
Relative importance and chemical effects of diffuse and focused recharge in an eogenetic karst aquifer: an example from the unconfined upper Floridan aquifer, USA

M. Ritorto · E. J. Screaton · J. B. Martin · P. J. Moore

Abstract Karst aquifer studies often focus on allogenic water inputs and large conduit flow. However, diffuse recharge can be significant, particularly in unconfined eogenetic karst aquifers that retain high matrix permeability. This study examines an unconfined region of the upper Floridan aquifer (USA) that hosts a sinking stream, its resurgence, and a large conduit system. Daily diffuse recharge was approximated using a water-budget method and ranged from 17% of precipitation during a low precipitation year to >53% during the highest precipitation year, illustrating the highly variable nature of diffuse recharge in this region. The total allogenic input via the sinking stream over the 5 years of the study was significantly larger than the volume of diffuse recharge. However, only about 2% of the allogenic recharge flows from the conduit into the surrounding aquifer. That flow is restricted to storm events when hydraulic heads in the conduits exceed those in the surrounding aquifer. The estimated volume of dissolution is similar for allogenic recharge and diffuse recharge to the unconfined region surrounding the conduits, but dissolution from the diffuse recharge is distributed over a larger area than dissolution from allogenic recharge. These results exemplify how recharge type impacts flow and water–rock interactions in eogenetic karst aquifers.

Keywords Karst · Floridan aquifer · Groundwater recharge/water budget · Carbonate rocks · USA

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Introduction

Many previous investigations of karst hydrogeology have focused on flow within large conduits due to their role in the rapid movement of water (e.g., Ryan and Meiman 1996; White 2002). Cave exploration, dye trace studies, and natural tracer studies have established connections between focused recharge areas (sinking streams or sinkholes) and springs (e.g., Padilla et al. 1994; Martin and Dean 1999, 2001; Florea and Vacher 2006). Analyses of spring hydrographs, thermographs, and chemographs have also been used to characterize aquifer flow and chemical processes (Dreiss 1989a, b; Grasso and Jeannin 2002; Grasso et al. 2003; Kovacs and Perrochet 2008). Although large conduits have dominated past research due to their rapid flow and the ease of access to this flow at springs, significant additional diffuse flow occurs through intergranular (matrix) porosity and fractures in the surrounding aquifer (e.g., Shuster and White 1971; Worthington et al. 2000; Martin and Dean 2001; White 2002; Screaton et al. 2004).

Diffuse flow is particularly important in carbonate aquifers that have not been deeply buried and retain high matrix permeability (e.g., Florea and Vacher 2006). These types of aquifers have been termed “eogenetic”, to distinguish them from “telogenetic” aquifers, in which deep burial and tectonism cause recrystallization to form dense rock with low matrix porosity and permeability (Vacher and Mylroie 2002). The matrix permeability in telogenetic aquifers can be low, resulting in minimal true intergranular flow (e.g., Palmer 2002; Florea and Vacher 2006).

Spring flow in some telogenetic karst aquifers can be entirely attributed to focused inputs due to allogenic input (sinking streams) or internal runoff. In these aquifers, diffuse recharge and interactions between the conduits and surrounding formation are minimal, and chemical reactions may be limited to surfaces of major fractures and bedding plane partings (e.g., Ryan and Meiman 1996; Greene 1997). In contrast, the high matrix permeability within unconfined and poorly confined eogenetic karst aquifers suggests that diffuse recharge will be a significant part of the aquifer water budget. Consequently, water–rock reactions may occur within the matrix, either directly

from diffuse recharge or from loss of water from conduits to the matrix, as well as within fractures and conduits. Some telogenetic karst aquifers may behave similarly to eogenetic karst aquifers where diffuse recharge and flow can be accommodated by distributed fine fracture systems (e.g., Shuster and White 1971; White 2002; Bailly-Comte et al. 2007; Jourde et al. 2007; Toran et al. 2007).

Although allogenic inputs through sinking streams can dominate karst aquifer water budgets, much of this water may flow through the system with little interaction with the aquifer matrix. Exchange of water between conduit and matrix can occur when conduit hydraulic head temporarily exceeds the hydraulic head in the surrounding aquifer during high discharge events (White 1999; Martin et al. 2006). Following passage of the discharge pulse, the water will drain from the matrix and fractures of the adjacent aquifer material into the conduit. This temporary storage effect is greatest in unconfined eogenetic karst aquifers, where intergranular permeability and storage (specific yield) are high. However, attenuation of allogenic fluid pulses has been observed in some telogenetic karst aquifers (e.g., Bailly-Comte et al. 2007; Jourde et al. 2007), suggesting storage of the allogenic water within the surrounding aquifer.

While allogenic recharge can be easily measured through observation of sinking stream discharge (White 1999), diffuse recharge is difficult to estimate in any aquifer and may require comparison of multiple methods (e.g., Scanlon et al. 2002). Long-term water budgets or calibration of groundwater models for specific basins yield average recharge values, but are not appropriate for short-term analyses or understanding temporal variability of diffuse recharge. As an example of the importance of temporal variability, Florea and Vacher (2007) used well hydrographs from the Florida Peninsula to conclude that a much smaller percentage of precipitation becomes recharge during summer thunderstorms than during fall hurricane events, likely due to difference in evapotranspiration. Similarly, previous work in north-central Florida calculated monthly potential evapotranspiration and noted that summer precipitation would be less likely to recharge the aquifer than precipitation at other times, due to the high summer evapotranspiration rates (Martin and Gordon 2000). The most accurate techniques for determining recharge on short time scales often require complex instrumentation or are data-intensive; thus, simple daily mass balance methods can provide a practical alternative (Dripps and Bradbury 2007).

This study examines the importance of diffuse recharge in an unconfined portion of an eogenetic karst aquifer region that is recharged by both precipitation (diffuse recharge) and a sinking stream (allogenic recharge). An important aspect of the study is characterizing the temporal variations in diffuse recharge. This was accomplished using a daily mass-balance method that incorporates the Penman-Monteith model to approximate evapotranspiration. Because detailed evapotranspiration parameters were not available for the site, the input values were adjusted to match long-term estimates based on

water budget studies (Hunn and Slack 1983; Grubbs 1998), and resulting estimates were compared to recharge values estimated from variations in conservative element concentrations. Comparison of diffuse recharge rates with allogenic input also allows us to evaluate the potential dissolution of the carbonate aquifer due to each fluid source. Although this study focuses on the unconfined Floridan aquifer, the results discussed here are relevant to other unconfined eogenetic karst aquifers and to unconfined telogenetic karst aquifers that exhibit diffuse flow behavior.

Study area

This research was conducted in the Santa Fe River basin of north-central Florida (Fig. 1), which covers an area of roughly 3,500 km² (Hunn and Slack 1983). The basin is underlain by Oligocene and Eocene carbonate rocks that make up the Floridan aquifer system. In the northeastern portion of the basin, the Floridan aquifer system is confined by overlying Miocene and younger siliciclastic sediment (Miller 1997). To the southwest, the upper Floridan aquifer is unconfined. In the study region, the upper Floridan Aquifer (UFA) is about 430 m thick, unconfined at the surface, and is covered by a thin veneer of unconsolidated sands and sediments (Miller 1986). In this area, no middle-confining unit exists; as a result, the UFA extends to the lower confining unit of the Cedar Key Formation (Miller 1986). Potable water extracted from the aquifer is estimated to come from the upper 100 m of the Eocene Ocala Limestone, with more mineralized water in deeper portions of the aquifer (Hunn and Slack 1983; Miller 1986). Porosity and matrix permeability of the Ocala Limestone average about 30% and 10⁻¹³ m², respectively (Budd and Vacher 2004; Florea and Vacher 2006).

The primary study area features an approximately 5-km gap in the surface flow of the Santa Fe River where it disappears into a 36-m deep sinkhole known as the Santa Fe River Sink and ultimately reemerges at a first magnitude spring called the Santa Fe River Rise (Fig. 1; Hisert 1994; Martin and Dean 2001). Between the Santa Fe River Sink and Rise, the river flows through a system of conduits that have been mapped by cave diving exploration or inferred from natural or introduced tracers. Flow rates within the conduits have been measured to be at least several km/day using a variety of tracers including SF₆ (Hisert 1994), Rhodamine WT (Moore and Martin 2005), and temperature (Martin and Dean 1999; Sreaton et al. 2004). The measured flow rate depends on the stage of the river, with flow velocity increasing with river stage (Martin and Dean 1999). The study area contains twelve monitoring wells, which are located various distances from known conduits (Table 1). Drilling of these wells allowed estimation of depth to carbonate rocks, and these wells allow monitoring of aquifer water levels, and sampling of groundwater chemical compositions outside of the conduits.

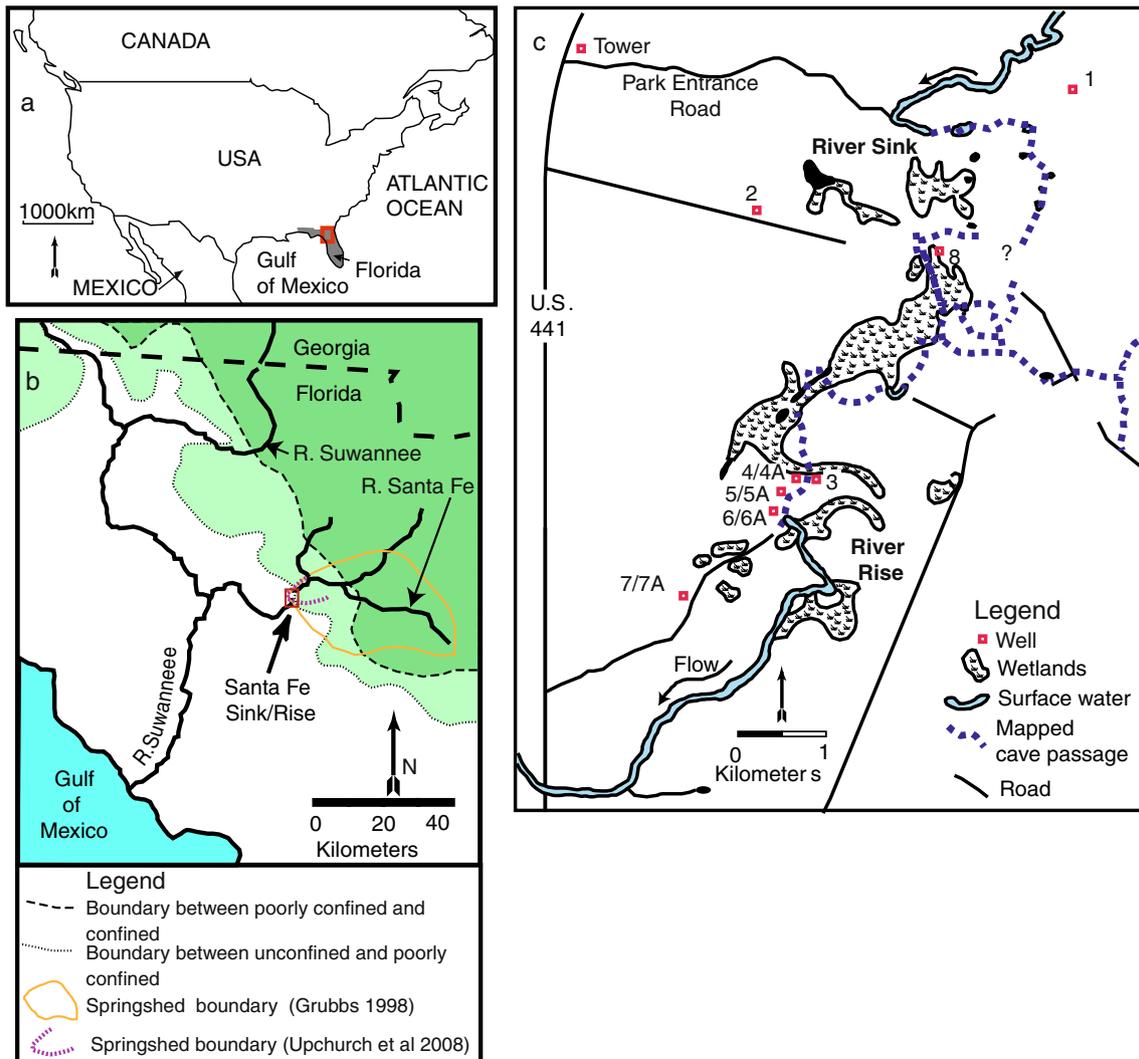


Fig. 1 Location and schematic map of the study area. **a** Location of Florida (*shaded*) within the United States. **b** General setting of the Santa Fe River Sink and River Rise. Location shown by box (**a**). **c** Details of the study area including the locations of the Santa Fe River Sink and River Rise, monitoring wells, and mapped and inferred conduits

Hydraulic connection between the conduits and the surrounding aquifer has been observed with chemical and physical hydrologic techniques. Following a major flood, chemical concentrations of Na^+ and Cl^- decreased by 40% in a water supply well approximately 2 km west of the conduit discharging to the Santa Fe River Rise. Martin and Dean (2001) interpreted this dilution to represent inflow of water from the conduit to the surrounding aquifer matrix. During most floods, more water flows into the River Sink than discharges from the River Rise, indicating that the surrounding aquifer gains water from the conduit (Screaton et al. 2004; Martin et al. 2006). This contrasts with base-flow conditions, when the discharge out of River Rise exceeds that into River Sink, indicating flow of water from the aquifer to the conduits. The exchange of water agrees with changes in head gradient between the conduit and monitoring wells (Martin et al. 2006). Water chemistry was examined at the deep monitoring wells (Table 1) and it was concluded that, in

addition to local diffuse recharge and allogenic input, upward flow from the deep aquifer provides water and dissolved solids to the conduit system (P.J. Moore, University of Gainesville, unpublished data, 2008). Although the volume of water flow could not be quantified because the concentration at depth is unknown, this source of water was observed to vary inversely with the Rise stage; contributions from depth are greatest during droughts.

This study focuses on the unconfined region of the UFA between Santa Fe River Sink and Rise. The region supplying groundwater to the Santa Fe River at the Rise (its springshed) was delineated at about 1,400 km² by Grubbs (1998), which consisted of 67% (940 km²) in which the UFA is well confined, 28% (390 km²) in which it is poorly confined and leakage to the UFA occurs through the confining layer, and 5% (70 km²) where the UFA is unconfined. Recent work using more detailed potentiometric surface maps (Upchurch et al. 2008)

Table 1 Summary of monitoring wells

	Installation date (mm/yyyy)	Screen interval (m bgs)	Screen interval (m asl)	Top of Floridan (m asl)	Ground surface elevation (m asl)
Well 1	12/2002	22.9–16.8	–8.4–2.3	–3	14.45
Well 2	12/2002	30.5–24.4	–14.5 to –8.4	10	15.96
Well 3	1/2003	28.4–22.3	–10.5 to –4.4	15	17.87
Well 4	1/2003	29.6–23.5	–11.7 to –5.6	13	17.89
Well 4a	3/2006	9.8–6.7	8.2–11.3	13	17.96
Well 5	3/2003	29.9–23.8	–13.7 to –7.6	11	16.22
Well 5a	3/2006	8.23–5.18	8.0–11.0	13	16.20
Well 6	1/2003	31.1–25.0	–17.6 to –11.5	9	13.51
Well 6a	3/2006	5.5–2.4	8.1–11.1	10	13.55
Well 7	1/2003	29.9–23.8	–14.7 to –8.6	10	15.22
Well 7a	3/2006	7.6–4.6	7.6–10.6	13	15.19
Well 8	4/2004	30.5–24.4	–17.2 to –11.1	10	13.32
Tower	pre-1976	26.5–?	–2.6–?	?	23.88

suggests that the springshed may be considerably smaller, with only ~20 km² of unconfined aquifer and 160 km² of poorly confined aquifer (Fig. 1). The confined portion of the springshed was not delineated.

In the unconfined UFA in north-central Florida, runoff is generally negligible and very little channelized surface drainage is present because the soils are permeable and the slope of the land surface is gradual to flat. Consequently, average annual aquifer recharge rates are high. Estimates range between 45 and 60 cm/year based on water budget analyses (Grubbs 1998). These values are between ~33 and 44% of the average precipitation of 137 cm/year (Hunn and Slack 1983). A value of 46 cm/year, near the lower end of the above range was reported by Hunn and Slack (1983).

The interaction between conduit and monitoring well hydraulic heads was analyzed by Martin et al. (2006) to estimate transmissivity values between the conduit and each monitoring well. Martin et al. (2006) assumed hydraulic heads at the monitoring wells were affected only by changes in conduit head; however, hydraulic head will also be influenced by diffuse recharge at the monitoring wells, a variable that was not included in the model. Resulting transmissivity values ranged from 900 to 500,000 m²/day. Monitoring wells closest to the conduit yielded lesser values and those at greater distances yielded greater values. The increase in transmissivity as measurement scale increased was interpreted to be a result of water flowing through preferential flow paths. With greater measurement scale, the likelihood of encountering a preferential flow path increases. This observation is consistent with conclusions from other karst and fractured aquifers (Rovey and Cherkauer 1995; Person et al. 1996).

Methods

Data and sample collection

Data analyzed during this study include daily precipitation, river stage, and chemical analyses of water from monitoring wells drilled to the water table a few tens of meters to about 1 km from the conduits (Table 1). Daily precipitation was recorded at the O'Leno State Park

station and was accessed through the database of the Suwannee River Water Management District (SRWMD 2007). River stage measurements were recorded daily by O'Leno State Park personnel from a staff gauge located approximately 0.5 km upstream of the Santa Fe River Sink. The gauge has a 2.09 m gap between 12.41 and 14.50 masl and thus elevation data are missing from this range. If data at other Santa Fe River stations and site monitoring wells indicated smoothly varying water levels, Santa Fe River Sink stage was interpolated across this gap. Water levels at the Santa Fe River Rise were measured with an automatic data logger installed within a stilling well constructed from 5.08 cm (2 inch) PVC pipe and located approximately 200 m downstream of the Rise.

Shallow monitoring wells, which were sampled to characterize shallow groundwater chemistry, have screened intervals that cross the water table (Table 1). All monitoring wells are constructed of 5.08 cm (2 in) PVC piping with a screened interval of 6.10 m (20 ft) for the deep wells and 3.05 m (10 ft) for the shallow wells. Information from other monitoring wells provides information on the depth to the carbonate bedrock which was estimated based on cutting returns and drilling response. The transition is gradational from unconsolidated sands to indurated carbonate rock. Variations in recorded depth likely reflect heterogeneous distributions of carbonate in the epikarst and differences in interpretation of whether the carbonate was intact.

Water levels were recorded with in situ Minitroll Loggers (accuracy of +/- 0.02 m), Van Essen Divers (accuracy of +/- 0.005 m), and Van Essen CTD Divers (10-m divers with an accuracy of +/- 0.01 m and 30 m divers with an accuracy of +/- 0.03 m). A separate barometric data logger (accuracy of +/- 0.0045 m) was used to correct the non-vented pressure transducers for ambient barometric pressure changes. The recorded stage at the River Sink was converted to discharge based on a rating table developed by the SRWMD (rating No. 3 for station No. 02321898, Santa Fe River at O'Leno State Park), and water level at the Santa Fe River Rise was converted using the rating curve produced by Sreaton et al. (2004). River Rise water levels were recorded at 10-min intervals. Water elevations were manually measured

or surveyed at the time the data were downloaded. Errors due to logger drift (either instrument drift or logger movement) were generally less than 0.035 m.

The shallow, water-table wells were installed in winter 2006 and were sampled seven times over the study period on 11 April, 15 June, 12 July, 28 August, and 12 October 2006 and 17 January and 10 April 2007, covering an entire water year. During this period, precipitation was low and the river remained at baseflow conditions (Fig. 2). Water was pumped from the wells using a Grundfos II submersible pump at a slow rate (0.5 L/min) until one well volume had been extracted, or about 2–4 L of water depending on water-table elevation at the time of pumping. While pumping, water was monitored for specific conductivity (SpC), temperature (T), dissolved oxygen concentration (DO), pH, and turbidity until at least three consistent values were obtained for each parameter. Samples were collected in a variety of PVC sampling bottles depending on the analyte to be measured. Samples for metal analyses were preserved in the field with nitric acid, and all samples were kept chilled until analyzed. Concentrations of major ions (Na, K, Ca, Mg, Cl, and SO_4) and alkalinity were analyzed either by a-NELAC certified laboratory (Advanced Environment Laboratories, Inc.) in Gainesville, FL or in the Department of Geological Sciences, University of Florida. Analyses were determined in accordance with Environment Protection Agency (EPA) regulations for each analyte (EPA 1983). Data from quality-assurance samples indicated no contamination and good analytical reproducibility. Precision of most analytes were <8% relative standard deviation (RSD) and charge balance for most samples are <5%, but may be larger in dilute samples which have concentrations close to instrument detection limits.

Chemical composition of precipitation in the region was obtained from National Atmospheric Deposition Program Site FL03 in the Bradford forest (NADP 2008), which is located approximately 15 km east of the field area. Major element compositions (Cl, SO_4 , Ca, Na, Mg, K, specific conductance, and pH) are available for the precipitation. Concentration data are available from 19

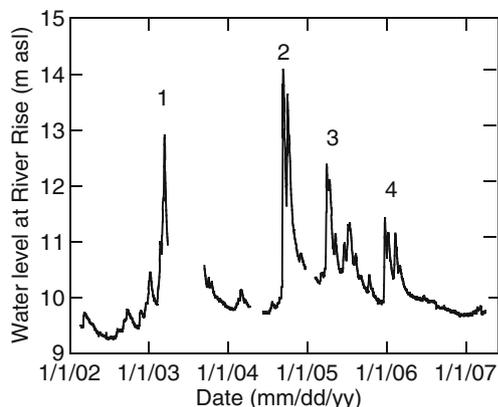


Fig. 2 River Rise water levels between February 2002 and March 2007. Missing data are indicated by gaps in the curve. Numbers denote storm events discussed in the text

December 2000 to 4 September 2007 and this complete data set has been included in the statistical summary of chemical composition (Table 3). There is no statistical difference in the precipitation composition over the 7 years of available data from its composition during the year that the wells were sampled.

Calculation of daily diffuse recharge

Diffuse recharge was calculated at a daily time scales using a mass-balance method similar to Dripps and Bradbury (2007), with runoff omitted:

$$\begin{aligned} \text{Recharge} = & \text{precipitation} - \text{interception} \\ & - \text{evapotranspiration} \\ & + \text{antecedent soil moisture} \\ & - \text{total soil moisture storage capacity} \quad (1) \end{aligned}$$

Evapotranspiration was approximated on a daily basis using the Penman-Monteith model for determining water lost to the atmosphere from a vegetated surface. Inputs to the Penman-Monteith model, including air and soil temperature, relative humidity, average solar radiation, and wind speed at 10 m elevations, were measured at a Florida Automated Weather Network (FAWN 2007) station located approximately 25 km south of the field area in Alachua, Florida. When data were missing from the Alachua station, FAWN data from Live Oak, Florida (~60 km NW of the site) were substituted.

The Penman-Monteith model combines the Penman equation of evaporation with an estimate of canopy conductance, C_{can} , with the assumption that a reasonably uniform vegetated surface can be represented as a single “big leaf” whose total conductance to water vapor is proportional to many small leaves (Dingman 2002). Canopy conductance is the product of three characteristics of the local vegetation: shelter factor, leaf conductance, and leaf area index (LAI). Vegetation in the O’Leno study area consists of a mixture of hardwoods, pine, and cypress with an understory primarily consisting of palmettos. Shelter factor (f_s), which adjusts transpiration for leaves sheltered from sun and wind, was chosen to be 0.5 based on a completely vegetated area (Allen et al 1989). Leaf conductance (C_{leaf}) was approximated based on solar radiation, air temperature, soil-moisture deficit, and absolute-humidity deficit (Stewart 1988). Solar radiation, air temperature, and absolute humidity deficit were obtained or calculated from the meteorological data, while the soil moisture deficit was determined by subtracting the antecedent soil moisture from the soil moisture storage capacity. Leaf area index is determined from the total area of leaf surface above a ground area. Typical values of 6.0 are reported for conifer and broadleaf forests (Federer et al. 1996).

A simplified approach to interception losses was included in the daily water budget. The canopy storage

was allowed to fill during each day with any occurring precipitation and empty by evaporation during and following precipitation. Canopy storage of 0.07 cm was assumed based on values reported by Liu (1996) for a cypress/pine wetlands located southwest of the study site. Because only daily values for precipitation were available for O'Leno State Park, duration of precipitation events was approximated through inspection of hourly precipitation data from the Alachua FAWN database. A representative precipitation duration of 3 h was selected. These simplifications will cause canopy interception to be overestimated for short duration precipitation events or those that occur at night, and underestimated for longer duration events. Limitation on evaporation of intercepted water due to canopy wetness below saturation was not included in the calculations.

Soil-moisture storage capacity was estimated to be ~10 cm, based on an estimated root zone depth of 1 m (Stewart 1988) and an estimated available water content of 0.10 for sands (Dingman 2002). The soil moisture was tracked through time by adding excess precipitation (precipitation minus evapotranspiration and interception losses) to the previous day's soil moisture (e.g., the antecedent soil moisture) up to the soil-moisture capacity. The remainder of the excess precipitation is assumed to become recharge, as shown in Eq. (1). For the start of the study period (January 2002), an antecedent soil moisture of 5 cm was assumed.

Because detailed LAI studies have not been conducted at the site, the LAI values were adjusted to yield an average recharge of ~46 cm/year for 2002–2006. This value corresponds to estimates presented by Hunn and Slack (1983) and is at the lower end of the range of Grubbs (1998), to provide conservative estimates of daily diffuse recharge. To simulate seasonal changes in leaf cover, a sinusoidal variation in LAI was assumed with variation from 3.5 in the winter to 6.5 in the summer, which provided the best match to long-term recharge. To observe the effect of this sinusoidal variation on results, the recharge was recalculated using a constant LAI of 5. The observed difference in annual and event recharge for the seasonally varied and constant LAI was small (<10%) because much of the recharge to the aquifer occurs in spring and fall and is not affected by the assumption of seasonality in LAI.

Errors in the calculated temporal distribution of recharge arise from a number of factors, including unknown effects of long-term variations in vegetation due to droughts and controlled burns. Evaporation from the surface water bodies was not included in the calculations due to their small surface area. Because there is only one precipitation station on the site, error will also be introduced by local variations in precipitation.

Geochemical modeling

The geochemical model PHREEQC (Parkhurst and Appelo 1999) was used to estimate the amount of calcite dissolution that may have occurred as diffuse recharge

equilibrates with the aquifer. The influence of evapotranspiration on chemical composition of the precipitation was estimated using mass-balance models constrained by differences in Cl^- concentrations of the precipitation and water collected from the top of the saturated zone. Following estimations of chemical concentrations through ET, PHREEQC was used to determine their partial pressure of CO_2 , ion-activity products (Q), and calcite saturation index— $\text{SI} = \log(Q/K)$, where K is the equilibrium constant for calcite. Samples within ± 0.1 SI are assumed to be in equilibrium with respect to calcite based on analytical errors in measurements of pH, alkalinity, and concentrations of Ca^{2+} (e.g., Langmuir

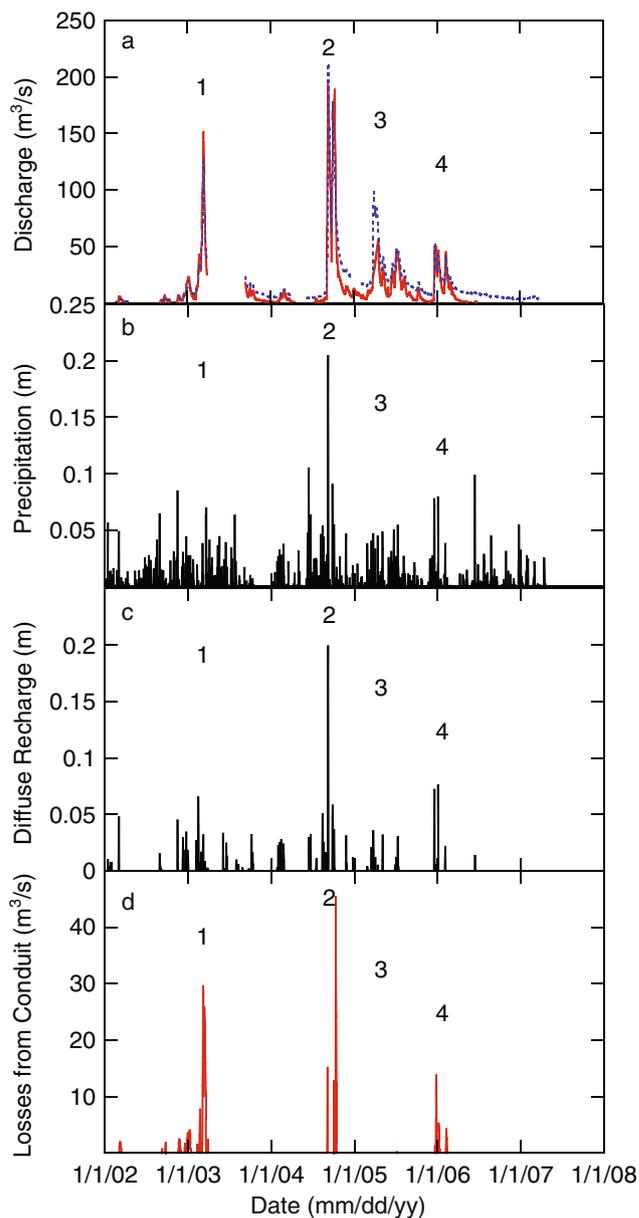


Fig. 3 a Discharge at River Sink (red solid line) and River Rise (blue dashed line) for February 2002 to March 2007. b Precipitation. c Estimated daily diffuse recharge. d Losses from the conduit system (V_{sink-Vrise}). Numbers denote storm events discussed in the text

1997). No temperature data were available for the precipitation, but precipitation should thermally equilibrate with the ground water so the average temperature measured at each well was used for the equilibrium modeling (Table 3). The P_{CO_2} values for groundwater were estimated from alkalinity measurements of the water; alkalinity values were not available for the precipitation, which was assumed to be in equilibrium with atmospheric P_{CO_2} with a value of $10^{-3.5}$. Thermodynamic data were obtained from the *phreeqc.dat* database. Equilibrium modeling consisted of estimating the mass transfer required to match the measured calcite saturation indices and P_{CO_2} of the well water after the composition of precipitation was corrected for concentration effects from ET.

Results

Between January 2002 and April 2006, four storm events significantly increased discharge on the Santa Fe River (Figs. 2 and 3, labeled 1–4). During the remainder of the study period, the system showed generally decreasing discharge, corresponding to decreasing water levels at the Santa Fe River Sink and decreasing hydraulic heads in the monitoring wells. Measured precipitation between 2002 and 2006 averaged 135 cm/year, similar to the long-term average estimated for the area (137 cm/year; Hunn and Slack 1983).

Because of the relationship between precipitation, ET, and soil moisture storage (Eq. 1), precipitation does not always result in estimated recharge (Fig. 3). Particularly in the summer months, precipitation can be completely transferred to ET or soil moisture storage. On 13 June 2006, 0.1 m of precipitation occurred but was almost entirely taken up by soil-moisture storage, due to previous dry conditions. In contrast, the largest single day estimate of diffuse recharge (0.2 m) resulted from the passage of

Hurricane Frances in September 2004. Little of the precipitation was lost to ET or transferred to soil moisture due to the meteorological conditions and previous rainfall. During baseflow conditions, much of the water that flows into the conduit system at the Santa Fe River Sink flows through the conduit system and out of the River Rise with little interaction with the surrounding aquifer and little change in its chemical composition (Martin and Dean 2001). Under these conditions, dissolution may be limited to the perimeter of the conduits. During storm events, hydraulic head in the conduits can exceed that in the surrounding aquifer, driving allogenic water into the matrix. The volume of water lost from the conduits was calculated as the difference between the discharge into the Santa Fe River Sink (V_{sink}) and the volume exiting the conduit system at River Rise (V_{rise}) on days that discharge into the sink exceeded from the outflow from the rise (Fig. 3). These daily values were summed for the study period to determine total losses (Table 2). Stage during events 1 and 2 exceeded the maximum measurement of the rating curve; as a result, the estimates of discharge and losses from the conduit are based on extrapolation of the rating curve.

Overall, the loss of allogenic recharge from conduits is small relative to the total volume of inflow in to the River Sink (~2%) and is similar in magnitude to the estimated volume of diffuse recharge. As discussed in the following, water lost from the conduit may have a significant potential impact on the evolution of the aquifer because dissolution is focused in the region surrounding the conduit system.

Water chemistry

Although most of sampled wells are separated by only a few hundred meters (Fig. 1), each is characterized by distinct water compositions. This spatial heterogeneity could be linked to variations in the composition of the

Table 2 Water budget estimates for the study period and for time periods surrounding storm events 1–4

Event	Period	No. of days	P^a (m)	Interception (m)	ET (m)	Diffuse recharge (m)	Volume diffuse recharge (10^8 m ³)	V_{sink} (10^8 m ³)	Losses from conduit system ^b (10^8 m ³)
	1/1/02–31/12/02	365	1.25	0.26	0.63	0.32	0.06–0.22	0.41	0.04
	1/1/03–31/12/03	365	1.42	0.29	0.72	0.46	0.09–0.32	3.08	0.31
	1/1/04–31/12/04	366	1.87	0.22	0.66	0.99	0.20–0.69	6.02 ^c	0.13 ^c
	1/1/05–31/12/05	365	1.33	0.27	0.68	0.37	0.07–0.26	4.47	0.03
	1/1/06–31/12/06	365	0.84	0.15	0.55	0.14	0.03–0.10	1.47	0.03
	1/1/07–31/03/07	90	0.20	0.03	0.15	0.07	0.01–0.05	0.00	0.00
	1/1/02–31/03/07 ^d	1,916	6.91	1.22	3.39	2.35	0.47–1.6	23 ^c	0.54 ^c
1	2/5/03–26/03/03	50	.31	0.02	0.07	0.23	0.05–0.16	2.25	0.28
2	9/2/04–10/11/04	70	0.72	0.05	0.14	0.55	0.11–0.38	5.23	0.13 ^c
3	3/24/05–21/04/05	29	0.15	0.02	0.08	0.08	0.02–0.06	0.93	0.00
4	12/14/05–01/02/06	50	0.31	0.02	0.05	0.21	0.04–0.15	1.09	0.05

^a Precipitation (P) does not equal the sum of evapotranspiration (ET), interception, and recharge due to changes in soil moisture storage during the calculation time period

^b Total losses from the conduit system were estimated from summing losses from days with $V_{sink} > V_{rise}$

^c A gap exists in River Sink stage data during a 2004 event that could cause the estimated Sink input and the loss from the conduit system to be an underestimate

^d Totals for the study period

sediments in the soil and vadose zone, particularly concentrations of organic carbon. The water composition of each well is fairly uniform through 2006–2007 with coefficient of variations (CV = standard deviation/mean) that are similar to the error of the measurements for each well (Table 1). Precipitation composition varies greatly through time as shown by large values of its CV (Table 3). The small temporal variability in water chemistry may reflect limited precipitation over the period of time the wells were sampled (April 2006 to April 2007) and thus limited diffuse input. Saturation state of groundwater with respect to calcite varied between -0.33 to -0.21 SI and averaged -0.28 SI. The saturation index of precipitation was -9.3 with respect to calcite. The large difference in saturation index between precipitation and groundwater suggests that diffuse recharge mixes with groundwater

previously equilibrated with calcite, rapidly equilibrates with calcite in the subsurface, or a combination of these processes.

In the study area, concentrations of Cl^- and Na^+ at the water table are about 8–14 times higher than in the precipitation. The increase in Cl^- and Na^+ concentrations is unlikely a result of dissolution of minerals in the vadose zone, which is thin (4–6 m) and lacks Cl^- and Na^+ bearing minerals, consisting mostly of unconsolidated quartz sands (Miller 1986). Assuming the increase in Cl^- and Na^+ concentration results from evapotranspiration, their elevated concentrations over precipitation reflect a loss of between 86 and 93% of the precipitation, slightly greater than the estimates based on interception and evapotranspiration losses (Table 2). The resulting estimates of recharge (7–14%) are slightly less than estimates of

Table 3 Summary of water samples from shallow wells and precipitation. *n* number of samples

Location		Well 4A <i>n</i> =7	Well 5A <i>n</i> =7	Well 6A <i>n</i> =7	Well 7A <i>n</i> =7	Precipitation <i>n</i> =249
Cl	Range ^a	0.282–0.344	0.310–0.361	0.169–0.225	0.198–0.274	0.0012–0.467
	<i>x</i> ^a	0.331	0.341	0.194	0.225	0.0239
	CV ^b	7	5	10	14	236
SO ₄	Range	0.058–0.164	0.101–0.129	0.264–0.481	0.323–0.427	0.0021–0.0727
	<i>x</i>	0.093	0.117	0.342	0.372	0.0170
	CV	38	9	22	11	74
Ca	Range	2.23–2.59	2.90–3.15	2.21–2.48	1.98–2.40	0.0004–0.0339
	<i>x</i>	2.48	3.02	2.33	2.26	0.0042
	CV	4	3	4	6	113
Na	Range	0.241–0.282	0.237–0.300	0.204–0.342	0.139–0.261	0.0006–0.422
	<i>x</i>	0.256	0.257	0.279	0.190	0.0210
	CV	6	9	15	21	245
Mg	Range	0.065–0.078	0.058–0.063	0.066–0.093	0.060–0.078	0.0001–0.0418
	<i>x</i>	0.071	0.061	0.076	0.070	0.003
	CV	5	4	14	9	211
K	Range	0.0026–0.0099	0.0001–0.0036	0.088–0.240	0.0051–0.0077	0.0001–0.0105
	<i>x</i>	0.0075	0.0020	0.17	0.0063	0.0011
	CV	37	75	29	17	173
Alkalinity	Range	3.90–4.82	4.86–5.68	3.60–4.40	3.04–3.94	- ^c
	<i>x</i>	4.47	5.32	4.01	3.55	-
	CV	7	6	8	8	-
DO	Range	2.75–4.43	0.36–0.99	0.60–0.88	0.23–1.1	-
	<i>x</i>	3.76	0.59	0.76	0.48	-
	CV	18	37	15	63	-
pH	Range	6.51–6.89	6.59–6.79	6.79–6.97	6.90–7.23	3.91–5.54
	<i>x</i>	6.75	6.69	6.86	7.02	4.65
	CV	2	1	1	2	6
Temp.	Range	20.8–21.5	20.9–21.7	19.2–21.4	20.4–21.4	-
	<i>x</i>	21.1	21.2	20.4	20.8	-
	CV	1	1	4	1	-
SpC	Range	460–515	543–584	458–504	400–470	0.8–57
	<i>x</i>	490	570.14	479.71	440.00	16
	CV	4	2	4	6	54
SI _{cal}	Range	-0.54–-0.13	-0.33 to -0.10	-0.38 to -0.13	-0.33–0.09	-
	<i>x</i>	-0.33	-0.25	-0.31	-0.21	-9.3
	CV	n/a ^d	n/a	n/a	n/a	n/a
Log P _{CO2} ^e	Range	-1.45– -1.11	-1.30 to -1.12	-1.58– -1.45	-1.88 to -1.60	-
	<i>x</i>	-1.35	-1.22	-1.51	-1.72	-3.5
	CV	8	5	3	6	-

^a Range and mean (*x*) in mmol/kg H₂O, except for DO in mg/L, Temp. in °C, SpC in μS/cm, pH, and SI_{cal}, are unitless and P_{CO2} is in atm

^b Coefficient of variation (CV) in percent

^c (-) is not measured

^d Not applicable due to possibility of both positive and negative values

^e Log P_{CO2} for precipitation assumed in equilibrium with atmosphere

recharge based on Cl^- concentrations at the water table in Bermuda, which found ~25% of precipitation recharged the aquifer (Vacher and Ayers 1980).

Assuming Cl^- and Na^+ are conservative, relative changes in other solute concentrations would reflect reaction with aquifer minerals. In this setting, the most likely process to alter water chemistry would be dissolution of calcite. The total amount of calcite dissolution was estimated by increasing concentrations of non-conservative solutes expected from evapotranspiration in the water based on differences in Cl^- and Na^+ concentrations in precipitation and groundwater. The mass of calcite dissolution was estimated to produce Ca^{2+} and P_{CO_2} concentrations required to reach saturation with calcite.

Following these calculations, estimated concentrations of some major components, including K^+ , Mg^{2+} , and SO_4^{2-} differ from their observed values, reflecting additional reactions between the water and the aquifer materials. There is no systematic difference in the discrepancies between modeled and observed values (Table 4). These components could be controlled by other processes that are not included in the model estimates, such as vegetative uptake (e.g., K^+), sources from non-stoichiometric calcite (e.g., Mg^{2+}) or dissolution of minerals other than calcite (e.g., Mg^{2+} and SO_4^{2-}), and sorption to mineral surfaces in the soil zone (e.g., K^+ and Mg^{2+}). While the chemical compositions of water differ between each well, the amount of calcite and CO_2 that were required to change precipitation composition to match the measured groundwater chemistry is similar among the wells with averages of 2.1×10^{-4} and 3.1×10^{-4} moles/kg of water, respectively.

Discussion

The influence of diffuse recharge on the water budget and water-rock reactions has often been neglected in karst systems because much recharge in telenetic karst regions is allogenic or is recharged through discrete fractures (e.g., Greene 1997; Bailly-Comte et al. 2007; Jourde et al. 2007). Furthermore, diffuse recharge can be

difficult to quantify, and methods that assess long-term average rates fail to reflect the significant variations through time. To understand this temporal variability, a daily water budget calculation was used that incorporated the Penman-Monteith model (Eq. 1) to estimate evapotranspiration, with LAI adjusted to match estimates of long-term average recharge.

Although the diffuse recharge in this study was constrained to average ~46 cm/year from 2002 to 2006, or 34% of precipitation, the relationship between recharge and precipitation varies significantly through time. Recharge is only 17% of precipitation in the driest year (2006), while it reaches ~53% of precipitation in the wettest year (2004). Although there is feedback between precipitation and evapotranspiration through soil moisture, which is included in the ET calculation, evapotranspiration does not change linearly with precipitation. A much lower percentage of precipitation is lost to interception and evapotranspiration when it falls in high intensity events rather than smaller, temporally distributed events (Fig. 3).

Comparison to estimated recharge ratios derived from groundwater chemistry from April 2006 to March 2007, when precipitation was very low, suggests that the water-budget method reported here may slightly overestimate net recharge during this time period. It is possible that the long-term average (46 cm/year) used to adjust the ET parameters is an overestimate. Alternatively, there might be greater temporal variability than suggested by this study, with diminished percentage of precipitation recharged during low precipitation periods such as during April 2006 to March 2007, and a greater percentage during high precipitation periods.

It is notable that >40% of the diffuse recharge calculated for the entire study period occurred during 2004 when two major hurricanes passed over the region. This observation shows the importance of extreme events to the water budget and potentially to dissolution. This conclusion is consistent with observations by Florea and Vacher (2007) indicating that significant recharge occurred due to the Fall 2004 hurricanes, whereas summer storms provided little recharge. The importance of tropical systems for aquifer recharge should be considered in hydrologic studies and

Table 4 Precipitation water composition modified by estimates of evapotranspiration and calcite dissolution compared to measured water composition at top of the saturated zone

		Alkalinity	Ca	Cl	K	Mg	Na	SO ₄	pH	Calcite ^a	CO ₂ (g) ^a
		mmol/kg H ₂ O								mole/kg H ₂ O	
Well 4A	Modeled composition	4.52	2.47	0.330	0.015	0.0345	0.290	0.234	6.75	-1.8×10^{-4}	-2.6×10^{-4}
	% difference	1	-0.2	-0.3	102	-51	13	152	0.02		
Well 5A	Modeled composition	5.41	2.92	0.341	0.016	0.0356	0.299	0.242	6.69	-2.0×10^{-4}	-3.3×10^{-4}
	% difference	2	-3	0	710	-41	16	107	0		
Well 6A	Modeled composition	4.08	2.17	0.194	0.0089	0.0203	0.170	0.138	6.87	-2.6×10^{-4}	-3.8×10^{-4}
	% difference	2	-7	0	-95	-73	-39	-60	0		
Well 7A	Modeled composition	3.69	1.99	0.225	0.010	0.0235	0.198	0.160	7.04	-2.1×10^{-4}	-2.5×10^{-4}
	% difference	-4	14	0.14	-39	199	-4	132	-0.2		
Average										-2.1×10^{-4}	-3.1×10^{-4}

^a Amount of mass transfer from aquifer minerals and atmosphere to water at the top of the saturated zone. *Negative sign* denotes uptake into water to achieve measured SI_{cal} and $\log P_{\text{CO}_2}$ at each well (Table 3)

may be a factor in predictions of impacts of future climate change on water resources in this region.

The balance between diffuse recharge and allogenic input (flow into River Sink) varies with hydrologic conditions. Inflow to the River Sink was significantly greater than diffuse recharge except during January to March 2007 when River Sink contributions were negligible and diffuse recharge was the primary contributor to outflow at the River Rise. Although the volume of allogenic input is high, only 2% of it was estimated to be lost from the conduits to the matrix; this occurred during the storm events when hydraulic heads in the conduit were temporarily greater than in the surrounding aquifer (Table 3).

The loss of water from the conduit reflects the relationship between conduit hydraulic heads, which are controlled by input into the River Sink, the hydraulic properties of the conduit system, and aquifer hydraulic heads, which are impacted by diffuse recharge and time scales of exchange with the conduit system. Although it was not the largest event in terms of precipitation or river stage, storm event 1 shows the largest amount of water lost from the conduit system to the surrounding aquifer (Table 2). This event had a similar amount of diffuse recharge as event 4, but shows ~5 times greater loss of conduit water to the surrounding aquifer. One cause for the difference could be antecedent water level. Diffuse recharge raises hydraulic head in the aquifer and will result in less inflow to the aquifer from the conduits. Accordingly, heavy precipitation following an extended drought (such as occurred in late 2002) will lead to greater losses from the conduit system than if aquifer water levels are elevated before the conduit flood wave passes through. An additional factor will be distribution of precipitation. If precipitation is heavier in the confined portion of the Santa Fe River Rise Basin than in the unconfined region surrounding the conduit, conduit losses will be greater than if precipitation is evenly distributed.

Dissolution of UFA from diffuse and allogenic recharge

The potential for dissolution of the UFA from diffuse recharge can be estimated by combining the recharge volume with the estimated change in saturation state as precipitation is altered by reactions to the compositions found at the water-table. The estimated diffuse recharge between 1 January 2002 and 31 March 2007 was 2.35 m (Table 2) and the average amount of calcite that would dissolve to alter precipitation composition to that found at the top of the saturated zone is 2.1×10^{-4} mole/kg of H_2O (Table 4). Assuming this magnitude of dissolution occurred over the period for which diffuse recharge has been estimated, approximately 0.5 moles of calcite per m^2 per unit area would be dissolved by diffuse recharge across the unconfined area of the basin. The molar volume of calcite is $3.69 \times 10^{-5} m^3$, and assuming porosity is 30%, denudation rates from diffuse recharge to the unconfined aquifer would have averaged approximately $2.6 \times 10^{-5} m$

over the 5 years of the study or about $5.0 \times 10^{-6} m/year$. Over the estimated area of unconfined aquifer contributing to the River Rise (~20–70 km^2), total dissolution due to diffuse recharge during the study period would be about 5.2×10^2 to $1.8 \times 10^3 m^3$. The water table in this study area averages about 4 m bgs (Table 1) and the sediments above the UFA consist primarily of quartz sands. Thus, most of the calcite dissolution occurs at the top of the UFA when the water table occurs within the overlying quartz sands or at the top of the saturated zone when the water table lies below the top of the UFA.

Estimated water losses from the conduits are $0.54 \times 10^8 m^3$ over the study period, similar in magnitude to the estimated diffuse recharge in the unconfined springsheds (Table 2). During high flow, water is lost from the conduit typically has a SI of <-4 (Martin and Dean 2001). Sreaton et al. (2004) used this value to estimate between 1 and 1.7×10^{-4} mole of calcite dissolved per kg of H_2O . Because the time that the conduit water remains in the matrix is not known, it is possible that it does not reach equilibrium; thus this assumed dissolution is an upper bound. This mass of dissolution by allogenic water equilibrating with calcite is less per kg of water than diffuse recharge, which is unexpected considering that the allogenic water typically has high values of P_{CO_2} and is highly tannic with large concentrations of organic acids. Assuming 1.7×10^{-4} moles calcite per kg H_2O was dissolved by conduit water lost to the matrix, a total of about 1×10^7 moles of calcite would be dissolved during the study period. Using the molar volume of calcite ($3.69 \times 10^{-5} m^3$) an estimated porosity of 30%, about $5 \times 10^2 m^3$ of aquifer would dissolve. This volume is similar in magnitude to the amount of dissolution estimated to result from diffuse recharge. Because large storm events account for most of the diffuse recharge during the study period and almost all of the losses of water from conduit to matrix occur during and following the major storm events (Table 2; Fig. 3), most secondary porosity formed in the region will be caused by these storm events.

The morphology of porosity increase will vary depending on whether diffuse recharge and allogenic recharge cause dissolution. Dissolution from diffuse recharge will be distributed across the region where the aquifer is poorly confined or unconfined, but should be broadly distributed across the water table. In contrast, dissolution from allogenic recharge will occur adjacent to the conduits or in the aquifer rocks invaded by conduit water following storm events. The allogenic water will advance further into the formation where preferential pathways exist, as suggested by the relationship between estimates of transmissivity and the scale over which the estimates are made (Martin et al. 2006). The form of the dissolution voids from diffuse and allogenic recharge will differ considerably, with diffuse recharge causing ramiform and spongework voids, concentrated at the water table (Ford and Williams 2007), while allogenic recharge would cause rudimentary branchwork caves (e.g., Palmer 1991) such as those mapped at this study area.

Summary

Daily diffuse recharge to an unconfined region of a karst aquifer was approximated for a ~5-year period with a water budget method. Results of these calculations illustrate the magnitude of diffuse recharge varies through time depending on precipitation and evapotranspiration. In this example, estimated diffuse recharge varies from 17% of precipitation during a low precipitation year to >53% during the highest precipitation year. The highest precipitation year (2004) accounted for >40% of the estimated diffuse recharge during the 5-year study period, with the majority of the 2004 recharge due to two tropical storms. The high variability of diffuse recharge, as well as the importance of storm events to aquifer recharge, is often obscured by use of long-term averages in hydrologic studies.

Through the ~5 years of data, total allogenic input is significantly larger than the estimated diffuse recharge volume; however, most of the allogenic recharge flows through the conduits discharging at the River Rise with little interaction with the surrounding aquifer. Calculated losses from the conduit to the surrounding aquifers during storm events were only small percentages (0 to ~10%) of the total allogenic recharge during those events. The volume of rock dissolved by diffuse recharge is estimated to be $5.2\text{--}18 \times 10^3 \text{ m}^3$; however, dissolution from diffuse recharge is expected to occur over an area significantly larger than from allogenic recharge, which will be focused within preferential flow paths within the aquifer. Consequently, diffuse recharge should result in more dispersed dissolution at the water table rather than dissolution concentrated at the boundaries of the conduits and high-permeability zones connected to the conduits.

Results of this study illustrate the contribution of diffuse recharge to an unconfined karst region, despite the presence of a large conduit system with allogenic recharge. This diffuse recharge will impact water budgets and dissolution patterns. As a result, it should be considered in aquifer management and springshed protection. Furthermore, understanding of recharge timing is necessary to infer aquifer hydraulic properties from precipitation response (Florea and Vacher 2007). Although these results are particularly applicable to eogenetic karst aquifers, it may also be important for telogenetic karst aquifers that exhibit diffuse flow behavior due to distributed fractures.

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