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GROUNDWATER RESIDENCE TIMES IN UNCONFINED CARBONATE AQUIFERS

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Abstract: Tracers have been widely used in unconfined carbonate aquifers to measure groundwater velocities and travel times. Injected tracers have largely been used to measure travel times from sinking streams to springs. Environmental tracers have largely been used to estimate overall residence times in an aquifer, and give times that are typically one hundred times longer than estimates from injected tracers. Use of both environmental and injected tracers has enabled residence times and storage volumes to be calculated for both diffuse and conduit components in a number of aquifers. With the addition of permeability data it is possible to calculate storage and flow components for the matrix, fracture and channel components. Results show that the matrix of the rock provides almost all storage, but has very long residence times, especially in older carbonates. Channels provide little storage, account for most of the flow, and have very short residence times. Fractures play an intermediate role between the matrix and channels and have low storage and moderate residence times. These same contrasts are found in many different aquifers and are likely to be found in all unconfined carbonate aquifers. Thus these aquifers are marked not so much by ranging from conduit flow to diffuse flow types, but rather in having triple porosity with contrasting flow and storage properties in the matrix, fractures and channels. The combination of environmental and injected tracers provides a powerful tool for elucidating these contrasting properties.

Introduction

There are widely divergent views on groundwater residence times in unconfined carbonate aquifers. One view is derived from the long history of measuring groundwater velocities; it has been estimated that more than 90% of all groundwater traces have taken place in carbonates (Quinlan, 1986). Such testing as well as cave exploration has led to the view that most carbonate aquifers are dominated by flow through conduits. A contrasting view usually comes from well tests, where transmissivity and hydraulic conductivity values are broadly similar to those from sand aquifers. Consequently, many hydrogeologists assume that carbonate aquifers function in a similar way to sand aquifers and behave as equivalent to porous media with the water, in general, moving slowly through the rock.

White and Schmidt (1966) recognized that carbonate aquifers have both localized flow in conduits and diffuse flow through fractures and the matrix of the rock, and Atkinson (1977) calculated the proportions of conduit and diffuse flow for the Cheddar groundwater basin in England. It appeared to be logical that there might be a range between carbonate aquifers where diffuse flow dominates and the water seeps slowly through the aquifer, and others where conduit flow dominates, and a number of such conceptual models have been proposed (White, 1969; Atkinson and Smart, 1981; Smart and Hobbs, 1986; Quinlan et al., 1992).

An alternative possibility is that both diffuse flow and conduit flow are present in most, if not all, carbonate aquifers, and that the perceived differences are largely a function of the types of measurements made. Thus tracer tests from sinking streams to springs are an excellent way to demonstrate conduit flow with rapid velocities, whereas a borehole is unlikely to intersect a major conduit so pumping test results generally reflect diffuse flow properties. Worthington et al. (2000) analyzed data from four contrasting limestone and dolostone aquifers in terms of flow and storage in channels, fractures and the matrix. They concluded that at least 96% of storage is in the matrix and that at least 94% of flow is through channels in the aquifers studied, thus showing that widely different carbonate aquifers function in similar ways.

Tracers have been very useful in helping determine the proportions of matrix, fracture and channel flow in carbonates, and this paper reviews a number of studies with contrasting results.

Injected and Environmental Tracers Used to Measure Travel Times

The most common tracing in carbonate aquifers is between sinking streams and springs, and well over ten thousand such tests have been carried out. Worthington (1999) compiled the data from 2,877 such tests, which have an approximately log-normal distribution with a geometric mean of 1,770 m d^{-1}. In the data set there is a wide range in distance traced, with the median distance being 4,000 m and 576 traces being over distances of at least 10 km

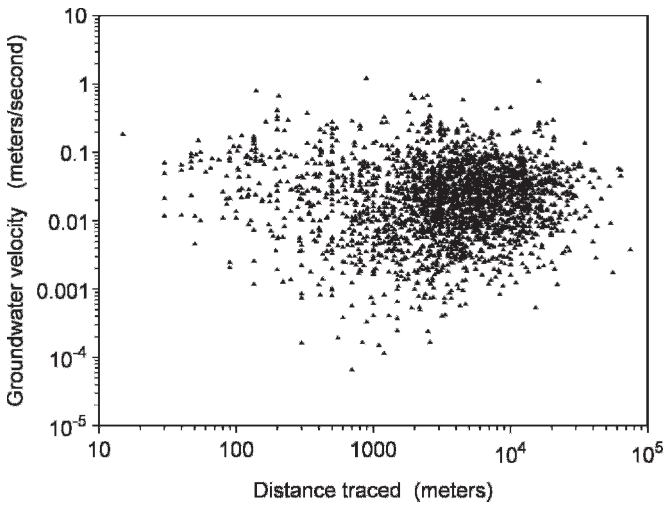

Figure 1. Ground-water velocities and traced distances for 2,877 sink to spring tracer tests.

(Fig. 1). The large number of traces over long distances with rapid flow clearly indicate that extensive networks of interconnected conduits on a scale of many kilometers are common.

There have been a number of studies from dolines or from the surface to drip points in caves 10–100 m below the surface (Friederich and Smart, 1981; Bottrell and Atkinson, 1992; Kogovšek, 1997). Tracer arrival times are typically minutes to hours, but there is commonly high dispersion so that mean residence times are much greater. There have also been a number of tracer tests between wells and these typically give travel arrival velocities of tens to hundreds of meters per day. The existence of velocities $>$100 m d^{-1} from sink to spring, surface to conduit and from well to well tracer tests clearly show that there are many pathways in carbonate aquifers where there is rapid flow.

A wide range of environmental tracers have been used to determine residence times, including water temperature, chemical variables such as total hardness and both stable and radioactive isotopes. Sampling in shallow conduits has shown that average residence times in the vadose zone are typically months or longer (Pitty, 1968; Yonge et al., 1985). These times are much longer than the tracer arrival times from injected tracers and demonstrate the large variance in residence time. Similarly, there have been many tritium measurements at springs that have demonstrated mean residence times of years while in the same aquifers tracers have shown flow-through times of days, and a number of these studies will be described below.

The broad conclusion to be made from all the tracer studies is that environmental tracers tend to give much greater aquifer residence times than injected tracers. This apparent anomaly can be resolved by accounting for the multiple porosity elements in a carbonate aquifer.

Calculation of Residence Times in Carbonate Aquifers

A simple and useful way to consider carbonate aquifers is in terms of flow and storage in one-, two- and three-dimensional elements of the aquifer (Worthington, 1999). The one dimensional elements have generically been called channels (Worthington and Ford, 1995). Channels with diameters less than a few centimeters commonly provide most of the inflow to boreholes during pumping tests, and in caves are best seen as the vadose flows and drips that form stalactites and stalagmites. Larger channels are called conduits when flow becomes turbulent, which is commonly at a threshold diameter of about 1 cm (White, 1988, p. 290–293). Caves are large conduits that a person can enter. The two dimensional elements in carbonate aquifers are joints and faults. The three dimensional elements are the matrix blocks that lie between the fractures.

The calculation of residence times in porous-medium aquifers is straightforward. In such aquifers flow lines are parallel and particle tracking numerical models such as the U.S. Geological Survey program FLOWPATH can give estimates of travel between two points in an aquifer and therefore of residence time. The calculation of residence times in carbonate aquifers is only straightforward in two simple situations. One is where all the flow is along a conduit from a sinking stream to a spring. In these situations there is no mixing between water particles of different ages and thus a simple piston-flow model of advective flow from sink to spring provides an accurate model. The second simple situation may occur where recharge is through a thick porous medium overburden such as sand. Soil is unlikely to behave as a porous medium because of preferential flow via channels caused by root casts, animal burrows or dessication shrinkage of clays. In a downgradient direction in carbonate aquifers there is increasing mixing between waters that have followed different flowpaths and thus have a range of ages. Consequently, the variance of the age will generally increase in a downgradient direction.

Residence Times from Environmental and Injected Tracers

There have been a number of studies where both environmental and injected tracers have been used (Table 1). Each of these studies involved analysis of a number of tritium samples as well as multiple traces from sinking streams to springs.

The east-flowing Danube River loses flow at sinkpoints in its bed in southern Germany. Tracer testing in 1877 using salt and the fluorescent dye uranine showed that the flow crosses the European continental divide and resurges 12 km to the south at Aach Spring, which is on a tributary of the west-flowing Rhine River. This spring is the largest in Germany with an average discharge of 8.5 m^3 s^{-1}, and

Table 1. Groundwater velocities from injected and environmental tracers.

Location	No. of ^{3}H samples	Mean flow path length (km)	Residence time ^{3}H (years)	Velocity from ^{3}H (m d^{-1})	Traced distance (km)	Velocity from injected tracer (m d^{-1})	Reference
Aach, Germany	10	9	10	2.5	12 – 18	1000 – 4800	Batsche et al., 1970
Areuse, Switzerland	23	6	0.75 – 2	8 – 22	6 – 14	350 – 4800	Müller and Zötl, 1980
Kiveri, Greece	40	15	2	20	3 – 42	160 – 4300	Morfis and Zojer, 1986
Vaucluse, France	57	30	10	8	23 – 46	200 – 2300	Puig, 1990; Mudry and Puig, 1991; Couturaud and Puig, 1992
Hölloch, Switzerland	24	5	0.5 – 1.7[a]	8	0.4 – 11	600 – 5300	Bögli and Harum, 1981; Jeannin et al., 1995

[a] From both ^{2}H and ^{3}H

losses from the Danube account for a major fraction of the flow (Batsche et al., 1970; Käss, 1998). Tracing from these sinks to Aach Spring gave travel times of 2.5 to 13 d, with the travel time being inversely related to discharge at the spring. However, tritium analyses gave a mean residence time of 6 to 14 yr. The age of water at two major sinks on the Danube is 2 to 6 yr and 6 to 14 yr, respectively (Batsche et al., 1970), so the actual residence time in the aquifer of the old component of flow is uncertain.

The Areuse Spring in the Swiss Jura Mountains has a mean flow of 4.7 m^3 s^{-1}. Tracer tests from five sinking streams to this spring helped delineate the catchment area and give conduit velocities. Tritium and discharge measurements showed that the rapid component of flow was 20% of total discharge, with the remaining 80% of discharge having a mean residence time of 9 months to 2 yr (Müller and Zötl, 1980).

In the Peloponnese peninsula in Greece there are a series of enclosed basins with large sinking streams, surrounded by mountains that rise up several hundred meters. The mean residence time of more than 80 springs in this area was determined from tritium samples, with most springs having residence times in the range of 2 to 10 yr (Morfis and Zojer, 1986). Some of the larger springs were selected for intensive tritium sampling. For instance, monthly samples were collected at Kiveri Spring for a period of three years and a further 14 samples were collected during a three month period while tracer tests were being carried out. Kiveri Spring is a coastal spring and is one of the largest springs in Greece. Six injected tracers were recovered at this spring, with flow paths of 3–42 km and much faster groundwater velocities than the tritium indicated (Table 1). There was similar intensive sampling at springs at Stymfalia, Ladon, and Kefalari which yielded groundwater ages of 5 yr, 4.5 yr, and 4 yr, respectively. Injected tracers recovered at these three springs days to weeks after injection gave similar results to Kiveri, with most tracers giving velocities >1000 m d^{-1} (Morfis and Zojer, 1986).

The Vaucluse Spring is the largest spring in France and has a groundwater catchment of about 1,100 km^2. The spring has been explored to a depth of −308 m by a remote-operated submersible vehicle (Mudry and Puig, 1991). Tritium measurements at the spring have shown that there is a mixture of water of different ages; at high flows recent precipitation predominates, while at low flow there is a large component of water with a residence time of more than 30 yr. Similarly long residence times have also been measured in boreholes in the catchment area (Puig, 1990). The short residence time component has been demonstrated by seven tracer tests over distances of 23–46 km, where tracer residence times have varied from 2 weeks to several months (Couturaud and Puig, 1992).

Hölloch is the longest cave in Western Europe, with a mapped length of 190 km. There have been extensive studies of the cave and its hydrology (Bögli and Harum, 1981; Jeannin et al., 1995; Jeannin, 2001). Measurements with deuterium and tritium gave estimated mean residence times of 1.6 yr and 1.7 yr, respectively, for the long residence-time component which accounted for a minimum of 30% of total discharge. Deuterium gave a mean residence time of 6 months for the total spring flow, and tracer tests gave residence times of 10 h to a week.

The residence times and velocities of the above five studies are summarized in Table 1. The tritium analyses gave an age for the groundwater that yielded an average velocity of 2–22 m d^{-1} whereas the injected tracers gave velocities that were about one hundred times faster.

Recent studies at Wakulla Spring (Florida) have given an even larger contrast between the results of the two techniques. Environmental tracers gave a groundwater residence time age of 39 years from $^{3}H/^{3}He$ analysis, and Katz (2001) suggested that such $^{3}H/^{3}He$ dating "provides a realistic assessment of the susceptibility of the UFA [Upper Floridan Aquifer] to contamination by approximating the travel time for contaminants to reach a particular zone in the aquifer." This interpretation is based on the assumption that the aquifer behaves as a porous medium. However, recent tracer testing with fluorescent dyes from the sinking streams of Munson Slough, Fisher Creek and Black Creek has given groundwater ages of just days to weeks (Loper et al., 2005). This confirms that the aquifer behaves as a double or triple porosity aquifer rather than a single porosity porous medium aquifer. Additionally there has been extensive cave exploration upstream from Wakulla Springs, which have a mean discharge of 11 m^3 s^{-1} (Wisenbaker, 2006). The combination of the massive discharge from a single location and the cave exploration gives further information on the conduit fraction of flow.

The very large differences between groundwater ages from injected tracers and environmental tracers in all the above studies are complementary rather than contradictory because they measure different aspects of the porosity. The tracers injected into sinking streams and recovered at springs give velocities and residence times of conduit flow, the fastest component of flow through the aquifer. The environmental tracers give an average age of the groundwater, including not only the rapid flow component through conduits, but also the slow flow component through the matrix and fractures in the bedrock as well as the soil and epikarst.

The combination of environmental and injected tracers in the above studies clearly shows that there are multiple residence times in carbonate aquifers and that residence time is a function of the parameter being measured. There have been a number of studies that have considered the volumes and residence times of the different porosity components in carbonate aquifers, and one single-porosity, three double-porosity, and two double-porosity models are discussed below.

Residence Times and Storage Volumes in Single- and Double-Porosity Models

Jordtulla Cave is an almost straight 580 m long submerged conduit in Paleozoic marble that drains Glomdal Lake in Norway and provides an example of a simple sink to spring conduit. The cave survey showed the conduit volumes is 1.35 $\times 10^4$ m^3 and continuous discharge measurements over a period of 20 months gave a mean discharge of 2.5^3m s^{-1} (Lauritzen et al., 1985; Lauritzen, 1986). The mean residence time of the flow through the conduit is thus 13,500/2.5 s or 90 min. This calculation ignores the gain along the conduit from autogenic recharge from matrix, fracture or conduit flow. The autogenic catchment is 2.6% of the total catchment and the proportions of flow through the rock matrix, fractures, or channels have not been measured or calculated. The matrix flow is likely to be extremely low in this low-porosity marble, so it is likely that almost all autogenic recharge flows rapidly through fractures and channels and consequently may also have a short residence time. Residence time in the conduit is inversely proportional to discharge, which varies substantially in this mountainous subarctic environment. The residence time has been measured by more than forty traces at flows between 1 m^3 s^{-1} and 10 m^3 s^{-1} (Lauritzen, 1986; Smart and Lauritzen, 1992). At extreme flows of 0.1 m^3 s^{-1} and 50 m^3 s^{-1} the calculated residence time is 38 h and 4.5 min, respectively.

The Cheddar Springs have a mean discharge of 0.73 $m^3 s^{-1}$ and drain an estimated 39 km^2 of the Mendip Hills in England, and both conduit and non-conduit fractions of flow and storage were calculated by Atkinson (1977). The lag between the arrival of a flood pulse and the arrival of low-conductivity sinking stream water was used to estimate a conduit volume of 1.1×10^5 m^3. Integration of the discharge recession curve gave a baseflow storage of 3.3×10^6 m^3, showing that conduits only account for 3% of total storage. A non-conduit transmissivity of 0.031 m^3 s^{-1} was calculated from the baseflow recession and from the storage coefficient, which enabled the fraction of non-conduit flow of 30% to be estimated, with the remaining 70% of flow being through conduits (Atkinson, 1977). The residence time for non-conduit flow can be calculated by dividing the non-conduit volume by the discharge of 0.22 m^3 s^{-1}, giving an average residence time of 170 d. Similarly, the average residence times for conduit flow can be calculated by dividing the conduit volume by the conduit discharge of 0.51 m^3 s^{-1}, giving a residence time of 2.5 d. The groundwater catchment is 10 km in length so this time would represent an average velocity of 2 km d^{-1} over an average flow path length of 5 km. Smart (1981) carried out repeat tracing along the Longwood Swallet to Cheddar Springs flow path and found that conduit velocity was directly proportional to discharge and ranged from 110 m d^{-1} to 6400 m d^{-1}, with 13 of the traces exceeding

2 km d^{-1} and 11 traces being less than 2 km d^{-1}. Thus the repeat tracing lends credence to the estimate of conduit volume by Atkinson (1977).

The Höllengebirge in the Northern Limestone Alps of Austria are a high mountain range with autogenic recharge. Seasonal discharge, ^{18}O variations and low-flow tritium concentrations were used to calculate storage volumes and residence times for conduit and non-conduit flow and storage (Benischke et al., 1988). Results showed that concentrated recharge and rapid flow through conduits accounted for 72% of flow, but this only accounted for 4% of aquifer storage.

The Central Styrian Karst in Austria has a major sinking stream, the Lurbach, as well as a limestone plateau with autogenic recharge. The sinking stream accounts for 64% of the spring discharge of 0.29 m^3 s^{-1}. Conduit volume was calculated from the spring discharge between tracer injection and recovery times during 17 repeat tracer tests, and non-conduit storage was calculated from 29 tritium measurements from samples collected over a period of two years (Behrens et al., 1992).

The results from the four areas described above are summarized in Figure 2. The three double-porosity models give broadly similar results, with 4% or less of storage being in conduits, but most of the flow being in them. There are also some substantial differences. The small conduit volume in the Styrian karst is because the calculation is only of the main conduit from the Lurbach sinking stream and does not include conduits in the autogenic fraction of the catchment. The large differences in matrix/fracture residence times are probably at least partly due to the differences in the method of calculation, with the two Austrian examples using tritium and Cheddar using baseflow recession. However, all three double-porosity models show that conduit residence times are orders of magnitude less than non-conduit residence times.

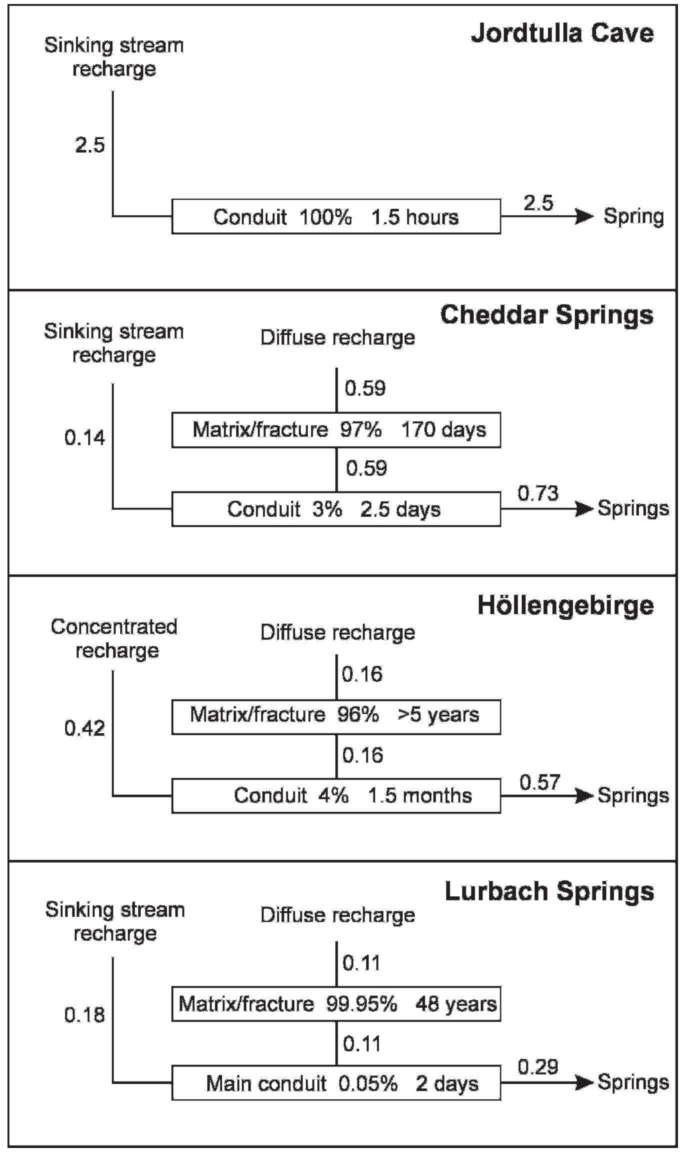

Figure 2. One and two-box models for carbonate aquifers, with fraction of storage (in percentage) and residence time in each box and flow in (m^3 s^{-1}) between boxes. See text for details.

RESIDENCE TIMES AND STORAGE VOLUMES IN TRIPLE-POROSITY MODELS

Triple-porosity models can potentially give a more accurate picture than double-porosity models of ground-water residence times in carbonate aquifers, and two examples are shown in Figure 3, the Manavgat River basin in Turkey and the Turnhole Spring basin in Kentucky.

The Manavgat River basin drains a topographic basin of 928 km^2 and in addition several closed basins, giving an estimated total drainage area of 9,100 km^2 (Yurtsever and Payne, 1986). This area has both the longest groundwater traces and one of the largest springs in the world (Bakalowicz, 1973; Chabert, 1977; Karanjac and Gunay, 1980). A total of 41 tritium samples were collected between 1963 and 1980 at the Oymapınar gauging station, where long-term discharge records are available. Tritium concentrations were found to vary by more than an order of magnitude, with the maximum of 684 tritium units being measured in a sample collected in April 1963. Part of the variation over time was due to decreasing atmospheric concentrations following the cessation of atmospheric nuclear weapons testing, but there was also a factor of four variation in concentration between high-flow and low-flow periods. From recession curve analysis, Yurtsever and Payne (1986) inferred that there were two storage elements in the aquifer with average residence times of about 3 months and 9 months, respectively, plus a baseflow component with a longer residence time and a discharge of 29 m^3 s^{-1}. Best-fit analysis to match modeled and measured tritium values gave mean residence times of 2 months, 9 months and 12 yr for the three components of

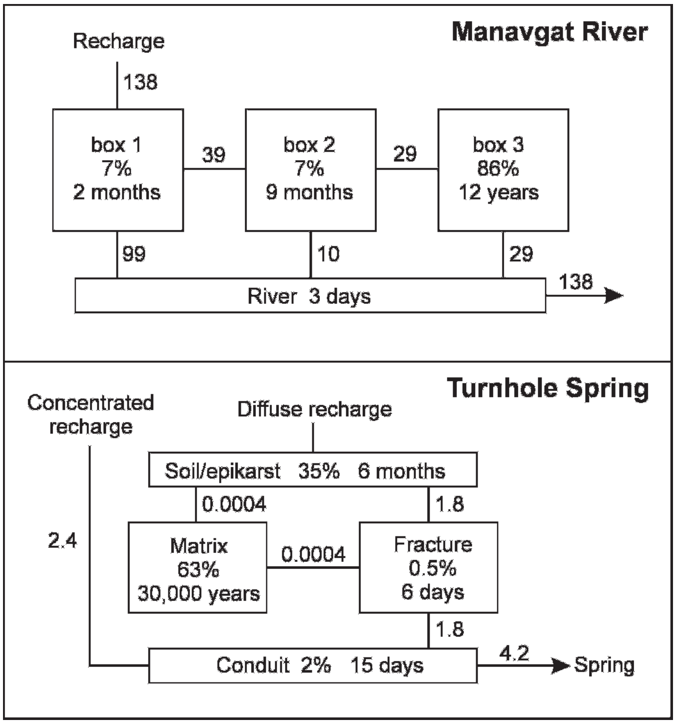

Figure 3. Multiple-box models for carbonate aquifers, with fraction of storage (in percentage) and residence time in each box and flow in (m^3 s^{-1}) between boxes. See text for details.

flow, with 86% of storage being in the long residence time component (Figure 3).

The Turnhole Spring basin drains an area of 217 km^2, including part of Mammoth Cave (Quinlan and Ewers, 1989). Worthington et al. (2000) calculated matrix, fracture and channel fractions of flow and storage. Matrix porosity and hydraulic conductivity were measure from core and hand samples. Fracture hydraulic conductivity was determined by pump and slug tests in boreholes, and fracture porosity was calculated from estimated fracture apertures. Channel porosity was determined from the lag between the arrival of a flood pulse and the arrival of low-conductivity sinking-stream water and from tracer-test velocities. Channel flow was determined from runoff calculations. Finally, the effective aquifer thickness was estimated from the looping of cave passages in Mammoth Cave, which are up to 23 m below the contemporaneous water table. Results gave 96–97% of storage in the matrix of the rock (Worthington et al., 2000). However, the study only considered bedrock storage and flow, and soil and epikarst properties were not included. Gunn (1986a, b) showed that such storage can be a considerable fraction of total storage where there is thick soil or overburden above a carbonate aquifer. The depth of soil and moisture content in the Turnhole Springs catchment have not been measured, but an estimated 300 mm of storage would have a mean residence time of 6 months and would then account for 35% of total storage in the groundwater basin (Fig. 3).

Residence Time Distributions of Flow and Storage

From the above studies it is possible to estimate residence time distributions for the respective aquifers. However, there are two very different definitions of residence time distribution (Worthington et al., 2000). These are

$$T_r = T_m R_m + T_f R_f + T_c R_c \tag{1}$$

$$T_s = T_m S_m + T_f S_f + T_c S_c \tag{2}$$

where T is residence time, R is recharge to the aquifer, S is the storage in the aquifer, the subscripts m, f, and c refer to matrix, fracture and channel, respectively; T_r is the residence time of water recharging the aquifer, and T_s is the residence time of the water within the aquifer. The three components of R and S are dimensionless fractions, the sum of which are both unity.

Jordtulla Cave and the Turnhole Spring basin are the simplest and most complicated models, respectively, of the examples that are shown in Figures 2 and 3. Residence time distributions for them were calculated using Equations 1 and 2 and assuming that the residence time of each flow component in the bedrock has a log-normal distribution. Examples of log-normal distributions include the tracer velocity distribution in Figure 1, which has a standard deviation of 0.54 log units. Similarly, hydraulic conductivity data also have a log-normal distribution, with the standard deviation usually being between 0.5 and 1.5 log units (Freeze and Cherry, 1979, p. 31). For instance, the slug test data from nine boreholes in the Turnhole Spring basin have a geometric mean of 6×10^{-6} m s^{-1}, with a standard deviation of 0.94 log units.

In calculating the residence time distributions, the residence times for Jordtulla Cave are based on the flow duration data (Lauritzen et al., 1986). For conduit flow at Turnhole Spring, residence times are based on a mean groundwater pathway of 11 km and on the histogram of tracer-velocity distribution in Worthington et al. (2000); these data are shown in Figure 1. For matrix flow and fracture flow it is assumed that the residence time distributions are log-normal with a standard deviation of 2.0 log units. This large standard deviation reflects not only the variation in hydraulic conductivity, but also the large variation in distance flowed. For the soil/matrix a standard deviation of 1.0 is used because flow through soil is likely to be approximated by piston flow and the substantial differences in residence time may be largely due to differences in soil thickness.

Results are shown in Figure 4. Jordtulla Cave is modeled as a single-porosity aquifer, so the residence time distributions from Equations 1 and 2 are identical (Fig. 4a). However, the two distributions for Turnhole Spring are very different. In terms of recharge to the

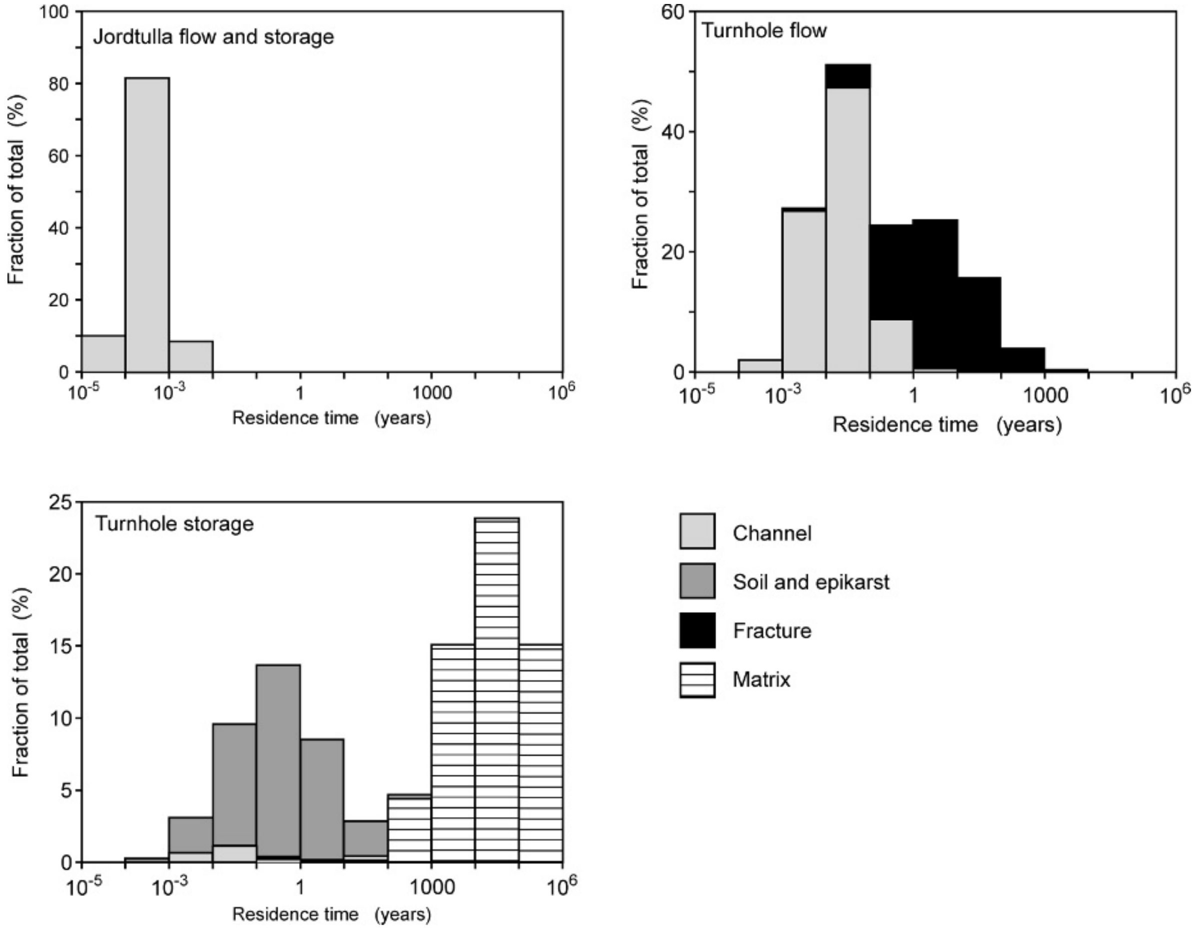

Figure 4. Residence times for both flow and storage in Jordtulla Cave (top left), flow in the Turnhole Spring basin (top right), and storage in the Turnhole Spring basin (bottom left).

aquifer (or discharge from the aquifer), most of the water passes quickly through it and the mode is 0.01–0.1 yr, or 4–37 d (Fig. 4b). This reflects the large proportion of concentrated recharge at sinking streams or dolines which has been shown by tracing to quickly travel to Turnhole Spring. The residence time of storage is bimodal and is dominated by soils and epikarst storage, with a residence time of months, and by matrix storage, which has a very long residence time (Fig. 4c). From Equation 1, the mean residence time of recharge to the aquifer is 4 years. The mean residence time of storage in the aquifer is given by

$$T_s = T_m S_m + T_f S_f + T_c S_c + T_e S_e \tag{3}$$

where terms for residence time (T_e) and storage fraction (S_e) in the soil and epikarst are added to the variables in Equation 2. Equation 3 gives a mean storage residence time of 19,000 years; this is dominated by the large fraction of total storage that is in the matrix and by its long storage time. The estimated residence times are only first approximations as they are based on very limited data.

Discussion and Conclusions

The models in Figures 2 and 3 are all simplifications of the carbonate aquifers discussed. The range in residence times may be more of a continuum rather than the discrete ages that these figures imply because there is a continuum of aperture sizes. These range from pore throats less than 1 µm in width to fractures, many of which have apertures in the 10–100 µm range, to channels. The smallest channels, such as those feeding slow-dripping stalactites, have calculated apertures in the 0.05–1 mm range (Worthington, 1999). The largest channels, such as those close to high-discharge springs, have apertures greater than 10 m.

There are a number of factors influencing the estimated residence times of the different aquifers discussed, including the use of different tracers and different methodologies to calculate residence times as well as differences in the aquifers themselves.

The aquifers discussed in this paper are all unconfined. In some confined carbonate aquifers, such as deep synclinal basins, extremely high total dissolved solids (TDS) concentrations show that flow is sluggish, and in these situations there may have been little karstification unless it occurs at an early pre-burial stage. However, in other confined aquifers such as the Edwards Aquifer in Texas, there are large springs with low TDS and the aquifer is well-karstified (Lindgren et al., 2004).

Detailed consideration of advective flow and of diffusion have shown that fractured rocks are unlikely to behave as porous media (Pankow et al., 1986). Furthermore, the self-organization due to the positive feedback loop between flow and dissolution means that carbonate aquifers are less likely than other fractured rocks to behave as porous media. The use of both injected and environmental tracers is an excellent way of demonstrating the multiple porosities and large range in residence times in carbonate aquifers. There have been a number of conceptual models that have suggested that carbonate aquifers range from conduit-flow to diffuse-flow types. However, the present study better supports the conclusions of Worthington et al. (2000) that unconfined carbonate aquifers all have great similarities, with all having triple porosity with contrasting flow and storage properties in the matrix, fractures and channels.

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