ABSTRACT

Determining the nature of water flow and contaminant dispersion in karst requires far more information than can be provided by simple dye traces. Tracing can delineate drainage divides, flow directions, and flow velocities at various stages, but from water management purposes it is also important to determine such variables as groundwater storage, retention times, patterns of convergence and divergence, and response to wet-dry cycles in the soil. These are most significant in the non-conduit portions of the karst aquifer, which supply most wells. Dye tracing can be augmented by hydrograph analysis at various stages, tracing with tagged solid particles or microbes, evaluation of dissolved solids and chemical equilibria, and isotopic analysis. This paper concentrates on some of the uses of chemical equilibria and isotopes. Stable isotopes (e.g. $^{18}$O and deuterium) and the various radium isotopes are among the most useful. Ratios among the four radium isotopes ($^{228}$Ra and $^{224}$Ra, with half-lives in years; and $^{223}$Ra and $^{226}$Ra with half-lives in days) are well suited to karst studies. These techniques are time-consuming and costly, so a full analysis of a karst aquifer is rarely feasible. Instead, it is recommended that selective analyses be made of representative parts of the aquifer, and that they be applied as follows: (1) Develop conceptual models based on field observation, which allow one to anticipate a range of probable scenarios of contaminant transport and remediation. (2) If digital models are used, it is most effective to design simple generalized models in which the boundary conditions are clearly defined, and then to gain insight into real aquifers by noting the differences between the model and field observations. (3) Use field techniques to become familiar with the local hydrology and then apply hydraulic and chemical principles to anticipating contaminant behaviour, rather than reacting only to emergencies. These approaches encourage the growth of interpretive skills based on the same scientific principles that govern the origin of caves and karst.

Keywords: hydrologic models, geochemistry, isotopes, contaminant tracking

1. INTRODUCTION

Maintaining a safe water supply is difficult in karst, where the physical setting and modes of water movement are complex. This paper addresses two issues: first, to introduce the great variety of interpretive field techniques that are available to the karst hydrologist; and second, to suggest a realistic strategy for applying the resulting information to karst.

Effective water management in karst requires several types of field data: (1) Delineation of drainage basins and drainage divides. This task is complicated by the overlap of catchment areas where perched vadose flow crosses phreatic divides, and by the shifting of divides with time as flow stage varies. (2) Flow directions, velocities, and discharge in solution conduits and in the dispersed flow outside the conduits. (3) Patterns of convergence and divergence of groundwater, and their role in chemical dispersion. (4) Effective pore and fissure sizes and their interconnectivity. This information helps the anticipation of likely paths of pathogen migration. (5) Volume and duration of water retained in storage between infiltration events (e.g., capillary water, perched pools, etc.).
2. ANALYTICAL TECHNIQUES

The variables listed above can be investigated in many different ways. Major categories of hydrologic field data are outlined here, mainly to demonstrate their utility and how they relate to each other. Most are time-consuming, and some are costly as well, so it is rarely feasible to apply them in sufficient detail to truly understand the behaviour of a karst aquifer. However, by considering them, we are forced to think about how karst aquifers behave. For further information see also MILANOVIĆ, 1981; BONACCI, 1987, and FORD & WILLIAMS, 2007.

2.1. Measurement of hydraulic head and gradients

The most direct way to measure local hydrologic conditions is to measure heads in water wells and to determine their spatial and temporal variation. Contouring of static water levels can give a good approximation of drainage divides and flow patterns, if the data are abundant enough and the geology is relatively simple (e.g., QUINLAN & RAY, 1989).

Natural variations in head with time, provide much information on proximity to turbulent-flow conduits, as well as flow convergence and divergence at different stages. Rapid rise and fall of head in response to rainfall or snow-melt events facilitates the delineation of major flow routes, with turbulent-flow solution conduits having the most extreme rates of response. Laminar-flow zones within the aquifer respond more slowly, with broad, long-term rises and declines in head. Volume of groundwater storage and rates of release can be estimated. Variations in head with time can demonstrate the dispersal of water during flood pulses.

As in other aquifers, pumping tests in karst provide considerable information on flow patterns, effective hydraulic conductivity, and anisotropy. Spatial variability tends to be much greater than in other aquifer types. Flow directions and anisotropy can also be anticipated from the geologic setting.

Hydraulic gradient is a critical component in all flow equations, whether laminar or turbulent. Discharge and velocity are directly proportional to gradient in laminar flow but are related more or less to the square root of the gradient in turbulent flow.

2.2. Discharge measurements

Combining discharge measurements with head data provides insight into the structural nature of the aquifer. Discharge at springs and in cave passages is proportional to catchment area. It is more useful in determining aquifer properties to measure variations in discharge with time, especially in response to storms and/or snowmelt. Differing responses of springs to what appear to be similar storm events can usually be accounted for by evapotranspiration loss and antecedent soil-moisture conditions, both of which show a strong seasonal effect. Where the hydrology is simple, as where ponors feed a single spring, the comparison of discharge in vs. discharge out is a simple method for assessing the presence of dispersion of water into the aquifer. During a flood pulse, the inflow at first typically exceeds the outflow, indicating accumulation of storage in conduits, abandoned upper-level cave passages, and neighboring fissures and pores. During the waning phase of a flood pulse, the outflow exceeds the inflow as storage is released. A long tail with a roughly logarithmic rate of decrease suggests the release of water as laminar flow, after the main turbulent-flow pulse has passed (ATKINSON, 1977). The volume released is found by integrating the area under the hydrograph (volume = \( \sum Q \Delta t \), where \( Q \) = discharge and \( t \) = time.

Response to storm events will vary with antecedent precipitation – for example, after a prolonged dry period when the infiltration capacity of soil and fill material in epikarst fissures is dominated by desiccation fissures, in comparison with a prolonged wet period when soils are moist and have expanded to fill available bedrock fissures. Much of the water that reaches the phreatic zone during an infiltration event is composed of capillary water that has been held in storage from prior events and displaced by the new water pulse (shown by PITTY (1966)).

2.3. Measuring travel times: quantitative tracer tests

Estimating the position of drainage divides with dye traces is a long-established technique. Detection of flow divergence, crossovers, and shifting of divides with flow stage are also important outcomes. These complexities increase with structural deformation. Dominantly convergent and well-defined drainage patterns are typical of undisturbed strata, as in the central U.S.A. (e.g. QUINLAN & RAY, 1981). In areas of greater structural complexity, such as the Dinaric chain (e.g., BAUČIĆ, 1968), features including divergent flow paths, crossovers, and overlapping groundwater divides are far more likely. Dye tracing is discussed in many other publications (e.g., KÄSS, 1998).

Much information can be gained by repeating quantitative dye traces at a wide variety of discharges. Dye concentrations at detection points are measured at short time intervals so the exact arrival times, peak dye concentrations, and mean travel times (to centres of mass) can be detected. Mean breakthrough times to each monitoring point are plotted as a function of discharge. A logarithmic scale allows coverage of a broad range of values and emphasizes differences in the shape of the plots (PALMER, 2007). Conduits that are mostly water-filled will show linear plots with slopes of \(-1\) (Fig. 1). Paths composed mainly of open channels, such as canyons, produce concave-upward curves: as discharge rises, water depth also increases, and the increase in wetted perimeter, \( p \), length of contact of water with solid surfaces in a cross section, can increase almost as fast as the cross-sectional area \( A \). Flow velocity is a function of the ratio \( A/p \), so velocity in a flooding vadose channel tends to increase more slowly than in a water-filled conduit. A combination of open channels and closed conduits will give linear plots at low discharge that change to concave-upward curves at high discharge. Complex patterns, such as overflow and divergence,
may complicate the analysis, but they can also be revealed by this method. Approximate conduit size and water volume within it can also be crudely estimated.

It is useful to know the approximate percentage of a conduit that is vadose. Low-density contaminants that are mainly insoluble in water will tend to float and accumulate at sumps. During flood pulses, much of a normally vadose conduit will fill with water and drive the contaminants upward into many narrow fissures. Leakage of volatile gases to the surface has been documented (e.g., in Bowling Green, Kentucky; Crawford, 1984), where volatile gases have accumulated in buildings to near explosive limits. Even if the entire interpretive procedure is not feasible, it is helpful merely to anticipate the field conditions that lead to this problem.

2.4. Use of tagged tracers

The ability of pathogens to be carried by groundwater can be estimated by tracing with solid particles of discrete size. An ideal tracer consists of natural indigenous microbes that have been tagged with an identifier that is incorporated into the living cells. Brahana, (2009) describes this technique in a karst basin in Arkansas that is isolated for hydrologic research. The bacteria are exposed to a europium solution in a karst basin in Arkansas that is isolated for hydrologic research. Samples of infiltration water must be collected where it first emerges from the rock or sediment matrix so there is no loss of dissolved gases. The pH is measured in situ, and precipitation of dissolved solids is prevented by HCl acidification of one of a pair of samples. Most seepage water is near saturation with calcite. Saturation with dolomite generally requires lengthy residence time in an aquifer (typically years). Significant supersaturation with either mineral generally indicates loss of CO₂ from the water, e.g., by air exchange through open cave entrances or fissures.

Dripwater chemistry in caves, combined with discharge of the drips, can clarify the nature of vadose flow routes. Is the water seeping slowly, with large areas of contact with fissure walls? Is it following discrete solution channels? Some of this information can be obtained from rate equations (e.g., Plummer et al., 1978, Dreybrodt, 1988). A generic rate equation for dissolution is

\[ \frac{dC}{dt} = \left( A' \frac{k}{V} \right) \left( 1 - \frac{C}{C_s} \right)^n \] (1)

where \( \frac{dC}{dt} \) = change in concentration with time, \( k \) = reaction coefficient, \( n \) = reaction order, \( C_s \) = saturation concentration, \( A' = \text{surface area in contact with the water} \), and \( V = \text{water volume} \). It is rarely possible to find a unique solution to this equation, but the range of possibilities becomes clear. An integral solution, as well as values for \( n \) and \( k \) for typical karst situations, are given by Palmer (1991). Note that \( \frac{1}{V} \) is dimensionally equivalent to \( Q \), and \( A' \) is proportional to flow length, so \( C/C_s \) relates directly to discharge and to the network of openings through which the water has passed.

A \( P_{\text{CO}_2} \) significantly greater than that of the soil suggests a hygogenic CO₂ source. For example, at Saratoga Springs, New York, water is actively degassing as it emerges from the springs. The flow is discontinuous, with spurs and bubbles. With the assumption that the water at depth was at equilibrium with calcite, back-calculation indicates that its \( P_{\text{CO}_2} \) was more than 6 atmospheres. Reaction-path software is useful in the calculations (see www.usgs.gov/software).

\( P_{\text{CO}_2} \) significantly less than atmospheric is common but difficult to measure. Seepage into carbonate rock through an insoluble cap-rock allows dissolution to take place under nearly closed conditions, because the reaction is isolated from the reservoir of soil CO₂. \( P_{\text{CO}_2} \) can drop to as little as \( 10^{-4} \) to \( 10^{-5} \) atm. This is difficult to measure, because local flow rates are very small, and CO₂ is absorbed rapidly from
the cave air. Results include rills, etching, and weathering of cave walls where seepage water suddenly becomes highly aggressive toward carbonates (PALMER, 2007). Discharge per unit area is low, but the total over large areas can be substantial. Infiltration through insoluble rock can be verified, and contaminant paths and filtering can be anticipated.

2.7. Stable-isotope chemistry

Flow rates and storage in non-conduit parts of a karst system can be assessed through the use of isotope chemistry. 18O and deuterium (\(\delta^2H\)) in precipitation vary seasonally, and when plotted on a graph of \(\delta^18O\) vs. \(\delta^2H\) they tend to fall on a straight line. This “local meteoric water line” is typically close to, and nearly parallel to, that of the global mean data, defined by \(\delta^{18}O = 10 + 8 [\delta^{2}H]\), as shown in Fig. 2. During the cold season, the points plot at the lower left (more depleted in the heavier isotopes); and during the warm season they plot at the upper right. As this water infiltrates and travels through the aquifer, it retains most of its initial isotopic signature. Changes due to CO2 uptake and dissolution of carbonates have little effect, because their total molar contribution to the water is only a tiny fraction. The discrepancy in isotopic signature between local precipitation and of a groundwater sample increases with time for the first half year, and then diminishes. This discrepancy forms a sinusoidal curve with time (Fig. 3), and therefore the “age” (residence time) of the water since it first precipitated can be estimated in most cases. A single measurement is not sufficient; a time series needs to be developed that shows the seasonal variation over a long time (ideally several years). A groundwater sample that tracks almost exactly with that of the precipitation is likely to have spent less than a single season reaching its present point in the aquifer. Large discrepancies indicate longer residence times in the ground. An erratic correlation requires more care in interpretation. Comparison of values in a variety of places in the aquifer is likely to clarify the overall picture of residence times.

Groundwater that is supplied by a wide range of water sources, typical of baryphreatic flow, tends to have a clustering of oxygen-deuterium values somewhat low on the meteoric water line, regardless of time of year (Fig. 1). This is because most of the infiltration takes place in the transition from cold to warm, when snow melt is high and evapotranspiration is low.

Points to the right of the local meteoric water line normally indicate evaporative enrichment of the heavy isotopes at the surface. (It may also indicate long-term inheritance from local bedrock, but this appears to be minor in karst aquifers.) For example, McFail’s Cave, New York receives many drips along its length of about 11 km. Some of the land above it is swampy, so there is great opportunity for evaporation. Some of the drips show a significant shift to the right, away from the meteoric water line, and these are interpreted as being fed by wetlands. The position of the drips relative to the wetlands supports this idea, but there are local discrepancies that appear to indicate lateral movement of vadose water down the dip of the strata.

Sulphate content can be used as an indicator of depth of groundwater flow. For example, in the same field area there are sulphate-rich springs that show a sulfur isotopic signature (\(\delta^{34}S\)) that is identical to that of the solid sulphates in a local Silurian dolomite, which in this area lies at a depth of up to 100–200 m below the surface. This same water shows a clustering of oxygen-deuterium values that does not vary significantly with time. The \(\delta^{34}S\) plot exactly in the range of values for Silurian marine sulphate rocks.

2.8. Use of radioactive isotopes: the example of radium

One of the most promising avenues for investigating karst hydrology is the interpretation of radium (Ra) isotopes. Little has been done in this field, and certain details have yet to be understood. Bedrock contains trace amounts of uranium and thorium; 235U, 238U, and 232Th. Decay of 238U produces 226Ra (half-life of 1601 yr), and 235U produces 223Ra (half-life of 11.1 days). 223Th produces both 224Ra (half-life of 5.7 yr) and 224Ra (half-life of 3.54 days). All Ra isotopes decay to radon (Rn) and eventually to lead (Pb).

Water in contact with bedrock or sediment acquires these isotopes by dissolution. The main governing variables are shown by Equation 1. With four radium isotopes of varied sources and half-lives, they provide a potentially great amount of information about flow patterns in karst. For general reference, see KRAEMER & GENEREUX, 1998. Those with long half-lives (years) are 226Ra and 223Ra. Those with short half-lives (days) are 224Ra and 223Ra. As water travels through narrow fissures or fine-grained material with large areas of contact and long residence times, it equilibrates with the local bedrock and sediment values. The ratio 222U/238U is about 0.0466, so that is the equilibrium ratio for the decay products 222Ra/226Ra. But 224Ra and 223Ra come from the same parent (224Th), so 224Ra/223Ra ideally approaches 1.0.
High activities of the long-lived Ra isotopes indicate lengthy and intimate contact with bedrock or sediment. High activities of the short-lived Ra (224Ra and 223Ra) indicate recent release of water from pores and narrow fissures into larger bodies of water, where they decay faster than they can be replenished from the solids. Zones of seepage into streams (at the surface or underground) can be identified in this way. The time since the seepage has entered the main body of water can be estimated by the amount of disequilibrium. For example, with time, the 228Ra/226Ra ratio decreases. This decrease can be caused by simple mixing between the incoming seepage and the stream or lake water, but if the seepage input retains its identity as a plume without substantial mixing (as in lakes fed by springs), the ratio decreases along an exponential decay curve instead of linearly.

Marine rocks (e.g., carbonates) have a low Th/U activity ratio (<0.1), so they produce low 228Ra/226Ra ratios in exponential decay curve instead of linearly. If the source is located near the surface of a solid, it can be ejected into the adjacent fluid. Alpha recoil has a significant effect only where there is a very large surface area, as in suspended fine-grained sediment. High 228Ra/226Ra ratios can result up to at least 6 in slow-moving groundwater. This suggests both considerable alpha-recoil and also long residence times (tens or hundreds of years; Tom KRAEMER, Reston, Virginia, personal communication).

Residence time of groundwater is often estimated with tritium, radiocarbon methods, etc., but the utility of those produced by human activity (e.g., tritium from atmospheric testing of nuclear devices) is diminishing with time. Radioactive and tritium methods, radiocarbon methods, etc., but the utility of those produced by human activity (e.g., tritium from atmospheric testing of nuclear devices) is diminishing with time.

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3. CONCLUSIONS

The interpretive techniques described above are all interrelated by several major concepts: the mass balance, fluid mechanics, dissolution kinetics, and chemical equilibrium. They share the same physical laws, concepts, and variables as those that govern the origin of karst. All require a fundamental understanding of the local geological setting. By applying these and similar techniques, one can understand the origin and development of karst in addition to how it behaves hydrologically.

These techniques require considerable time and expense, so they are feasible only for long-term academic or government-sponsored research projects. It is important to develop suitable strategies for contaminant remediation by anticipating problems, rather than by reacting after a spill or leakage has already taken place.

Today the most common approach to groundwater management is digital modelling, in which the goal is to predict outcomes on the basis of a few simple field measurements. This is rarely successful. Instead, it is more appropriate to design simple digital models that are not expected to be correct, but the output of which can easily be compared to field observations. Confronted with the differences between the ideal model and reality, we are forced to visualize the field conditions that can account for those differences. Another approach to digital modelling is to develop interactive models of specific aspects of karst that allow one to explore the effects of varied field conditions (e.g., DREYBRODT et al., 2005). These methods encourage professional growth, in contrast to the typical accumulation of digital outputs that involve only repetitive data types and thought processes.

A recommended strategy is first to use field techniques such as those described in this paper to gain insight into the behaviour of karst aquifers, and only then to progress to aquifer modelling, whether it be conceptual, analytical, statistical, or digital. Field information should ideally be held in a central repository, (e.g., in a government-sponsored or academic karst centre), rather than scattered widely in the literature or in personal files. Hydrologic and chemical field measurements give personal insight into the internal workings of karst – an important step in the training and advancement of karst scientists.

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