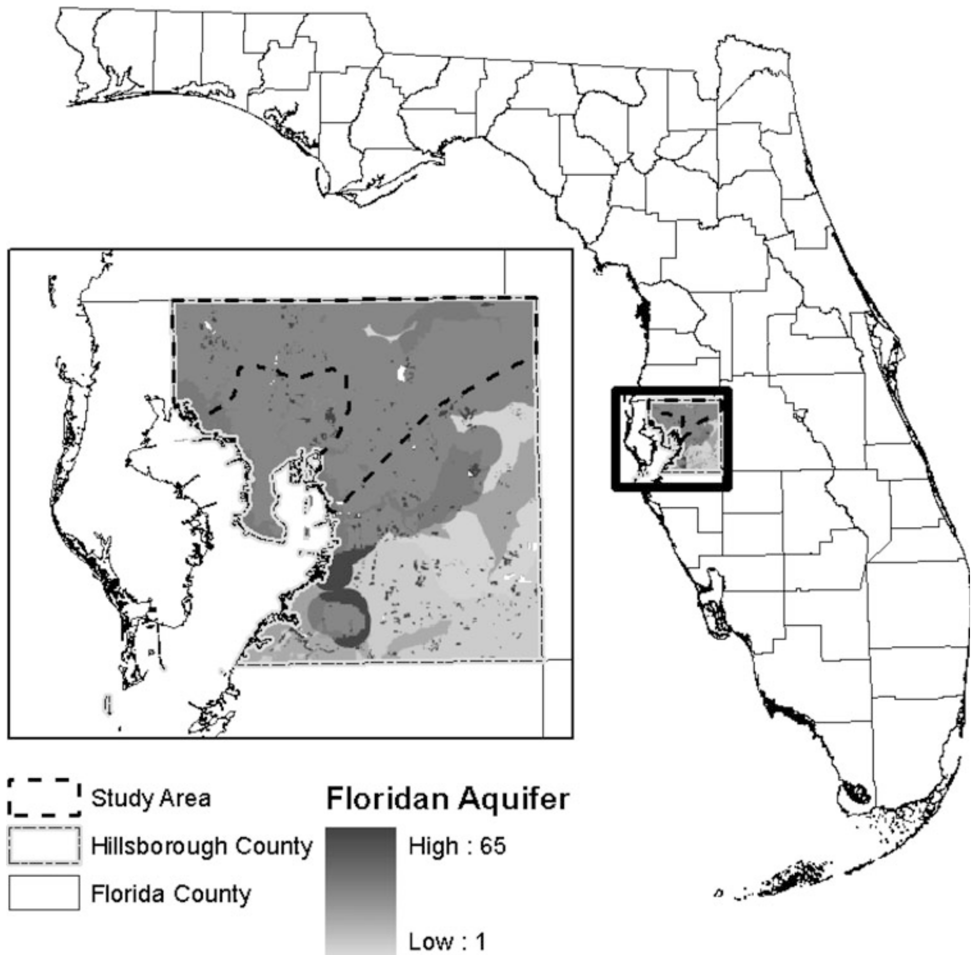


Fig. 1 Unconfined Floridan aquifer within Hillsborough County, Florida

Hutchinson 1992; Armstrong et al. 2003; Arthur et al. 2007). These shapefiles were freely available from the state, county, or local water management district. Testing of the accuracy of these data was undertaken by the previous studies and for further information on that process, please consult the above references. Because our study area did not have a confining layer above the aquifer, such a parameter was not included for this particular study. However, in other parts of Florida, the FAS is overlain by a confining layer and therefore such a coverage would be included if the study area was to be expanded.

Soil permeability was originally created by the digitization of county soil surveys, which permeability measurements for each identified soil unit. This GIS layer as used for our study was extracted from the FAVA model for the FAS in Hillsborough County. The scores assigned in Table 1, based on a range from 1 (lowest) to 5 (highest), were subjectively defined based on the classification of soil permeability used in the county soil survey.

Aquifer hydraulic conductivity was extracted from Megamodel (Sepulveda 2002), a groundwater model that simulates hydraulic conductivity and that was previously applied and verified in our study area (Armstrong et al. 2003). Verification undertaken by these authors involved measuring hydraulic conductivity that was derived from well data.

Epikarst in Hillsborough County is dominated by sinkholes which were termed closed topographic depressions by Arthur et al. (2007), the creators of the FAVA model. Consequently, their terrain model shapefile was used to delineate the epikarst layer for KAVI.

Finally, data for depth to water table were extracted from the DRASTIC study carried out in our study area where groundwater wells were the source for this parameter. Although there was additional depth to water table models available from Megamodel and FAVA, the decision was made to employ the same parameter utilized by the Susceptibility Index (SI) in order to better compare and contrast the two GVMs.

All hydrogeologic coverages (GIS layers) were scored from 1 to 5 depending on their characteristics, and scores increased with greater vulnerability to the aquifer (Table 1). Whereas the groupings for other layers were based on parameters from previous models, the scoring scheme for the Epikarst layer utilized kernel analysis to create a density grid

Table 1 Scoring of layers for KAVI (1 = lowest, 5 = highest)

Layer	Physical characteristic	Score
Hydraulic conductivity (permeability) (in/h)	Surface water	1
	<0.6	2
	0.7–6.0	3
	6.1–19.9	4
	>20	5
Depth to water table (ft)	36–45	1
	26–35	2
	16–25	3
	1–15	4
	0	5
Hydraulic conductivity (ft/day)	1–100	1
	100–300	2
	300–700	3
	300–700	4
	>1000	5
Epikarst (closed topographic depressions)	No sinkholes	1
	Moderate density	3
	Highest density	5
Landover	Natural-protected	1
	Pasture	2
	High-intensity agriculture, low-density residential	3
	Industrial, high-density residential	4
	Mining	5
Roads	No major highway	1
	Major highway	5

to recognize clusters of sinkholes which would increase aquifer vulnerability. A 500-m bandwidth was used for the analysis, and the highest densities were scored a 5, the next highest scored a 3, and where sinkholes were not present a 1.

Class breaks for the combined physical component of the KAVI model were established at the midpoint between the input vulnerability values so as to reflect the increased precision of output values generated by the raster processing. Except for the grouping of the two lowest input values of 1 and 2, where KAVI values less than 2.5 represent low vulnerability, the remaining KAVI values were classified around a single input vulnerability value in the following way: 2.51–3.5 is low to moderate vulnerability; 3.51–4.5 is moderate to high vulnerability; and greater than 4.5 is high vulnerability.

A similar scoring system to the hydrogeologic layers with regard to high−low vulnerability was used for the land-use layer (Table 1). However, major highways were categorized according to their presence (score of 5) and absence (score of 1). The final anthropogenic layer was then combined with the other hydrogeologic layers to create the final vulnerability scores of the KAVI model. A variable weighting scheme was applied to KAVI using the following percentages: anthropogenic 30%, epikarst 25%, and soil permeability, aquifer hydraulic conductivity and depth to water table 15% each. Thereby, the resulting equation for the KAVI model is as follows:

$$\mathrm{KAVI} = 0.15 \times D + 0.15 \times S + 0.15 \times A + 0.25 \times E + 0.30 \times \mathrm{LU}$$

where

D	Depth to water table
S	Soil permeability
A	Aquifer hydraulic conductivity
E	Epikarst
LU	Overall anthropogenic layer

The land-use layer was given the highest weighting because of the number of layers combined together and its overall importance in karst aquifer systems. Epikarst received 25% of the total available weight with the rationale that sinkholes are the quickest avenue of contamination to the aquifer and thereby pose significant risks to the aquifer below. Such an approach is justified because Gogu and Dassargues (2000), who when undertaking a sensitivity study of the EPIK method, found that overall vulnerability was most sensitive to the epikarst layer.

The Susceptibility Index (SI) was adapted from DRASTIC with the intention of evaluating aquifer vulnerabilities on a medium to large scale (1:50,000–1:200,000) with respect to diffuse pollution in hydrogeological settings (Ribeiro 2000; Stigter et al. 2006). The SI differs from DRASTIC in its inclusion of a parameter for land use and its exclusion of three parameters found in DRASTIC, for reasons explained below. According to previous studies, the types of land use and their assigned ratings used in SI follow those provided by a team of Portuguese scientists (Ribeiro 2000). These ratings, shown in Table 2, are different in scale from the ratings used in KAVI's anthropogenic layer, though this is somewhat irrelevant as the scales of vulnerability are proportionally the same.

The three parameters of DRASTIC that were removed from the previous applications of the SI (Ribeiro 2000; Stigter et al. 2006) are soil (*S*), unsaturated zones (*I*), and aquifer hydraulic conductivity (*C*). In attempting to truthfully reproduce this index for our particular study area, we intentionally omitted these parameters as well. Previous studies employing SI argued that soil type is indirectly represented through land use and thus unnecessary for inclusion in the model (Frances et al. 2001). It is suggested that the unsaturated zone serves only as a time lag (Stigter et al. 2006) and hence was not included. Hydraulic conductivity was also excluded by Stigter et al. (2006), for they felt it was already represented by aquifer media. The land-use layer used for the SI was simply a reclassified version of the layer used in KAVI, with SI's weights replacing those of KAVI. Remaining layers for the Susceptibility Index were created by clipping the necessary data from DRASTIC as it was previously applied to Hillsborough County, and then adding those layers to the land-use component. Weights were also included for the SI as stipulated by Stigter et al. (2006): depth to water 18.6%, net recharge 21.2%, aquifer media 25.9%, topography 12.1%, and land use 22.2%. The resulting equation is as follows:

$$\mathrm{SI} = 0.186 \times D + 0.212 \times R + 0.259 \times A + 0.121 \times T + 0.222 \times \mathrm{LU}$$

where

D	Depth to water
R	Net recharge
A	Aquifer media
T	Topography
LU	Land use

Similar to KAVI, SI utilizes a number system in which the higher the number assigned, the greater the assumed vulnerability of that area. SI was designed for a study area that included both carbonate rocks and detritic sediments. Corresponding vulnerabilities are categorized according to the same scale utilized for an agricultural study in Portugal (Stigter et al. 2006) which were adjusted to correspond with the four-class scheme of the KAVI. Classes are as follows: 70–90 is high vulnerability, 60–70 is moderate to high vulnerability, 50–60 is moderate to low vulnerability, and 0–50 is low vulnerability.

Sensitivity analysis tests how human subjectivity affects vulnerable scores for the entire domain by removing one parameter/map from the index (Lodwick et al. 1990;

Table 2 SI ratings for land cover (0 = lowest, 100 = highest)

Land use	Rating
Agricultural areas	
Irrigation perimeters (annual crops, paddy fields	90
Permanent crops (orchards, vine yards)	70
Heterogeneous agricultural areas	50
Pastures and agro-forested areas	50
Artificial areas	
Industrial waste discharges, landfills	100
Quarries, shipyards, open-air mines	80
Continuous urban areas, airports, harbors, (rail) roads, areas with industrial or commercial activity, laid-out green spaces	75
Discontinuous urban areas	70
Natural areas	
Aquatic environments (salt marshes, salinas, intertidal zones)	50
Forests and semi-natural zones	0
Water bodies	0

Napolitano and Fabbri 1996). The equation that outlines the test in our article is

$$S_{\mathrm{KAVI}} = [(V_{\mathrm{KAVI}}/N - V_{\mathrm{KAVI-1}}/n)/V_{\mathrm{KAVI}}] \times 100$$

where

- S_{KAVI} sensitivity related to the removal of one parameter
- V_{KAVI} vulnerability index
- $V_{\mathrm{KAVI-1}}$ vulnerability index computed without one parameter
- N number of parameters used to compute KAVI (5)
- n number of parameters after one layer removal (4)

The accuracy of the weights assigned for the KAVI parameters can be determined by calculating the effective weights (W_{KAVI}) of each parameter:

$$W_{\mathrm{KAVI}} = ([R_{\mathrm{KAVI}} \times W_{\mathrm{KAVI}}]/V_{\mathrm{KAVI}}) \times 100$$

where

- R_{KAVI} parameter rating value
- W_{KAVI} weight for each parameter
- V_{KAVI} final vulnerability score

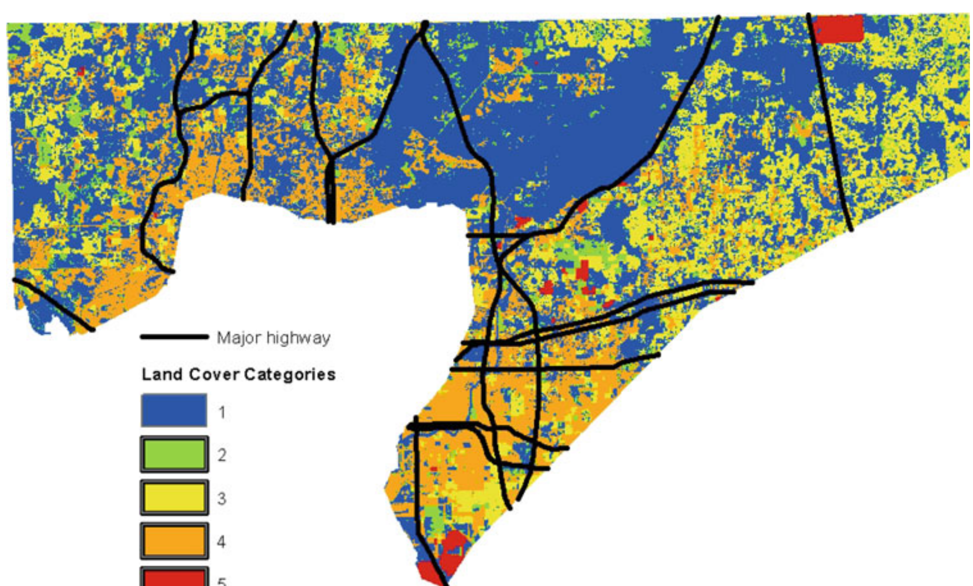
4 Results and Discussion

4.1 Application of KAVI

The anthropogenic layers of KAVI display, in detail, the heterogeneity of human activity within our study area (Fig. 2) which is understandable considering the urban–rural nature of the county. Such variability is absent from physical layers of S and A (Fig. 3) which is due in part to overall homogeneity of the lowland coastal plain but may also reflect the data classification system. This system is designed to encompass all ranges of permeability and conductivity (Table 1) found in the natural environment, and due to the low relief and uniform nature of the soil cover for our particular area, values almost entirely fall within the lowest (conductivity) or highest (permeability) categories of vulnerability for these two layers. E and D parameters show greater variability and consequently have the greater potential on influencing overall vulnerability. KAVI, being a karst related index, places more weight (25%) on E than the other physical parameters (15%), and high densities of sinkholes can be found in the western and southern portions of the area.

Overall vulnerability for the FAS is generated by combining the weighted layers as KAVI (Fig. 4). High concentrations of sinkholes combined with the dense residential–industrial areas generate the highest overall vulnerability. However, where high densities of sinkholes coincide with major highways, the lines of high vulnerability are also apparent, as expected. Clusters of higher vulnerability are located in southern and western portions of the study area (Fig. 4). Central-northern Hillsborough County has low FAS vulnerability due to few sinkholes but also minor human alteration of the natural environment. The Hillsborough River which flows through this area and its surrounding swampland has limited development. In addition, a major source of the city of Tampa's water supply comes from this catchment, both from well fields and the river (which is dammed); hence, the future low vulnerability of this area is assured.

Fig. 2 Potential anthropogenic sources of pollution for the Floridan aquifer system



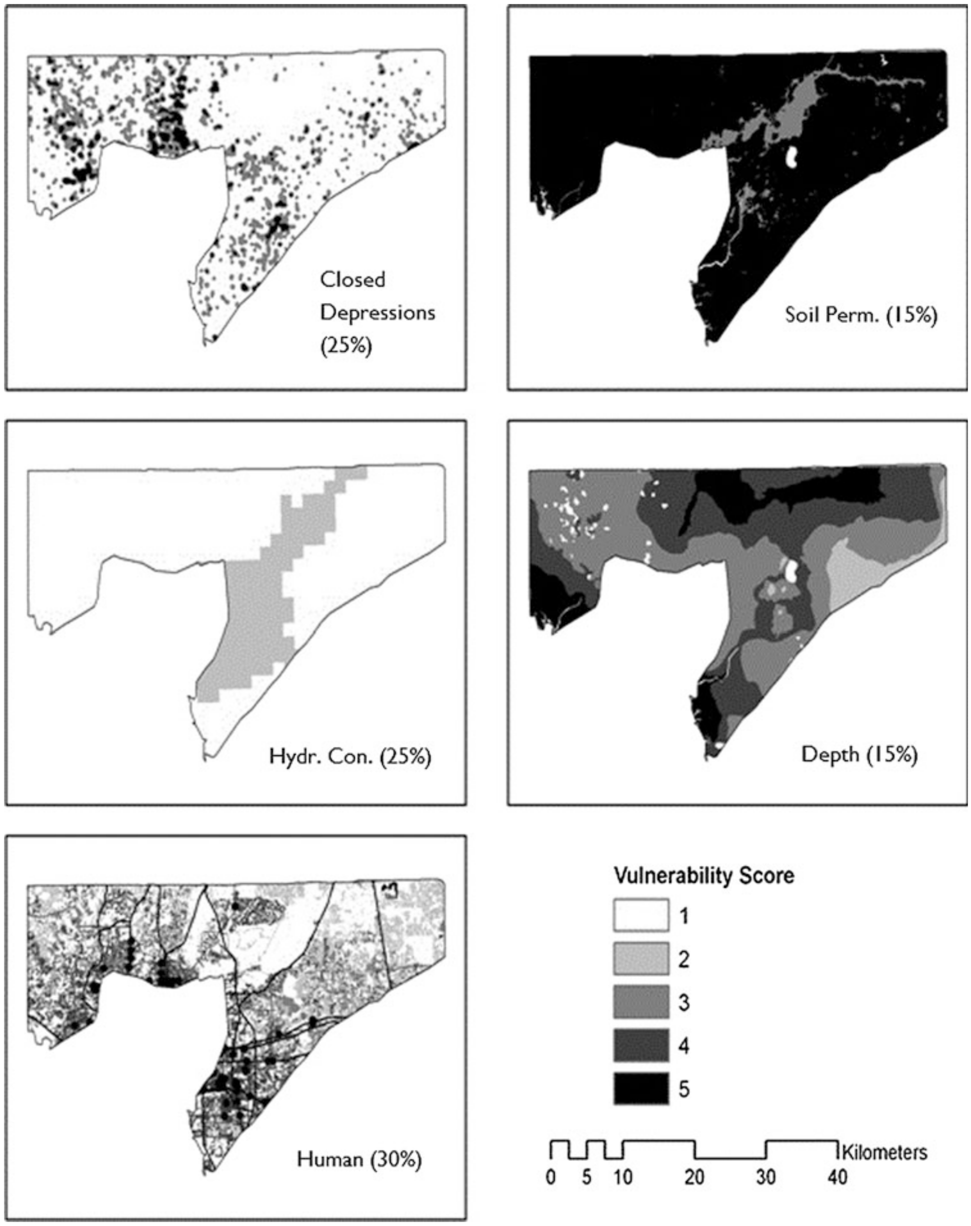


Fig. 3 Physical input layers into KAVI

4.2 Application of Susceptibility Index (SI)

Application of SI was undertaken as a means to determine whether our specific vulnerability index (KAVI) which designed for karst landscapes outperforms another specific vulnerability index (SI) that was not created for a karst setting.

Input layers for SI are depicted in Fig. 5, and it is apparent that these layers vary significantly from those of KAVI, consequently the two final vulnerability maps are quite different (Fig. 6). SI's use of DRASTIC as the basis for its physical parameters is quite apparent in the final vulnerability map. The "blocky" nature of the zones is indicative of the R layer of SI, which has the highest weighting of all the layers (Fig. 5). What is somewhat surprising the percentage of the county that is classified in the two highest vulnerability categories. There are certainly some similarities with KAVI, such as the western and southern sections of the FAS, but considerably larger areas fall within the very highest level of vulnerability as denoted by SI. The reason why SI assigns such large areas as high vulnerability is due to the contribution of the layers *R*, *A,* and *T* (Fig. 5), which as a result makes SI appear extreme in highlighting problem zones for the FAS. A major discrepancy between the two indices is in the western section of the study area as well as the very southern portion which SI deems as moderate to high vulnerability. The reason for this difference once again is the weight SI places on the *R*, *A,* and *T* layers.

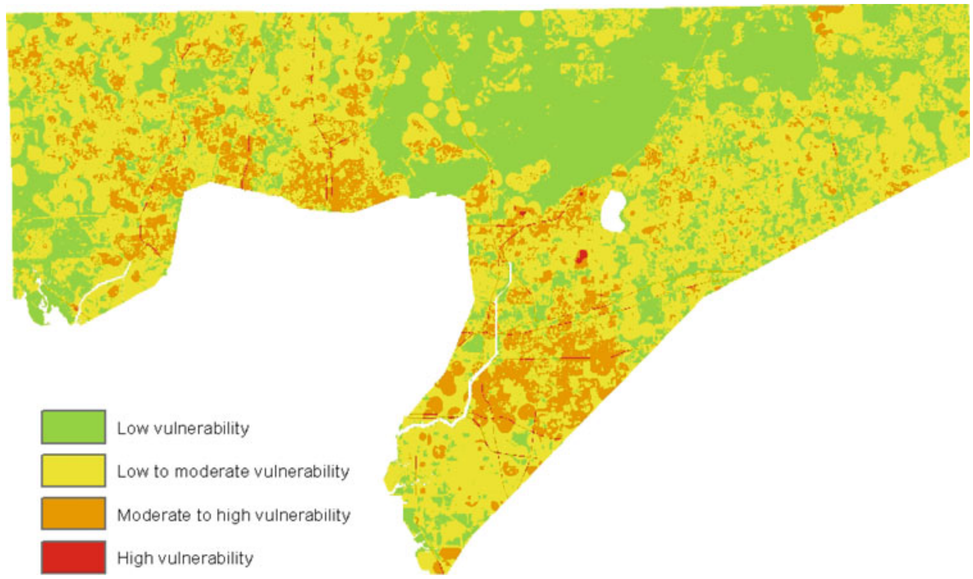


Fig. 4 Combined weighted layers depicting KAVI for the Floridan aquifer system

4.3 Comparison Between KAVI and SI

To better quantify the difference between KAVI and SI, GIS was used to show areas of agreement and divergence based on vulnerability classes (Fig. 7). The more negative values depict areas that SI classifies as more vulnerable compared to KAVI while more positive values are areas that KAVI classifies as having higher vulnerability compared to SI. It is not surprising that the preponderance of negative values confirms the above conclusion that SI is skewed toward higher vulnerability values. However, to truly quantify the differences between SI and KAVI, *GIS spatial analyst* was used to calculate the percentage measured by each index for the four vulnerability classes (Table 3). The results clearly show that SI suggests a serious threat is posed to the FAS with ~77% of the study deemed moderate to high and high vulnerability. In comparison, KAVI only states that ~13.5% falls in these categories.

Another measure of their difference is to calculate what percentage of the area KAVI values exceed SI and vice versa. KAVI vulnerability values only exceed SI for 3.47% of the area: conversely, SI exceeds KAVI for 85.3% of the area, with 11.25% in agreement (Table 4). Stitger et al. (2006) found that for SI, overestimation of vulnerability seems to occur frequently. Hence, by any measure KAVI appears to be the more conservative of the two indices pertaining to assessing FAS vulnerability.

One approach to determine whether KAVI is too conservative or SI too extreme is to validate the indices using the data of an actual water quality parameter measured in the groundwater of the study area.

4.4 Validation

Ravbar and Goldscheider (2009) state that there is no standard practice of validating vulnerability maps. They were referring to intrinsic vulnerability which considers only physical parameters and ignores human land use. However, specific vulnerability does incorporate the latter, and as such other approaches are available. Human activity can produce various chemical constituents that will vary in concentration due to both land-use and physical characteristics of the environment above and within the aquifer. While Ravbar and Goldscheider (2009) proposed using water tracer tests as surrogates for contaminants and as a method to validate their maps, the lack of springs within our area precluded such an approach.

Nitrate data collected from 75 wells by the Southwest Florida Water Management District (SWFWMD) that withdraw water from the FAS provided the opportunity for a validation test to determine which index could best reproduce the concentration of this parameter. The number of wells provided a certain degree of confidence of the results of the statistical analyses undertaken. Nitrate was chosen as it is deemed by the local water authorities as the most significant contaminant for the Floridan aquifer due to the high fertilizer use.

Well locations were plotted on the vulnerability maps of KAVI and SI in ARCGIS®, and then, maximum nitrate concentrations for these wells were portrayed on these same maps (Fig. 8a, b). None of the constituent values for the wells exceeded the recommended maximum concentration of nitrate (10 mg/L). Inspection of these maps appears to suggest that KAVI corresponds more closely with nitrate than SI as is confirmed by the Pearson Correlation test (KAVI: $r = 0.341$, $p = 0.001$; SI: $r = 0.026$, $p = 0.461$) for each index.

4.5 Sensitivity Analysis: S_{KAVI}

With the creation of any intrinsic or specific GVM, a certain amount of subjectivity is unavoidable when assigning rating values and weights for each parameter. Sensitivity analysis can test for this subjectivity by removing one parameter/map from the model and measuring how that affects the vulnerable score for the entire domain (Lodwick et al. 1990; Napolitano and Fabbri 1996).

The results of this sensitivity analysis (Table 5) found that the parameter with the highest sensitivity was LU followed closely by *S*. It is not surprising that LU is the most sensitivity because of its high weighting and hence a large impact on vulnerability. The low sensitivity to *A* is because this coverage has the lowest range in values consequently a small contribution to the overall scores. However, we cannot ascertain why KAVI is most sensitive to *A*. The individual layer for this parameter has the least variability of any in KAVI (Fig. 3). A possible reason for this result is the extreme variability of this parameter across the study area. The parameter with the lowest sensitivity, *S*, could be a result of the fairly uniform soil thickness across the study area.

4.6 Effective Weights for KAVI: W_{KAVI}

When calculating the final vulnerability score for KAVI, each parameter has been assigned a weight according to what we deemed was its relative contribution to the overall vulnerability of a karst environment. To determine whether the weights assigned for KAVI are truly representative of the relative importance of each parameter for vulnerability, effective weighting analysis provides insight to this question.

The weights that were originally assigned for calculating KAVI were found to be quite accurate for the parameters *D*,

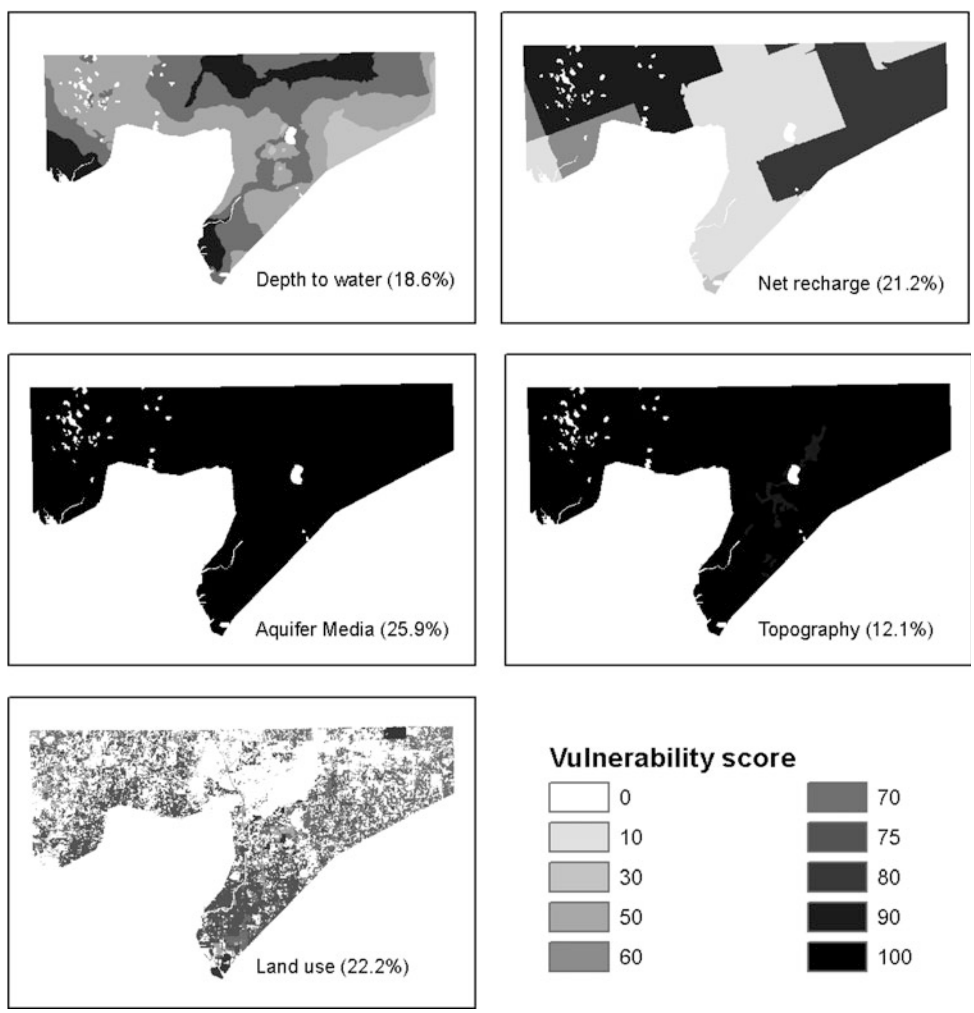


Fig. 5 Physical input layers into SI

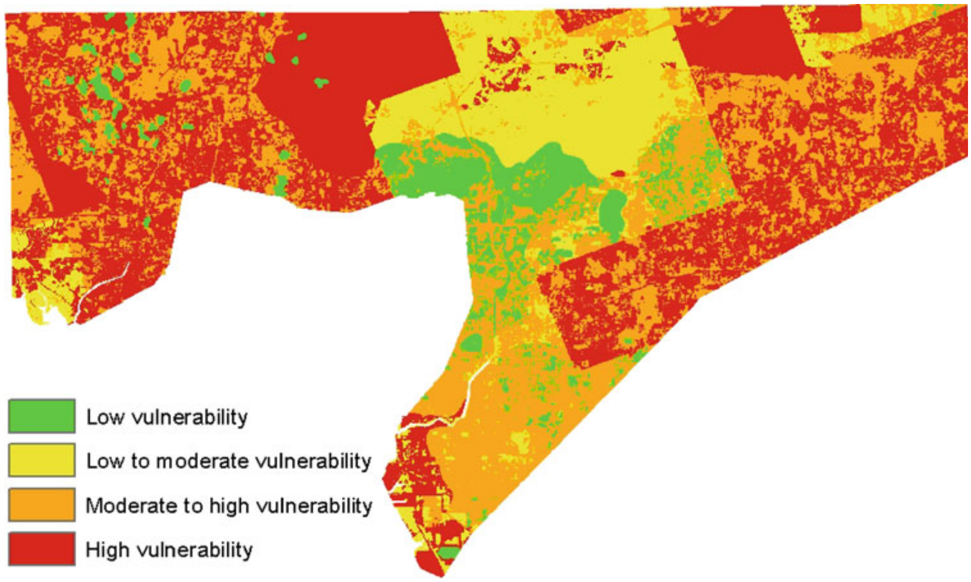


Fig. 6 Susceptibility Index overall layer for the Floridan aquifer system

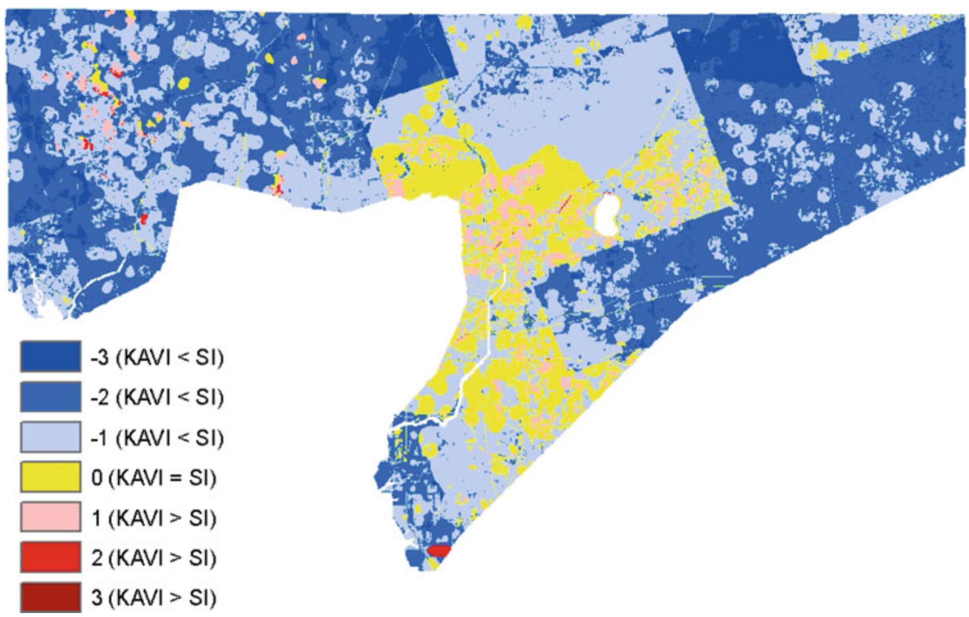


Fig. 7 Vulnerability class-based comparison between KAVI and SI

Table 3 Percentage of study area in each vulnerability class by index

Vulnerability	KAVI (%)	SI (%)
Low	37.55	7.95
Low to moderate	48.85	15.11
Moderate to high	13.29	36.58
High	0.30	40.36

Table 4 Percentage of study area by difference in vulnerability classes

Difference in class values	% of total
KAVI > SI	3.47
KAVI = SI	11.25
KAVI < SI	85.3

Fig. 8 **a** Overlay of maximum contaminant concentrations over KAVI vulnerability layer; **b** overlay of maximum contaminant concentrations over SI vulnerability layer

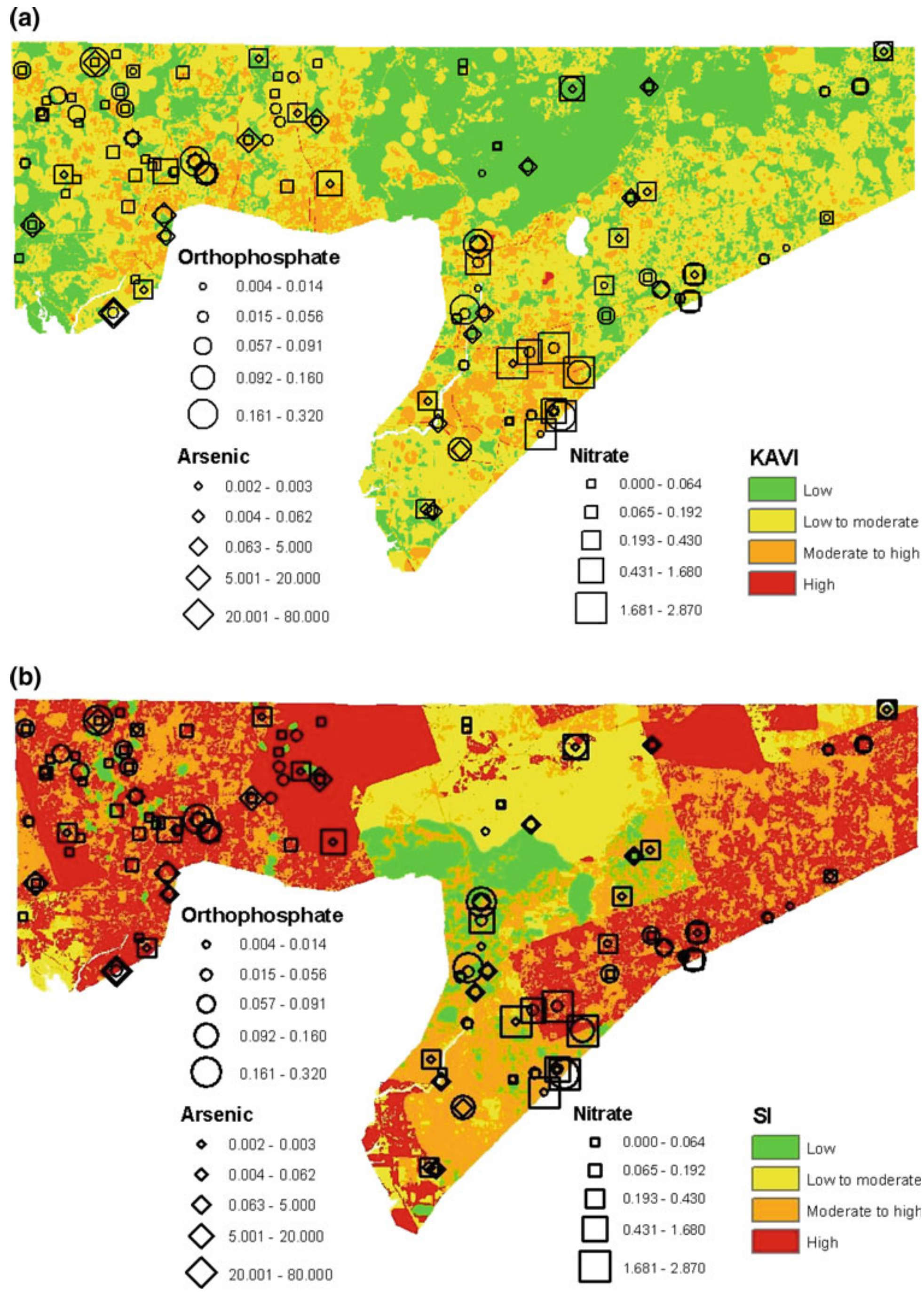


Table 5 Sensitivity analysis with the removal of one parameter (%)

Parameter removed	Mean	Minimum	Maximum	Standard deviation
D	13.35	3.0	30.0	4.69
S	28.0	11.39	39.47	5.87
A	6.95	2.75	21.95	3.13
E	17.68	5.43	45.45	8.82
LU	33.94	17.14	72.97	9.22

Table 6 Determining the results of changing the effective weights

Parameter	Theoretical weights		Effective weights (%)			
		%	Mean	Minimum	Maximum	Standard deviation
D	0.15	15	15.14	3.95	34.09	5.38
S	0.15	15	31.87	12.33	46.88	7.49
A	0.15	15	7.92	3.66	25.71	3.66
E	0.25	25	19.91	7.35	51.02	9.64
LU	0.30	30	25.09	9.38	56.6	11.12

CD, and LU (Table 6). However, the result shows that the importance of land use and closed depressions was slightly overestimated: LU's theoretical weight of 30% compared to the effective weight 25.09% and CD overestimation was approximately 5%. The major discrepancies were for the *S* and *A* layers. Soil permeability was vastly underestimated because of the sandy soils in the area while major aquifer hydraulic conductivity difference was mostly likely due to the low value for the study area of <1.5 cm/h.

5 Conclusions

GVMs have been used during the last 20 years to determine the potential for contamination for groundwater. Many GVMs focus on intrinsic vulnerability and thus base their predictions on solely hydrogeologic parameters. In contrast, KAVI is a specific vulnerability model, similar to the SI, but differs in that it incorporates the karst topography of a region and that topography's potential to lead to contamination events within an aquifer system. While the vulnerability maps of SI and KAVI have some common zones of vulnerability, SI is prone to overestimating vulnerability, as evidenced by designating most of the study area as moderate to highly vulnerable. Both models were subjected to validation using water quality indicator nitrate that was measured from wells in the FAS. Statistical tests found that KAVI outperformed SI in correlating vulnerability levels with concentrations of nitrate. Such a result indicates that KAVI has the capability to highlight zones that are vulnerable to surface contamination. The emphasis KAVI placed on epikarst (captured as sinkholes) probably accounts for this result as sinkholes represent rapid flow paths of contamination to the FAS. Finally, sensitivity analysis and effective weighting calculation justified the importance of including land use in defining the vulnerability of aquifer to the influence of surface human activities.

From this study, it would appear that GVMs such as KAVI that are specifically designed for karst areas provide a reliable tool for environmental managers to delineate zones of protection for the aquifer. Areas denoted as high vulnerability could be given top priority for restricting certain land-use types while future development may be directed to those areas of low vulnerability. Future research to improve KAVI will require its application to other karst areas to determine whether it can replicate contaminant levels in those areas.

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Part VI

Aquifer Studies

Lithofacies and Transport for Clastic Sediments in Karst Conduits

Rachel F. Bosch and William B. White

Abstract

Karstic aquifers carry a load of clastic sediment as part of their hydrologic function and these 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 are usually well delineated, sediments from multiple sources are mixed and redistributed within the aquifer to produce the sediment deposits that remain stored in caves or the load of sediment discharged from karst springs. As an aid to the interpretation of clastic sediments in karst aquifers, we have modified a previously proposed facies concept with an emphasis on its implications for contaminant transport and storage. Five facies are defined in terms of particle size, degree of sorting, and sedimentary structures: backswamp facies, channel facies, diamicton facies, slackwater facies, and thalweg facies. The deposits represented by each set of facies characteristics in turn can be interpreted in terms of depositional mechanisms. The slackwater facies and channel facies are the most significant in terms of implications for contaminant transport and therefore receive greater emphasis than the other three in this discussion. The facies labeled 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 labeled 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.

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1 Introduction

One of the most important characteristics of karstic drainage basins is the ability of their subsurface conduit systems to transmit insoluble materials in a range of particle sizes from colloids and clays to cobbles and (occasionally) boulders. Clastic sediments are derived from a variety of sources including surface stream sediments washed in by sinking streams; materials from the overlying land surface injected through shafts, sinkhole drains, and open fractures at the base of the epikarst; and insoluble residues from the dissolution of the bedrock. The conduit system acts as a mixing chamber so that the sediments deposited in caves or discharged from karst springs are typically derived from multiple source areas and further have often lost the characteristics of the source material. There are also multiple mechanisms for transport of clastic sediments. Cave deposits provide a useful representation of the types of materials being transported through the aquifer so it would be helpful to devise a means for labeling and classifying these deposits. Much discussion of sediment sources, description of deposits, and mechanism of transport can be found in two reviews (White 2007; Herman et al. 2012).

Labeling various clastic sediment deposits as facies appeared in a discussion of sediment transport (White and White 1997) and in a study of cave sediments in the Cheat River Gorge, West Virginia (Springer and Kite 1997). The facies concept was expanded and given a new labeling by the present authors (Bosch and White 2004). That labeling was used in the review papers cited above and was found useful in the description of clastic sediments in the Butler Cave-Sinking Creek System, Virginia (Chess et al. 2010). Given the importance of clastic sediments in contaminant transport, we here further refine the facies concept of clastic sediments in caves and suggest their relevance to the storage and transport of certain classes of contaminants. We made changes to better integrate the nomenclature of cave sediment facies with traditional sedimentation terminology, as well as to calculate the hydrologic conditions that would have likely been required to produce the observed sediment deposits. More detail may be found in the thesis from which this paper is drawn (Bosch 2015).

2 The Facies Concept as Applied to Caves

The facies names presented in Bosch and White (2004) are backswamp facies, channel facies, diamicton facies, slackwater facies, and thalweg facies. The original classification was based on particle size and particle sorting but mixed a physical description with an interpretative mechanism. The locales described in the original publication were reanalyzed and objectively described, according to Miall's (1996) facies codes (Table 1). The facies types are sketched (Fig. 1) to show the populations in terms of particle size and sorting. The facies are drawn as separate areas for clarity. For most real sedimentary deposits, there would be no blank areas and the facies types would be less distinct and probably overlap.

The names given to the facies imply a mechanism of deposition as outlined below. Further detail and explanation are given in the original publication (Bosch and White 2004).

Channel facies are the subsurface equivalent of surface stream sediments. Like surface stream deposits, their movement is episodic, carried by flood flow events. Unlike surface streams, however, karst conduits can shift from open channel flow to pipe flow if the flood discharge is sufficient to fill the conduit. This partially contributes to the discontinuous sequence of clays, sands, gravels, and cobbles distributed along the conduit at deposition sites dictated by the irregular geometry of the conduit itself.

Thalweg facies are well-winnowed remnants of the channel deposits. Base flow and moderate flows in cave

Table 1 Classification of sedimentary facies in caves

Facies code	Facies	Sedimentary structures	Interpretation
Fsm	Clay to silt	Massive with possible chert fragments and/or fossils	Backswamp cave deposit (insoluble residue)
Gcm, Srh	Crudely bedded to massive gravel, granule to cobble; very fine to coarse sand	Horizontal bedding to unbedded, ripple cross-bedding to horizontal bedding	Channel cave deposit
Gmm	Massive, matrix-supported clay to boulder	Chaotic, unsorted, unbedded	Diamicton cave deposit (debris flow)
Fl	Clay to very fine sand	Fine lamination	Slackwater cave deposit (overbank or waning flood)
Gh	Gravel, pebble to boulder	Well-sorted, open framework; well-winnowed	Thalweg cave deposit

In these facies codes, *F* indicates a facies dominated by fine-grained sediment; *G* gravel-dominated; and *S* sand-dominated. The lowercase letters refer to sorting and sedimentary structures present: *c* crudely bedded, *m* massive or matrix supported, *r* ripple cross-bedding, *h* horizontal bedding, and *l* laminated

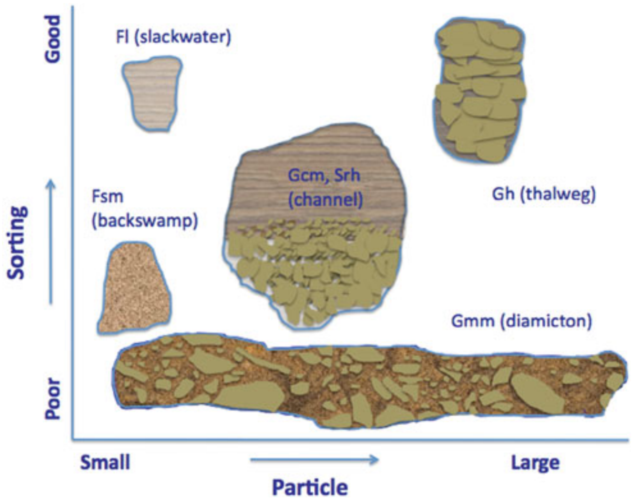

Fig. 1 Qualitative sketch showing the division of cave sediments into facies based on grain size and sorting, including Miall's (1996) facies codes

streams winnow out clays and sands leaving the coarse fraction as a stream bed deposit.

Slackwater facies are deposited from suspended particles in muddy floodwaters that entered either as overbank flows or as backflooded water from surface streams. As a result, they are fine-grained and thinly laminated with the laminae marking subsequent flood events. Channel facies, thalweg facies, and slackwater facies are all very common and are associated with aquifers containing (or that contained in the past) active conduit systems.

Diamicton facies are the result of debris flows where materials of all particle sizes are taken into suspension and flow down high gradient passages. Diamicton facies are uncommon because the geological conditions needed are uncommon.

Backswamp facies is the not entirely satisfactory name given to the residual insoluble material left by dissolution of the bedrock and sifted down from the epikarst. The composition of the backswamp facies depends entirely on the characteristics of the insoluble fraction of the bedrock. Backswamp facies are found in caves formed by percolating groundwater with little stream action.

3 Calculation of Transport Thresholds for Channel Facies

Cave deposits can be examined to interpret the paleohydraulic conditions that would have been necessary for their deposition. We may then observe present-day flows and make good predictions as to what kind of sediment deposits and therefore what kind of contaminants we would expect to result. These implications can be applied to contaminants

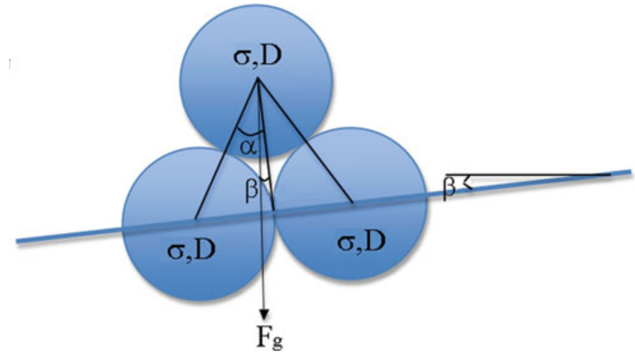

Fig. 2 Sketch for entrainment of a particle resting on identical particles

that are transported in similar modes to the sediments discussed here, as well as to contaminants that move in aqueous solution. We present the calculations here for transport of channel facies as one example of deriving paleohydraulic conditions. Similar derivations, with differing levels of complexity, may be performed for the other four facies, ranging from straightforward analytical calculations to multi-component computer modeling.

In the real world, there is the fairly complex arrangement of sediment grains of varying density, size, and shape resting on several other grains, each of a different size and shape from the first grain and from each other. That situation can be addressed using modeling software. For this work, to simplify the mathematics and to obtain rough estimates for the flow conditions that may have been present to transport sediments, several assumptions have been made. We first choose to address a two-dimensional problem of one grain resting on two grains. Second, we assume that all three of these grains are spherical and have the same diameter, *D*. These three grains are assumed to be resting on a streambed of uniform, linear slope, *S* as illustrated in Fig. 2.

An expression for determining the threshold shear stress necessary to entrain a given particle can be obtained from balancing the torques exerted on a grain about the contact points with the grains below. This balance of torques, as presented by Allen (1985), yields Eq. (1). This can only be applied to grain sizes larger than 60 µm since it does not account for grain-to-grain cohesion forces (Huang et al. 2015). Here, we will take the simplest case, where each grain is spherical and is resting on a bed of same-sized grains, also having diameter *D*.

$$\tau_{cr} = \frac{2D(\sigma - \rho)g}{3\cos\beta}\tan(\alpha - \beta) \quad (1)$$

where

τ_{cr} is the critical shear stress at the threshold of entrainment (N m^{-2}),

D is the diameter of the sediment grain to be transported (m),
σ is the density of the grains (2650 kg m^{-3}),
ρ is the density of the fluid (1000 kg m^{-3}),
g is acceleration due to gravity (9.80 m s^{-2}), and
α is the angle between the line connecting the centers of the grains and the perpendicular to the bed, and β is the angle that the bed tilts away from the horizontal.

Therefore,

$$\tau_{cr} = \frac{10,780D}{\cos\beta}\tan(\alpha - \beta) \quad (2)$$

Examining Fig. 2, it is apparent that because we have assumed equal diameters for the grains being considered, the triangle connecting the center points of the three spheres is equilateral, with each side of length D, and therefore, $\alpha = \frac{\pi}{6}$. Here, then, is the equation that will be applied to each set of field data:

$$\tau_{cr} = \frac{10,780D_{50}}{\cos(\tan^{-1}S)}\tan\left(\frac{\pi}{6} - \tan^{-1}S\right) \quad (3)$$

where D_{50} is the fiftieth percentile grain size sampled at the given field site and S is the slope of the streambed at the sampling site.

τ_{cr} can be used to calculate shear velocity (m s^{-1}), $u_* = (\tau_{cr}/\rho)^{1/2}$, which can then be used to estimate a stream flow velocity, u, also in m s^{-1}.

$$u = \frac{u_*}{\kappa}\ln\left(\frac{z}{z_0}\right), \text{ or substituting } u = \frac{(\tau_{cr}/\rho)^{1/2}}{\kappa}\ln\left(\frac{z}{z_0}\right) \quad (4)$$

where κ, 0.40, is the von Kármán constant (Bailey et al. 2014), and z/z_0 is the roughness factor, which has been found to be about 9 for rough cave floors and walls through simulation of cave flow conditions (Bird et al. 2009). Applying these values yields an estimation of flow velocity needed to move the fiftieth percentile diameter of the sediments that were sampled:

$$u = 0.17\sqrt{\tau_{cr}} \quad (5)$$

Equation (5) was used to calculate the flow velocities needed to move the channel facies sediments from the Hawkins and Logsdon Rivers in Mammoth Cave (KY) and from Tytoona Cave (PA) using the data published by Bosch and White (2004). These velocities, presented in Table 2, are in the same range as flow velocities observed in cave streams (Palmer 2007). The fastest flows calculated, at 1–2 meters per second, match what would be expected during flood flow conditions in Tytoona Cave. It appears that these very rough calculations of the hydraulics of channel facies produce a reasonable agreement between sediment size and the stream velocity needed to move them.

4 Application of the Facies Concept to Contaminant Transport

The different sediment facies have different implications for the type of contaminant transport and the extent of contamination possible. The two most important are the channel facies and the slackwater facies.

Channel facies are stream deposits in conduits which have, or have had in the past, water moving at velocities comparable to those shown in Table 2. Boundary shears sufficient to carry sand, gravel, and even cobbles are also sufficient to carry solid waste in the form of cans, bottles, garbage, and in some cases old tires. Trash dumped in sinking surface streams can be carried underground and transported long distances. When velocities decrease due to ponding behind some blockage in the conduit, the trash becomes incorporated into the channel facies sediments where derivative decomposition products can be leached out over long periods of time.

Channel facies sediments themselves are porous media. Contaminants in the form of non-aqueous phase liquids (especially DNAPLs) can be adsorbed into the sediment pile which acts as a storage site. Channel facies sediments are moved during extreme floods so there is the potential for contaminant release long after the original spill.

A portion of the same suspended fine-grained particles that settle to become the slackwater facies are also discharged directly from karst springs, especially during flood flow when the spring waters may become muddy. It has been well-established from examination of spring waters that pathogens and metals are transmitted adsorbed onto clay particles. The sediments that remain in the conduit as

Table 2 Sediment data, stream water surface slope, and sediment transport characteristic calculations for cave streams

Site	D_{50} (m)	S	τ_{cr} (N m^{-2})	u_* (m s^{-1})	u (m s^{-1})
Logsdon River	0.00018	0.001*	1.12	0.033	0.180
Hawkins River	0.00050	0.002	3.10	0.056	0.299
Tytoona Cave—bed surface	0.016	0.01	97.3	0.312	1.70
Tytoona Cave—deep bed	0.0040	0.01	24.3	0.156	0.839

Water surface slopes estimated based on present stream geometries with the exception marked * where S was obtained through measurement of water surface slope at time of sediment sampling slackwater facies are likely to carry contaminants which become incorporated in the sediment pile to be released at some later time when the pile is mobilized by floodwaters.

5 Conclusions

Clastic sediments deposited in conduit systems can be divided into five categories based on descriptive facies: backswamp, channel, diamicton, slackwater, and thalweg. These facies can be interpreted in terms of depositional conditions, which provide evidence of transport conditions that were present during contamination events. Such findings may be used to predict expected distribution of contamination in karst systems. Coarse debris injected by sinking streams and from sinkhole dumps is most likely to be associated with the channel facies. Pathogens and some organic molecules are adsorbed onto clay particles and may be associated with the slackwater facies.

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Delineation of a Major Karst Basin with Multiple Input Points, Roaring River, Tennessee

Ryan Gardner, Evan Hart, and Chuck Sutherland

Abstract

Karst aquifers that are dominated by conduit recharge are at high risk of contamination because there is little filtration or sorption of contaminants in the water. Identifying flow paths through conduit aquifers is required in order to delineate basin boundaries and potential areas at risk from groundwater contamination. In this study we report on the first continuous (~1 year) discharge and water quality data set ever collected from the Boils spring on the Highland Rim of middle Tennessee. The Boils drains the Roaring River-Spring Creek system, a State Scenic River and Wildlife Management Area. We also report on the results of a quantitative dye trace that was done to identify surface contributions to this spring. At the Boils, we measured discharge, temperature, and specific conductance for an approximate one-year period. The average annual discharge of the Boils during 2015 was 2.1 m^3/s, with storm discharge reaching as much as 14 m^3/s. Conductivity at the Boils spring ranged from 310 µS at baseflow to 290 µS during storm events. Water temperature of the spring varied seasonally from 9 to 22 °C. The dye trace revealed a direct connection to the Boils from a sink located 9 km away (straight-line distance), with a travel time of about 12 h. A second trace at another sink covered a straight-line distance of 1.5 km in 4 h. The rapid travel times suggest that this aquifer is dominated by conduit flow and that further research to sample water quality is warranted. Our data help to fill an important gap in data about major spring discharge and water quality in Tennessee.

1 Introduction

Karst aquifers are characterized by conduits that transport large volumes of groundwater quickly over long distances (White and White 1989). Karst conduits have short water residence times and increase the bulk permeability of the overall aquifer. Although karst aquifers supply up to one-quarter of the world's population with drinking water (Ford and Williams 2007), the susceptibility of these aquifers to contamination has been widely reported (Du Preez et al. 2016; Vesper and White 2003; Field 1993). Due to these reasons, numerous techniques have been employed to characterize groundwater flow in karst aquifers, including spring flow water analysis, both chemical and physical properties (Liñán Baena et al. 2009; Goldscheider and Drew 2007; White 2002; Ryan and Meiman 1996; Padilla et al. 1994; Shuster and White 1972) and tracer studies (Pronk et al. 2007; Greene 1997; Keswick et al. 1982). In spite of these advances in karst hydrology, the vast majority of karst springs have never been monitored for discharge or water quality, and this is especially so for Tennessee, where most of the large karst springs have never been monitored. In this study we report on the first continuous discharge and water quality data set (~1 year), as well as the results of a quantitative dye trace, for the Boils spring on the Roaring River, Tennessee.

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Fig. 1 The Boils spring on Roaring River. Discharge shown is in winter and is approximately 3 m^3/s. Water sampling for dye trace was done just downstream from this location

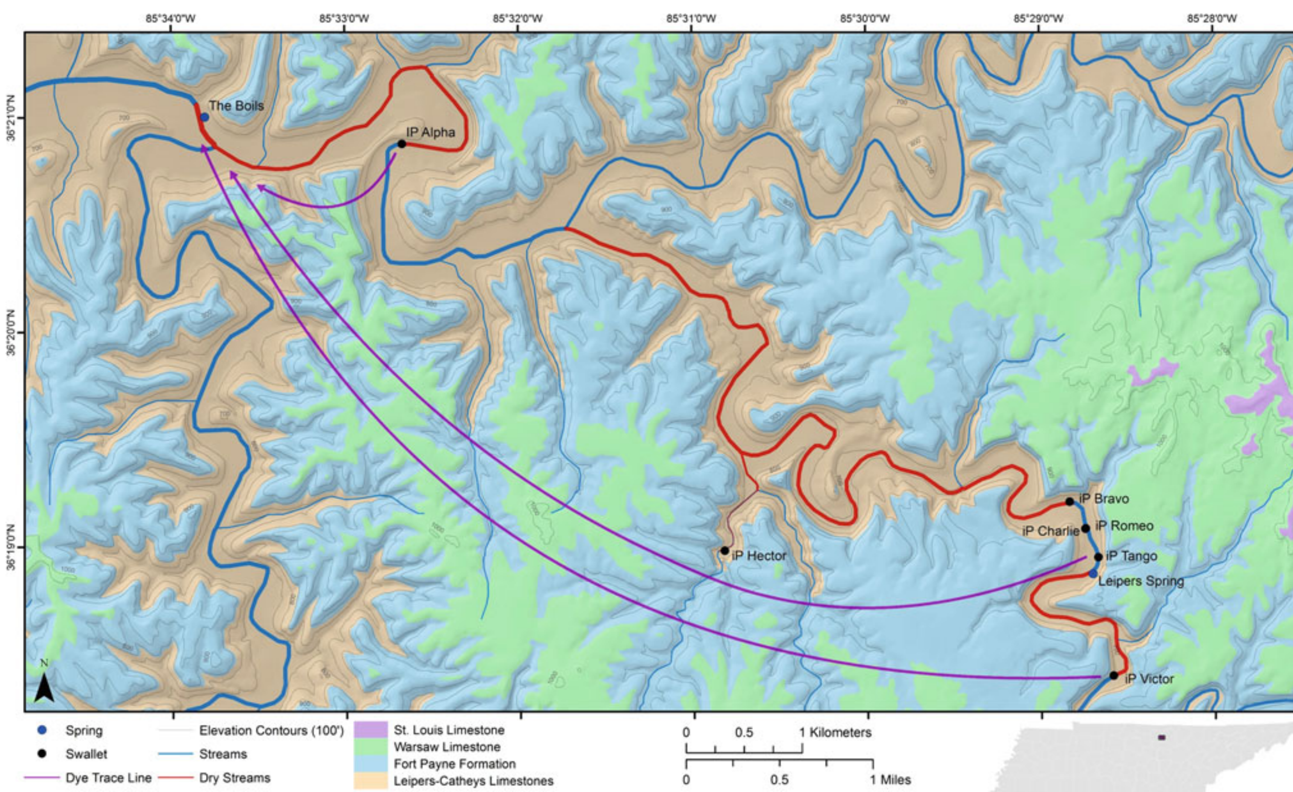

Fig. 2 Map showing the Roaring River-Spring Creek system. The two input points for dye trace were IP-Alpha and IP-Tango. Dye collection with automatic sampler was done at the Boils

2 Study Area

The Highland Rim region of Tennessee is characterized by a classic fluvio-karst landscape where sinking streams and conduit networks leave miles of streambed mostly dry, punctuated with stagnant pools of water. These systems are drained by one or more major springs often located at contacts with less permeable strata. The Roaring River-Spring Creek system is a major tributary of the Cumberland River and has been designated as a State Scenic River and Wildlife Management Area. The major perennial spring on the Roaring River is the Boils, named for the fact that water erupts vertically from conduits on the streambed, creating a noticeable boil on the water surface (Fig. 1). The watershed area for the Roaring River above the Boils is approximately 200 km^2 according to topographic maps (Fig. 2).

Land use in the watershed is mostly rural residential, forest, and light agriculture. The streams in the basin originate on the Pennsylvanian clastics of the Cumberland Plateau, and many of them sink into the Mississippian carbonates. In the lower reaches, Spring Creek and Roaring River flow west over the Ft. Payne Formation, a silica-rich limestone that acts as an aquiclude, until they intersect the Ordovician Chattanooga Shale. The Chattanooga Shale is underlain by the soluble Leipers Limestone, a dark gray, fossil rich, and medium-bedded Odrovician carbonate unit. Large cave systems are not typical of the Leipers; however, many dry streams in the area suggest that underflow conduits are large enough to drain the entire baseflow for these systems. This study focuses on karst features (sinkholes and the Boils spring) which are found within the Leipers limestone.

Fig. 3 In-stream swallet IP-Bravo is shown here taking almost all of the baseflow of Spring Creek in summer

3 Materials and Methods

The first step in the project was to identify the locations of karst features in the basin. It was noted in the field that the entire flow of Spring Creek at baseflow enters the subsurface at a series of sinkholes in the streambed, leaving most of the stream dry at baseflow (Fig. 3). Locating swallets was accomplished by talking to local residents, paddling remote stream sections, and walking the streams at baseflow. To accurately record the high-amplitude short-term variations in water quality at a karst spring following runoff events, a high-frequency flow-dependent sampling strategy must be implemented (Quinlan and Ewers 1985; Quinlan and Alexander 1987). An automatic stage recorder, water sampler, and conductivity logger were installed to record discharge, temperature, and conductivity continuously at the Boils during 2015. Two dye traces were carried out during the summer of 2015 from three different swallets on Spring Creek and one swallet on the Roaring River, and all dyes were recovered at the Boils in water samples and activated carbon. The first trace was qualitative and carried out at high baseflow, and the second trace was quantitative and carried out the day after a rain event. Precipitation was recorded at several weather stations located in Cookeville, TN, and in the Roaring River watershed. Rhodamine WT (RWT) and uranine dyes were used and an ISCO automatic water sampler was used to take samples at the Boils spring at 30 min intervals. Water was drawn out of each sample bottle and placed into 10-mL cuvettes, to be analyzed for fluorescence with a spectrofluorophotometer.

4 Results

RWT was injected at iP Tango and uranine was injected simultaneously at iP Alpha at 14:00 on October 10, 2015 (Fig. 2). The dye recovery curve at the Boils spring indicates a travel time of 4 h from iP Alpha, a straight-line

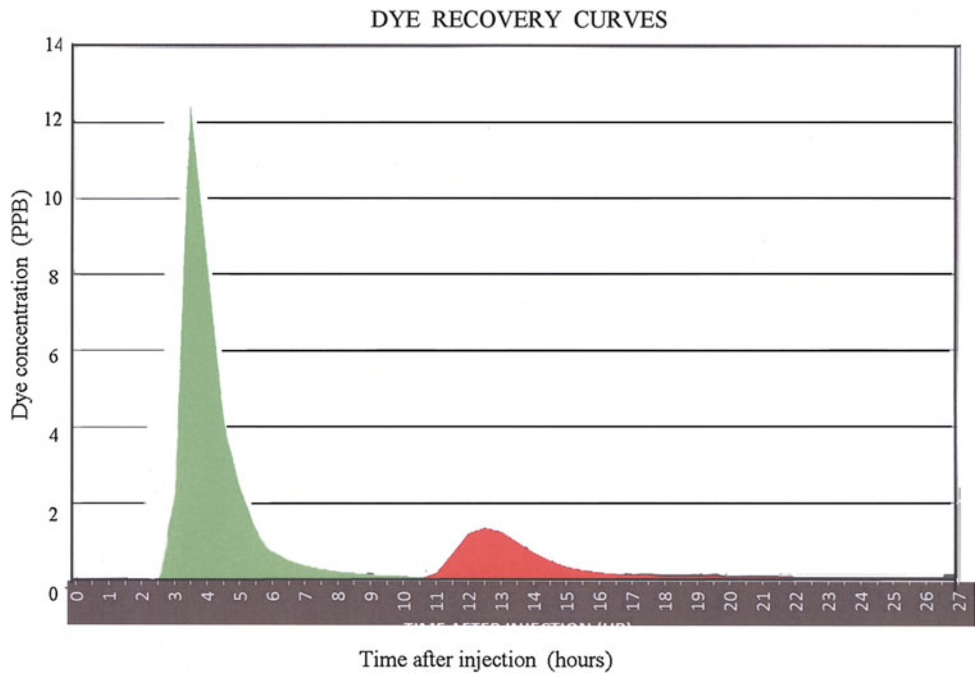

Fig. 4 Results of quantitative dye trace from IP-Tango to the Boils (RWT) and IP-Alpha to the Boils (Uranine) are shown. See Fig. 2 for map of showing these points. Sampling with activated carbon was also done downstream from the boils and on another tributary, but in each case no dye was detected showing that the Boils is the main spring output

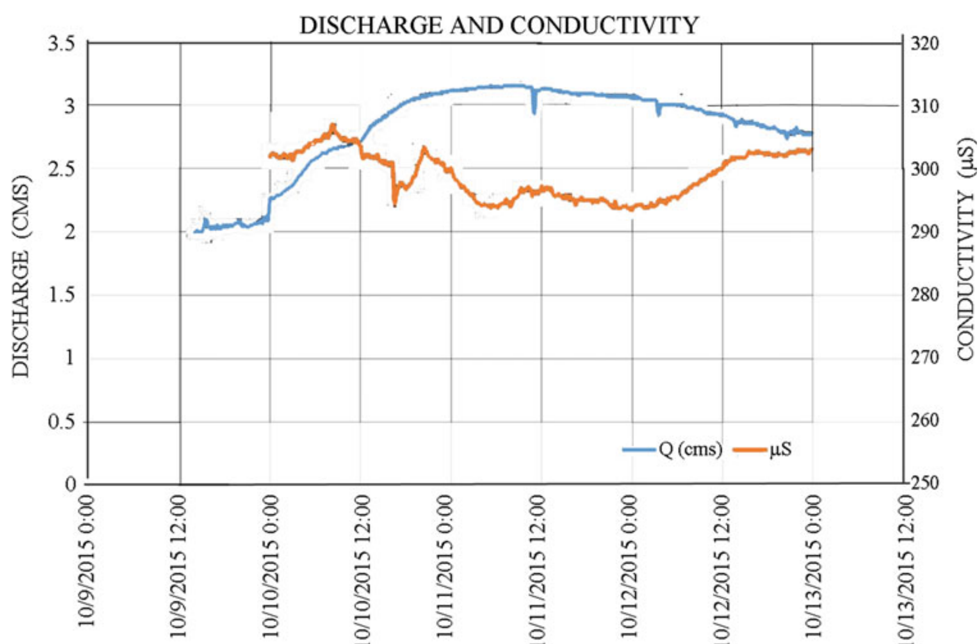

Fig. 5 Conductivity and discharge measured during the dye trace on October 10, 2015

distance of 1.6 km (Fig. 4). The dye recovery curve for the longer trace (iP-Tango to the Boils) covered a straight-line distance of 10 km in 12 h (Fig. 4). Discharge during the dye trace increased from 2 to 3 m^3/s because of a rain event (Fig. 5). Thus, the travel times were likely shorter than would be case had the trace been done at baseflow. Conductivity during the time of the dye trace decreased as discharge increased, typical of dilution (Fig. 5). Although not measured, turbidity markedly increased at the Boils during storm events. Four storm events each reaching a peak of approximately 14 m^3/s were recorded during 2015 (Fig. 6). Hydrograph time to peak for these storms was approximately 6 h and baseflow during the monitoring period averaged about 2 m^3/s.

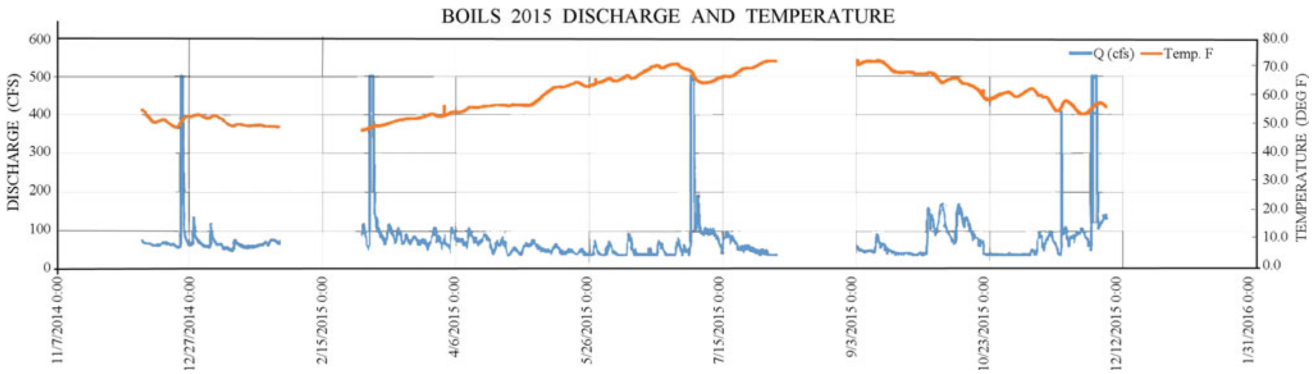

Fig. 6 Long-term discharge and temperature data measured at the Boils during 2015

5 Conclusions

Dye breakthrough curves in this study suggest that dispersion is minimal in the Spring Creek-Boils system. According to the dye trace results, conduit recharge appears to dominate, while diffuse recharge accounts for less of the total spring discharge. The average discharge of the Boils was approximately 2.1 m^3/s for the calendar year 2015, making it one of the largest measured springs in Tennessee. However, due to the lack of dispersion and the rapid travel times, potential contaminants entering the surface streams in the basin would remain concentrated and be transmitted through the system quickly. An increase in turbidity seen at the spring during each flood event suggests a direct connection to areas of sediment erosion upstream, perhaps agricultural areas. Although Spring Creek is designated as a State Scenic River, the spring is highly susceptible to point and non-point source contaminants such as pesticides, fertilizers, and bacteria coming from outside the State Scenic River area.

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Karst Geology and Regional Hydrogeology in Denmark

Bertel Nilsson and Peter Gravesen

Abstract

Upper Cretaceous chalk and Danian limestone aquifers supply about a third of the drinking water for Denmark. Quaternary sediments cover the carbonate aquifers, and at places with less than 15 m of Quaternary sediments, the aquifers, springs, and adjacent ecotones are especially vulnerable to contamination. The near-surface situated chalk and limestones are related to thin Quaternary sediment cover and karst features (springs, lakes, disappearing streams, caves, dolines). This paper categorizes the various observed karstic features into geological, hydrogeological, and structural settings of the chalk and limestone types that are important for management of this important groundwater resource in Denmark.

1 Introduction

Karst aquifers supply more than one-fifth of the world's drinking water (Ford and Williams 2007) and about third of Denmark's (COST 1995; Vangkilde-Pedersen et al. 2011). These aquifers contain fractures from tectonic episodes and larger conduits developed by dissolution of the carbonate host rock. While water storage in karst aquifers is in the porosity of the low-permeable host rock (matrix), groundwater follows fast preferential flow paths through a network of fractures and conduits (e.g., Jakobsen and Klitten 1999; Worthington et al. 2000; Rosenbom and Jakobsen 2005). This dual-porosity property has large implications for contaminant transport. The fast routing of groundwater through the conduits and fractures allows little time for chemical reactions, which could reduce contaminant concentrations before the water discharges in karstic springs or streams (Barker 1993; Taylor and Greene 2008). Thus, carbonate aquifers, springs, and adjacent ecotones are especially vulnerable to contamination (Vias et al. 2006; Mahler and Garner 2009) and groundwater extraction (Johansen et al. 2014).

Due to large-scale exploitation of karst groundwater and rapid urbanization, continuous lowering of the groundwater level takes place resulting in decreased or even ceased flow from karst springs, and groundwater-quality deterioration often occurs (Qian et al. 2006; Kang et al. 2011). Climate change and diffuse nitrate contamination of karst regions from agriculture are global problems, while also causing severe environmental problems in groundwater, surface water, and for the groundwater-dependent ecosystems (Jost et al. 2011; Hartmann et al. 2014). National action plans in Denmark implemented since 1986 have significantly reduced nitrate leaching to the groundwater aquifers (Hansen et al. 2011), but in carbonate aquifers with karstic features only a few monitored streams show a downward trend in nitrate concentration (Kronvang et al. 2008). It is likely that most karst systems represent drainage basins that are very large, and nitrate stored in the matrix continues to cause elevated nitrate concentrations in the karstic springs and streams for many years. The conceptual understanding of dynamic karst-groundwater-stream systems in Denmark remains yet unexplored. This article will categorize various observed karstic features into geological, hydrogeological, and structural settings of the chalk and limestone types that are important for management of the important groundwater water resource in Denmark by assembling the scattered knowledge that exists in Danish literature and make plausible that karstic chalk and limestone aquifers occur in Denmark.

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2 Geological Setting

The description of the geological setting is focused on the Upper Cretaceous (99.6–65.5 Ma), Danian (65.5–61.1 Ma) and Quaternary (last 2.6 Ma) time intervals.

2.1 Cretaceous

The uppermost Cretaceous marine chalk deposition in Denmark occurred in a part of the large North European carbonate sea where Denmark was totally covered by the sea (Fig. 1). The Maastrichtian chalk crops out on the pre-Quaternary surface in the northern part of Jylland and in the southern and eastern parts of Sjælland and Møn in the Baltic area. The Campanian (Mandehoved Formation) and Maastrichtian (Møns Klint Formation) (Surlyk et al. 2013) consist of at least 450 m of chalk deposits (Fig. 1). The Maastrichtian chalk is exposed in several pits in northern Denmark where the Quaternary cover is thin, in the centers of some of the salt diapirs produced domes, and in famous cliffs Stevns Klint and Møns Klint in south eastern Denmark, in the last as a glaciotectonic complex (Fig. 2). The white and yellow white micrite chalk is generally soft except for thin yellow hard grounds, black chert layers, and occasionally thin marl layers. The main component is coccoliths, but small clay content occurs.

2.2 Danian

The Cretaceous/Tertiary boundary forms the lower boundary of the Danian limestone, which is dominantly present in the subsurface of Denmark (Fig. 2) and exposed at Stevns Klint

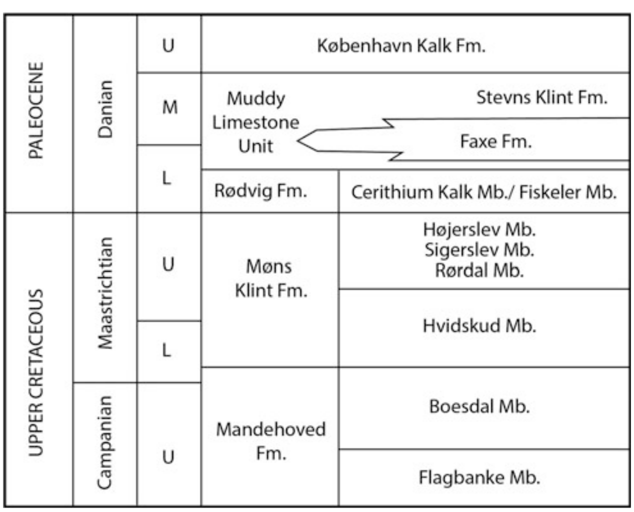

Fig. 1 Lithostratigraphy of the chalk and limestone deposits in Denmark (Based on Surlyk et al. 2006, 2013)

(Fig. 3b). The Danian sea covered the whole land area of Denmark. The Danian crops out on the pre-Quaternary surface in eastern Jylland and on Sjælland. The Danian limestone consists of several limestone types on the pre-Quaternary surface as bryozoan reef limestone interbedded with chert (Stevns Klint Formation; Surlyk et al. 2006) and the muddy or micritic limestone (Muddy limestone Unit, at present unnamed) (Håkansson and Hansen 1979; Thomsen 1995). The youngest unit is the often hard, massive limestone (København Kalk Formation; Stenestad 1976). In a few localities, coral limestone is present (Faxe Formation; Wesenberg et al. 2012) and the Rødvig Formation with Cerithium limestone Member and Fish Clay Member has also limited thickness and distribution (Surlyk et al. 2006) (Fig. 1). The Danian limestone has been found in many pits in northern Jylland, Djursland, and Sjælland (Ødum 1926; Pedersen and Petersen 2000). The best known locality for the Danian limestone is Stevns Klint (eastern Sjælland), where the Fish Clay Member with a high iridium content contributes to the interpretation of the asteroid impact hypothesis for the mass extinction at the exposed boundary (Surlyk et al. 2006). In northern Jylland, the boundary is formed as a thin marl layer or a hard ground (Håkansson and Hansen 1979), and in many areas in Sjælland, the boundary layer is removed by erosion but marked by the thin marl layers just below (Larsen 1988).

2.3 Quaternary

The Cretaceous chalk and Danian limestone are covered by Quaternary deposits. The Quaternary deposits in Denmark are between 0 m and more than 400 m thick. In some regions around Limfjorden in Jylland, Djursland, and Stevns, the cover is below 10 m and sometimes chalk and limestone crop out on the ground surface. The Quaternary Period is characterized by repeated glacial events, when glacial advances resulted in thick deposition interrupted by interglacial deposition in shallow seas, lakes, and bogs during warmer periods. Denmark is low-lying land with hills generally less than 150 m high, and the surface deposits are dominated by Weichselian successions. During the 100,000 years of Weichselian glaciation, the ice advances came from the Baltic, Norway, Sweden, and again from the Baltic (Pedersen 2012).

The deposits are characterized by proglacial meltwater successions capped by basal clayey till except for the outwash plains located in the areas beyond the main stationary line that formed during the last glacial maximum around 20,000 years ago. The deposits are often deformed by glaciotectonic thrusting and folding. The tills above the chalk and limestone deposits are often strongly calcareous and contain many limestone clasts.

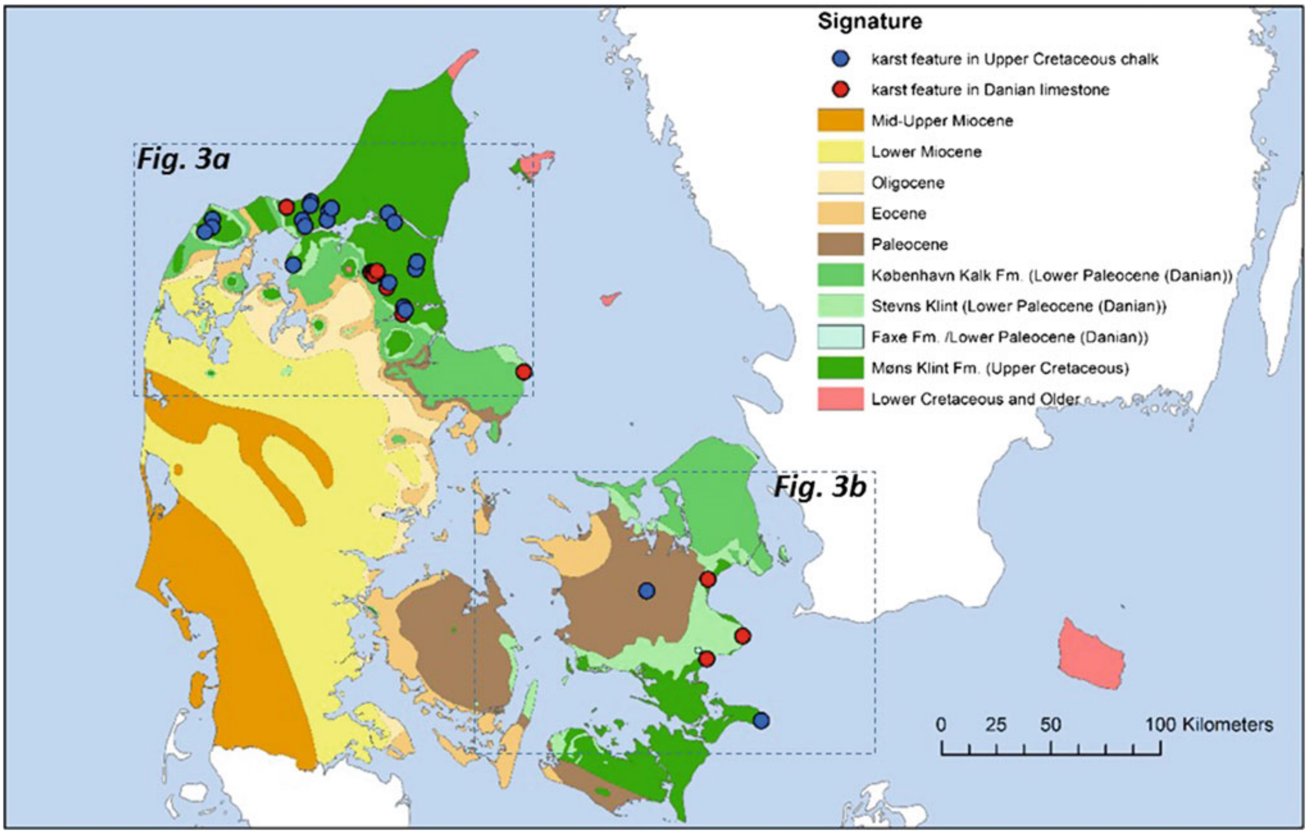

Fig. 2 Pre-Quaternary surface of Denmark (www.geus.dk). Parts of the surface are consisting of the Cretaceous chalk and Danian limestone covered by Quaternary deposits. Locations with karst phenomena in Cretaceous chalk (*blue dots*) and Danian limestone (*red dots*) are indicated

During Holocene time, the eustatic sea level rise resulted in deposition of marine fine-grained sand and clay in the northern part of the country. After the Atlantic transgression 8–7000 years ago, the glacioisostatic rebound brought these deposits up to the surface. Thin layers of sand and clay from the Atlantic transgression are occasionally resting on chalk and limestone deposits.

2.4 Structural Conditions

The chalk and limestone deposits are cut by tectonic faults, fractures, and conduits. The faults are mainly vertical or subvertical, while the fractures are vertical, horizontal, or oblique. The horizontal fractures and conduits often follow bedding planes, and the fractures and conduits are stained with yellow brown Fe components from water flow.

The top layers have been disturbed by the Quaternary glaciers, and large-scale glaciotectonic thrusting and folding is found in Møn Cliff as thick inclined chalk sheets. Isolated bodies of chalk or limestone are often included in the Quaternary layers. The upper parts just below the Quaternary deposits can be intensely brecciated, fractured, or reworked. The erosion of the surface has also formed shallow depressions which have been further eroded by meltwater streams or depressions left in the land surface when ice, formerly covered by sediment, melts (also called kettle hole or dead ice) (Gry 1979). This gives a pattern on the pre-Quaternary surface which is not related to karst processes alone, but shows a combination of karst processes and fluvial erosion and deposition known as fluviokarst (Stenestad 2006).

3 Karst Features in Chalk and limestone

This section describes the relationship between the Danish near-surface situated chalk and limestones with thin Quaternary sediment cover and karst features (Fig. 3a, b). The karst features in Denmark can be separated into sinkholes (Danish: *jordfaldshuller*) that are funnel-shaped (incl. fluviokarst) or vertical-sided dolines (Danish: *skorstene*), karst-lakes or sinkhole ponds with subsurface outlets, small caves, karst springs, karrenfelder, and streams with disappearing water flow (Stenestad 1982, 2006; Sigsgaard and Korsgaard 1998; Bakalowicz 2005; Taylor and Greene 2008). Table 1 summarizes karst features, type of rock, and locations mentioned in this paper.

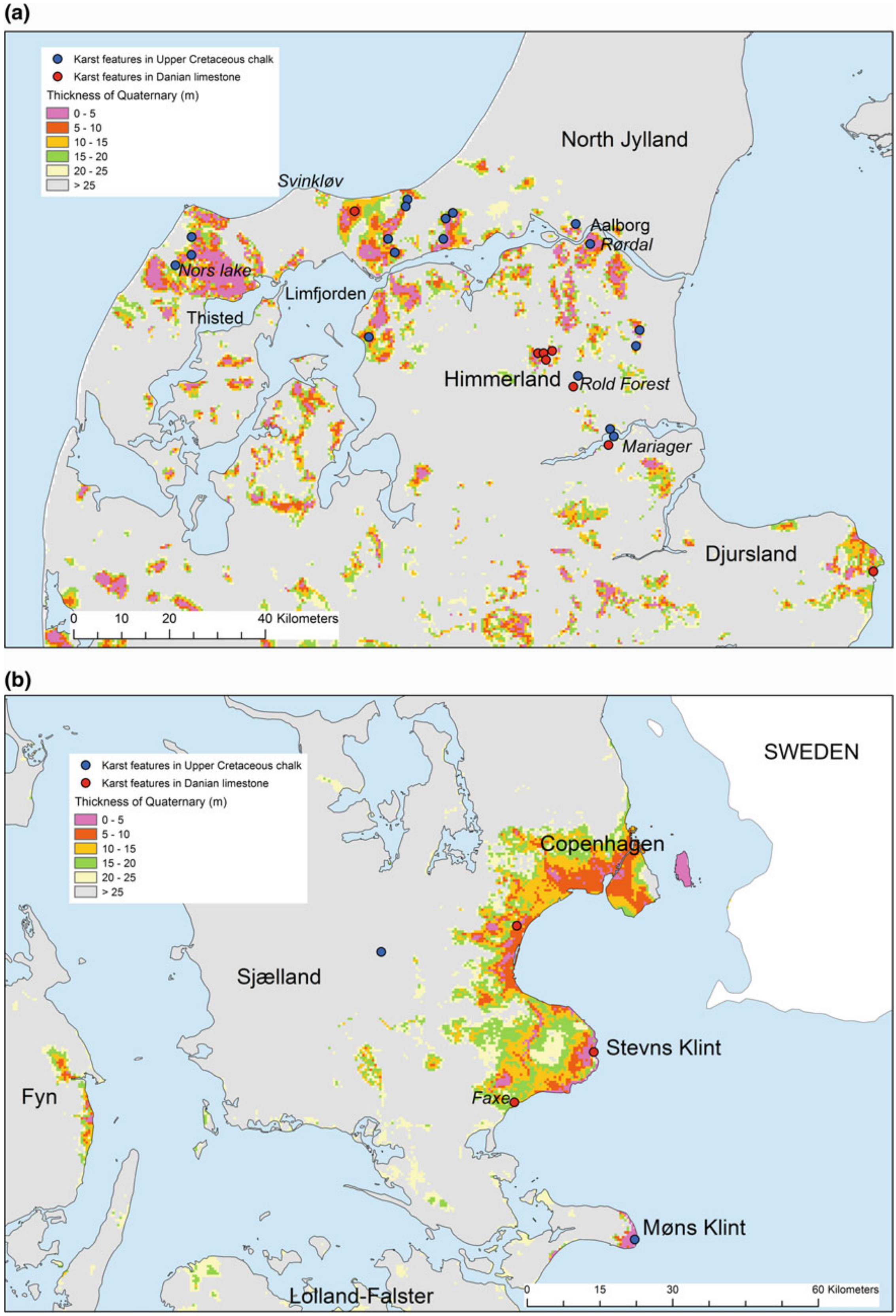

Fig. 3 Thickness of the Quaternary deposits in **a** North Jylland, Himmerland, and Djursland **b** Sjælland, Møn, and Stevns. Karst phenomena in upper Cretaceous chalk (*blue dots*) and Danian limestone (*red dots*) are located where the quaternary deposits have less than 15 m thickness

Table 1 Summary of karst features, carbonate rock types, and locations mentioned in the paper

Karst features	Carbonate rock types	Locations
Karst springs	UC, D	Rold Forest
Disappearing streams	UC	Borup Møllebæk, Slette stream, Rold Forest
Sinkholes	UC, D	Svinkløv, Klim Bjerg, Slette, Rørdal, Attrup, Rold Forest, Møns Klint, Faxe
Small caves	UC, D	Rørdal, StevnsKlint, Faxe
Karst lakes	UC, D	Nors lake, Vandet lake, Blegsø, Rold Forest
Karrenfelder	UC	Møns Klint

Upper Cretaceous chalk (*UC*) and Danian limestone (*D*)

3.1 Northern Jylland and North and South of Limfjorden

The Maastrichtian chalk deposits from Møn Klint Formation are in many areas covered by a thin Quaternary cover of 0–5 m thickness but also crop out on the ground surface (Gravesen 1988; Kiørboe 1988) (Fig. 3a). Sinkholes are distributed over the whole area. In cliffs and limestone pits, it is possible to find two types: funnel-shaped and vertical-sided. Both types have originated as areas of intense fracturing where acid water has percolated downward and dissolved the chalk. Afterward, the dolines have been filled up by material from above or altered by fluvial erosion and deposition (Stenestad 2006).

In the western part of the area, large karstic lakes such as Nors, Vandet, and Blegsø are found located along fault zones and in the middle of a salt structure (Hansen and Håkansson 1980). In this area, 5–10 m wide and 3–4 m deep sinkholes are located.

In some more local land areas, the bryozoan limestone from the Danian Stevns Klint Formation or the micritic limestone from the Danian Muddy limestone Unit are the pre-Quaternary surface (Figs. 1 and 2). In the city of Thisted, small dolines are found in the Danian limestone filled with Paleocene clay (Gravesen and Jakobsen 2016) (Fig. 4).

In the area along the north coast at Svinkløv, Klim Bjerg, and Slette, many sinkholes and dolines are registered in the chalk and limestone cliffs (Andersen and Sjørring 1992; Berthelsen 1987; Gry 1979; Jessen 1905) (Fig. 3a). In the Slette stream, the water often disappears in holes and appears again at lower sections of the water course. South of Fjerritslev on the high-lying chalk, numerous sinkholes are observed (Jessen 1905; Gry 1979), and also on the high chalk, several dolines and sinkholes are registered at Brovst (Jessen 1905). South of Limfjorden at Ranum, sinkholes in chalk are found.

Near the city of Aalborg, several funnel-formed sinkholes and lakes with subsurface outlets in the large Rørdal chalk pits are demonstrated by Stenestad (1976). The chalk is cut by abundant fractures and faults which have facilitated the development of the karst. The dolines are 0.5–1 m wide and

Fig. 4 Shallow doline in Danian limestone tilled with redeposited Upper Paleocene brown clay from the Thisted area (*Photograph* Peter Roll Jakobsen). *Scale red label* on stick is 20 cm long

1–2 m deep with spacing of 5–10 m, but occasionally, the spacing is as small as 2–3 m. The dolines are funnel-formed and filled with Quaternary sediments which is why Stenestad (2006) suggested a combined formation by karst and fluvial processes. Other chalk pits north and south of Aalborg demonstrate sinkholes and dolines (Jessen 1905).

3.2 Himmerland and Jylland

Danian bryozoan limestones from the Stevns Klint Formation show several karstic features in this area especially concentrated in Rold Forest, where the lakes of Madum and Øksø are regarded as karst lakes (Mathiassen 1920; Corbel 1947; Gry 1979) (Fig. 3a). In the area, several springs occur in the Stevns Klint Formation and the Muddy limestone Unit. The springs are located in lowland areas mainly along the fault bounded Gravlev river valley and are originally formed in fracture zones which have been enlarged by karstic processes (Larsen and Kronborg 1994). In the seven largest springs, the groundwater discharge varies from 80 to 150 L/s. Another feature is the occurrence of streams with low flow rates that disappear along losing sections. Some small streams are fed by several minor springs with discharge rates of 80–85 L/s. The famous "Store Blåkilde" karst spring (Fig. 5) is regarded as a subsurface discharge from the 20 m higher located Lake Madum. Nests of sinkholes are abundant in the area just west of Rold Forest near Oplev with a width of 6–8 m and depth of 3–4 m Mathiassen (1920). At Mariager Fiord located south of Rold Forest are several vertical-sided dolines occurring in a limestone pit at Fladbjerg (Ødum 1966) (Fig. 6), and in a chalk pit at Vive north of Mariager Fiord Stenestad (1982) has described a large doline.

3.3 Eastern Sjælland

In eastern Sjælland, many outcrops have existed in the past although only few are available today and locations with karst phenomena are restricted (Rørdam 1899; Milthers 1908, 1935; Stenasted 1976; Surlyk et al. 2006). The main part of the area consists of Danian limestone just below the Quaternary cover. In the Faxe limestone quarry with coral limestone belonging to the middle Danian Faxe Formation, several vertical-sided dolines to a depth of 1.7 m and minor

Fig. 5 Store Blåkilde karst spring in Himmerland, Jylland

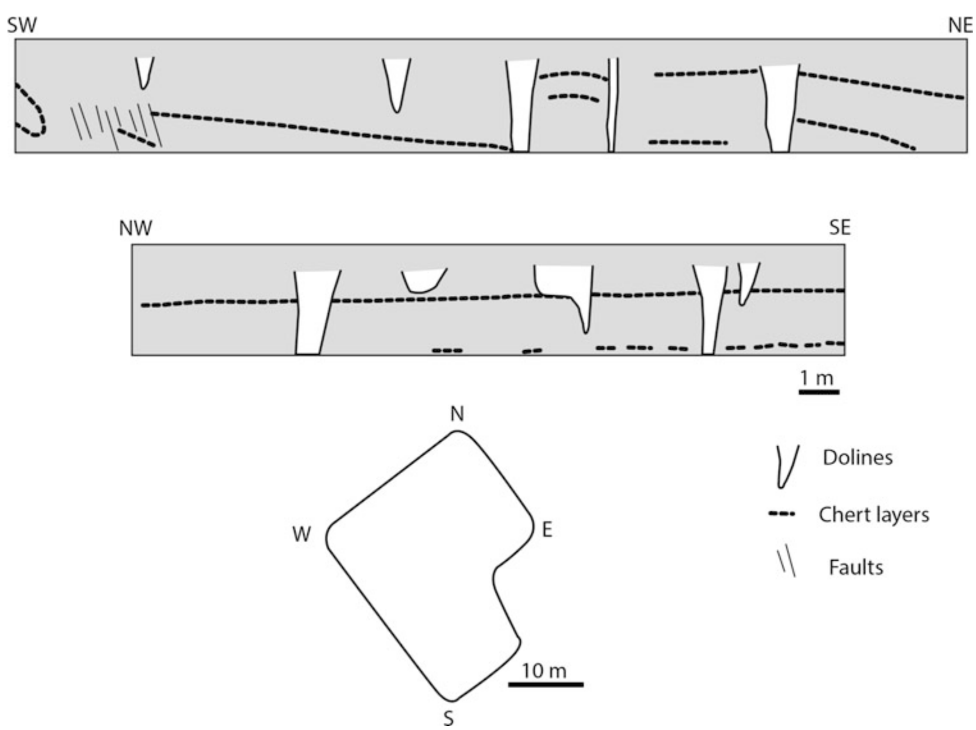

Fig. 6 Vertical-sided dolines in limestone pit at Fladbjerg (From Ødum 1966)

dissolution caves and fractures with stalagmites and stalactites has been described by Milthers (1908). In the large bryozoan limestone mounds from Stevns Klint Formation, some small dissolution caves have been found. In Allindelille Forest, a 20-m-thick glaciotectonic chalk sheet is situated just 25–40 cm below the ground surface with several sinkholes down to 10 m depth (Troels-Smith 1964).

3.4 Møn

On the island of Møn, two areas of sinkholes are found on the top of Maastrichtian chalk deposits from Møns Klint Formation in glaciotectonic sheets in the cliff of Høje Møn, where subvertical fault lines are modified by dissolution of the chalk and formation of the sinkholes, and some of the small lakes are also regarded as sinkholes (Ussing 1899; Hintze 1937). Karrenfelder as long shallow furrows occurs on the surface of the chalk sheets. In some of the sinkholes, all water disappears in the bottom. At the south coast of Møn, just north of Klintholm nests of sinkholes also occur.

4 Regional Hydrogeology and Implication of Karst Features

In Denmark, the chalk and limestone deposits represent the oldest aquifer containing freshwater (Fig. 7), except for a limited water extraction from the Precambrian basement and Paleozoic sediments at the island of Bornholm (Gravesen et al. 2014). The area of most importance for the groundwater water supply in chalk and limestone aquifers is an area extending east–west from the northern Jylland to Djursland and continuing to major parts of the islands of Sjælland, Møn, and Lolland-Falster (Nygaard 1993). The Quaternary aquifers are the most important for supply of potable water (approximately 50%). The chalk and limestone aquifers contribute about 35% of the total exploitable groundwater resource in Denmark, of which 10% is abstracted from Cretaceous chalk, 10% from Danian limestones, and 15% from the Selandian Green sand limestones (61.1–58.7 Ma) (Nygaard 1993). Particularly, in the chalk and limestone regions of Jylland and at Sjælland, the chalk and limestone aquifers are the main or only producing aquifers. Annual net

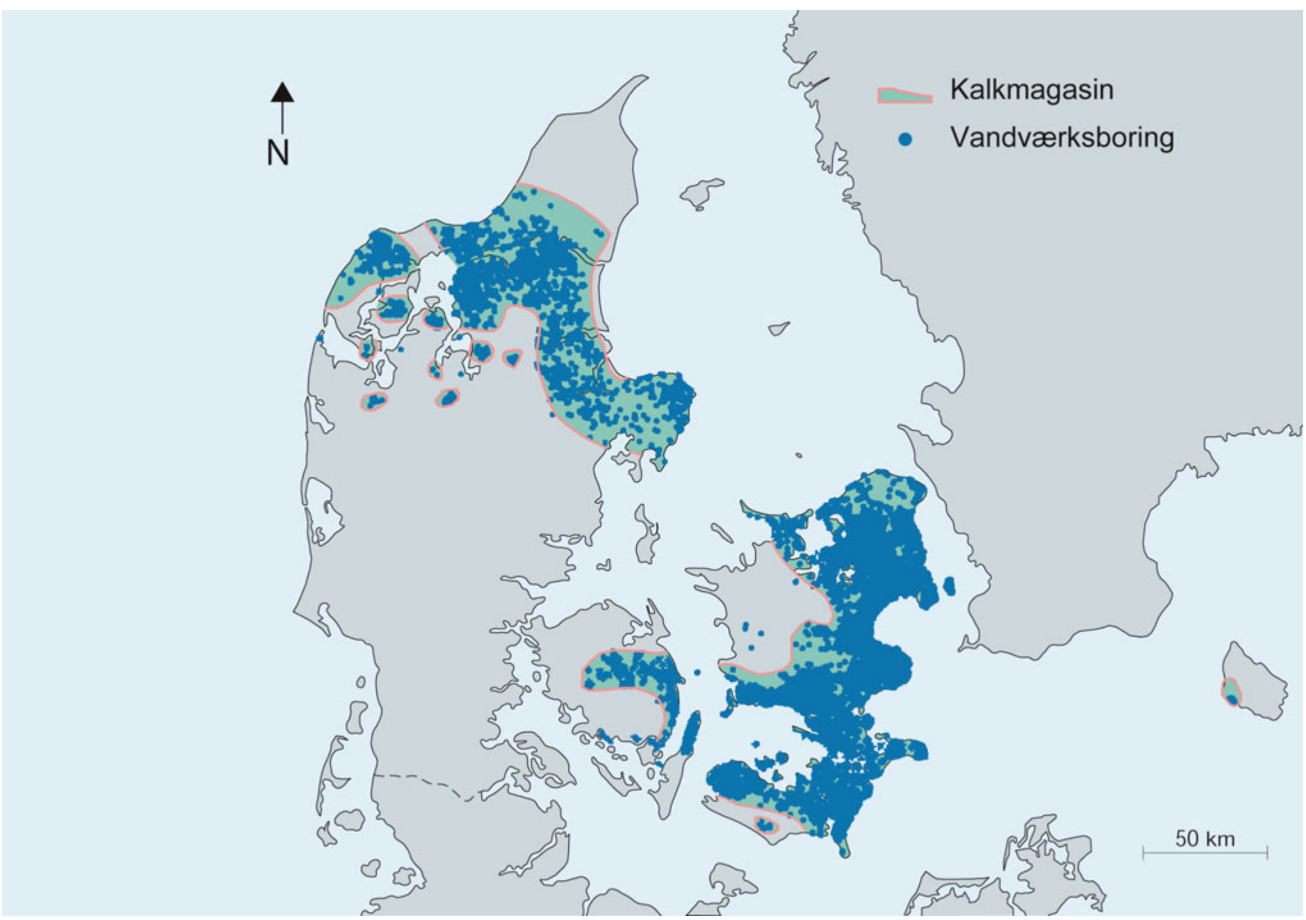

Fig. 7 The distribution of the chalk and limestone as freshwater aquifers and location of groundwater abstraction wells in the chalk and limestone is shown as *dots* (From Nygaard 1993)

precipitation (precipitation subtracted evaporation) within the chalk and limestone areas ranges from less than 200 to 400 mm/year with lowest values in Sjælland. Recharge to the deep regional chalk and limestone aquifers is estimated by a national water resource model to be approximately 100 mm/year in the western part and less than 50 mm/year in the eastern part of country (Henriksen et al. 2003). Higher recharge rates will occur in areas with no or thinner covers of Quaternary deposits. The total area of chalk and limestone covered with a few meters of Quaternary deposits (or even outcropping) in Denmark consists of about 6000 km^2 or 15% of the entire land area (COST 1995). The majority of the infiltrating water is lost to the densely distributed tile drainage system in cultivated areas.

Regionally, the hydraulic characteristics of the chalk and limestone vary considerably. In the areas important for water supply in the chalk and limestone areas, all dominant bedded rock types described in Sect. 2 occur with visible open fracture zones at 0.5- to 1-m intervals in the uppermost tens meters of the sequence. Along the eastern coastal line of Sjælland, one or two highly permeable zones of horizontal fractures appear at 30–70 m depth likely caused by rebound effects after glacial compression followed by unloading upon melting of the Weichselian ice shield. The same characteristics have been reported from the Aalborg region (Nielsen and Jørgensen 2008).

Most hydraulic parameters belong to model-calibrated values representing a watershed scale where the model is conceptualized without any karst features. Only few detailed investigations of porosity and hydraulic conductivity have been carried out in the type of chalk and limestone sediments that are of interest for this paper: Stevns Klint (Frykman 2001), in the Copenhagen area as part of the metro tunnel construction (GEO 2014) and in the Karlstrup chalk pit (Jakobsen et al. 1993; Brettmann et al. 1993). These investigations show, based on plug matrix measurements, that the Cretaceous chalk is soft and friable with a matrix porosity of 35–50% and Danian limestone contains alternating hard and soft layers and has a porosity of 10–35%. The hydraulic conductivity varies by orders of magnitude between 10^{-6} and 10^{-10} m/s. No measurements have been reported on fracture hydraulic conductivity in Danish investigation on hydraulic properties in chalk and limestone.

The conceptual understanding of dynamic karst-groundwater-stream systems in Denmark remains yet unexplored, and we believe that karst features may need to be incorporated in relation to the hydrogeological parameterization of an existing national water balance model (Henriksen et al. 2003), where the chalk and limestone aquifers are conceptualized as non-karstic aquifers.

5 Conclusion and Perspectives

Most karst features in Denmark are recognized in Jylland, around Limfjorden, and in Himmerland where near-surface-lying chalk and limestone are covered by thin Quaternary sediments. In the remainder of the country, only a few karst phenomena are found. The sinkholes are mainly recognized in the soft chalk deposits, although the Rold Forest area in Danian limestone shows many different karst features. It is obvious that there is a relation in some areas between the groundwater flow in the chalk and limestone aquifers and the karst features, which can give highly uncertain directions for the groundwater flow on both local and watershed scale. Karst features may need to be incorporated in relation to the hydrogeological parameterization of an existing national water balance model.

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Recharge and Water-Quality Controls for a Karst Aquifer in Central Texas

Brian A. Smith and Brian B. Hunt

Abstract

The Edwards Aquifer is a prolific karst aquifer system in Central Texas that provides drinking water to about 2 million people. Because a significant portion of the water recharging the Barton Springs segment of the Edwards Aquifer enters the subsurface through caves and enlarged fractures in the bed of Onion Creek, 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. 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. When the storm water passes, the valves open and allow the cleaner baseflow water to enter the cave. 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 1105 kg (2436 lbs) of nitrogen from nitrate/nitrite, 134 kg (295 lbs) of total phosphorus, and 86,385 kg (190,480 lbs) of sediment were prevented from entering Antioch Cave. This amount of sediment is equivalent to about eight dump-truck loads that are prevented from entering the aquifer.

1 Introduction

The Onion Creek Recharge Project was conducted by the Barton Springs/Edwards Aquifer Conservation District to improve the quality of water recharging the Barton Springs segment of the Edwards Aquifer (herein called Barton Springs aquifer) through Antioch Cave. This cave is situated within the bed of Onion Creek about 2 km (1.3 miles) west-southwest of the center of Buda, Texas (Fig. 1), and is capable of recharging large amounts of water to the aquifer when it is not filled with sediment and other debris. The most common contaminants in Onion Creek are sediments, bacteria, nutrients, and other nonpoint source pollutants that are brought into Onion Creek during storm events. Because the Barton Springs aquifer provides drinking water to about 60,000 people plus industrial, commercial, and irrigation users, and is the source of water at Barton Springs where endangered species live (BSEACD 2007), the quality of water recharging the aquifer is very important.

In 1997, a Best Management Practices (BMP) structure was constructed over Antioch Cave by the District with funding provided by a Clean Water Act Section 319(h) grant from the US Environmental Protection Agency (EPA). The grant was administered by the Texas Natural Resources Conservation Commission (TNRCC). These grants are awarded to address environmental issues associated with nonpoint source pollution. The purpose of the BMP at Antioch was to control the flow of water into the cave and to prevent clogging of the cave with sediment and storm debris. Opening and closing a valve on the BMP controls the flow of water from Onion Creek into Antioch Cave. During and following storm events, the valve is manually closed to

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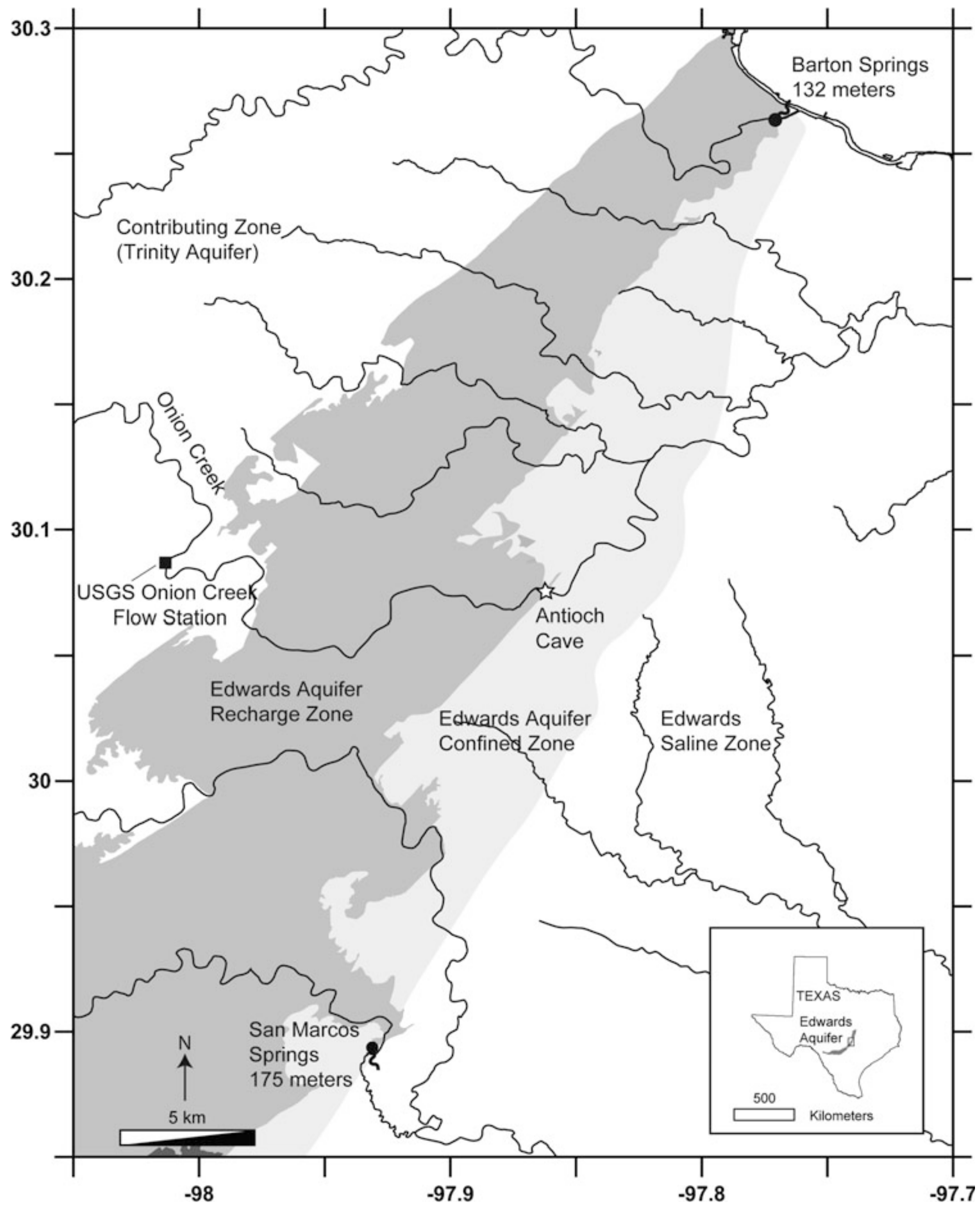

Fig. 1 Location map of the study area and a portion of the Edwards Aquifer

prevent entry of storm water and associated contaminants into the cave and subsequently into the Edwards Aquifer. When better quality water is flowing in Onion Creek, the valve is opened to allow recharge to occur. The system at Antioch Cave has been permitted by the Texas Commission on Environmental Quality (TCEQ) as a Class V injection well.

In 2006, the District was awarded another grant by EPA and TCEQ. The goal of this grant was to provide real-time monitoring of water quality and quantity at Antioch with a Continuous Water Quality Monitoring Network (CWQMN) system, to improve the intake system on the BMP, and to automate the opening and closing of the valve. As completed in 1997, the valve was operated manually by District staff and the grate over the valve was prone to clogging with storm debris. An automated system for opening and closing the valve based on water quality was deemed to be more efficient and protective of the aquifer than a manual system. The automated system was designed to close the valve when the turbidity of water in Onion Creek rises to 100 NTUs. This would prevent entry of contaminated storm water from entering Antioch Cave. As the storm pulse passes and the turbidity drops below 50 NTUs, the valve opens automatically. An intake screen with a large surface area allows for maximum recharge without being clogged with storm debris.

2 Background

Onion Creek is a major contributor of recharge water to the Barton Springs aquifer of Central Texas. Because thousands of people depend on this aquifer for their sole source of drinking water, and because the endangered salamanders at Barton Springs need a sufficient quantity of flow of high-quality water, the quality of water recharging the aquifer from surface streams is very important. Numerous studies have shown the relationship between these surface streams and the flow of groundwater through the aquifer to water-supply wells and the springs (Slade et al. 1986; Hauwert et al. 2004).

2.1 Purpose and Scope of Project

The TCEQ lists the Barton Springs aquifer as an impaired groundwater resource (TNRCC 1999). Onion Creek is listed on the TCEQ 303(d) list of impaired streams. Increases in sediment, bacteria, and other contaminants in groundwater as a result of storm-flow events in the Barton Springs aquifer have been documented by analysis of water samples from monitor and water-supply wells and Barton Springs (Fieseler 1998; Mahler et al. 2006a, 2011). The purpose of the project was to increase recharge to the Barton Springs aquifer while minimizing the amount of contaminants entering the aquifer during storm events.

To reduce the amount of sediment and other storm-related contaminants entering one of these recharge features, an automated control system was designed and installed at the BMP that was previously constructed over Antioch Cave on Onion Creek (Fig. 2). Two valves on the BMP control flow into the cave.

Fig. 2 Photograph ca. 1996 showing recharge and the entrance to Antioch Cave before the BMP was constructed. The debris over the entrance and also sedimentation within the cave decrease the amount of recharge entering the cave (Photograph from Fieseler 1998)

2.2 Previous Work: 1993–1998 Onion Creek Recharge Project

When District staff became aware of the existence of Antioch Cave, they quickly realized the significance of the cave for recharge to the Edwards Aquifer. Figure 2 is a photograph of the entrance to Antioch Cave prior to construction of the BMP. In 1992, the District began discussions with TNRCC about using federal 319(h) funds for conducting studies on Onion Creek and constructing a BMP at Antioch to improve the quality and increase the quantity of water entering the cave. Construction began on the BMP in August 1997 and was operationally completed by December 1997. A final report on the project was issued in December 1998 (Fieseler 1998). The BMP that was constructed was a steel-reinforced concrete vault. The BMP was situated directly over the cave entrance and is approximately 2 m (7 ft) high, 2.4 m (8 ft) wide, and 3.7 m (12 ft) long. Figure 3 is an aerial photograph of the study site showing the location of the upgraded BMP in the bed of Onion Creek. Figure 4 is a schematic cross section of Onion Creek showing the BMP and a portion of Antioch Cave. The BMP has two steel manhole accesses on top and two 91 cm-(36-in.) diameter spools to hold 91-cm diameter (36-in.) pneumatically operated butterfly valves. Only one valve was installed during the original project, and the other spool was sealed with a steel plate. Air hoses connected the valve to a 1-ft by 1-ft by 2-ft concrete box on the north bank of Onion Creek. From this box, the valve could be opened using either an air compressor or a tank with compressed air. A 4-in. diameter PVC pipe was the conductor pipe for air hoses from the valve in the BMP to the concrete box. In addition, a 6-in. PVC pipe connected the BMP to the concrete box to allow air from the cave to vent to the surface when water is flowing into the cave entrance. Such venting prevents undue pressure build-up in the BMP and allows more water to recharge the aquifer.

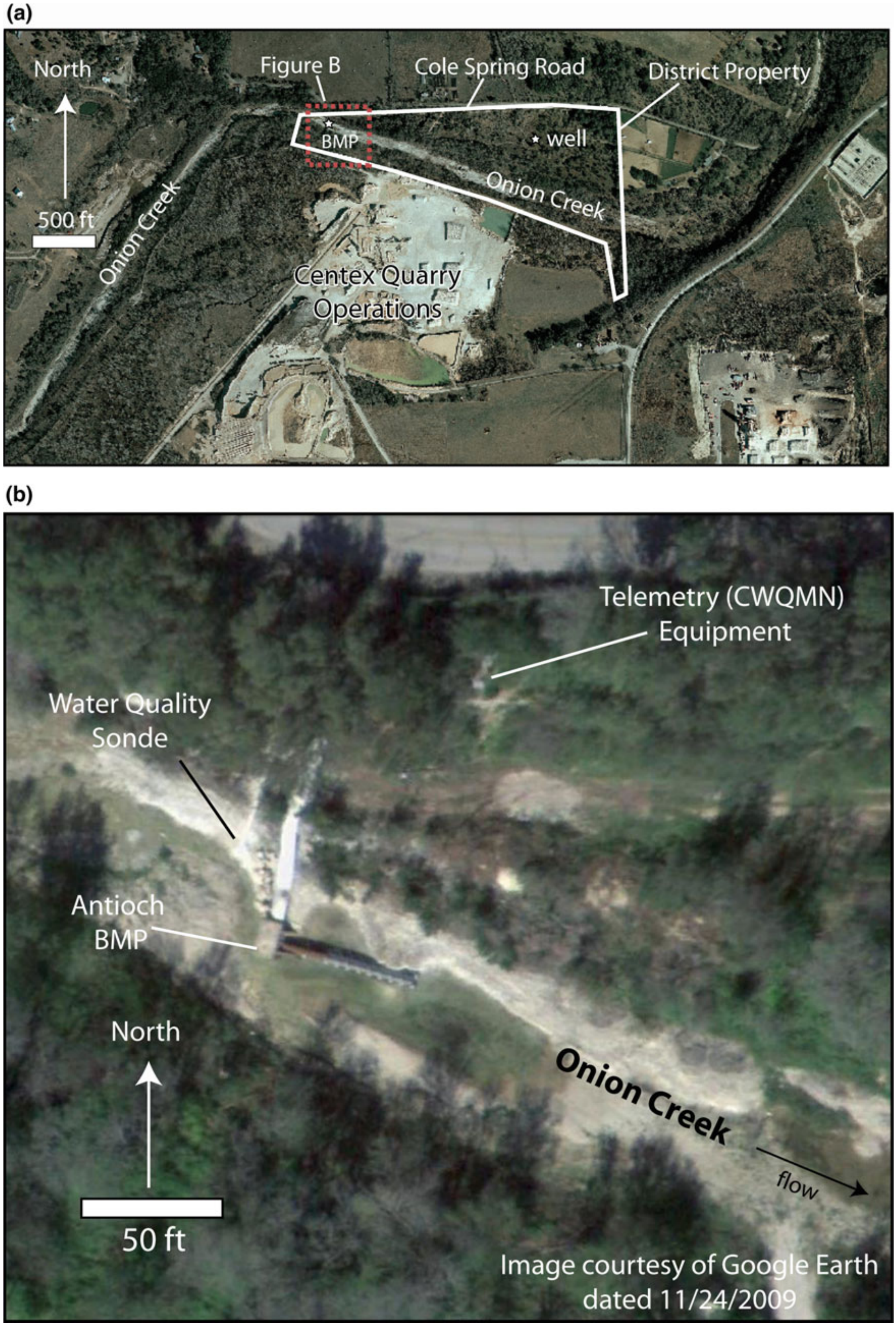

Fig. 3 **a** Aerial photograph showing major features near Antioch Cave including Onion Creek. **b** Close-up of aerial photograph showing the BMP after the upgrade

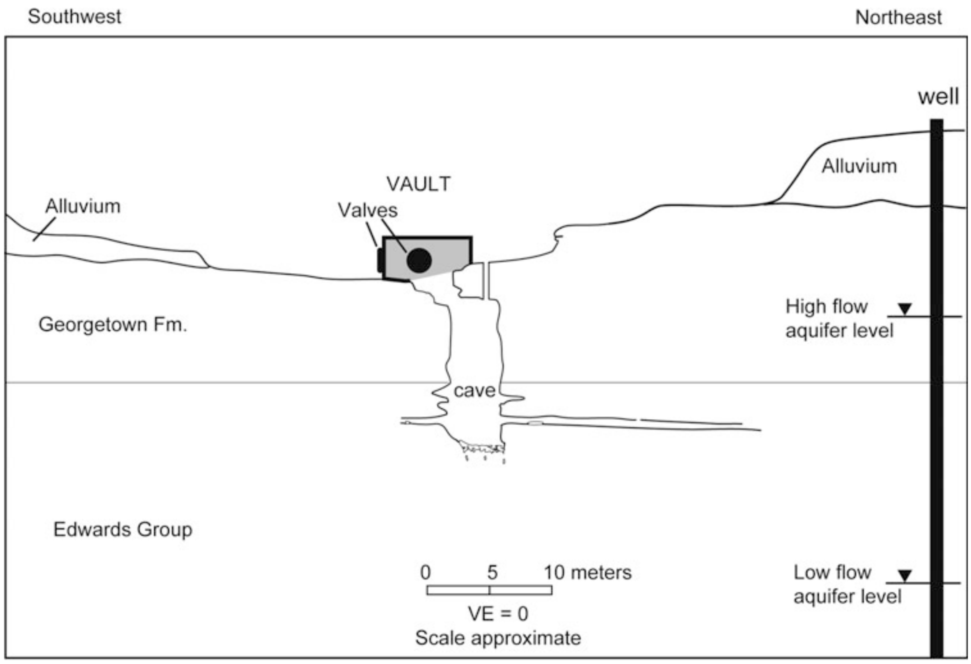

Fig. 4 Schematic cross section across Onion Creek and Antioch BMP looking upstream

The following text from the December 1998 final report (Fieseler 1998) describes the procedures and protocol for opening and closing the valve:

> The 36″ [91 cm] butterfly valve remains closed during non-flow conditions. Any spring flow, seepage or low flow recharges via the 4″ [10 cm] weep hole. When flooding occurs or whenever the creek is in a flow condition, the valve will remain closed during "first flush" conditions. This first flush condition contains heavy sediment loads, high bacteria counts, and large quantities of trash, debris, and organic material. Once conditions have improved, based on visual observations and turbidity measurements by District personnel, the air compressor will be turned on and the valve opened to allow recharge to occur. The valve will remain open as long as the water level in Onion Creek is approximately one foot deep or greater. Should subsequent flood events and/or first flush pulses occur which increases the turbidity, sediment load, or trash and debris content, or if some hazardous condition presents itself, the valve will be closed until conditions warrant re-opening the valve to continue recharge.

As this description indicates, management of the BMP is labor intensive and is dependent on District staff being available at key times when conditions are changing in Onion Creek. Recommendations were made in the 1998 report for adding a second valve to the BMP and for automating the system. An opportunity for doing this additional work arrived in 2006 when 319(h) funds became available.

3 Hydrogeologic Setting

3.1 The Edwards Aquifer

The Edwards Aquifer of Texas is a karst aquifer developed in faulted and fractured Cretaceous-age limestones and dolomites. Ford (2004) defines karst as terrain with distinctive hydrology arising from the combination of high rock solubility and well-developed solution channel porosity underground. Karst terrains and aquifers are characterized by sinking streams, sinkholes, caves, springs, and an integrated system of pipe-like conduits that rapidly transport groundwater from recharge features to springs (White 1988; Todd and Mays 2005).

The Edwards Aquifer system lies within the Miocene-age Balcones Fault Zone (BFZ) of south-central Texas and consists of an area of about 10,900 km^2 (4200 mi^2) (Fig. 1 inset). The aquifer extends about 435 km (270 miles) from the Rio Grande River along the Mexico/US border at

Del Rio, east to San Antonio, then northeast through Austin to Salado. Groundwater from the Edwards Aquifer is the primary source of water for about 2 million people plus numerous industrial, commercial, and irrigation users. Hydrologic divides separate the Edwards Aquifer into three segments. North of the Colorado River is the northern segment of the Edwards Aquifer, and south of the southern hydrologic divide near the City of Kyle is the San Antonio segment (Fig. 1). The Barton Springs segment is situated between the northern and San Antonio segments. Ryder (1996) and Lindgren et al. (2004) provide detailed and regional information on the overall Edwards Aquifer.

Development of the Edwards Aquifer was influenced significantly by fracturing and faulting associated with the Miocene-age BFZ and dissolution of limestone and dolomite units by infiltrating meteoric water (Sharp 1990; Barker et al. 1994; Hovorka et al. 1995). In addition, development of the aquifer is also thought to have been influenced by deep dissolution processes along the saline–fresh water interface, what is known as hypogenic speleogenesis (Klimchouk 2007).

Environmental Protection Agency identifies karst aquifers as one of the water supplies most vulnerable to pollution because of rapid groundwater velocities and limited ability to filter contaminants (Schindel et al. 1996). Numerous tracer tests have been performed on portions of the Edwards Aquifer demonstrating that rapid groundwater flow occurs in an integrated network of conduits discharging at wells and springs (Hauwert et al. 2004; BSEACD 2003). During higher flow conditions, a portion of this groundwater flows from the conduits into the diffuse matrix of the aquifer building up storage in the aquifer. Water from storage flows diffusely to wells or back into the conduit network during lower flow conditions (Mahler et al. 2006b). This dual flow system results in contamination having the potential to rapidly impact wells and springs, as well as slowly accumulate and move within the matrix of the aquifer.

3.2 Barton Springs Aquifer

The Barton Springs aquifer is the focus of this project. Approximately, 60,000 people depend on water from the Barton Springs aquifer as their primary or sole source of drinking water. Groundwater use is characterized as 80% public supply, 13% industrial (quarry operations), and 7% irrigation (golf courses and athletic fields). The various spring outlets at Barton Springs are the only known habitat for the endangered Barton Springs salamander (*Eurycea sosorum*). To protect existing users of the aquifer and the endangered salamanders, pumping from the Barton Springs aquifer has been capped at 14 million m^3/yr(3.77 billion gallons/yr) under non-drought conditions. During periods of drought, permitted users are required to make significant reductions in groundwater use with reductions of 50% of permitted volume during droughts equivalent to the drought of record in the 1950s.

The Barton Springs aquifer is 400 km^2 (155 mi^2) in area, with about 80% of the area consisting of unconfined aquifer conditions, although the percentage fluctuates according to hydrologic conditions. The primary discharge point is Barton Springs located in Barton Creek about 0.4 km (¼ mi) upstream of its confluence with the Colorado River (Fig. 1). The Barton Springs aquifer is bounded to the north by the Colorado River and by the outcrop and saturated thickness of the Edwards Group to the west. The eastern boundary of the aquifer is the interface between fresh and brackish water (>1000 mg/L total dissolved solids (TDS)) and is a complex three-dimensional boundary commonly known as the "saline" or "bad-water" interface. The saline zone of the Edwards Aquifer is characterized by a decrease in relative transmissivity (Flores 1990). Hovorka et al. (1998) describe this boundary as hydrodynamically controlled rather than separated by a distinct hydrologic barrier, although local fault control was noted. The southern hydrologic divide between the Barton Springs aquifer and the San Antonio segment of the Edwards Aquifer is located approximately between Onion Creek and the Blanco River near the City of Kyle. This divide may fluctuate according to hydrologic conditions, as supported by potentiometric surface elevations and recent tracer testing results (LBG-Guyton Associates 1994; Hunt et al. 2005; Land et al. 2010; Johnson et al. 2012).

Mapping of the Barton Springs aquifer has delineated geologic faults and several informal stratigraphic members of the Kainer and Person Formations of the Edwards Group (Rose 1972), each having distinctive hydrogeologic characteristics (Small et al. 1996). In the District, faults trend predominantly NE–SW and are downthrown to the southeast, with total offset of about 1100 ft across the study area. As a result of faulting and erosion, the aquifer ranges from about 450 ft at its thickest along the east side, to 0 ft along the west side of the recharge zone (Slade et al. 1986). Dissolution along fractures, faults, and bedding-plane partings and within certain lithologic units has created numerous sinkholes, sinking streams, conduits, caves, and springs.

3.3 Recharge

The majority of recharge to the aquifer is derived from streams originating on the contributing zone which is underlain by units of the Trinity Group and located primarily west of the recharge zone. Water flowing onto the recharge zone sinks into numerous caves, sinkholes, and fractures along its six major (ephemeral to intermittent) losing streams. Slade et al. (1986) estimated that as much as 85% of recharge to the aquifer is from water flowing in these streams. The remaining recharge (15%) occurs as infiltration through soils or direct flow into recharge features in the upland areas of the recharge zone (Slade et al. 1986). However, current studies indicate that upland recharge may constitute a larger fraction of recharge (Hauwert 2006). Mean surface recharge should approximately equal mean discharge, or about 1500 L/sec [53 cubic feet per second (cfs)]; however, maximum recharge rates during flooding may approach 11,300 L/sec (400 cfs) (Slade et al. 1986). Studies have shown that recharge is highly variable in space and time and focused within discrete features (Smith et al. 2001). For example, Onion Creek is the largest contributor of recharge to the Barton Springs aquifer (34% of total creek recharge) with maximum recharge rates up to 4530 L/sec (160 cfs) (Slade et al. 1986). Antioch Cave is located within Onion Creek and is the largest capacity discrete recharge feature known in the Barton Springs aquifer with an average recharge of 1300 L/sec (46 cfs) and a maximum of 2690 L/sec (95 cfs) during a 100-day study (Fieseler 1998). Figure 5a, b are cross-sectional views of the Antioch vicinity from a 3D geologic model (Hunt et al. 2010). Figure 5c illustrates the potentiometric mound from the high rates of recharge due to the cave and BMP. Increased recharge due to "urban leakage" from leaking water and wastewater lines, septic tanks, and applied lawn irrigation in the contributing and recharge zones is another potential source of water to the aquifer (Sharp 2010).

In the Barton Springs aquifer, the amount of cross-formational flow (subsurface recharge) occurring through adjacent aquifers is unknown, although it is thought to be relatively small on the basis of water-budget analysis for surface recharge and discharge (Slade et al. 1985) and multiport monitor well studies (Smith and Hunt 2009). Under drought and low water-level conditions, there could be an increased potential for cross-formational flow from the saline zone. Recent studies (Johnson et al. 2012) have documented recharge to the Barton Springs aquifer from the Blanco River, previously thought to only provide recharge to the San Antonio segment. In addition, recent studies (Land et al. 2010) have documented the potential for groundwater flow to bypass San Marcos Springs and flow toward Barton Springs.

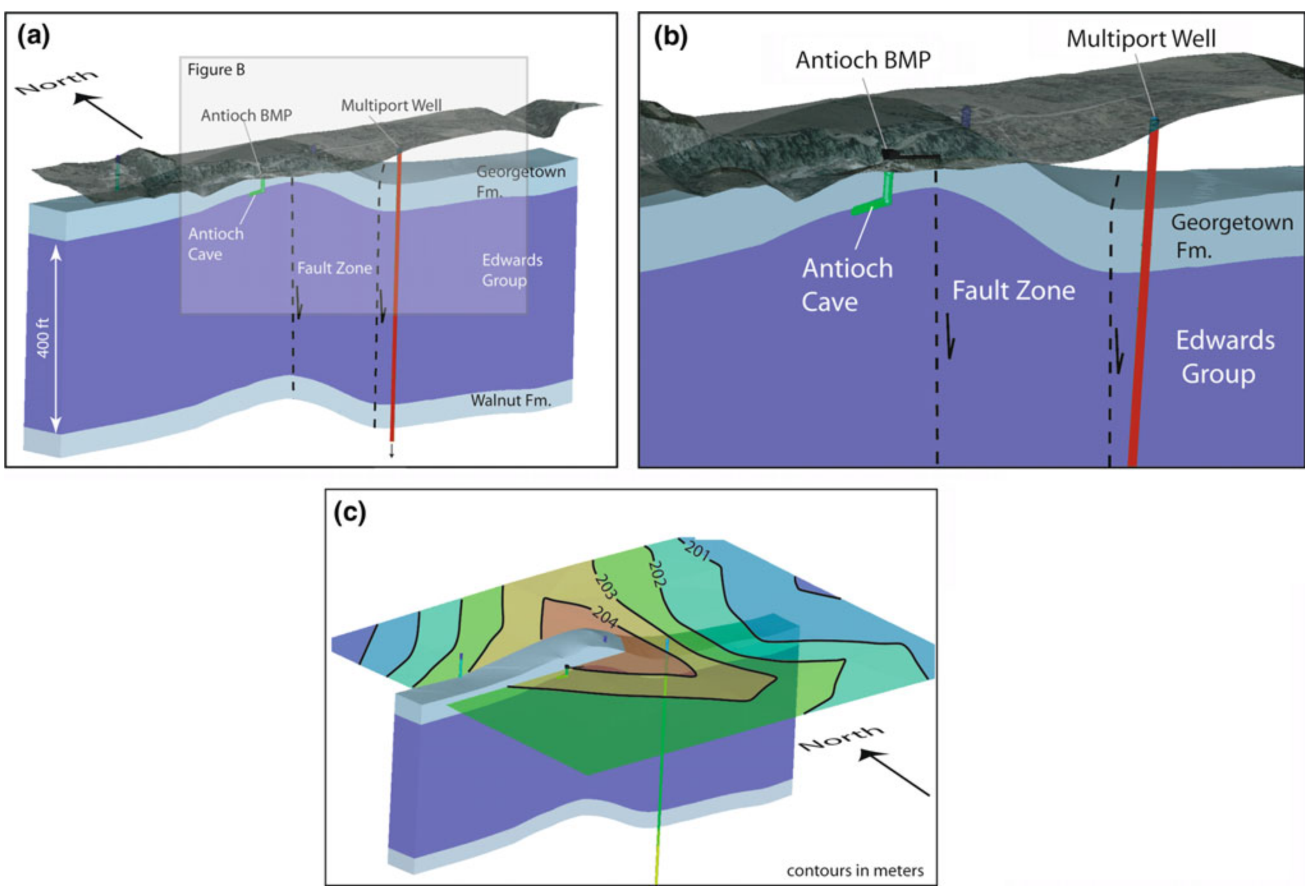

Fig. 5 **a** Oblique cross-sectional view of the Edwards Aquifer in the Antioch vicinity from the 3D geologic model. **b** Close-up view illustrating Antioch Cave and the BMP in relation to the fault zone. **c** Oblique cross-sectional view of the Edwards Aquifer with a high-flow potentiometric surface showing groundwater mounding due to high rates of recharge along Onion Creek and Antioch Cave

3.4 Groundwater Flow

The Edwards Aquifer is inherently heterogeneous and anisotropic, which strongly influences groundwater flow and storage (Slade et al. 1985; Maclay and Small 1986; Hovorka et al. 1996, 1998; Hunt et al. 2005). The Edwards Aquifer can be described as a triple porosity and permeability system consisting of matrix, fracture, and conduit porosity (Hovorka et al. 1995; Halihan et al. 2000; Lindgren et al. 2004) reflecting an interaction between rock properties, structural history, and hydrologic evolution (Lindgren et al. 2004). In the Barton Springs aquifer, groundwater generally flows west to east across the recharge zone, converging with preferential groundwater flow paths subparallel to major faulting and fracturing, and then flowing north toward Barton Springs.

Groundwater dye tracing and other studies demonstrate that a significant component of groundwater flow is discrete, occurring in a well-integrated network of conduits, caves, and smaller dissolution features (Hauwert et al. 2002a, b). Interpreted flow paths from tracer testing generally coincide with troughs in the potentiometric surface and are parallel to the N40E (dominant) and N45W (secondary) fault and fracture trends presented on geologic maps, indicating the structural influence on groundwater flow. Rates of groundwater flow along preferential flow paths, determined from dye tracing, can be as fast as 6.4–11.2 km/day (4–7 mi/day) under high-flow conditions or about 1.6 km (1 mi/day) under low-flow conditions (Hauwert et al. 2002a; Johnson et al. 2012).

In one trace, dye injected into Cripple Crawfish Cave on Onion Creek displayed diverging flow paths to Barton and San Marcos Springs (Hunt et al. 2006). This has implications for the groundwater divide separating the Barton Springs and San Antonio segments of the Edwards Aquifer. Traces from Cripple Crawfish Cave and Antioch Cave in Onion Creek have demonstrated divergent flow paths that appear to converge before discharging at Barton Springs. Dye-trace tests were performed three times from Antioch Cave in Onion Creek (Hauwert et al. 2004; Hunt et al. 2005). The first trace was performed under drought conditions (March 2000), and the dye was tentatively detected at a few nearby wells. Subsequent injections under wet, creek-flowing conditions (November 2000 and August 2002) resulted in repeated dye detections in up to 17 water-supply wells, including some public water-supply wells, and at Barton Springs. The paths of flow demonstrated by dye tracing revealed several divergent flow paths that appear to converge before discharging at Barton Springs. Arrival of dye at Barton Springs from Antioch Cave under high-flow (August 2002) conditions was about 7-day travel time with an apparent velocity of about 3.2 km/day (2 mi/day) (Hunt et al. 2005).

3.5 Water Levels and Storage

Water levels in the Edwards Aquifer are very dynamic and heterogeneous. Water levels do not show long-term declines in storage, but generally recover quickly from low levels reached during drought to previous high conditions typical of wet periods (Smith et al. 2001). Water levels and discharge at the springs respond very quickly to recharge events and then decline at variable rates, influenced by both conduit and matrix permeability and storage (Lindgren et al. 2004; Worthington 2003).

Figure 6 shows a potentiometric mound, or ridge, from recharge along Onion Creek and paths of dye injected into Antioch Cave (Hunt et al. 2007). Even under low-flow conditions, the mound is still present. The presence of a mound beneath Antioch and much of Onion Creek indicates that water recharging along Onion Creek is going into aquifer storage in addition to more direct, conduit flow to Barton Springs. The conduits that have been demonstrated through dye-trace studies to connect with Barton Springs are not of sufficient capacity to carry all of the recharging water directly to Barton Springs. The excess water must be entering storage that consists of a matrix of non-conduit dissolution features and primary porosity.

3.6 Geology of the Antioch BMP Vicinity

Antioch Cave is located on District property within the bed of Onion Creek about 2 km (1.3 miles) west-southwest of the center of Buda, Texas. The cave is located about 244 m (800 ft) upstream of a significant fault (Mountain City Fault Zone) delineating the eastern extent of the Edwards Aquifer Recharge Zone for this area. Geologic units at the surface include Cretaceous-age limestones (Georgetown and Buda) and claystones (Del Rio and Eagle Ford), which are in places overlain by more recent terrace, alluvium, and fill deposits.

The entrance and uppermost 6 m (20 ft) of the cave is formed along a solution-enlarged fracture within the highest stratigraphic unit of the Edwards Aquifer, the Georgetown Formation. The cave continues downward into the Edwards Group to a depth of about 12 m (40 ft) below the entrance (Fig. 4). The cave passage then extends laterally along a bedding plane about 15 m (50 ft) to the north then about 23 m (75 ft) to the northwest where it splits into two passages, one continuing northwest for about 45 m (150 ft) and the other trending west about 53 m (175 ft) (Fig. 7). All passages become too tight for a person to continue exploring. The Mountain City Fault Zone, trending NE-SW with about 30 m (100 ft) of vertical throw, is mapped on the property. The fault zone creates unconfined aquifer

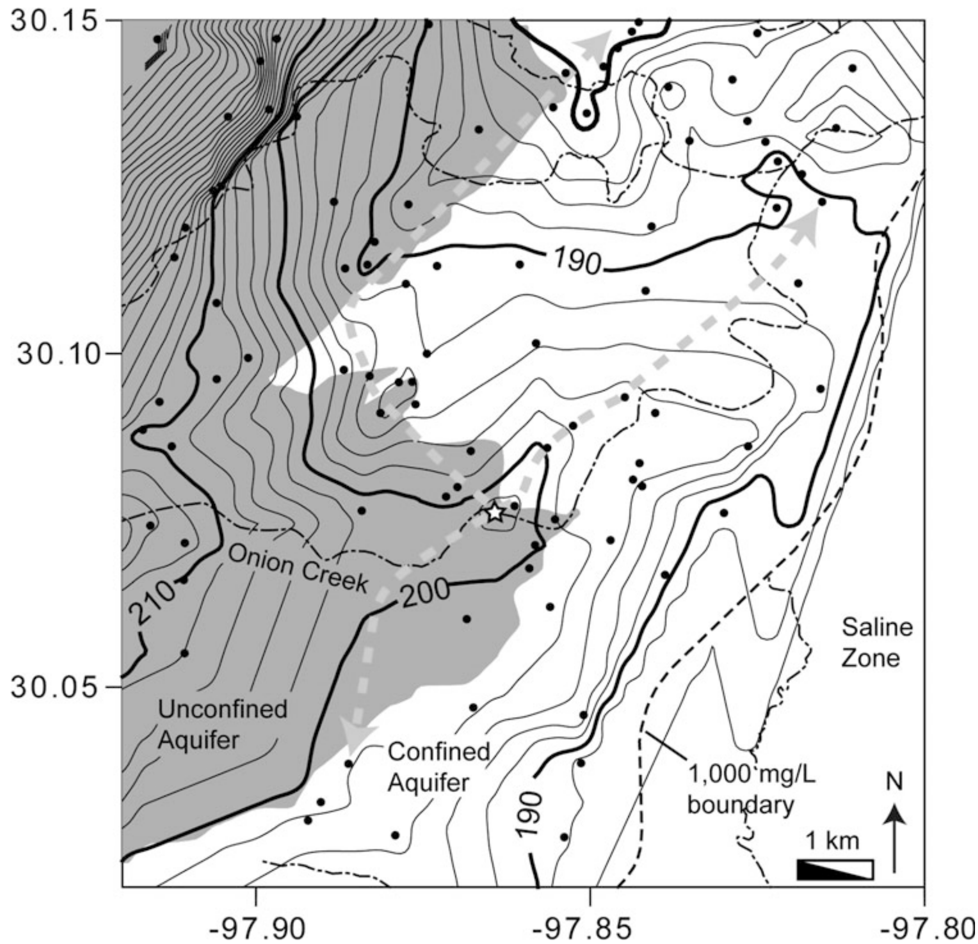

Fig. 6 **a** Regional potentiometric map along Onion Creek during high-flow conditions (February 2002). The 200-m contour illustrates the mounding effect due to discrete recharge from Antioch Cave. *Lines with arrows* indicate direction of groundwater flow from dye-trace studies

conditions on the upthrown side of the fault where the BMP is located and confined aquifer conditions on the downthrown side (Fig. 5).

3.7 Storm Water Contaminants in Onion Creek

Studies by the USGS (Web site data) indicate that high levels of bacteria and lead are associated with storm events in Onion Creek. The USGS collected water samples at their Onion Creek Driftwood station during multiple storm events between February 1994 and March 1998. Analyses were conducted for major cations and anions plus selected constituents commonly found in storm water.

A more recent study by the USGS (Mahler et al. 2011) finds that nitrate levels in Barton Springs and the five major streams that cross the recharge zone are significantly higher than samples collected between the early 1990s and November 2008. Samples were collected from these streams and Barton Springs during November 2008 and March 2010. Another conclusion of the study is that the probable source of nitrate in the recharging streams is biogenic (human and animal) sources.

Mahler and Lynch (1999) collected samples of water discharging from Barton Springs to determine the quantity, chemistry, and grain sizes of sediment discharging from the spring following two storm events in November 1995 and May 1996. They calculated that 805 kg (1775 lbs) and 1012 kg (2233 lbs) of sediment discharged from the spring during the two storm events, respectively. An analysis of the sediment and sediment peaks on the discharge hydrographs suggests that much of the sediments are derived from outside of the aquifer, meaning that the sediments are carried into the aquifer by recharging surface streams. Antioch Cave and other caves are potential pathways for sediment to enter the aquifer and eventually discharge at Barton Springs.

4 Methodology

This project involved the installation and operation of a continuous water-quality monitoring network (CWQMN), upgrade of the BMP at Antioch, and storm water sampling. Using CWQMN data and results of storm water sampling, the amount of contaminant reduction due to operation of the Antioch BMP was calculated.

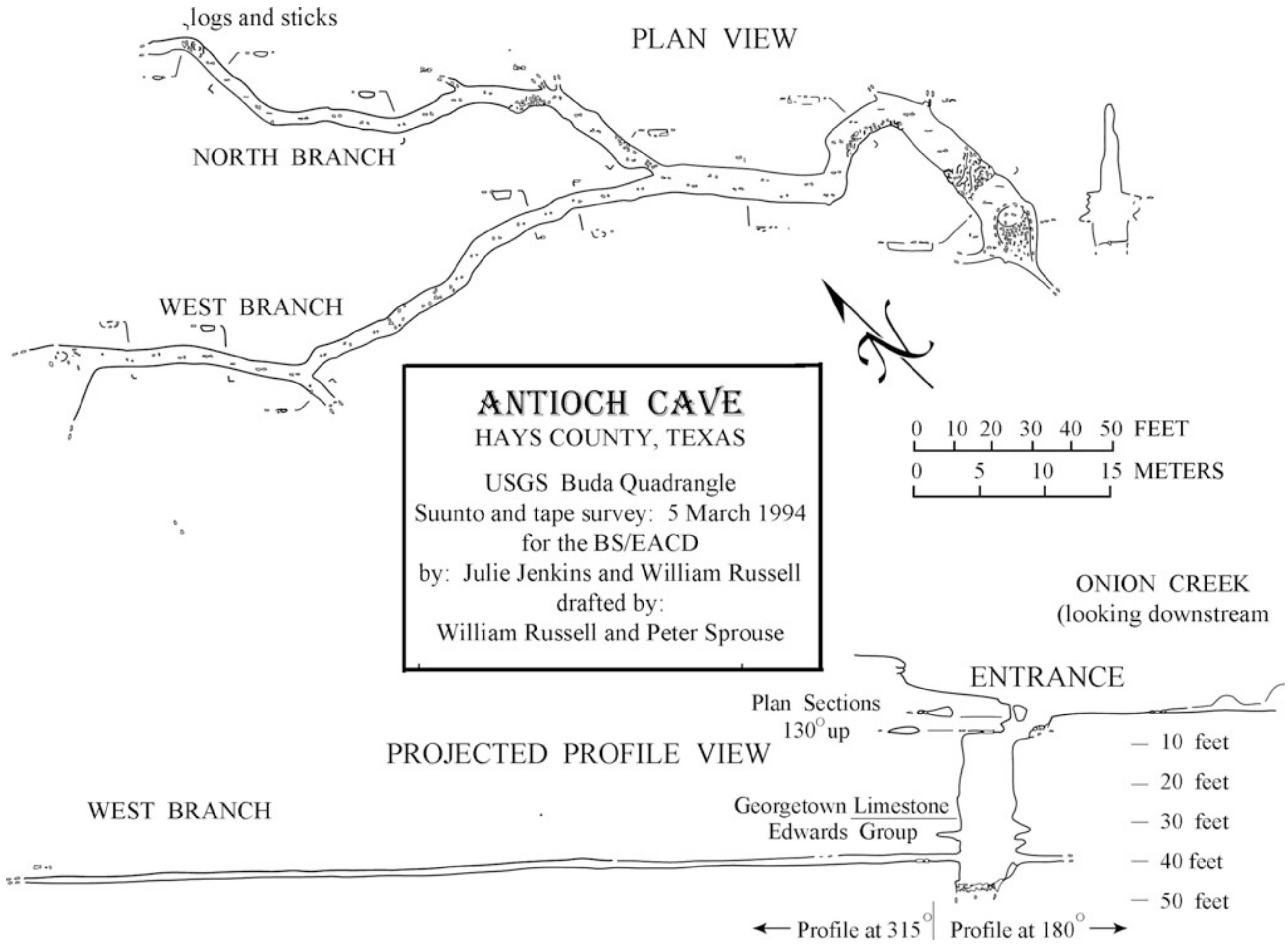

Fig. 7 Map of Antioch Cave showing plan and profile views

4.1 Continuous Water Quality Monitoring Network Sites

A CWQMN system was installed at the Antioch Cave site in Onion Creek to monitor water quality. This system provides real-time continuous data for surface water entering Antioch Cave and leaving the recharge zone within the Onion Creek watershed.

Data from the sensors are collected and stored in data loggers at the site and transmitted via wireless modem to the TCEQ MetroStar/Leading Environmental Analysis and Display System (LEADS) in Austin, Texas, where the data are processed and archived. Hourly averaged data are then posted to appropriate TCEQ Web sites for public use and review. Monthly site visits are conducted to verify or calibrate the multiparameter water-quality sensor, provide complete system maintenance, and monitor the CWQMN site for vandalism and acts of nature.

The Antioch CWQMN site includes the following equipment:

- In Situ Troll 9500 water-quality sensor (T, conductivity, DO, turbidity, pressure)
- Zeno data logger
- Enfora modem and cellular telephone
- Isco 2150 flow meter with area velocity/pressure
- Air compressor and tank
- Solar panel and 12-volt batteries.

District staff began the construction phase for the Antioch CWQMN system in April 2008. This monitoring site was brought onto the TCEQ real-time data collection system on August 16, 2008. The Troll 9500 was installed in a perforated 10-cm (4-in.) diameter PVC conduit about 4 m (15 ft) upstream of the BMP. The flow meter was installed in the 91-cm (36-in.) diameter pipe that connects the intake screen to the BMP. A stainless-steel equipment housing was installed above flood stage to house the Zeno data logger, modem, communications equipment, air compressor, and tank. Cables connecting the data logger to the probes run through the PVC conduit buried in a trench for a portion of the distance between the BMP and the equipment housing. From September 2009 to September 2010, water-quality measurements were made at Antioch for six storm events. Data continue to be collected to the present.

4.2 Upgrade of Antioch BMP

The original BMP, constructed at the Antioch site in 1997, was upgraded as part of this project to improve and automate the function of the BMP. The goal for the BMP when it was constructed was to reduce the amount of nonpoint source pollution entering the aquifer from storm water flow in Onion Creek. As part of this current project, modifications were made to improve the efficiency of the BMP by automating the opening and closing of the intake valves and by installing an intake screen over the second valve so that less storm debris and sediment could enter the cave and that the intake structure would not get clogged with debris.

An intake structure for the Antioch BMP, consisting of a 91-cm (36-in.) diameter screen and pipe, was installed in September 2008. The screen is 10 m (32 ft) long, and the pipe is 5 m (16 ft) long. The function of the intake structure is to allow water to flow into the cave while filtering out most of the debris that is carried in Onion Creek. A second 91-cm (36-in.) diameter valve was installed in the BMP on September 9, 2008 (Fig. 8). The valve controlled by the CWQMN equipment is programmed to close when turbidity of the water in Onion Creek rises to 100 NTU and to open when turbidity drops to 50 NTU. The default position of the valve is open since the turbidity meter is either sensing low turbidity water between storm events or air when there is no flow in the creek. When a storm pulse first arrives and turbidity levels increase above this threshold, the valve will automatically close. After the storm pulse passes and turbidity levels decrease, the automated valve opens to allow water to enter the BMP.

An Isco 2150 velocity meter was installed near the midpoint of the 5-m (16-ft) long pipe. This velocity meter measures flow of water into the second valve. From the velocity data, a volume of flow can be calculated by multiplying the velocity by the cross-sectional area of the pipe. By measuring the volume of water entering the system when the valve is first opened following a flow event, the mass of storm contaminants prevented from entering the aquifer when the valves are closed can be calculated (Eq. 1—Calculation of Contaminant Reduction). Figure 9 is a photograph of the completed system.

4.3 Storm Water Sampling

District staff selected storm water parameters for analysis that include total suspended solids (TSS), total dissolved solids (TDS), turbidity, nitrate and nitrite as nitrogen (N), and total phosphorus (P). Storm water sample collection followed field sampling procedures for conventional parameters documented in the TCEQ Surface Water Quality Monitoring Procedures Manual (TCEQ 2008).

Samples were collected from an open channel environment using a Teledyne Isco system (3700 series). An Isco bubbler flow meter (4230 series) initiates the sampling program for the automatic sampler. The flow meter logs water levels every 5 min and triggers the automatic sampler to start sampling when there is a rise of water level in the creek indicative of a storm pulse. The sampler and flow meter were placed about 6 m (20 ft) in elevation above the BMP so that the sampler pump will be capable of delivering

Fig. 8 Installation of second valve (automated) on Antioch BMP

Fig. 9 View of Antioch BMP following upgrade completion. View looking upstream

samples to the bottles in the sampler, but will not be subjected to flooding by all but the most severe storms. Volumetric calibration of the automatic sampler was performed to verify correct volumes were being collected. The automatic sampler fills two 1-L (about 1 quart each) bottles for every sample collected.

The collection of samples focused on peak flows from a given storm event with sampling continuing as the storm subsides. Samples were collected at intervals ranging from every 15 min to every 6 h. A selected number of samples thought to represent the storm hydrograph were sent to the laboratory for analysis. From October 2009 to September 2010, samples were collected from five storm events. Five to seventeen samples were analyzed for each storm event.

4.4 Calculation of Contaminant Reduction

Currently, the CWQMN system is set to close the intake valve when turbidity values rise to 100 NTU and to reopen when the turbidity value of storm water drops to 50 NTU. The contaminant reduction Eq. (1) is used to quantify the mass of contamination being prevented from entering the BMP.

$$Q * C_{\mathrm{N,P,S}} * T = M_{\mathrm{N,P,S}} \tag{1}$$

where

- Q Rate of flow into Antioch BMP when valve is first opened after storm pulse.
- $C_{\mathrm{N,P,S}}$ Concentration of N (nitrate/nitrite), P(phosphorus), or S (sediment) during storm pulse.
- T Duration of time that valve on BMP was closed.
- $M_{\mathrm{N,P,S}}$ Mass of contaminant prevented from entering aquifer.

5 Results of Sampling and Data Collection

As described in the methodology section, the data collection part of this project consisted of continuous water-quality monitoring with a CWQMN system at Antioch Cave and storm water sampling at Antioch. Data collection at Antioch began in May 2009. Other than some brief periods when the system was not functioning or data were not transmitted, there is a nearly continuous record of temperature, specific conductivity, turbidity, dissolved oxygen, and gage height for the Antioch site. However, between May 2009 and September 2009, there was no flow in Onion Creek at Antioch due to a severe drought.

5.1 Sampling of Storm Events

A summary of the six storm events recorded at the Antioch CWQMN site is presented in Fig. 10, which includes data from flow in Onion Creek at the U S Geological Survey (USGS) Driftwood station and maximum gage height at the Antioch CWQMN. Table 1 is a compilation of CWQMN and laboratory data shown in a chart format for each of the six storm events. Laboratory data include turbidity, nitrogen from nitrate and nitrite, total phosphorus, suspended solids, and total dissolved solids. A description of each of the six storm events is provided below.

5.1.1 Storm Event 1 (September 29–30, 2009)

At the beginning of September 2009, most of Texas was experiencing a severe drought that had been going on for close to 2 years. The District had declared an Alarm Stage Drought on June 23, 2008, for the Barton Springs aquifer. By the beginning of December 2008, the District was in Critical Stage Drought, and was on the verge of entering into Exceptional Stage Drought in September 2009. Heavy rain, up to 250 mm (10 in.) in some parts of the recharge and contributing zones, fell between September 9 and 12. However, this significant amount of rain did not cause any flow in Onion Creek at the USGS gaging station in Driftwood. Because of the extremely hot and dry conditions at the time of this rain, there was very little runoff of rainfall to the creeks.

On September 28 and 29, light rain of less than 13 mm (½ in.) fell over much of the study area. However, a small area on the north side of Onion Creek, upstream of Antioch, received about 76 mm (3 in.) over a few hours on September 29. This led to flow in some tributaries to Onion Creek starting about 3 km (2 miles) upstream of Antioch, but there was no flow at the Driftwood station. The flow soon reached the Antioch BMP with a maximum gage height of about 1.4 m (4.6 ft). Water-quality data were collected by the CWQMN system, but the automated sampler was not activated for sample collection. CWQMN data show a short but brief peak for flow at Antioch. Within less than 24 h, flow had decreased to virtually zero. The turbidity of the water first reaching Antioch was 776 NTU. Turbidity values dropped steadily until the end of the flow event. Conductivity values spiked initially, then declined sharply, then rose steadily until the end of the flow event, which lasted less than 17 h.

5.1.2 Storm Event 2 (October 27–28, 2009)

The second storm event recorded at Antioch occurred following a moderate amount of rain of about 50 mm (2 in.) on

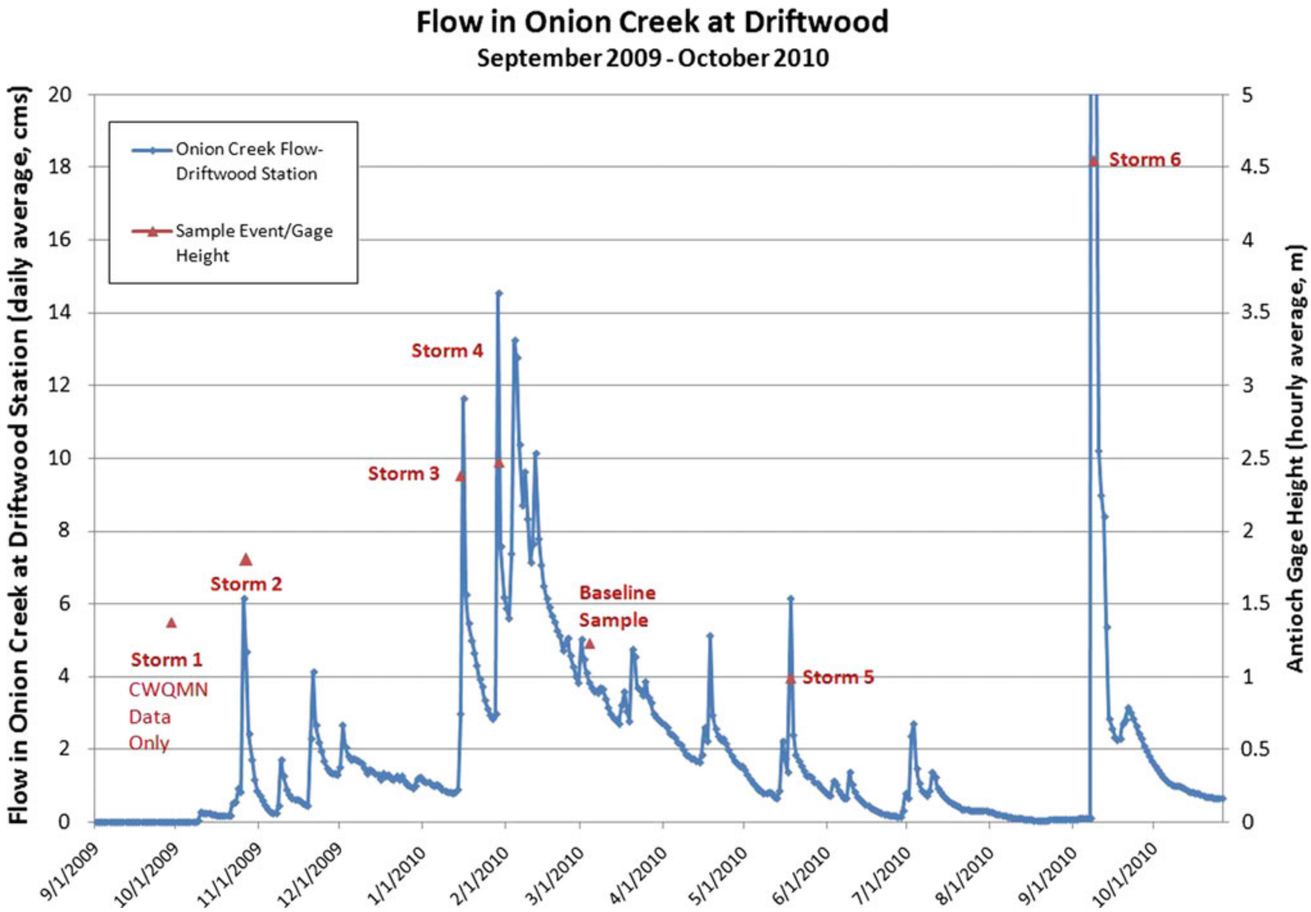

Fig. 10 Storm events sampled for this project are shown superimposed on a hydrograph of Onion Creek at the USGS Driftwood station from August 2009 to October 2010. The Driftwood station is about 21 km (13 miles) upstream of the Antioch Cave site

Table 1 Mass of contaminant reduction from operation of Antioch BMP for five storm events

Storm event	Start (NTU > 100)	End (NTU < 50)	Duration (days)	Duration (hours)	Average peak storm values[b] (mg/L)			Contaminant reduction[c] in lbs (kg)		
					N[a]	P[a]	TSS	N[a]	P[a]	TSS
1	Samples not collected for laboratory analysis									
2	10/27/09 1:41	10/27/09 2:27	0.03	0.8	6.16	0.075	57.5	**106** (48)	**1.3** (0.6)	**990** (449)
3	1/15/10 21:30	1/16/10 8:15	0.45	10.7	0.53	0.195	70.0	**128** (58)	**47** (21)	**16,905** (7666)
4	1/29/10 11:15	1/31/10 0:30	1.55	37.3	0.92	0.02	30.2	**770** (349)	**17** (7.6)	**25,271** (11,461)
5	5/18/10 2:56	5/18/10 12:31	0.40	9.6	0.33	0.005	31.2	**71** (32)	**1.1** (0.5)	**6717** (3046)
6	9/9/10 14:26	9/7/10 21:46	1.69	40.7	1.49	0.25	153.9	**1361** (617)	**228** (104)	**140,597** (63,763)
		Total duration	**4.1**	**99.0**			Totals (lbs)	**2436**	**295**	**190,480**
							Totals (kg)	1105	134	86,385

[a] N is nitrogen from nitrate and nitrite; P is total phosphorus. [b] For period during which the valve was closed. [c] Mass of contaminants not entering Antioch Cave while valves are closed

Fig. 11 Photograph of the top of the BMP about 8 h past the peak storm pulse on October 27, 2009, with a whirlpool near the corner of the vault due to water entering the original valve

October 26, 2009. This followed a very wet September, as described in Sect. 5.1.1, that had a rainfall total of about 330 mm (13 in.) over much of the recharge and contributing zones. Total rainfall in October was about 170 mm (6.5 in.) as measured at the District office in Manchaca, Texas. The maximum gage height at Antioch during this storm event was 2.0 m (6.2 ft). Turbidity reached a peak of 782 NTU at the very beginning of the storm pulse which quickly declined to less than 50 NTU within 50 min. Conductivity values spiked initially, then declined sharply, then rose steadily before leveling off for the remainder of the storm event. Figure 11 is a photograph showing water flowing in Onion Creek and the top of the BMP about 8 h past the peak storm pulse on October 27, 2009.

5.1.3 Storm Event 3 (January 15–17, 2010)

The third storm event occurred between January 15 and 17 following a 76-mm (3-in.) rain on January 15 and 16. January was also a very rainy month with a rainfall total of about 120 mm (4.7 in.), about 60 mm (2.5 in.) above average rainfall for the month. The gage height at Antioch reached a maximum of 2.4 m (7.9 ft) within 9 h of the start of the event (Fig. 12). A turbidity peak of 144 NTU occurred about 1 h after the start of the event. A second peak of 151 NTU occurred about 5 h after the first peak. Three conductivity peaks occurred during the first 12 h of the storm event followed by a slow decrease for the next 12 h, then a slow but steady rise in conductivity.

5.1.4 Storm Event 4 (January 29–31, 2010)

The fourth storm event was brought about by 41 mm (1.6 in.) of rain between January 28 and 29. Prior to the storm, flow in Onion Creek at the Driftwood station had been about 100 cfs, but there was no flow at Antioch prior to the storm. The gage height at Antioch reached a maximum of 2.5 m (8.2 ft) within about one hour of the start of the event. A turbidity peak of 144 NTU occurred immediately when the storm pulse reached the instruments at Antioch. Two conductivity peaks occurred during the first 12 h of the storm event followed by a slow decrease for the next 20 h, then a slow, but steady, rise in conductivity. Following this storm event, flow at Antioch continued until March 15 when the instruments recorded a gage height of 0 m. On that date, the USGS station on Onion Creek at Driftwood was recording flow of about 2831 L/sec (100 cfs).

5.1.5 Storm Event 5 (May 18–19, 2010)

The fifth storm event followed about 43 mm (1.7 in.) of rain between May 14 and 17. Flow began on May 18 and continued until May 19, for a total of about 42 h of flow. The peak gage height of 1.0 m (3.3 ft) occurred 5 h after the commencement of flow at Antioch. Of the five storm events sampled for this project, this event had the lowest recorded gage height. A turbidity peak of 962 NTU occurred immediately at the beginning of the storm pulse. Conductivity immediately peaked at the beginning of the storm pulse, then peaked again about an hour later, then decreased for another 5 h before rising steadily until the end of the flow event.

On June 30, 2010, Hurricane Alex landed in northern Mexico and brought more than 130 mm (5 in.) of rain to parts of the Edwards recharge zone. Flow in Onion Creek at the Driftwood station increased to about 2831 L/sec (100 cfs), but no flow occurred at Antioch as a result of this rain.

5.1.6 Storm Event 6 (September 7–10, 2010)

The sixth storm event was the largest storm event of the project. It followed about 190 mm (7.5 in.) of rain from Tropical Storm Hermine from September 7 through 8. Two days of light rain, that totaled about 15 mm (0.6 in.), preceded the storm by 4 days, so soil conditions were fairly wet. Hermine arrived in Central Texas on September 7 with about 167 mm (6.6 in.) of rain. The rain continued into September 8 with about 23 mm (0.9 in.). Flow began at Antioch at about 8:00 pm on September 7. A peak gage height of about 4.6 m (15 ft) occurred about 13 h later. A second gage height peak of about 4.0 m (13 ft) occurred about 12 h later. The maximum flow rate recorded at the USGS Driftwood station was 74,300 L/sec (2630 cfs) (hourly average). Five peaks were recorded at Antioch for turbidity during this storm event. The greatest turbidity reading was 1210 NTU that occurred 13 h after the beginning of flow at Antioch. There were three conductivity peaks within the first 26 h of the storm event followed by a steady rise. Flow at Antioch ended on September 13 for a total duration of about 6 days.

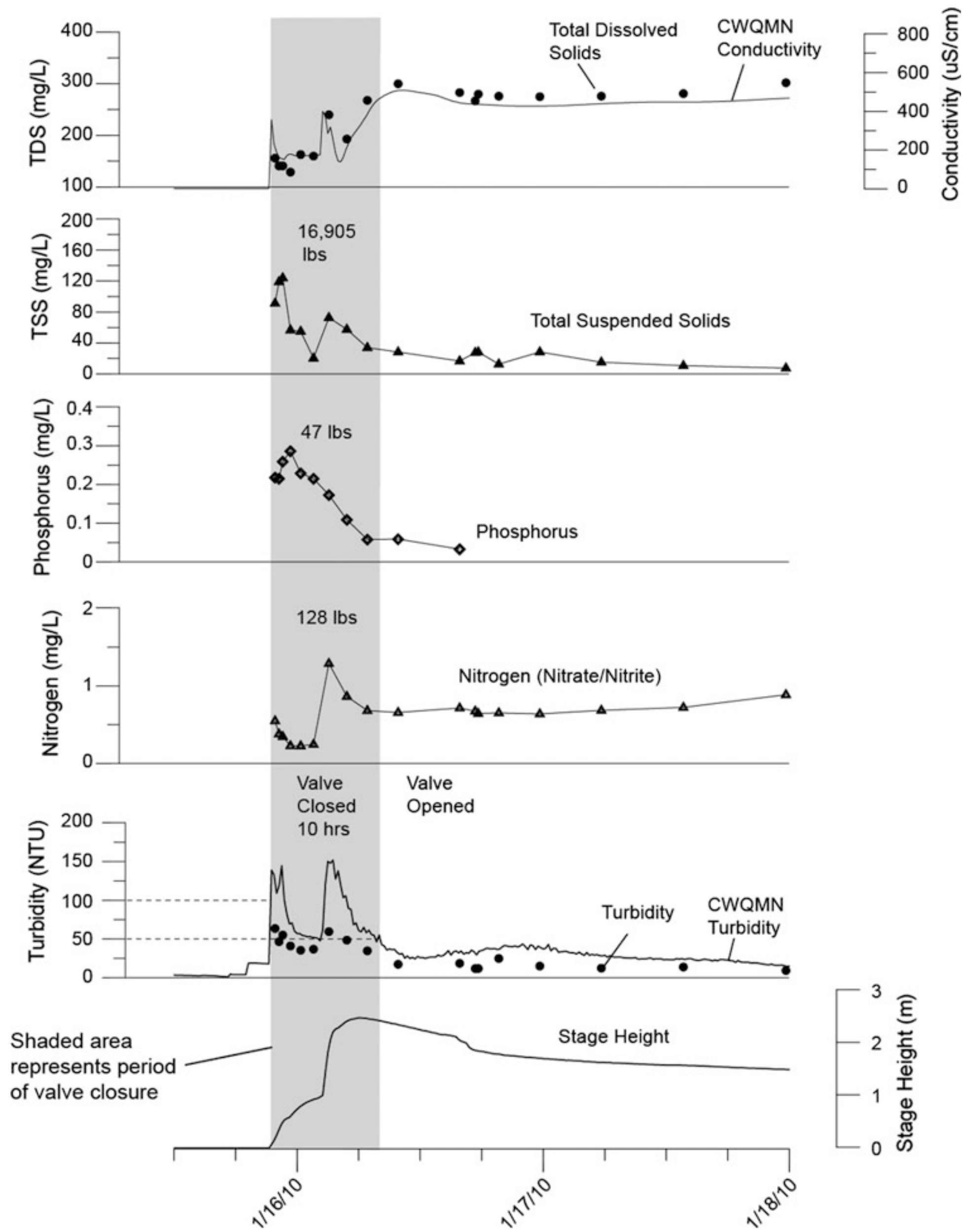

Fig. 12 CWQMN and laboratory analytical data for Storm Event 3

5.2 Comparison of Storm Events

Laboratory and CWQMN data for the five storm events show considerable variation in the relationships between the various parameters analyzed by the laboratory or recorded by the CWQMN system. A comparison of stage height to turbidity data from the CWQMN system at Antioch does not indicate any distinct pattern. The analytical results follow mostly irregular paths throughout the progression of each storm event. Many factors need to be considered in the analysis of each storm event. Antecedent conditions such as soil moisture and the amount of water in Onion Creek can significantly affect storm water runoff and subsequent flow in the creek. The intensity of rainfall and location of that rain can also affect the amount of flow and the variation in contaminant load of the storm water.

Unlike the storm events sampled for this project at Antioch, each storm event in the USGS study (Web site data) shows a clear trend with high turbidity levels associated with high flow rates. However, both studies show that each storm event is unique with respect to contaminant loads.

Figure 13 shows the results of laboratory analyses of samples from five storm events. Values for a given parameter vary considerably during the first 10 h of the storm event. Values tend to either rise or fall slightly after the first

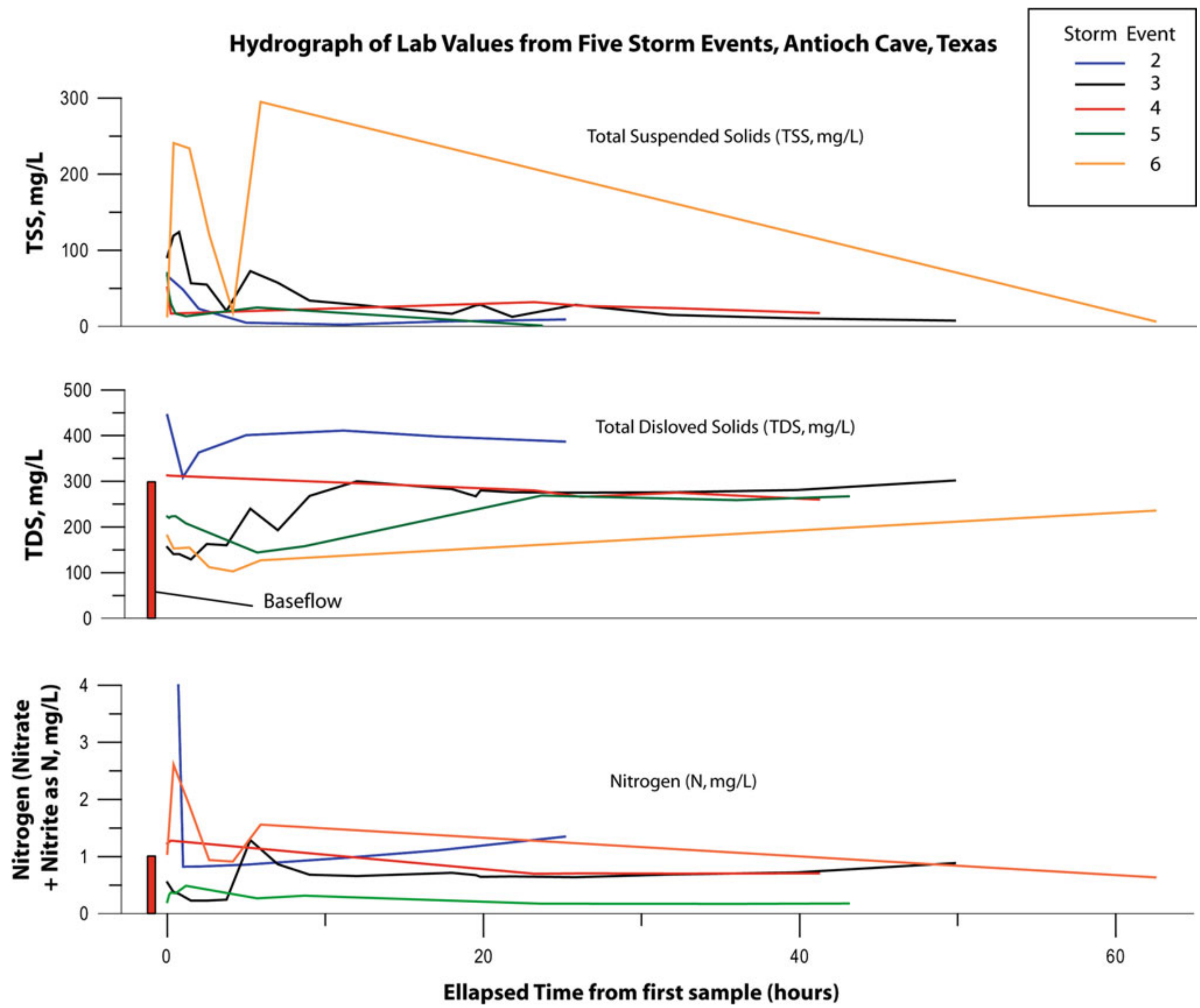

Fig. 13 Hydrograph of laboratory analytical results for five storm events at Antioch Cave. Also shown are the results from the baseflow sample as a *bar graph*. TSS was below the detection level for the baseflow sample

10 h. This pattern applies to each of the five storm events. A sample was collected from Onion Creek at Antioch on March 4, 2010, that is considered to be representative of baseflow conditions. Laboratory analytical results for TDS, nitrogen (nitrate/nitrite), and TSS were 299, 1.01 mg/L, and below detection level, respectively. The trends of each of these parameters for each storm event show that over time, the values are heading in the direction of the baseflow sample values.

5.3 Contaminant Reduction from Operation of BMP

The principal goal of the BMP constructed over Antioch Cave has been to reduce the amount of storm water contaminants entering the aquifer through Antioch Cave. This had been accomplished with the construction of the original BMP and has been improved with the recent upgrades made to the BMP.

The amount of contaminants not entering the aquifer due to operation of the BMP can be calculated by measuring the flow of water entering the BMP the moment the valve is opened, then multiplying that value by the concentration of contaminants in the water and by the duration of time that the automated valve was closed. The manually operated valve (original valve) is left in the closed position following passage of each storm pulse. The automated valve is closed when turbidity from a storm pulse goes above 100 NTU and is opened when turbidity drops below 50 NTU. Of these parameters, the most difficult to determine is the amount of flow that would be going into the aquifer during the peak storm pulse if both valves are open. This is accomplished, in part, by measuring the flow into the new valve and intake screen when the valve is first opened following passage of the peak storm pulse, which is the point at which turbidity in Onion Creek drops below 50 NTU. An Isco 1250 velocity meter is situated in the 5-m (16-ft)-long, 91-cm (36-in.)-diameter pipe placed between the intake screen and the new valve. Because the velocity meter was damaged during a storm event, there are limited velocity data from storm events. Flow data were collected for the January 15–16, 2010 storm event (Storm Event 3). At about 17:45 on January 16, the valve opened automatically and the instrument recorded a velocity of 3.9 m/s (12.5 ft/sec) that converts to a flow rate of about 2435 L/sec (86 cfs), or 2.4 cubic meters per second [cms]. As soon as possible after the new valve is opened, the original valve is manually opened to maximize flow into the cave. Although it is difficult to measure flow into the original valve, the combined flow into the cave is certainly greater than the measured flow into the new valve. For this evaluation, an estimated total flow into the system of 2831 L/sec (100 cfs) is used for the contaminant reduction calculations. This assumes that the additional flow into the original valve is a least 400 L/sec (14 cfs). This is a minimum flow value and it is likely that total flow into the system is greater than 2831 L/sec (100 cfs), but additional studies are needed to better determine this flow. The intake system for the BMP was designed to handle up to 7000 L/sec (250 cfs). However, it is not known what the upper limit of flow into the cave is.

The results of the contaminant reduction calculations are shown in Table 1. Calculations were made from data for five storm events. The first storm event recorded at Antioch with the CWQMN system did not include laboratory analytical data because the automated sampler was not yet programmed to operate during a storm event. The average duration of the storm events for which the turbidity level of the water in Onion Creek was greater than 100 and 50 NTU was 20 h. The longest time that the valve was closed was 40.7 h, and the shortest time was 0.8 h. As shown in Table 1, concentrations of contaminants and the amount of contaminant reduction varied considerably between storm events. Storm Event 6, with the longest duration of valve closure and the highest level of contaminants, except for nitrogen in Storm Event 2, had the highest amount of contaminant reduction with 617 kg (1361 lbs) of nitrogen, 104 kg (228 lbs) of phosphorus, and 63,763 kg (140,597 lbs) of sediment. These numbers show that by closing the valves on the BMP during storm events, a significant amount of contaminants from nonpoint sources can be prevented from entering the aquifer. This is certain to provide some protection to nearby water-supply wells and ultimately to lessen degradation of groundwater in much of the Barton Springs aquifer and Barton Springs. Contaminant reduction due to operation of the BMP also applies to other contaminants that were not included in the analytical program such as bacteria, lead, biological oxygen demand (BOD), and pesticides.

5.4 BMP Operation During Storm Event 3

Laboratory analytical and CWQMN data for Storm Event 3 are shown in Fig. 12, including the amount of contaminant reduction for each parameter and an indication of where on the hydrograph the automated valve closed and opened. Based on 15-min CWQMN data, the first storm water to reach the CWQMN multiparameter sensor had a turbidity value of 139 NTU. The automated valve closed immediately upon sensing a turbidity level of 100 NTU or greater. During the next 5 h, the turbidity of the storm water in Onion Creek decreased to 48 NTU. It is presumed that the valve opened due to a turbidity value of 50 NTU or less. However, turbidity then rose above 100 NTU within less than 30 min and presumably closed the valve again. The valve stayed shut for another 5 h until turbidity dropped below 50 NTU again.

As shown in Table 1 and Fig. 12, the amount of sediment, nitrogen (from nitrate and nitrite), and phosphorus prevented from entering the aquifer during Storm Event 3 was 76,668 kg (16,907 lbs), 58 kg (128 lbs), and 21 kg (47 lbs), respectively. Greater amounts of contaminants could be kept out of the aquifer by having the valve open at a lower turbidity level, but that would also decrease the amount of water recharging the aquifer. The results of Storm Event 3 indicate that below a turbidity of 50 NTU, the decrease in total suspended solids is at a slower rate than at levels above 50 NTU.

6 Conclusions

The upgraded BMP at Antioch Cave has demonstrated that such a system is capable of reducing the amount of storm water contaminants entering the Barton Spring aquifer through Antioch Cave. These contaminants can potentially impact water-supply wells and water quality at

Barton Springs where endangered salamanders live. The key findings and conclusions derived from this study are summarized below:

- The upgraded Antioch BMP is capable of significantly reducing the amount of nonpoint source contaminants entering the aquifer through Antioch Cave.
- It is estimated that during this period of operation of the upgraded BMP, 1105 kg (2436 lbs) of nitrogen from nitrate/nitrite, 134 kg (295) lbs of total phosphorus, and 86,385 kg (190,480 lbs) of total suspended solids (TSS) were prevented from entering the aquifer.
- Although bacteria concentrations were not a parameter monitored during this study, previous studies suggest that bacteria are a significant contaminant in Onion Creek during storm events and were reduced as a result of the operation of the BMP.
- The best water-quality indicators of storm flow are turbidity and TSS.
- Because the vault prevents the cave from plugging with debris, a greater quantity of water enters the aquifer. Water-level measurements from wells near the cave show that at times of maximum recharge, a groundwater mound develops below the cave. This increase in storage can help reduce the impact of drought on the aquifer.
- Installation of a flow meter near the main valve provides more accurate and reliable data for determining volume of flow into the BMP. This flow value is also used to estimate how much storm water is not entering the BMP when the valves are closed.
- A CWQMN system installed at Antioch Cave provides flow and water-quality data for water recharging the aquifer and leaving the recharge zone.
- Data provided by the CWQMN system and laboratory analyses of grab samples can be used to compare future water quality in Onion Creek as the Onion Creek watershed becomes more developed.
- During moderate to severe drought conditions, significant rainfall is needed for water to flow in Onion Creek. During non-drought conditions, much less rainfall is needed to get water flowing or to increase the rate of flow in Onion Creek.

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Monitoring of Cueva Larga, Puerto Rico—A First Step to Decode Speleothem Climate Records

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Abstract

This study presents results of an ongoing cave monitoring program at Cueva Larga, Puerto Rico. The monitoring includes monthly analyses of stable isotope ratios of rain and drip water, and trace element ratios of drip water and cave air parameters. Drip sites are above growing speleothems offering the unique chance to calibrate geochemical variations in speleothems in order to reconstruct past climate conditions. Seasonal rainfall patterns above Cueva Larga show characteristic stable isotope values. The wet season is characterized by more negative $\delta^{18}O$ and δD values and a maritime deuterium excess (+10‰). The dry season has more positive $\delta^{18}O$ and δD values and elevated deuterium excess (>15%). The seasonal variations in the $\delta^{18}O$ and δD values are smoothed by the soil and karst system which acts as a low-pass filter, indicating that climate proxies derived from speleothems growing in Cueva Larga may only show multiannual changes. The seepage water reservoir appears to be well-mixed. The transmission time of atmospheric signals into the drip water is site-specific ranging most likely from several months to years.

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1 Introduction

Here, we present results from a cave monitoring program at Cueva Larga. The goal of monitoring the Cueva Larga (CL) cave system is to understand and quantify the processes controlling the geochemical composition of cave drip waters which is ultimately recorded in speleothems. Calibrating the speleothems' geochemical composition to climate variables is the key to correctly interpret the proxy record encoded in speleothems in terms of past climate variability.

Speleothems have successfully been used as paleoclimate records (e.g., Fairchild and Baker 2012; Fairchild et al. 2006a; Lachniet 2009). Stable oxygen isotopes and trace element ratios have proven to be reliable paleoclimate proxies in many settings (e.g., Winter et al. 2011; Lachniet 2004; Wang et al. 2001; Spötl and Mangini 2002; Fairchild and Treble 2009; Cruz et al. 2009). However, interpretation of these proxies is not always straightforward. Cave

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monitoring and drip site monitoring play a key role prior to paleoclimate reconstruction based on speleothems (James et al. 2015; Lachniet 2009; Riechelmann et al. 2011, 2013).

Speleothem geochemical composition and growth are affected by the seepage water flow systematics through the soil and karst as well as the cave environment (Fairchild and Baker 2012). Seasonal variations in the cave environment can bias the recorded signal and might lead to aliasing if not resolved at a sufficiently high resolution (Banner et al. 2007; James et al. 2015; Weedon 2003). Moreover, processes such as evaporation, temperature variations, prior calcite precipitation (PCP), and changes in drip rate and pCO_2 can potentially alter the geochemical composition of speleothems, including trace elements and stable isotopes (Deininger et al. 2012; Fairchild and Baker 2012; Mickler et al. 2006). Cave monitoring results, as presented here, are important to understand the transmission of climate signals from the surface through the vegetation cover, soil, and karst into the cave (Fairchild and Baker 2012; Fairchild et al. 2007).

In the tropics, the speleothem $\delta^{18}O$ value is commonly used to reconstruct variations in local rainfall amount over time (Lachniet 2009). Variations in $\delta^{18}O$ and δD values of rainfall in the tropics are inversely correlated with the monthly rainfall amount, which is referred to as the “amount effect” (Sect. 2.1; Dansgaard 1964). The “amount effect” is variable, and other processes such as temperature, seasonality, and moisture source can modulate the “amount effect” and result in a more complex $\delta^{18}O$ signal (Dansgaard 1964; Rozanski et al. 1993). Trace element ratios of Sr/Ca and Mg/Ca show high potential as a complementary recorder of rainfall changes (Fairchild and Treble 2009; Fairchild et al. 2000; Stoll et al. 2012).

Adjustments of rainfall patterns to future climate change scenarios are still uncertain, and changes in the hydrological cycle will affect freshwater supplies (Intergovernmental Panel on Climate Change 2014; Winter et al. 2015). Multiproxy paleorainfall records offer a unique opportunity to evaluate climate models (Braconnot et al. 2012), and speleothem records can elucidate important climate forcings on regional rainfall (e.g., Asmerom et al. 2007; Cruz et al. 2005).

Our study investigates the transmission of the atmospheric signal into cave drip water feeding growing speleothems in Cueva Larga, Puerto Rico. The focus lies on tracing variations in the water cycle, expressed by changes in local precipitation. One part is to investigate the “amount effect” to ensure that variations recorded by speleothem isotopes can be linked to changes in past rainfall amount. Rainfall samples are collected above the cave site in the northern karst region of Puerto Rico and in Mayagüez at the western coast of the island to detect the stable isotope signal of precipitation. Another part is to characterize the cave environment and record changes in drip water chemistry to study whether there is a connection to atmospheric rainfall anomalies.

The setting of Cueva Larga appears ideal for paleoclimate studies due to its remote location, the lack of an active water stream and its small entrance limiting cave ventilation. In addition, the cave is unknown to the public restricting the risk of measurement disturbances. The monitoring results are documenting the natural undisturbed conditions in Cueva Larga and are providing important insight into the climate signal transmission into the cave.

2 Background

2.1 Isotopic “Amount Effect”

Rainwater $\delta^{18}O$ values depend on complex interactions in the hydrological cycle (Dansgaard 1964; Lachniet 2009; Rozanski et al. 1993). In the tropics, the “amount effect,” first described by Dansgaard (1964), usually outweighs other stable isotope effects. The “amount effect” describes a negative correlation between the monthly rainfall amount and its $\delta^{18}O$ values. Deep vertical convection systems, including tropical storms and hurricanes, have more negative $\delta^{18}O$ values than most other tropical rain events (Dansgaard 1964; Lawrence and Gedzelman 1996). In tropical cyclonic systems, atmospheric water ascends to high altitudes and Rayleigh distillation in the deep convection leads to an enrichment in light isotopes during the system’s evolution (Lachniet 2009). Furthermore, the extent of subcloud raindrop evaporation has also been related to rainfall amount and intensity (Dansgaard 1964; Lachniet 2009).

In Puerto Rico, easterly waves and low-pressure systems during the rainy season have higher cloud altitudes and lower condensation temperatures than trade-wind orographic rainfall of high-pressure systems during the dry season. More recent results obtained in Puerto Rico have shown a stronger correlation between $\delta^{18}O$ values of precipitation and maximal cloud heights (Scholl et al. 2009). This implies that the “amount effect” appears to be infuenced by cloud height and varying condensation temperatures of precipitation as well. Speleothem $\delta^{18}O$ values record variations in the drip water’s stable isotope composition reflecting rainfall’s $\delta^{18}O$ values and allowing reconstruction of tropical rainfall amount and weather patterns over time (Fairchild and Baker 2012; Lachniet 2009).

2.2 Global Meteoric Water Line (GMWL) and Deuterium Excess (d-Excess)

The Global Meteoric Water Line (GMWL) was defined by Craig (1961) as the relationship between the δD and $\delta^{18}O$ values of monthly rainfall water samples around the globe (Eq. 1). It results from the proportional fractionation difference during phase changes between δD and $\delta^{18}O$ and kinetic isotope fractionation during evaporation at relative humidity below 100% creating a d-excess. The d-excess (Eq. 2) is caused by the higher diffusivity for the lighter deuterium carrying molecule $^{2}H^{1}H^{16}O$ than for the heavier $^{1}H^{1}H^{18}O$. The d-excess of 10‰ in the GMWL represents an average relative humidity of 85% at the water source region (Clark and Fritz 1997; Merlivat and Jouzel 1979):

$$\delta D = 8 * \delta^{18}O + 10‰ \tag{1}$$

$$d = \delta D - 8 * \delta^{18}O \tag{2}$$

During condensation, the d-excess does not change and it is an indicator of the water vapor source region (Merlivat and Jouzel 1979).

2.3 Speleothem Trace Element Ratios (Sr/Ca and Mg/Ca)

Trace element ratios of Sr/Ca and Mg/Ca in cave drip water and speleothem may be used as hydrological proxies (Fairchild and Baker 2012). In certain cave settings (Fairchild et al. 2000, 2006a), it has been shown that seepage water during drier conditions exhibits higher ratios due to increased prior calcite precipitation (PCP) and selective leaching due to longer water residence times. PCP occurs upstream from the drip site and preferentially incorporates Ca in the crystal's lattice increasing the trace element ratio downstream. This may also be the case in Cueva Larga.

3 Site Description

Puerto Rico is the easternmost island of the Greater Antilles located in the northeastern Caribbean between the island of Hispaniola and the Virgin Islands (Fig. 1). From east to west, the northern karst region stretches along the north coast reaching heights of more than 400 m. Cueva Larga (CL), also known as Cueva Coroso (Fig. 1), is located in the north-central karst region (N 18°19; W 66°48) at a height of 350 msl. The area is a developed holokarst characterized by sinkholes and mogotes. A thick tropical forest covers the surface above the cave. The cave is dominantly vadose with some phreatic features. It developed in the Oligocene Lares Limestone (Monroe 1980). The entrance of CL is located along the flank of a sinkhole at the lower edge of a small hill. A narrow vertical pit forms the entrance, followed by two U-shaped depressions along the cave ceiling (Fig. 1). The main passage is nearly horizontal, strikes west–east, and forms a tube with ceiling heights of up to 30 m. The cave ends in the Collapse Room, a chamber whose roof collapsed, which is separated from the main chamber by a rise in the cave passage floor. The Collapse Room splits up in a small

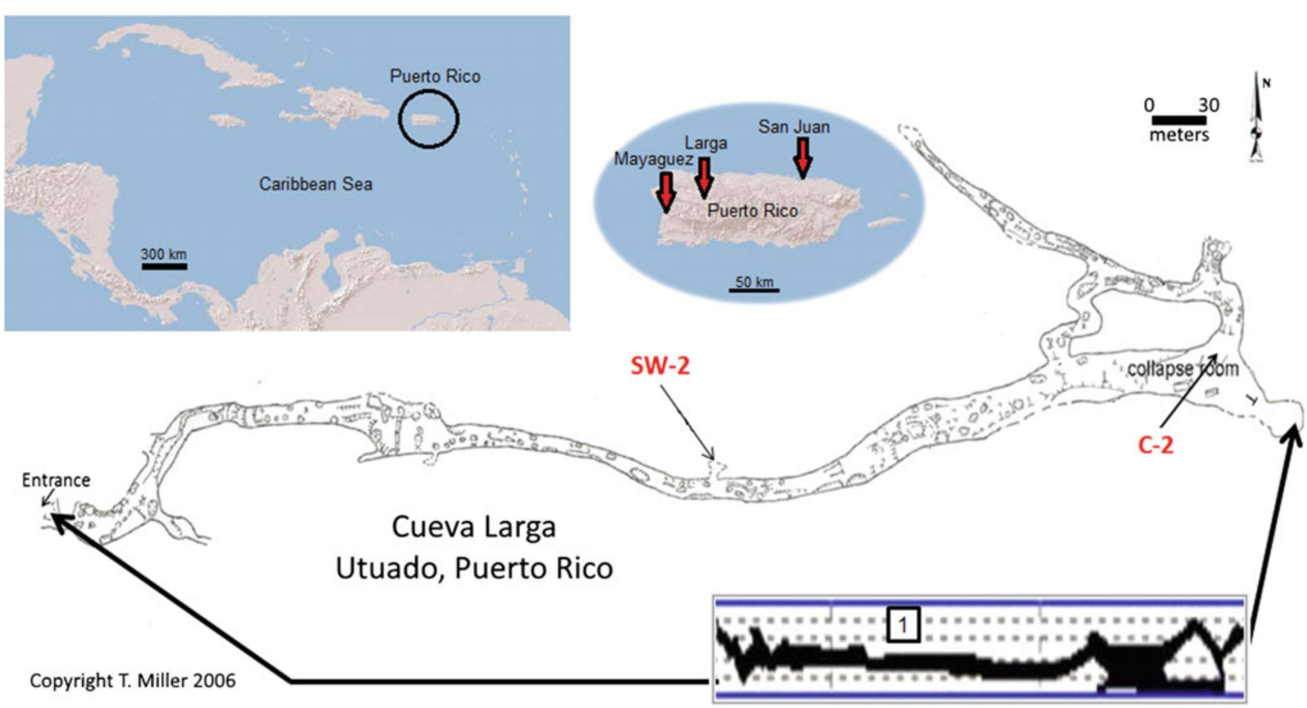

Fig. 1 Plan view of Cueva Larga (after Miller 2010) with monitored drip sites SW-2 and C-2 (*marked in red*). Also shown is an overview map of the Caribbean and a map of Puerto Rico with the locations of Cueva Larga, Mayagüez, and San Juan (*red arrows*). *Inset 1* Longitudinal section of the cave (Miller 2010)

lower- and a large upper-level passage which reconnects at the end of the cave (Fig. 1). The horizontal extent of CL is about 1440 m (Miller 2010). Here, we discuss the drip water data of drip site SW-2, located in the main passage, and site C-2, located in the Collapse Room (Fig. 1). Both sites were chosen because they feed actively growing speleothems and their drip rate is fast enough to allow instantaneous drip water sampling during each cave visit. Site SW-2 is in close proximity to a fallen speleothem which grew during the last 35 to 17 ka and the moitoring aims to improve the speleothem based climate reconstruction.

Most of the Caribbean shows a dry (Dec–Mar/Apr) and wet (Apr/May–Nov) season. The hurricane season starts at beginning of June and ends in November. During the wet season, precipitation declines during the summer months, which is referred to as the midsummer drought (Chen and Taylor 2002; Magaña et al. 1999). This rainfall pattern is also visible at Mayagüez and the Arecibo Observatory (Fig. 2). At the Arecibo Observatory, the annual rainfall amount is larger with 2137 mm/year compared to 1510 mm/year in Mayagüez. The midsummer drought is very pronounced at the mountainous Arecibo Observatory site with highest monthly rainfall amounts occurring during May. In Mayagüez, the midsummer drought is marked by a slight rainfall decrease in June, and the rainfall maximum is reached in September. Trade winds are the dominant control (85%) of air flow over Puerto Rico (Jury and Chiao 2013). In Mayagüez, the diurnal land and sea breeze are pronounced (Bennett et al. 1998), and the topography of Puerto Rico weakens the trade-wind flow creating a wake to the west of the islands, which promotes the formation of high convective afternoon thunderstorms (Jury and Chiao 2013).

Different weather patterns cause rain events throughout the year. Low-pressure systems embedded in easterly waves, tropical storms, and occasional cold fronts from the north are the main contributors of Caribbean rainfall. During the rainy season, easterly waves and low-pressure systems with cloud altitudes reaching up to 8000 m deliver the majority of rainfall, while during the dry season, trade-wind orographic rainfall of high-pressure systems with significantly lower cloud heights occurs (Scholl et al. 2009).

4 Methods

4.1 Sampling Procedure

Cueva Larga was visited every month in 2013 and 2014 and about every two months in 2015. The monitored drip site SW-2 is located in the middle section of CL about 425 m inside the cave, and site C-2 is located in the Collapse Room on top of a boulder field at the end of the cave about 790 m inside (Fig. 1). During each cave visit, pCO_2, temperature (T), and relative humidity (RH) measurements were recorded at each site. An Amprobe CO_2-100 handheld carbon dioxide meter (precision of ±30 ppm, ±5% of the reading for pCO_2 between 0 and 5000 ppm; ±0.6 °C for T and ±5% for RH above 90%) was used from January 2013 to July 2013, whereas from July 2013 to January 2015, a handheld Vaisala GM 70 with a 2000 ppm CO_2 probe (accuracy ±30 ppm + 2% of reading for pCO_2 between 0 and 2000 ppm) and a HM70 humidity and temperature probe (precision ± 0.2 °C for T and ±1.7% for RH above 90%)

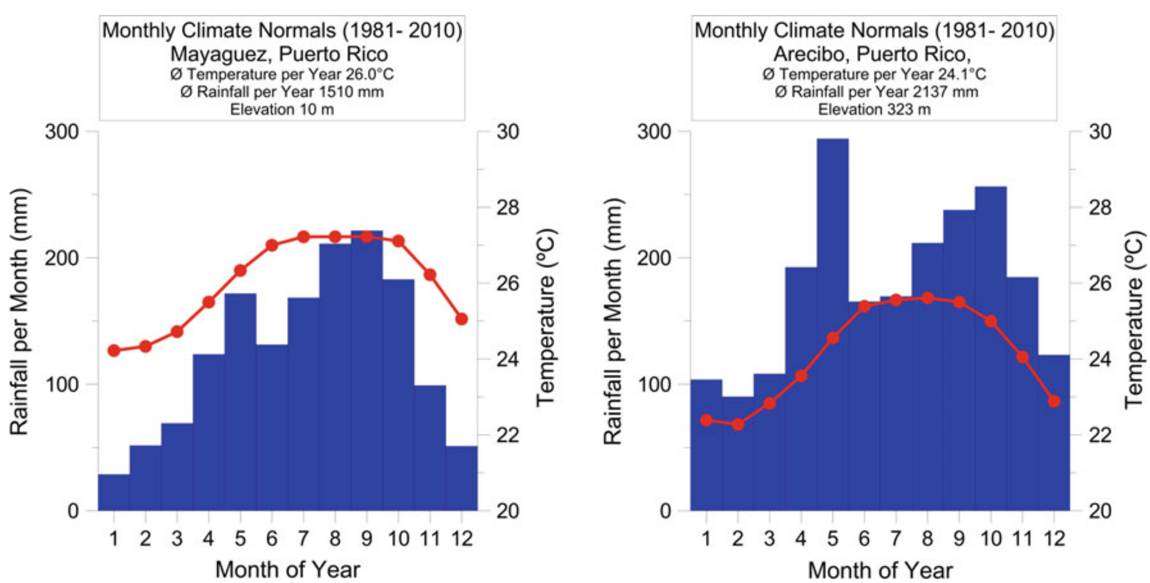

Fig. 2 Monthly climate normal 1981–2010 for Mayagüez (*left*) and Arecibo Observatory (*right*). The data were downloaded from the data query tool xmACIS (http://xmacis.rcc-acis.org/) developed and maintained by NOAA's Northeast Regional Climate Center

were used. During two cave visits, both devices were used and the measurements agreed within uncertainty.

Outside atmospheric temperature data for Cueva Larga were taken from the Arecibo Observatory weather station, located at 323 msl (about 7 m lower than the entrance of CL) about 10 km north of the cave site. (Data source: http://xmacis.rcc-acis.org/). Monthly rainwater samples were collected both above the cave site and at the University of Puerto Rico in Mayagüez (N 18°12; W 66°08, 10 msl). Rainwater samples were collected according to the GNIP (Global Network of Isotopes in Precipitation) station operation manual (IAEA 2012). At the beginning of each sampling period, the collection bucket was filled with paraffin oil that covered the buckets surface area by a height of at least 0.5 cm to prevent evaporation of the rainwater stored inside the bucket over the sampling period. After a settling period of about one week, to allow the oil to separate completely from the rainwater, the monthly rainwater sample was transferred via siphoning into transportation vials. For the Cueva Larga site, the weighted average rainfall δD and $\delta^{18}O$ values were calculated. At the cave site, rainfall samples were collected during each cave visit. In Mayagüez, rainwater samples were taken in close temporal relation to the cave site visitation in 2013. Starting in 2014, the rainwater samples in Mayagüez were taken at the beginning of each month.

Cave drip water samples were collected during each field trip. Depending on the drip rate, the collection of enough water took up to 1.5 h. Drip rates were determined via counting the number of drips within 1 min. For cation analyses, pre-acidified 15-ml Falcon tubes were used.

4.2 Analytical Methods

Monthly rainwater samples from Mayagüez were measured in the Isotope Hydrology Laboratory of the IAEA (International Atomic Energy Agency) in Vienna. Hydrogen and oxygen isotope analyses were conducted by off-axis integrated cavity output laser spectroscopy and/or dual-inlet isotope-ratio mass spectrometry.

Stable isotope ratios of rain and drip water from the CL site were analyzed at the University of Innsbruck, Austria. A first set of samples was analyzed for $\delta^{18}O$ using the CO_2 equilibration method (Thermo Scientific Delta^{plus}XL with Gasbench II) and for δD using a Thermo Scientific Thermal Combustion/Elemental Analyzer (TC/EA) and a Delta V Advantage mass spectrometer. The uncertainty was 0.15‰ for $\delta^{18}O$ and 1‰ for δD. Later samples were analyzed on a Picarro L2140-*i* CRDS. The uncertainty is 0.08‰ for $\delta^{18}O$ and 0.5‰ for δD. All results are reported relative to VSMOW.

The analyses of the cation concentrations of drip waters were performed at Heidelberg University with a Agilent ICP-OES 720 (Varian) with an internal 1σ-standard deviation of <1% for Ca^{2+}, Mg^{2+} and Sr^{2+}. An external standard, the SPS SW2 with a long-term 1sigma-reproducibility of 2.2% for Ca^{2+} (conc. 10 mg/L), 3.4% for Mg^{2+} (conc. 2 mg/L) and 3.6% for Sr^{2+} (conc. 250 μg/L) was used.

5 Results

At both sites, Mayagüez and Cueva Larga, the rainwater $\delta^{18}O$ values show a trend towards more negative values when the amount of rainfall is larger (Fig. 3). The sample period has not always been exactly one month. For Cueva Larga, the rainwater sampling period varied between 16 and 58 days and for Mayagüez the sampling period started to be monthly in the year 2014 but varied between 15 and 48 days in 2013. To account for different sampling durations, the average daily rainfall amount over the sampling period has been calculated and was multiplied by 30.4 days (the length of an average month) to express the average rainfall intensity over the sampling period in terms of monthly rainfall amount. In Fig. 3, the raw results (rainfall amounts over initial variable sampling periods) and normalized monthly results (normalized to 30.4 days) are shown together with GNIP data from San Juan between the years 1968 and 1973. The monthly rainfall $\delta^{18}O$ values show a wide scatter, but in general, lower values are observed during periods of higher rainfall amount. The linear trend indicates that a decrease of 1‰ in $\delta^{18}O$ roughly corresponds to a rainfall increase of about 220 mm/month in Mayagüez and 250 mm/month at Cueva Larga.

All data from Mayagüez plot close to the GMWL (Fig. 4). The rainfall measurements from Cueva Larga split up into two groups. One group is located near the GMWL, while the other group plots above the GMWL with elevated d-excess values between 15 and 20‰ (blue box in Fig. 4). Some of the cave drip water samples from drip sites SW-2 and C-2 were analyzed for both δD and $\delta^{18}O$. These results are also shown in Fig. 4. Only one result falls on the GMWL. The other drip water samples plot between the GMWL and the elevated d-excess. These have been sampled between April and August 2014. All drip water values show lower stable isotope values than the weighted mean of rainfall $\delta^{18}O$ and δD ($\delta^{18}O = -2.04$‰ and $\delta D = -5.24$‰).

The d-excess values were plotted against time to investigate the temporal distribution of both rainfall groups at Cueva Larga in Fig. 5. The rainfall measurements with an elevated deuterium excess (d-excess > 15‰) were taken during the end of the dry season and early wet season (February–May; Fig. 5). While Figs. 4 and 5 point out that

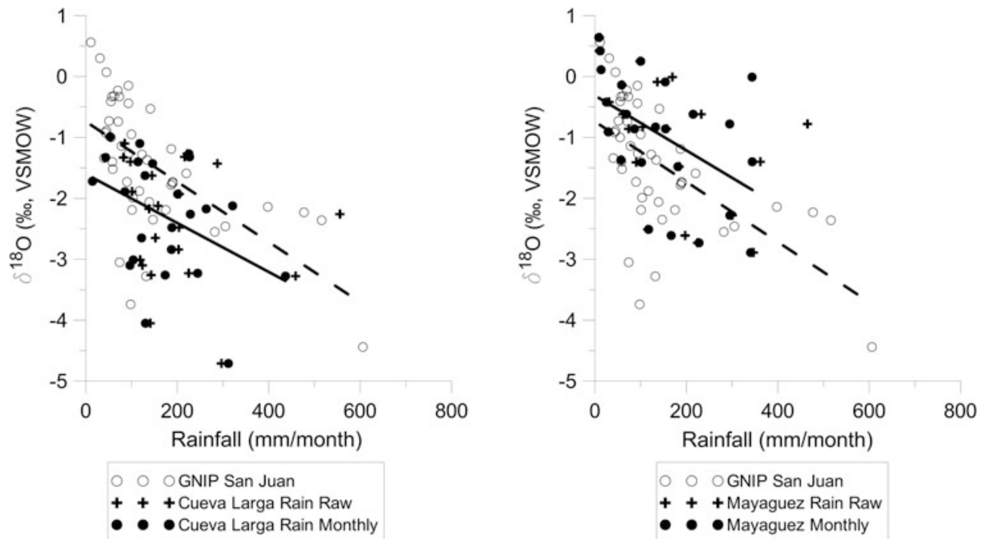

Fig. 3 δ^{18}O values of rainfall collected at Cueva Larga (*left*) and in Mayagüez (*right*). *Crosses* show the measured values for each sampling period (raw data). *Filled circles* show the rainfall δ^{18}O value relative to the normalized to rainfall amounts occurring over one month (30.4-day sampling period). *Open circles* show GNIP rainfall data from San Juan between 1968 and 1973 (downloaded from GNIP's WISER data-platform https://nucleus.iaea.org/wiser IAEA/WMO 2015). The *solid-and-dashed line* shows the linear trends of the normalized data from our measurements and the GNIP data from San Juan, respectively

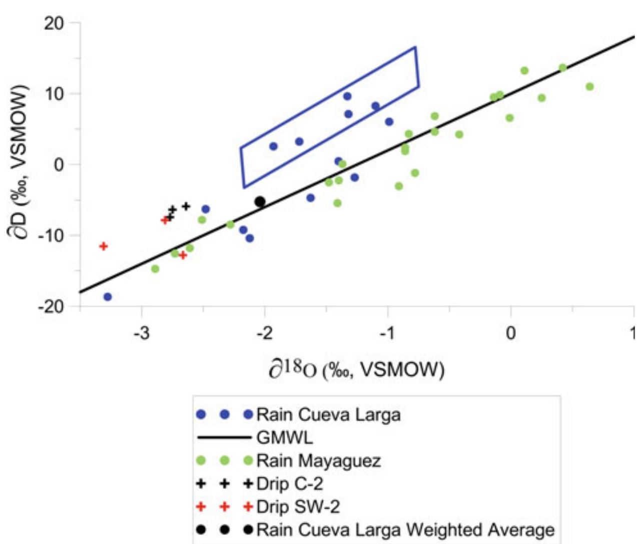

Fig. 4 Comparison of rain (*points*) and drip water data (*crosses*). The Global Meteoric Water Line (GMWL: $\delta D = 8*\delta^{18}O + 10‰$) is represented by the *black solid line*. The *blue box* marks elevated rainwater d-excess values >15‰ at Cueva Larga. The *black filled circle* shows the average isotopic composition of the rainfall weighted by rainfall amount ($\delta^{18}O = -2.04‰$ and $\delta D = -5.24‰$)

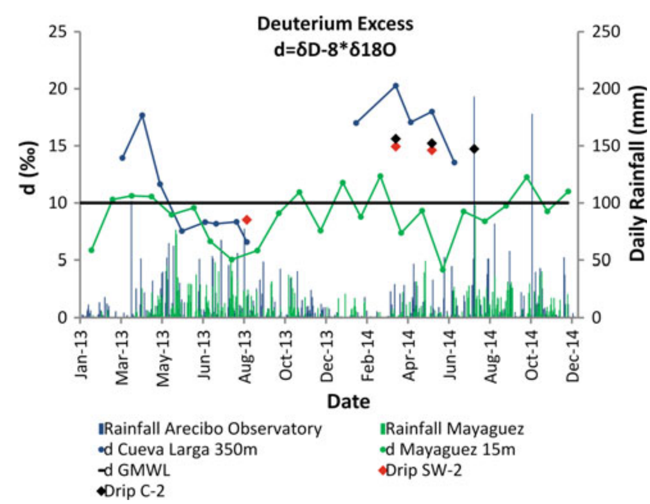

Fig. 5 Deuterium excess (d) of rainwater compared to the daily rainfall amount. The time series for Cueva Larga shows gaps, because some monthly samples have been measured only for δ^{18}O

there is a seasonality of the deuterium excess, yet insufficient data are available to establish seasonal meteoric waterlines for the Cueva Larga mountain site.

Figure 6 shows the results of cave monitoring compared to the temperature and rainfall outside the cave. The rainfall pattern shows the dry season in the winter and wet season in the summer period. Extreme daily rainfall events are related to tropical depressions and hurricanes. The highest daily rainfall amount (193 mm) was measured during hurricane Bertha (3 August 2014). Tropical depressions delivered large rainfall amounts of 178 mm (27 October 2014) and 142 mm (16 May 2015). The monthly rainfall anomaly is the difference between the observed monthly rainfall to the rainfall normal from 1981 to 2010. Figure 6 shows that monthly rainfall anomaly was negative during summer 2013 and early 2014. This trend is interrupted by the strong positive anomaly in August 2014 when hurricane Bertha passed by Puerto Rico. The following month showed normal

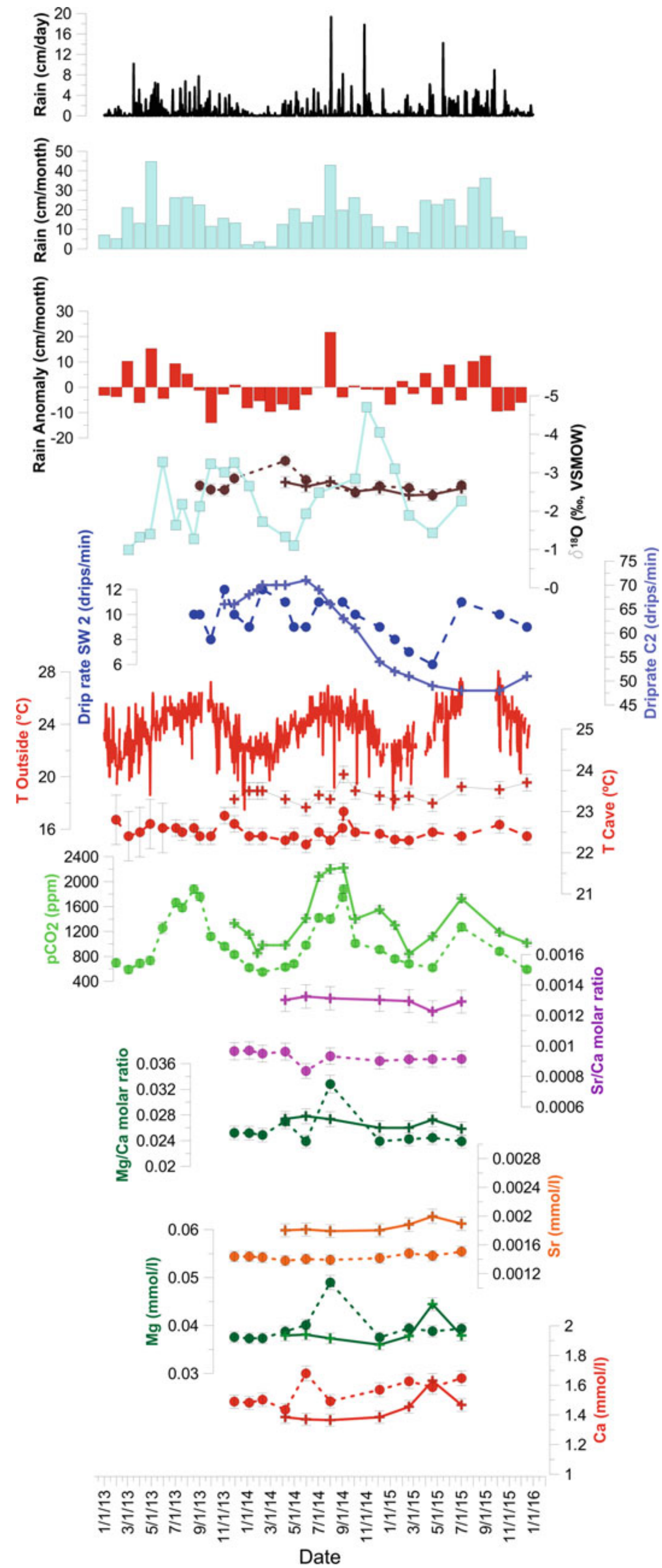

Fig. 6 Weather observation and cave monitoring results in Cueva Larga from 2013 to 2015. Data are shown for drip site SW-2 (*circles on dashed line*) and C-2 (*crosses on solid line*). The *first three plots* show the daily rainfall amount, the monthly rainfall amount, and the rainfall anomaly of each month compared to the monthly climate normal from 1981 to 2010 from the Arecibo Observatory weather station (Fig. 2). The *blue squares* show $\delta^{18}O$ results of rainwater compared to the $\delta^{18}O$ results of drip water (*in brown*). This is followed by the temperature outside and inside Cueva Larga (*red*), the cave atmospheric pCO_2 at each site (*green*), and the Sr/Ca (*pink*) and Mg/Ca (*dark green*) values. The *lowest plots* show the concentrations of Sr (*orange*), Mg (*green*), and Ca (*red*) in the drip water

rainfall amounts and some positive and negative anomalies at the end of 2015.

Inside Cueva Larga, the variations in drip rate are site-specific. The monthly observations at drip site C-2 show constant trends exceeding the annual period. Drip rate increased from November 2013 to May 2014 and then continuously decreased until October 2015. In contrast, drip site SW-2 shows variations on a shorter timescale. Rapid increases in drip rate were observed in November 2013, February 2014, July 2014, and July 2015 followed by drip rate decreases occurring over time frames of several months (Fig. 6). Assuming a drip volume of 0.23 mL/drip (Collister and Mattey 2008), we calculated the drip rate in L/s and were able to classify both drips (after Fairchild et al. 2006b) as dominated by seepage flow.

Rainfall $\delta^{18}O$ values show a seasonal signal. More negative values (down to −4.7‰) are recorded during the wet season and vice versa. In 2013, one negative peak in May (−3.28‰) is observed followed by a second negative peak (below −3‰) at the end of the rainfall season (September to December). In 2014, the negative $\delta^{18}O$ values of the summer season do not show the bimodal signal observed in 2013. More negative values are measured from July to December/January. The most negative values are up to 1.4‰ more negative than in 2013 and occur during October and November. The drip water $\delta^{18}O$ composition of drip sites C-2 and SW-2 inside Cueva Larga does not reflect the surface pattern between dry and wet season. The drip water of drip site C-2 shows no significant variations and has an average $\delta^{18}O$ value of −2.59 ± 0.12‰. Similar $\delta^{18}O$ values were measured in drip water at site SW-2 (−2.69 ± 0.23‰). Except for April and May 2014, when drip water $\delta^{18}O$ values were more negative.

Temperatures in Cueva Larga are nearly constant over time compared to the annual cycle outside the cave. In the main cave passage at site SW-2, the average temperature is 22.51 ± 0.18 °C. This is similar to the average annual temperature outside the cave, 22.5 ± 0.1 °C (calculated for two years from 4 November 2012 to 3 November 2013 and 4 November 2013 to 3 November 2013). At site C-2 in the Collapse Room near the end of Cueva Larga, the average temperature is almost 1 °C higher (23.43 ± 0.19 °C). At the transition from summer to winter (September and October), a short-lived temperature maximum was observed where temperatures increase by +0.5 °C. This is probably related to a change in cave air circulation.

Cave pCO_2 values follow the seasonal temperature cycle at the surface. Summer maxima reach up to 1880 ppm at drip site SW-2 and up to 2220 ppm at drip site C-2. Winter minima are as low as 550 ppm at drip site SW-2 and 850 ppm at drip site C-2. In contrast to temperature, the annual pCO_2 pattern is asymmetrical showing a gradual rise from May to August and a relatively rapid decrease in September.

The trace element to Ca ratios is nearly constant over the monitoring period. At drip site C-2, the average Sr/Ca ratio is $1.293 \times 10^{-3} \pm 0.029 \times 10^{-3}$ and thus higher than at drip site SW-2 with an average of $9.25 \times 10^{-4} \pm 0.38 \times 10^{-4}$. The Mg/Ca ratio is similar at both sites with an average of $2.55 \times 10^{-2} \pm 0.26 \times 10^{-2}$ at site SW-2 and $2.681 \times 10^{-2} \pm 0.077 \times 10^{-2}$ at site C-2. The Ca concentration is generally higher at drip site SW-2.

6 Discussion

Rainfall and temperature outside Cueva Larga show a seasonal cycle with increased rainfall during the summer season (Fig. 6). Plotting the $\delta^{18}O$ values of rainfall against rainfall amount (Fig. 3) reveals that periods of increased rainfall amount correspond to more negative $\delta^{18}O$ values. The linear trend at both sites shows a rainfall "amount effect" of about 4.5×10^{-3} to 4.0×10^{-3}‰/mm monthly rainfall. This "amount effect" is in agreement with the trend observed in rainfall collected in San Juan between 1968 and 1973 (Fig. 3). Unfortunately, the rainfall data (Fig. 3) show a large scatter, which makes quantification of absolute rainfall amounts from the rainfall's isotopic composition difficult. Nonetheless, the rainfall results document the general isotopic "amount effect", suggesting that $\delta^{18}O$ values recorded in speleothems from Cueva Larga reflect primarily variations in rainfall amount similar to other speleothem records from tropical regions (e.g., Lachniet 2004; Winter et al. 2015).

The differences in rainfall $\delta^{18}O$ values between 2013 and 2014 above Cueva Larga appear to be related to different weather patterns reaching the site. In 2014, maximum daily rainfall amounts are larger than in 2013 due to large convective rainfall systems including hurricane Bertha. Large tropical convective systems may have $\delta^{18}O$ values lower than −6‰ (Lawrence and Gedzelman 1996). The contribution of these systems seems to be responsible for the lower $\delta^{18}O$ values in 2014. The observed bimodal summer in the $\delta^{18}O$ values of 2013 may be related to the lack of large convective rainfall systems allowing the midsummer drought to appear in the rainfall $\delta^{18}O$ data. In the summer of 2014, the sampling interval was larger than in 2013 which may also have prohibited the detection of a bimodal $\delta^{18}O$ rainfall signal.

The currently available two years of observations from Cueva Larga indicate inter-annual variations in rainfall $\delta^{18}O$ values. Extending the observations to several years might resolve inter-annual isotopic rainfall variations, which are likely to be recorded in speleothems. Detailed rainfall stable isotope studies in Puerto Rico revealed that the $\delta^{18}O$ value of rainfall is complex (Scholl et al. 2009; Scholl and Murphy 2014). The correlation between maximum cloud height and rainfall $\delta^{18}O$ values is larger than the correlation to rainfall amount (Scholl et al. 2009), indicating that condensation temperature plays an important role. The evolution of rainfall downstream of Puerto Rico leads to characteristic rainfall $\delta^{18}O$ values distinguishing trade-wind orographic showers, low-pressure systems, and convective systems (Scholl and Murphy 2014). Thus, changes in weather patterns over multiannual time-spans seem to have an influence on the isotopic signal of drip water in Cueva Larga, highlighting the potential for speleothem $\delta^{18}O$ time series from this site for revealing changes in weather patterns and rainfall amounts. However, the complexity of the process occurring in the soil and karst above the cave as well as inside the cave during precipitation of speleothem calcite may make the interpretation of speleothem $\delta^{18}O$ values on inter-annual timescales difficult (Mischel et al. 2015).

In Mayagüez, $\delta^{18}O$ and δD values of the rainwater plot close to the GMWL (Fig. 4). These samples seem to be primarily controlled by different degrees of Rayleigh fractionation during rainout (Rozanski et al. 1993). At the location of Cueva Larga, the rainwater samples appear to form two groups, one group plotting on the GMWL and the other group plotting above the GMWL with d-excess values between +15 and +20‰. Currently, we do not have enough data to establish a seasonal Local Meteoric Water Line (LMWL), but it appears that the season of elevated d-excess agrees well to a LMWL ($\delta D = 8.2 * \delta^{18}O + 14$) established for the mountainous Eastern Puerto Rico by Scholl and Murphy (2014). Elevated d-excess values occur between the middle and end of the dry season and have been measured in April 2013 and from February to end of May 2014 (Fig. 5). The seasonality might be related to a greater fraction of recycled rainwater via the process of evaporation from surface and forest canopy upstream the cave site (Aemisegger et al. 2014; Peng et al. 2010; Lee et al. 2009; Price et al. 2008; Victoria et al. 1991) among other processes.

Since elevated d-excess values have not been observed at Mayagüez (Fig. 5), rainwater recycling seems to be negligible during both seasons. Mayagüez lies on the west coast of Puerto Rico in the trade-wind wake zone of the island. At this location, winds typically come from the west (Jury and Chiao 2013) bringing marine moisture with a d-excess of about 10‰. Similar observations have been made at the south coast of Puerto Rico where the primary moisture source is also maritime (Govender et al. 2013).

Inside Cueva Larga drip water $\delta^{18}O$ and δD results indicate that the wet season rainfall contributes proportionally more to the drip water than the rainfall during the dry season because all drip water measurements are more negative than the amount of weighted average isotopic composition of the rainfall (Fig. 4). This seems plausible because during the dry season a greater fraction of the rainfall will be lost to evapotranspiration than during the wet season. Currently, only three drip water samples at each site have been analyzed for δD. These results are insufficient to reveal drip water seasonality. More frequent cave drip water $\delta^{18}O$ and δD values could be used to investigate the transmission of seasonal atmospheric signals into the cave drip water in addition to the $\delta^{18}O$ drip water time series at this site. An indication of the transmission of d-excess seasonality into Cueva Larga is the observation that during the wet season in September 2013, the drip water at site SW-2 falls near the GMWL, having similar d-excess values than the rainwater at that time (Fig. 5). The rest of the few drip water d-excess observations have been made during the end of the dry season (April and May 2014) and show elevated d-excess values similar to the rainfall at that time. Additional drip water δD data with monthly sampling resolution are required for more meaningful interpretations concerning the transmission of the seasonal d-excess signal from the rainwater into the cave drip water.

Cave atmosphere pCO_2 shows an annual cycle. It reaches a minimum during winter and a maximum during summer season. Comparing the buoyancy of cave air to the outside atmosphere reveals that the combination of the seasonal temperature cycle outside the cave and the cave geometry of Cueva Larga is the main driver of alternation between a well-ventilated winter mode and a near-stagnant summer mode (Vieten et al. 2016). In particular, during winter nights, the buoyancy of the cold outside air drops markedly below the cave atmosphere's buoyancy, leading to maximal cave ventilation. During the summer mode, cave ventilation is at a minimum because most of the time the buoyancy of the cave air is lower than outside leading to stagnant ventilation conditions. Similar observations in the seasonality and magnitude of pCO_2 have been documented in temperate regions (Frisia et al. 2011; Spötl et al. 2005). Other caves show similar seasonal ventilation systematics, but different pCO_2 amplitudes, such as in Austria (Boch and Spötl 2008); Ireland (Baldini et al. 2008); France (Bourges et al. 2006); Arizona, USA (Buecher 1999); Texas, USA (Cowan et al. 2013); and Germany (Meisner et al. 2010).

The documented cave atmosphere seasonality probably leads to seasonal variations in carbonate precipitation (e.g., Kaufmann and Dreybrodt 2004; Fairchild et al. Fairchild et al. 2006a, b; Baldini et al. 2008) because cave pCO_2 is directly linked to the growth rate of speleothems where lower pCO_2 values result in higher supersaturation with respect to calcite and increasing carbonate precipitation rates (Baker et al. 2014; Dreybrodt 2012). Variations in growth rate might cause a bias toward the fast growing season in climate records deduced from speleothems and also affect the incorporation of trace elements into the crystal lattice (Fairchild et al. 2006a; Gabitov and Watson 2006). Assuming all other factors being equal, seasonal ventilation appears to cause increased growth rates during the low pCO_2 winter season even though it rains more in the summer. In the most extreme case, speleothems in Cueva Larga would only grow during winter when the cave pCO_2 falls below a threshold value allowing carbonate precipitation. Carbonate precipitation seasonality is especially important for drip sites which feed from seepage water with short transition times and negligible water mixing along the seepage path from the surface to the cave. Such sites usually exhibit seasonal variations in the drip water geochemistry linked to the seasonality above the cave. The drip water stable isotope and trace element data from Cueva Larga do not show seasonal patterns (Fig. 6). Thus, the soil and karst above the cave appear to act as a low-pass filter.

A seasonal signal similar to the rainfall $\delta^{18}O$ seasonality is not clearly detectable in the drip water data. Drip site SW-2 appears to show a slight response to rainfall seasonality in early 2014. More negative $\delta^{18}O$ values are recorded at site SW-2 (Fig. 6). This could be the signal transmitted of 2013 summer rainfall. Delay times of similar length have been observed at other cave sites (e.g., Riechelmann et al. 2011). In 2015, a corresponding signal is not visible in the drip water of site SW-2. This might be related to the relatively dry year in 2014 with most months showing a negative rainfall amount anomaly (Fig. 6). A lack of recharge during 2014 is also indicated by the decreasing drip rates at both drip sites starting in summer 2014. At site SW-2, drip rates decrease by about 45% from 11 drips/min in September 2015 to 6 drips/min in April 2015. Thus, less recharge of more negative summer rainfall during the drier summer 2014 might be the reason for the missing negative peak in drip water $\delta^{18}O$ values at drip site SW-2 in 2015. At drip site C-2, drip rates decrease by about 40% from 69 drips/min in July 2014 to 48 drips/min in July 2015 and remain low, while drip site SW-2 shows an increase in drip rate in July 2015. The increase in drip rate at drip site SW-2 seems to be related to a large rainfall event in May 2015 (140 mm rain on May 16, 2015). During 2013/2014, drip site SW-2 also shows higher drip rate variability than drip site C-2, indicating that drip rate at site SW-2 responds more directly to rainfall and recharge events above the cave.

Trace element ratios indicate that the residence time and/or the host rock composition is different above both drip sites. Sr/Ca is higher at drip site C-2 (Fig. 6) indicating longer residence times above drip site C-2 than above drip site SW-2 (Verheyden et al. 2000). This is in agreement with the slower responding drip rates and the lack of any seasonality at drip site C-2.

Sr/Ca and Mg/Ca show no seasonal variation. We do not find evidence for varying degrees in PCP. Figure 7 shows a comparison of the drip water results from both drip sites at Cueva Larga to drip water data from Brown's Folly Mine, UK (Fairchild et al. 2006b). The variable drip water composition in Brown's Folly Mine is represented by the outlined area in Fig. 7 and has been interpreted to be the result of varying degrees of PCP. In Cueva Larga, there is no evidence for such variable degrees of PCP above the cave on the annual timescale.

The water reservoir above Cueva Larga seems to be large enough to buffer seasonal rainfall variations causing no detectable changes in PCP over the monitored period. However, trace element variability in speleothems from Cueva Larga may be related to long-term changes in climate above the cave.

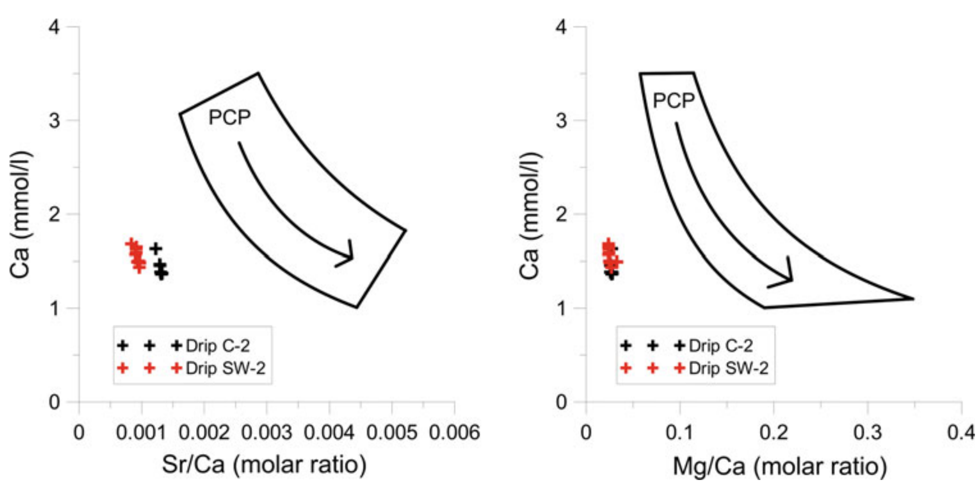

Fig. 7 Geochemical relationships of trace element ratios (Sr/Ca *left* and Mg/Ca *right*) to Ca concentration for drip sites SW-2 and C-2 in Cueva Larga. The outlined area in each plot shows similar evaluation in Brown's Folly Mine, UK (Fairchild et al. 2006a, b). The *arrow* labeled with PCP (prior calcite precipitation) shows the direction in which higher degrees of PCP along the seepage water flow path would shift the results

7 Conclusions

Two years of cave monitoring in Cueva Larga, Puerto Rico, represent a first step to investigate the response of cave drip water to climate fluctuations above the cave. The drip water geochemistry provides insight into seepage water flow and mixing processes resulting in important implications for speleothem climate records. The isotopic rainfall “amount effect” has been detected in rainfall above the cave and in Mayagüez. This is an important prerequisite for speleothem $\delta^{18}O$ values to reflect changes in the rainfall amount over Puerto Rico. Rainfall deuterium excess shows elevated values during the dry season only at Cueva Larga, whereas Mayagüez seems to be dominated by maritime water vapor sources. Drip water d-excess may enable us to estimate seepage water transition time.

Seasonality in cave ventilation results in low cave air pCO_2 in the winter season which might cause accelerated speleothem growth rates and bias speleothem climate records toward the winter season. Drip water trace element ratios lack variations, implying that changes in PCP along the seepage flow path do not have a significant effect over the monitored period.

Both drip sites seem to be fed by well-mixed sources. The lack of clear seasonality makes estimations of residence and transmission time difficult. Drip site SW-2 appears to show a response to annual rainfall changes indicating a transmission time of several months, while the transmission time for drip site C-2 appears to be larger. The well-mixed and slowly responding drip sites monitored here favor speleothems to record multiannual paleoclimate changes because the seepage water system acts as a low-pass filter.

This study shows that monitoring of drip sites is useful to decipher the effects influencing the climate signal recorded in speleothems. Environmental observations will improve speleothem paleoclimate interpretations and extending the monitoring to several years may even enable us to calibrate the speleothem proxy record to absolute changes above the cave. Some of the here presented results are preliminary and need to be verified by continuation of the cave monitoring program in Cueva Larga.

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Part VII

Conference Summary

Abstracts of Additional Conference Papers

William B. White

Abstract

This chapter reproduces short abstracts of 14 papers presented at the conference for which complete papers were not submitted. These were extracted from the conference program published by the Karst Waters Institute. The abstracts summarize research on the assessment of karst groundwater contamination, contamination and public health, and hydrogeologic studies of karst aquifers and are arranged under these headings.

1 Introduction

A portion of the papers presented either orally or as posters at the conference were not submitted for formal publication in the Proceedings volume. Short summaries of these papers are given in the sections that follow. These excerpts were taken from the pre-conference abstracts that were published by the Karst Waters Institute as part of the conference program. Affiliations and addresses for the authors are also found in the conference program (White et al. 2016).

2 Karst Groundwater Contamination and Tools for Their Evaluation

The primary thrust of the conference was the interface between the hydrogeology of karst aquifers and their exceptional ability to transmit contaminants and the public health impacts on those who wish to use the karst groundwater. This section deals with investigations of groundwater contamination and the methods and tools for evaluating the degree and distribution of groundwater contamination.

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2.1 Mobility of *Escherichia coli* Compared to Traditional Groundwater Tracers Within Karst Terrains (Ashley Bandy, Alan Fryar, Kim Cook, Jason Polk, Kegan McClanahan, and Stephen Macko)

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-µm-diameter fluorescent microspheres). *E. coli* is quantified by molecular methods (qPCR) and dual stable isotope analyses using enrichment levels of ^{13}C and ^{15}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

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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.

2.2 Phytoforensics: Using Plants as Biosentinels of in-Home Exposure Pathways (Joel G. Burken)

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-planta* 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 is not subject to the variability of in-home sampling and thereby provides reliable assessment of subsurface pollutants and an additional protective, cost-effective protection of human health.

2.3 Current State of Metal Toxicity and Remediation in the Tri-State Mining District, USA (Aaron W. Johnson, Douglas R. Gouzie, Melida Gutierrez, and L. Rex McAliley)

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 have 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. The full paper has been published (Johnson et al. 2016).

2.4 Hydrologic Analysis of a Poplar-Based Phytoremediation System (Felix L. Santiago Collazo, Alan J. Rabideau, and Beynan Ransom)

An evaluation of the performance of a poplar-based phytoremediation system (phytobarrier) for hydraulic containment of 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 groundwater monitoring wells at the site, the method of White (1932) (Fig. 1) 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 wells. Furthermore, the analysis demonstrated that for some years the wells with the highest median ET_G values were located distant (more than 15 m 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.

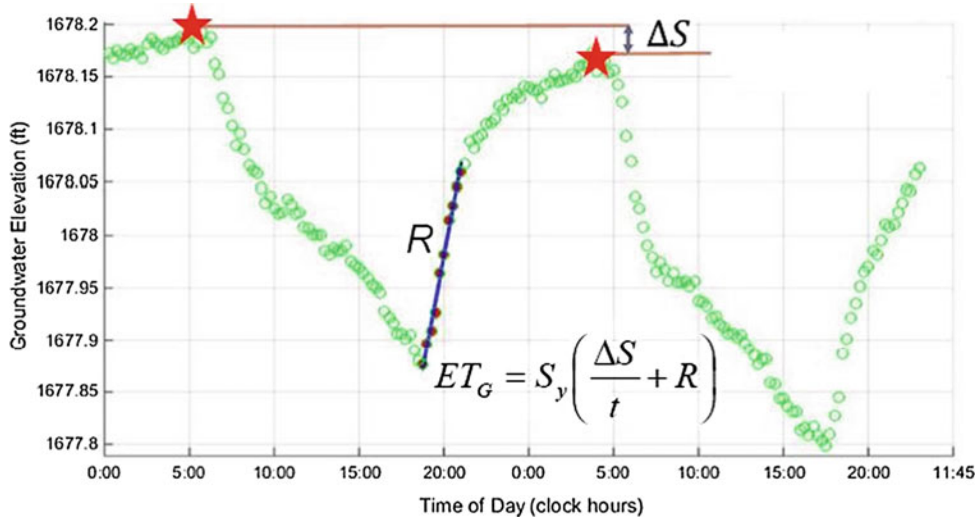

Fig. 1 Application of White method to estimate poplar evaporation (ET_G) from water table fluctuations (y-axis), where ΔS = change in storage, R = recharge (slope), S_y = aquifer specific yield, and t = elapsed time (x-axis)

Possible reasons include the lack of complete areal coverage by the phytobarrier, the young age and incomplete root penetration of the trees, data scatter in the observed hydrographs, and a variety of simplifying assumptions associated with the method.

2.5 Microbial Contamination in Karst: From Monitoring to Process Comprehension (Michael Sinreich)

Microbial 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, and inactivation during storage or particle-attached transport. Monitoring data in conjunction with in situ techniques provide the basis for process comprehension and allow the establishment of enhanced conceptual and transport models in relation to microbial contamination and karst systems in general.

2.6 Assessment of Flow and Transport Properties in an Intermediate Karstified Laboratory-Scale Physical Model Using Hydraulic and Tracer Response Analysis (Jonathan Toro-Vázquez and Ingrid Y. Padilla)

Karst 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 laboratory 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 laboratory-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 TCD 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.

2.7 Selected Micropollutants as Indicators in a Karst Catchment (Johannes Zirlewagen, Ferry Schiperski, Olav Hillebrand, Karsten Nödler, Tobias Licha, and Traugott Scheytt)

Event-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^2 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^{-1}. 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.

3 Contaminant Exposure and Public Health

Wells and springs in karst aquifers are used as both public and private water supplies. Questions addressed concern exposure of the public to contaminated water and the health issues implicit in the exposure.

3.1 Protecting the Karstic Corner: A Challenge to Minnesota's Drinking Water (James L. Berglund, Justin L. Blum, and Emily Berquist)

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.

3.2 Environmental Exposures Among Pregnant Women in the Northern Karst Region of Puerto Rico (John Meeker)

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. Some initial results are given in Meeker et al. (2013).

3.3 Beyond Case Reports: Placing Karst in Context in Public Health Response to Groundwater Contamination (Marian Rutigliano)

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 USA, 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.

4 Aquifer Studies

Karst aquifers store and transmit water differently than porous media aquifers. They also have highly variable hydrologic properties depending on structure, lithology, and geologic setting. A great deal of research has gone into observing, measuring, and modeling karst aquifer behavior.

4.1 Storm water Runoff Characterization and Treatment System Efficiency Analysis in Mammoth Cave National Park (Hung-Wai Ho, David Solomon, and Rick Toomey)

Mammoth 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 compound (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 h. The lessons learned from this study show that the chemistry of parking lot runoff varies by parking lot size and storm properties, and alternative storm water management practices should be considered to improve the treatment efficiency.

4.2 Improving the Karst Groundwater Catchment Area Isohyet Map of Río Tanamá, Arecibo, Puerto Rico, Using a Geographic Information System Software Method (Orializ Martínez Román and Thomas E. Miller)

This investigation focuses on the improvement of the Charco Hondo (CH) isohyetal map method created in the investigation by Martínez in 2014. It is important since there is no catchment area determined for CH by the US 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.

4.3 Where Is the Greatest Potential for Superficial Contamination in the North Coast Limestone Aquifer of Puerto Rico? (Ronald T. Richards, Anastacio Emiliano, and Rafael Méndez-Tejeda)

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 whether 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 May 22, 2015, and September 18, 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 h and 40 min 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.

4.4 Tennessee Cave Life Relational Geodatabase (Chuck Sutherland)

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 is 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 are 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.

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The Intersection of Groundwater Contamination and Human Health: Summary of an Interdisciplinary Conference

Janet S. Herman

Abstract
Some characteristics of karst aquifers make them particularly susceptible to contamination. The reliance on groundwater for drinking supplies in karst regions creates the potential for public health effects. Elucidating potential human exposure and health effects requires an unexploited multidisciplinary approach that was the focus of this conference. Diverse perspectives on the hydrology, geochemistry, and microbiology of karst systems, contaminant transport, exposure concentrations and human health, and regulatory approaches bring us closer to our goal of protecting human health. Summaries of the keynote and research talks are given here. Group discussions are reported as conclusions and recommendations from the conference. New investigative tools, improved quantitative approaches, innovative data analysis, and true multidisciplinary studies are necessary to advance knowledge in this field.

1 Theme of the Conference

Notable public health concerns in the karst regions of Puerto Rico provided initial motivation for this conference convened to explore karst groundwater contamination, consequences for human health, and regulatory issues in karst water resources. This chapter includes summaries of the presentations organized along the same structure as the conference: context for contaminant transport in karst, research advances in tools for investigating hydrological transport, and new findings from studies of exposure concentrations and human health, followed by presentations on regulatory and legal perspectives. Each presentation summary is attributed to the speaker, and their papers or abstracts can be found elsewhere in this volume. The group discussions held after each group of presentations identified emerging themes of needed research directions and management reform. A summary of the group discussions is presented as the conclusion of this chapter without attribution to the individual among the 71 conference participants who articulated the idea.

The question driving this conference was whether and how people's health might be affected by contamination of karst groundwater. The broad scope of topics needing the attention of scientists, health professionals, and policy specialists in order to address that question was established in the welcoming talk by Heather Henry. Recognizing karst aquifers as an important source of drinking water for much of the world, the occurrence of infectious agents and various inorganic and organic contaminant chemicals in karst groundwater requires new multidisciplinary approaches integrating expertise drawn from the domains of human and environmental health, geology and hydrology of karst, and laws and regulations. Henry asserted that a multidisciplinary research approach holds promise as a framework to understand the interactions between contamination in karst aquifers and human exposures as well as developing best practices for engaging communities and stakeholders to protect public health.

Negative public health outcomes in Puerto Rico were elucidated in the conference-opening lecture by José

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Cordero. Cordero described the extent to which preterm birth plagues Puerto Rico. Connections to chemicals in drinking water are suspected, and the Puerto Rico Testsite for Exploring Contamination Threats (PROTECT) team is conducting research funded by the National Institute of Environmental Health Sciences (NIEHS) to test these connections. The geographic association of karst groundwater used for drinking supplies, presence of organic contaminants, and hot spots of preterm births strengthens the likelihood of a causal relationship between the manufacture of birth control pharmaceuticals with its attendant wastewater discharge and the downstream consumption of water leading to deleterious human health outcomes. Additional connections between human health and contaminated water in karst terrains require further elucidation.

1.1 Current State of Knowledge in Karst Contaminant Transport

The stage for groundwater in karst being vulnerable to contamination was set in two initial keynote lectures. William White presented the systematics and mechanisms by which contaminants enter and migrate through karst aquifers. The physical properties of karst systems allow hydraulic behavior that ranges from slow groundwater flow through porous media to swift surface water flow in open channels. As a result of the broad range of aquifer characteristics, contaminants can move into and through the karst subsurface, contaminant transport can occur quickly, and contaminants can sometimes end up in unexpected places. Ingrid Padilla brought the focus of the discussion to the geologically young karst of Puerto Rico. There are 22 Superfund sites in Puerto Rico, and 55% of them are on karst even though only 20% of Puerto Rico is underlain by karst. Padilla pointed out that published maps of contaminant occurrence are artifacts of the way in which groundwater is monitored. Maps neither fully describe contaminant occurrence nor reveal sources of contaminants, because the maps reflect only the available data that come from monitored wells. Overlain on spatially non-uniform monitoring, the monitoring period for some contaminants has been long while only shorter records exist for other contaminants. Data that reflect in time and space what investigators were purposefully looking for resulted in maps of contaminant occurrence that are not true representations of overall groundwater quality. Taken together, the White and Padilla presentations demonstrate the need for improved approaches to investigating contaminants in karst and for making connections to human health.

2 Research Advances

The fundamental question regarding environmental contamination and human health is, first and foremost, "Was anyone exposed?" Establishing exposure is neither straightforward nor part of typical health studies. Knowledge about exposure is built from information on sources of contaminants and their subsequent fate and transport in the environment. Sources, fate, and transport of contaminants are studied by environmental scientists. The hydrogeological, geochemical, and microbiological conditions of a given environment determine the processes controlling contaminant fate and transport. Only after release, biogeochemical alteration, and hydrological migration through the environment can exposure be considered. The medium of exposure is often water, the same medium of transport. Exposure may be by direct consumption through drinking, indirectly through water use in food preparation, or by contact in the environment such as by swimming. Finally, degree of exposure is very difficult to quantify, especially in the analysis of historical data. The goal of elucidating potential human exposure and health effects from the occurrence of contaminants in the environment requires new multidisciplinary studies and research discoveries. Information from studies of the hydrology, geochemistry, and microbiology of karst systems, contaminant transport, exposure concentrations, and regulatory approaches are all needed to bring us closer to our goal. Results of such investigations were presented at this conference.

2.1 Contaminants and Tools for Investigating Contaminant Transport

The Swiss experience with delivering drinking water safe for human consumption is focused in part on microbial contamination. Michael Sinreich described a detailed monitoring study in which bacteria, viruses, and protozoa were all found in higher concentrations in karst waters than in non-karst regions. Although total bacterial cell numbers were stable over the course of storm events, the proportion of *E. coli* was higher directly after storms. Molecular markers revealed a mix of human and ruminant fecal contamination of rural karst springs. A large number of molecularly traced viruses, some of which were pathogens, have been detected, but this study did not include an assessment of outcomes for human health. One conundrum that emerged from this research was the revelation that molecular markers are more persistent in water than are live bacteria, causing new questions about the appropriate connection between concerns for human health and the targets of monitoring by water supply purveyors.

Ashley Bandy studied the transport of bacteria with different tendencies to attach to solids in comparison to the transport of inert particles and of dye. The multiple tracers released into the epikarst overlying a cave system in Kentucky revealed that all particles broke through in advance of the dye, sticky and non-sticky bacterial breakthrough behavior depended on flow conditions, and overall mass recovery of all tracers was extremely low. Although quantification was not possible, clear differences in solute, particle, and bacterial transport were illustrated. The future success of any predictive transport models in capturing the behavior of bacteria in karst systems depends upon a vastly improved understanding of transport mechanisms.

Elucidation of the contamination scenario in each case is key to an effective cleanup response and to improved management of water resources in general. Correct source identification is an invaluable tool to achieve that end. Organic micropollutants indicative of untreated sewage and treated sewage as sources were described in the research presented by Johannes Zirlewagen. By analyzing pharmaceuticals and food additives with inherently different degradation rates and with different histories of usage, Zirlewagen used the presence and ratios of various compounds to indicate the source of contamination. Further, the results were not simply qualitative indication of source but quantitative partitioning of sources into their respective magnitudes of contribution. Ferry Schiperski extended the case for the utility of organic micropollutants detected in karst springs as a powerful tool for revealing hydrological transport processes in karst aquifers. The analysis of both currently used and legacy herbicides proved conclusive in distinguishing a surface water source from an aquifer matrix source of storm flow. Analysis of a food additive provided indication of sewage overflow during some storm events. In contrast to easier-to-measure constituents such as electrical conductivity and turbidity that are routinely monitored, the details of micropollutant concentrations revealed a great deal more about quantitative source contributions than is commonly known for water emerging at karst springs. These investigators are using the insights they have gained to interpret hydrosedimentary evolution of the aquifer as influenced by particle transfer from the land surface, deposition and resuspension within the aquifer, and emergence at the spring. Future research may focus on wider adoption of such analytical methods by other investigators with a view toward informing water management and aquifer protection strategies.

Karst springs in the Alps hundreds of kilometers distant from Vienna supply high-quality water to the capital that has undergone as little treatment as possible. This strategy for minimal treatment is critically dependent upon careful source-water monitoring so that abstraction from any individual spring can be managed to achieve the best water quality. The target for monitoring is any indication of fecal pollution, and Hermann Stadler collected measurements over the course of rainfall events using automatic samplers and satellite communication. Spectral absorption at 254 nm, a function of dissolved organic carbon concentration plus turbidity levels, can be measured remotely with an automatic probe. During rainfall events, absorption increased along with increasing *E. coli* numbers. Because spectral absorption began to increase slightly in advance of *E. coli* appearing at the springs in concerning numbers, it proved a useful early indicator for water management decisions. Andreas Farnleitner advanced fecal hazard assessment for the Austrian alpine springs using molecular source tracking. The great variability in *E. coli* occurrence in springs was shown to be in part due to its growth outside the enteric system, casting suspicion on its usefulness as an indicator of human pathogens. Instead, *Bacteroides* spp. are clear indication of fecal contamination, but quantitative molecular RNA analysis is required to distinguish human from ruminant (cows, mountain goats) sources. Now, the water supply managers are using quantitative microbial risk assessment to plan the level of treatment necessary for protection of human health.

Non-infectious agents such as metals in drinking water present potential risk to human health. The processes controlling metal mobility in karst waters in Florida illuminated the role that flow conditions played in mobilization of metals. In the study system, high dissolved organic carbon concentrations are characteristic of organic-acid-rich surface waters, low dissolved oxygen levels are typical of most of the limestone aquifer with some anoxic groundwater in the deep matrix, and fully oxygenated conditions prevail in cave passages. Amy Brown explained how groundwater–surface water interactions contrasted greatly between intense summer thunderstorms that tended to recharge high-DOC surface water to the subsurface and the steady rain of the winter wet season that tended to displace old anoxic water from the matrix into conduits and cave passages. The contrasting patterns of water influx and efflux within the highly heterogeneous karst system were the ultimate controls on metal mobilization.

Biodegradation of organic contaminants such as fuel hydrocarbons may reduce the concentrations of constituents of concern for human health effects, yet the rapid transport of groundwater in karst aquifers is often assumed to minimize the potential for biodegradation. Thomas Byl showed, however, that plenty of bacteria to affect biodegradation are present. Although attached bacteria may not find sufficient surface area in karst aquifers to maximize biofilm formation, free-floating bacteria use flagella and buoyancy control to move toward biodegradable contaminants. The rate of biodegradation can be enhanced by the addition of electron acceptors, co-metabolizing substrate, and vitamin B that is used by many redox enzymes, and Byl found improved rates of biodegradation when soy infant formula was introduced to the contaminated aquifer.

Ljiljana Rajic took a different approach to experimentally manipulating groundwater redox conditions without the addition of chemicals. With trichloroethylene (TCE) as the target contaminant, solar-powered electrolysis showed promise for reduction to ethane at the cathode. Coupled to TCE reduction, oxidation of ferrous iron at the anode to ferric oxyhydroxide precipitate can act as sorption substrate for other contaminants such as chromium, arsenic, and selenium. In practice, a simpler application of solar-powered electrolysis may be more immediately useful. Using palladium to catalyze the production of hydrogen peroxide in the presence of Fe(II) resulted in the release of hydroxyl radicals to a flow cell emplaced in a well. Pumping contaminated groundwater through the flow cell resulted in lowered contaminant concentrations. The continuous generation of reactive oxygen species for the degradation of organic contaminants may be a useful point-of-use treatment strategy.

Numerical models that identify land areas with a particular susceptibility index for potential contamination are used as part of the regulatory strategy to protect drinking water supplies. Whether these models are suitable for application to karst regions has not been determined. A test of a widely used model for a problem of nitrate contamination of groundwater in Florida revealed shortcomings in its application to karst aquifers. Philip van Beynen proposed a new karst aquifer vulnerability index and argued that it was a necessary tool in successful water resources management.

The fundamental dilemma of addressing groundwater contamination in karst is the great uncertainty about where within the karst subsurface the contaminant is located. Malcolm Field presented a scenario for karst aquifers in which dense non-aqueous phase liquids (DNAPL) might have drained into a sinkhole and might be present in spring discharge, but in between the input and output, the investigator knows nothing about where the contaminant is and what is happening to it. From a regulatory perspective, remediation success is evaluated by recovery of the contaminant, but such an assessment may be impossible for karst systems. If karst is then technically impractical to remediate, prevention becomes the only employable strategy. Therein lies a regulatory disconnect: although the national US Environmental Protection Agency (EPA) controls remediation requirements, it is some local entity that establishes land-use policies that would affect prevention. EPA is not an effective agency in prevention strategies, but other national-level agencies may successfully play a role in proactively protecting karst. For instance, the US Fish and Wildlife Service can use the Endangered Species Act to change local land and resource use that effectively prevents contamination of the karst subsurface.

2.2 Exposure Concentrations

The hydrogeological transport presentations touched on numerous contaminants of demonstrated deleterious effects on human health: metals, fuel hydrocarbons, synthetic organic compounds such as pesticides and solvents, inorganic chemicals, bacteria, and viruses. The occurrence and fate of such compounds were the focus of the transport studies. Direct demonstration of consequences for human health was beyond the scope of the fate-and-transport studies. Human health was more explicitly the focus of investigations by the next set of speakers.

In 2015, the World Health Organization published a Global Action Plan on antimicrobial resistance that included recognition of the role for water and the environment in any effective plan for the future protection of human health. Fabienne Petit described research into the occurrence of antibiotic resistance of *E. coli* in karst groundwater in France. Quantification of the distribution of various strains in the overall *E. coli* population was the basis for assessing the prevalence of antibiotic-resistant bacteria. Human and bovine *E. coli* showed more resistance, and their relative prevalence in the overall pool of *E. coli* cells collected in water samples depended upon prevailing hydrological conditions. During rainfall events, there were more antibiotic-resistant strains in water samples. In fact, these *E. coli* tended to associate with non-settleable organic floc. In contrast, under dry conditions, there were more antibiotic-sensitive strains present, and these cells tended to associate with mineral particles. To devise an effective disinfection scheme, detailed monitoring of bacterial strains in environmental waters is appropriate yet rarely employed. All *E. coli* persisted for more than 2 days in the environment, and Petit concluded there was a permanent reservoir of genes in the aquifer such that the potential for gene transfer existed, causing significant concern for future human health.

Teasing apart human from bovine fecal contamination is fundamentally important to assessing the risk to human health. Maureen Muldoon demonstrated extreme fecal contamination of karst groundwater in Wisconsin where confined animal feeding operations generate a liquid waste slurry that is applied to the sometimes snow-covered land surface. Currently, manure application is based on nitrogen needs for corn production and to minimize surface water runoff. Snowmelt or rain-on-snow events result in brown, smelly, high-nitrate groundwater in domestic wells. Federal regulations managing nutrients apply to runoff not infiltration, so regulatory policy is not preventing manure contamination of groundwater. The practical issue for human health outcomes is the question of if and when viruses or bacteria arrive at wells. Anecdotal evidence of gastrointestinal illness abounds, but direct confirmation of enteric organisms in drinking water has proved elusive. Although qPCR analyses of human and bovine viruses and of bovine *Bacteroides* are possible, collecting a large volume of water from a domestic well in a time series that includes samples prior to, during, and after the "brown-water event" has proven difficult.

Measuring actual human exposure to pathogens or contaminants is a special challenge. Instead, public health professionals ordinarily turn to epidemiology, or the study of patterns and occurrences of disease in a population in which co-variants can be well measured. John Meeker explained the complex ways the introduction of a contaminant into the human body can nonetheless lead to many different physiological and biochemical pathways, transformations, and outcomes. In seeking to better understand the connection of exposure to health, biomarkers are emerging as useful tools. Biomarkers can help reveal details of physiological processes acting upon compounds or pathogens without subjecting study participants to direct risk. For the assessment of hypothesized exposure–health connections in a population, the National Health and Nutrition Examination Survey (NHANES) contains useful information on human health; however, making connections to environmental exposures is limited by the privacy restrictions on the health data that remove location information. Giving scientists knowledge of location would allow the identification and assessment of environmental factors associated with human disease outbreaks.

Marian Rutigliano presented a different perspective on making the environment–health connection. Rather than start with human health data and try to assess causative environmental factors, some success has been realized by starting with the environmental occurrence of suspect chemicals and then looking at health data. Some notable traits of karst waters include high lithium concentrations, widespread occurrence of culturable enteric viruses, and elevated *E. coli* associated with high rainfall. Knowing some of these environmental facts about karst, the question then becomes whether there are connections to health outcomes. For high lithium concentrations, public health records show fewer suicides, fewer hospital admissions, and greater incidence of hypothyroidism, all plausible direct health outcomes. The consequence of the presence of viruses and bacteria is more difficult to relate, because unusual numbers of transient illnesses are difficult to detect. Given the role of local hydrological processes in creating exposure events, having spatially distributed human health data would go a long way toward making this type of analysis possible. Recommendations for high-frequency chemical and biological monitoring of karst waters, including preceding and during peak discharge events, arise from the desire to make these connections. Rutigliano also points out that human health is not only influenced by drinking water quality. Vapor exposure to volatile compounds and dermal exposure in recreational waters may also influence human health.

Research into the geographic association of health outcomes and mining activity was presented as an example of the direct connection of environmental contamination to public health. Michael Hendryx used mortality data by county in West Virginia to establish the location of health outcomes, because reports of deaths are easier to obtain than reports of disease occurrence. To test correlations between environmental contamination and public health, geographic information must be included in data about disease occurrence. Hendryx made a strong case for economics being important to building a compelling argument for environmental regulation, because the balance of the cost of restrictions on contaminating industries pales in comparison to the costs associated with diseases and deaths.

A tiered approach to monitoring and regulating water quality was suggested by Samuel Dorevitch. EPA guidance for characterizing and reporting on recreational water quality was presented as a better model for monitoring karst groundwater than the guidance for drinking water in a distribution system. The difference in approaches is that the first results in prioritization of monitoring for more susceptible waters while the second demands uniform monitoring that may not detect rare occurrences of pathogens. Local public health departments have several tools that can be applied to the nexus of human health and water quality. They can (1) order limitations on water usage through advisories, (2) issue permits for on-site septic systems, and (3) collaborate in environmental studies with the disease data that they collect. Dorevitch recommends that environmental scientists interact more with public health officials to gain the type of insights desired by the participants in this conference.

3 Directions in Regulation

Most regulatory policies for protection of drinking water supplies were developed for non-karst regions. Strategies effective for other geological terrains do not work well for karst systems. New approaches to ensuring high-quality drinking water in karst regions are needed.

3.1 Regulatory Issues in Karst Water Resources

Well-head protection is widely used with great success in many regions of the world. In practical terms, this policy limits land use and excludes contaminant release to areas outside a contributing area for a water supply well. James

Berglund explained how practitioners interpret the rule in Minnesota: according to a radial distance equivalent to an anticipated 10-year time-of-travel for water to reach a community well. But, unequivocally, time-of-travel delineation does not work in karst. Yet, state regulations do not allow variance in the application of regulations from site to site, even if the underlying geology is different.

Jesse Richardson emphasized that, legally, legislated regulations must be generally applied, because allowing case-by-case decisions invites arbitrary and capricious enforcement. Further, for laws to be useful, they cannot be vague. Because most regulatory power resides in the states, there are variations in regulations that can be examined for effectiveness. Interestingly, Puerto Rico has the best law for protecting karst water quality, although the Act for Protection and Preservation of the Caves, Sinkholes, and Caverns of Puerto Rico was not devised with that goal in mind. This example points to the role that land use restrictions play in the secondary outcome of water quality. Most zoning of land use is decided at the local level, and local governments are typically underfunded. Establishing a buffer zone around identified karst features is the most common strategy employed, even though the expertise necessary to thoroughly identify such features is often not available. Richardson recommends turning to non-regulatory approaches to restrict land use. Conservation easements and the transfer of development rights may prove to be more successful in preventing the contamination of karst groundwater than existing state regulations meant to protect water resources.

Regulations for emergency response to contaminant spills are usually oriented toward protecting surface waters. Geary Schindel documented hazardous material spills in Texas for which the response is to flush with large volumes of freshwater. In regions underlain by karst, the excessive release of water on the surface can lead to pushing contaminants into the subsurface, thereby entering the drinking water supply. Sewage line breaks with attendant infiltration of wastewater into shallow karst can result in pathogens in groundwater. Ingrid Padilla corroborated the San Antonio experience with sewage leaks by adding observations from Puerto Rico where water distribution lines lose 60% of their supply and the loss rate from sewer lines is even greater. James Berglund had also pointed out concern for water supply contamination in karst arising from abandoned and unsealed wells creating a direct connection to groundwater even if the land surface is adequately protected.

Acts of environmental conservation can be consequential for the protection of human health. Abel Vale related the history of the preservation of natural areas in Puerto Rico as an example of the vital ways in which karst, water, and humans intersect. Laws enacted to protect caves and other karst features as natural resources had cascading positive effects. Initially safeguarding natural areas from urban sprawl and infrastructure development, these laws also brought about the protection of water quality that led to the protection of human health. The non-profit, non-governmental organization Ciudadanos del Karso (Citizens of Karst) in Puerto Rico has actively supported legislation to conserve karst features. Vale presented this strategy as a successful approach to the difficult challenge of protecting water quality and human health.

4 Emerging Themes and Conference Conclusions

Through several days of moderated discussion including all the conference participants, agreement emerged on identification of knowledge gaps, research needs, and future directions.

Karst is particularly prone to contamination. Strong agreement that karst is particularly prone to groundwater contamination is the starting point for summarizing the meeting conclusions. Depending upon the nature of the contaminant, it will behave differently in terms of fate and transport. The amount and timing of contaminant release will determine whether the result is a long-term problem or an immediate emergency. Rapid transport is the key trait of migration in karst, with conduit–matrix interaction critical to determining transport phenomena. Different tracers yield different travel times, a problem that also applies to different contaminants. Rapid transport of constituents with differentially enhanced or retarded breakthrough requires thoughtful and continuously revised decisions about sampling frequency for water quality monitoring. Dealing with highly variable concentrations in monitoring remains an issue in terms of management, because which value should guide the application of regulations is not clear.

Site-specific studies play a crucial role. Karst is such a heterogeneous terrain that it is difficult to generalize its properties for the purposes of developing the best regulations. Explicit consideration of the connection of the land surface to groundwater through epikarst should be part of every hydrological study. Even for all the efforts to move past case studies, site-specific studies are needed for the best regulatory protection or remediation outcome.

Pollution prevention is essential. Pollution prevention strategies are particularly needed in karst. The community of scientists should determine the best tools for assessing susceptibility of karst to contamination, thereby maximizing prevention. More attention is required in developing remediation strategies for the unavoidable or legacy contamination issues. New modeling tools may prove useful in generalizing the phenomena observed in karst aquifers. In addition, some looming issues have not yet been researched, such as the potential for climate change to alter the microbiology in karst. Bacteria that cause gastrointestinal disease or that cause oxidative stress (a contributing factor in preterm birth) may be more widespread in the warming climate of the future.

Documentation of human health effects requires additional data and a new approach to data analysis. A knowledge gap hinders identification of the environmental cause that directly results in human health effects. The lack of compelling connections stems from several factors. There is a time lag between exposure to a contaminant and the expression of disease. There are both acute and chronic health effects that present at different times. The dilemma was characterized as a time series analysis problem, one that might benefit from creative analysis of big datasets. We need to collect disparate information into an integrated database that includes public health statistics. In epidemiological and multivariate analyses that endeavor to use lots of data, a big problem is finding studies that were conducted and reported in comparable ways. Sharing data is important to make studies intercomparable. In human health studies, there is more uncertainty in any individual variable of study than in nearly any other science. Significant work is required on how to best account for uncertainties.

Collaboration between health and environmental scientists is necessary. Feedback is needed from health scientists to contaminant hydrogeologists and karst scientists about what environmental variables are most useful in predicting or protecting public health. Medical specialists might provide information to field and laboratory scientists on what subtle water quality or microbial changes might have the largest consequences for human health. That is, what environmental knowledge is most useful to human or environmental health studies? In general, scientists need to work with local health departments. Public health departments are the basis for discerning health effects and yet are underfunded. To make progress on the relationship of environmental contaminants and health outcomes, increased workforce —both in terms of expertise and in numbers—is needed.

Revised regulatory approaches are required for karst systems. Appropriate protection of karst groundwater is a highly valued goal. Standard regulations do not sensibly apply to karst, and unique regulations appropriate to the protection of karst are needed. The legal requirement that state regulations be uniformly applied is indefensible given existing scientific knowledge. Scientists might collaborate with lawyers to bring lawsuits challenging current laws. It is possible to make laws to avoid certain activities in karst; some states forbid the construction of landfills on carbonate bedrock and allow no room for negotiation. The fact that some states have more protective regulations than other states argues for national standards. Perhaps a national standard for well construction in karst is appropriate. Failing the establishment of a legal standard, even a national guidance document would be useful in overcoming local variations in regulations. There may be no foolproof strategies for the environmental protection of karst, but we have far more scientific knowledge about the contaminant hydrogeology of karst aquifers than is reflected in the laws and regulations that currently prevail. Meeting participants expressed concern that environmental agencies are underfunded.

Human health is critically dependent upon environmental health. The consensus of the inextricable connection between environmental health and human health should be adopted by all investigators so that all future work is conducted from the point of view that if environmental health is degraded, human health is degraded. Working from this premise offers the best hope for protection of human health. It is public policy, usually motivated by health issues, that drives research in karst.

Cross training in multiple disciplines and effective communication are keys to the future. Broad recommendations emerged from discussions about how to generate new ideas and approaches. Increasing diversity and inclusion in the population of scientists and in the communications at meetings was thought to be a promising approach. Cross training young scientists in all the collaborating disciplines represented at this conference was recommended as appropriate preparation for future professionals. Scientists need to communicate well with the lay public and with politicians. Successful communication to the public requires the delivery of science content to people so they can know how to act, whether in personal or commercial realms. Successful communication of scientific findings in understandable terms will help achieve the desired outcome of engaging stakeholders to protect public health by protecting karst waters.