

VARIATIONS IN THE DISCHARGE AND ORGANIC MATTER CONTENT OF STALAGMITE DRIP WATERS IN LOWER CAVE, BRISTOL

ANDY BAKER,¹ WILLIAM L. BARNES² AND PETER L. SMART³

¹*University of Exeter, Department of Geography, Amory Building, Rennes Drive, Exeter, EX4 4RJ, UK*

²*University of Exeter, Department of Physics, Stocker Road, Exeter, EX4 4QL, UK*

³*University of Bristol, Department of Geography, University Road, Bristol, BS8 1SS, UK*

ABSTRACT

Six drip waters, which were actively depositing stalagmites in Lower Cave, Bristol, were analysed both for discharge and luminescence properties. Drip discharges were determined for two different years, and show a complex response to surface precipitation variations. Inter annual variability in drip discharge is demonstrated to be significantly higher than intra-annual variability, and discharge was demonstrated both to increase and decrease non-linearly with increased precipitation. Drip waters demonstrate a correlation between their luminescence intensity and drip discharge, with increased luminescence in winter as more organic matter is flushed through the aquifer. The strength of the relationship between luminescence intensity and discharge increases with increased discharge. The results presented here have implications for the palaeoenvironmental interpretation of annual growth laminae and the growth rates of stalagmite samples. © 1997 John Wiley & Sons, Ltd.

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INTRODUCTION

Detailed investigation of the relationship between precipitation and discharge for slow cave drips is required to provide important information for the characterization of karst aquifers. Flows within the unsaturated zone are recognized to be very varied, ranging from slow drips to considerable flows, with a wide range of discharge variation and a complex dependence on both surface precipitation and evaporation, soil moisture storage, surface detention, the subcutaneous zone storage and the geological characteristics of the aquifer; see Figure 1 (from Smart and Friedrich, 1987). This latter theorization is the most complex of many attempts to categorize karst groundwater flow (see also work by Gunn, 1981; Williams, 1983; Atkinson, 1985). Smart and Friedrich (1987) classify the hydrological characteristics of inlet flows in one cave system (G.B. Cave, Mendip Hills, England) by their maximum discharge and discharge variability (Figure 1). For example, seepage flows have relatively low discharge and coefficient of variation, and often exhibit seasonal variations in discharge related to storage replenishment in winter followed by recession in the periods of soil moisture deficit. Shaft and vadose flows have higher coefficients of variation and higher discharge, often with a more peaky, storm response. Subcutaneous flows have high coefficients of variation owing to their intermittent action, and are commonly found in the top 30 m of the aquifer, which is more highly fissured. Using this classification system, drip feeds to stalagmites, with a typical observed drip rate of 1 drip every 1–1000 s ($0.0005\text{--}0.5\text{ l h}^{-1}$), should fall into the seepage flow category and exhibit continuous flow with low variability. Such low discharge flows were not analysed by Smart and Friedrich (1987) in their study.

As well as providing important information as to the hydrological characteristics of karst aquifers, the measurement of stalagmite drip discharge is also important in a palaeoclimatological context. Recent

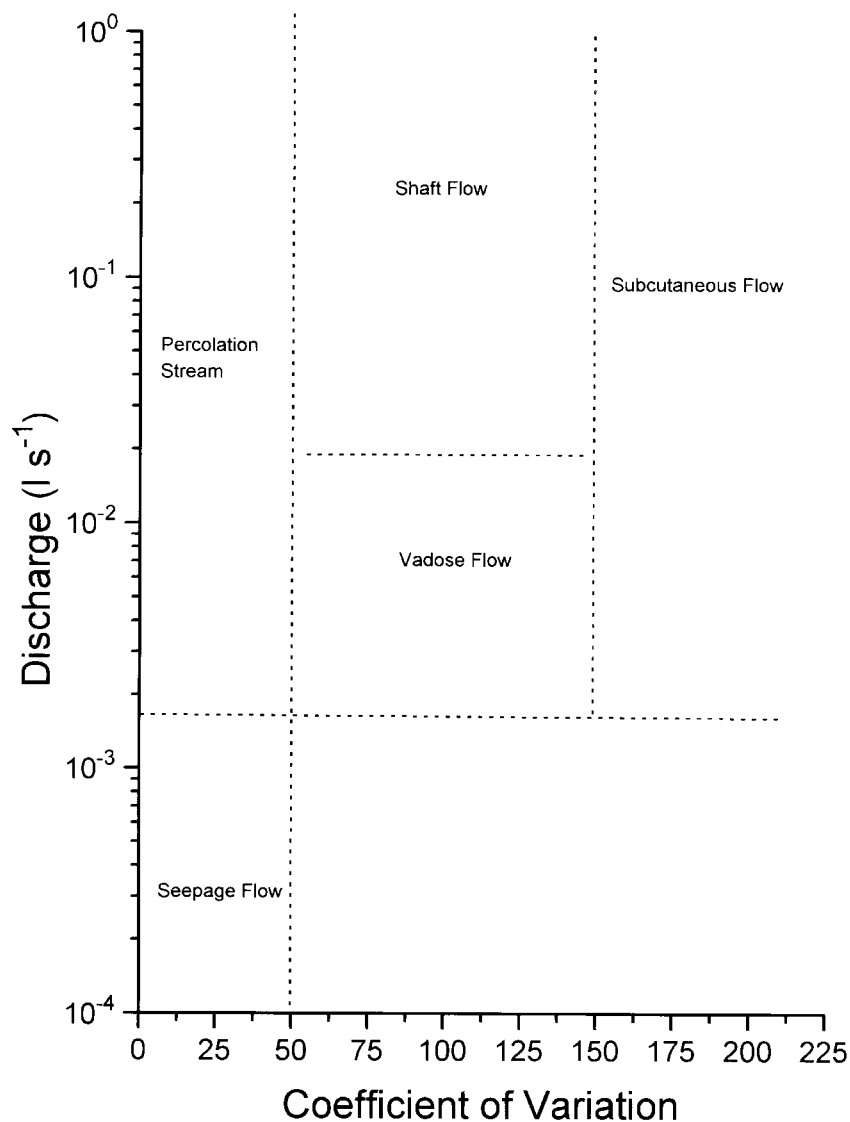


Figure 1. Classification of karst groundwater flow types from their discharge and discharge variability. From Smart and Friedrich (1987)

advances in the development of high resolution records of environmental change from cave stalagmites include the measurement of visible and luminescent annual bands (Genty, 1992; 1993; Baker *et al.*, 1993, 1995a; Railsback *et al.*, 1994; Shopov *et al.*, 1994; Genty *et al.*, 1996). Banding in stalagmites is generally caused by the presence of humic and fulvic acids, which alter both the visible optical properties as well as the luminescence of the samples when excited by ultraviolet light. In some instances variations in the width of the annual laminae have been demonstrated to correlate with annual variations in precipitation (Railsback *et al.*, 1994; Genty and Quinif, 1996), and differences in the structure of the brightness of the banding have been suggested to correlate with seasonal variations in precipitation (Genty *et al.*, 1997a). Stalagmites have the advantage of being datable by uranium series techniques, with a precision of up to 1% by thermal ionization mass spectrometry (Edwards *et al.*, 1987), and thus the annual records can be temporally constrained and

provide high resolution records of palaeoprecipitation change for the last 300 000 years. The latter is particularly significant as palaeoprecipitation has generally proved difficult to determine from other palaeo-environmental indicators. In order to obtain a better understanding of the palaeoenvironmental records contained within the annual banding of stalagmites, calibration experiments need to be undertaken for samples that are actively forming and for which precipitation and discharge measurements can be undertaken. Such data has not been frequently collected for two reasons. First, the discharge on to stalagmite samples is very low, with typical values in the range of 1 drip every 5–1000 seconds. With a typical drip volume of $0.17 \pm 0.05 \text{ cm}^3$, this is equivalent to a discharge of $3 \times 10^{-5} - 2 \times 10^{-7} \text{ l s}^{-1}$. Such low discharges limit the water sample size available for collection for chemical analysis (100 ml of water can take 24 hours to collect), and limits the use of geochemical variations as an aid to flow characterization as a result of samples degassing during collection. Secondly, although many studies have been undertaken on the intra-annual variability of discharge on to stalagmites (see, for example Pitty, 1966; 1974; Stenner, 1973), to our knowledge, only one has considered interannual variations (Genty *et al.*, 1997b).

In order to determine the relationship between the drip discharge on to stalagmites and precipitation change, and its palaeoenvironmental applications to annually laminated stalagmites, data were collected from Lower Cave, Bristol, England. Discharge data were collected over two annual field cycles; the first in 1991–1992, after five years of below average precipitation; the second in 1994–1995, after three years of above average precipitation. Over the second annual cycle, samples were also collected for luminescence and total organic carbon (TOC) analysis, in order to determine the relationship between annual luminescence banding preserved in stalagmites and their hydrological characteristics.

SITE DESCRIPTION

Lower Cave, Bristol ($51^\circ 27' \text{ N}$, $02^\circ 36' \text{ W}$; National Grid Reference ST566732) is a short 18 m long cave in Lower Carboniferous limestone (Figure 2). This limestone is massive, well jointed, pure limestone dipping at 40° ; the cave follows a weakness along a bedding plane in the direction of dip. The cave contains both active

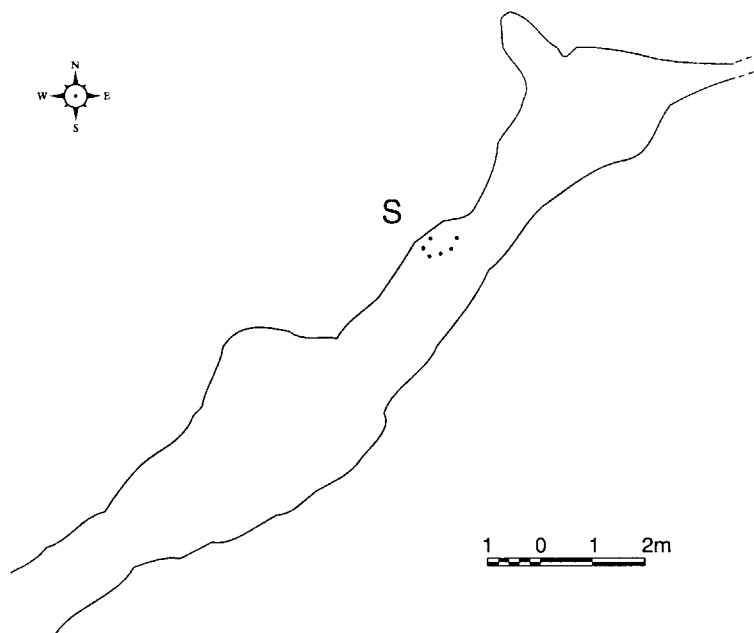


Figure 2. Survey of Lower Cave, Bristol. Location of sample sites LC-1 to LC-6 are labelled by 'S'

and inactive flowstone and stalagmite deposits, the former including recent samples that have been deposited over the last 50 years, since the cave was last used as a storage site. The cave contains a high density of drip sources (an average straw stalactite density of 7 samples m^{-2}), the drip sources did not appear to be associated with fissures or fractures and are thus likely to be associated with intergranular storage. The overlying surface consisted of a steeply inclined cliffed slope (at a 50° angle), which comprised of 50% bare rock and 50% vegetation cover, the latter of scrub (50% of total vegetation; *Rubus fruticosus* agg, *Syringa vulgaris*, *Crataegus monogyna*, etc.), tall calcareous grassland (40% of total vegetation; *Bromopsis erecta*, *Festuca rubra*, *Veronica spicata*, etc.) and short calcareous grassland (10% of total vegetation; *Thymus praecox*, *Plantago lanceolata*, etc.). The soils over the cave consisted of 1–5 cm of humic layer, with occasional litter layers and rooting throughout. The climate of the region is cool temperate oceanic, with a 30-year mean annual precipitation of 842 mm with a winter maximum, and a mean annual temperature of 10.0°C with a winter minimum of 3.9°C (January) and a summer maximum of 16.5°C (July). In summer, evaporation exceeds precipitation.

Seven drip sites (LC-1, LC-2, LC-3, LC-4, LC-5, LC-6a, LC-6b) were analysed within the back 5 m of the cave, the sites chosen were such that the drip water would have passed through a significant volume of limestone (> 15 m) (Figure 2). The drip waters all originated from actively depositing straw stalagmite sources; the straws were within a 2 m^2 area but were not visibly connected hydrologically. Each drip had an associated actively forming stalagmite deposit of 4–6 cm in diameter, which was being deposited on a man-made gravel floor emplaced when the site was used as a store.

EXPERIMENTAL METHOD

The hydrological characteristics of the drip feeds supplying the seven stalagmites were measured over the course of two annual field cycles, the first of which covered the period July 1991–August 1992 (with a two month gap in May and June 1992 when the first author was unable to collect data), and the second between March 1994 and April 1995. Discharge measurements were made at 2–3 weekly intervals throughout these time periods by taking multiple readings of the elapsed time between drips and then taking the average to get a measure of drip rate, assuming a constant drip volume of 0.17 cm^3 (the measured average volume of drips at the site). In 1994–1995, 10–25 ml water samples were collected in glass bottles (the time for collection averaged 4–8 hours), before being preserved for organic matter analysis by freezing. In order to determine the relationship between discharge and organic matter, measurements were made of both drip water luminescence properties and total organic carbon (TOC) content (the volume of sample collectable in 8 hours being too small to allow direct measurement of humic and fulvic acid concentration). Although absorption at 360 nm has been correlated with TOC in river and peat waters (Grieve, 1985), such a relationship has not been demonstrated for either the absorption or luminescence of cave drips. Therefore, luminescence was measured by analysing water samples with an ultraviolet (325 nm, HeCd) laser; water samples were held in 5 ml UV transparent cuvettes and the luminescence intensity at 420 nm was collected using a photomultiplier. TOC analyses were performed on 10 ml water samples using a standard TOC analyser.

RESULTS AND INTERPRETATION

Stalagmite Discharge Data 1991–1992

The drip discharges for the seven sample sites, together with the precipitation record, are presented in Figure 3, and data on the mean discharges and cross-correlations of discharges between drip sites are presented in Tables I and II, respectively.

Figure 3 demonstrates that there is no response of drip rate to summer storm events owing to the increased evaporation, and hence soil moisture deficit, at the time, and that there is a slight lag between winter precipitation and an increase in drip discharge. Visual examination of the figure suggests that an increase in

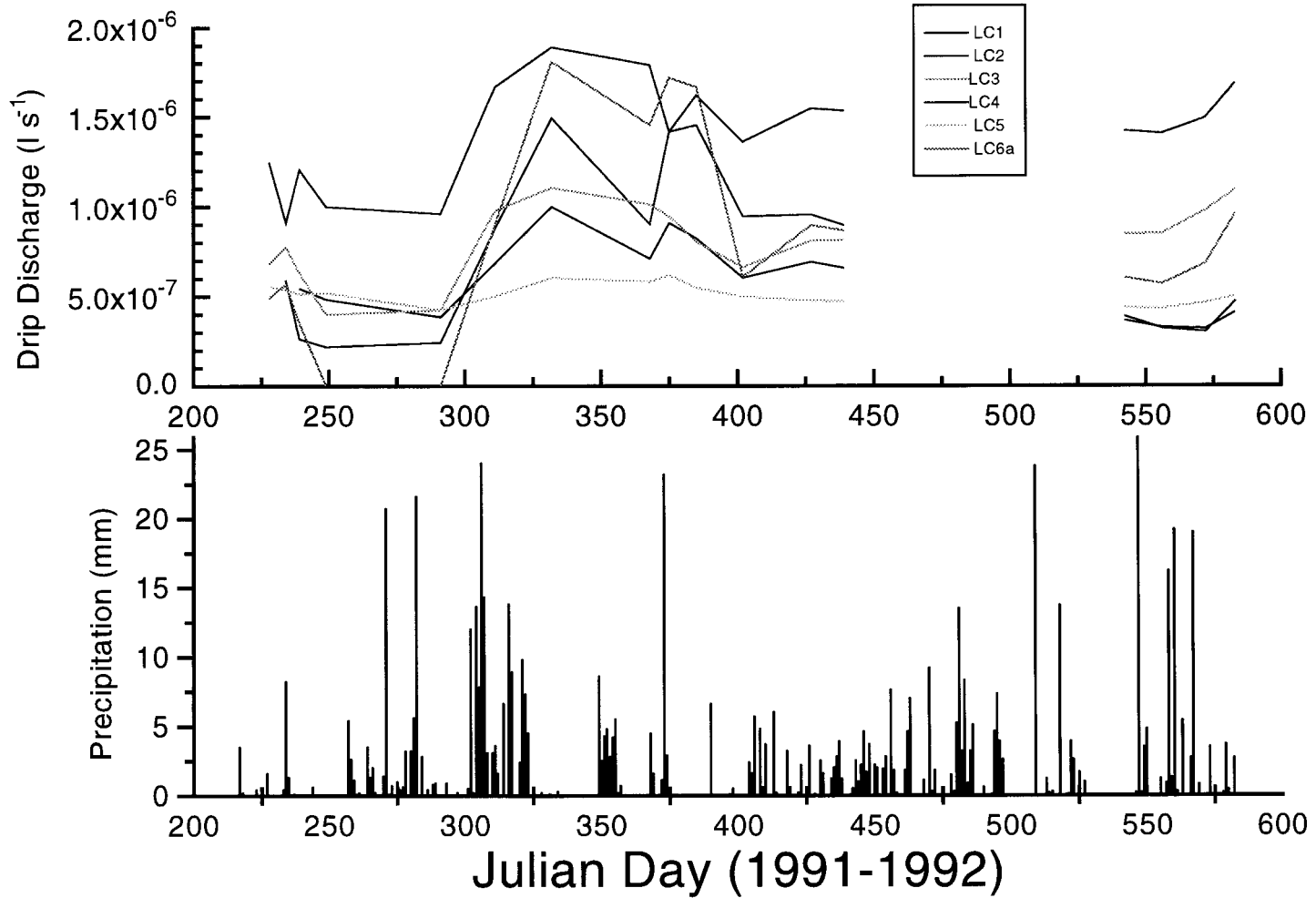


Figure 3. Daily precipitation for the period 1991–1992, together with the drip discharge for samples LC-1 to LC-6

Table I. Descriptive statistics for Lower Cave sites in 1991–1992 and 1994–1995

Site	Discharge 1991–1992 ($\times 10^{-7}$ l s $^{-1}$)				Discharge 1994–1995 ($\times 10^{-7}$ l s $^{-1}$)				Change in discharge between 1991–1992 and 1994–1995
	<i>x</i>	1 σ	CV	<i>n</i>	<i>x</i>	1 σ	CV	<i>n</i>	
LC-1	6.07	2.21	36%	13	0.80	0.61	77%	16	$\times 0.13$
LC-2	7.84	4.66	59%	13	55.2	57.5	104%	18	$\times 7.05$
LC-3	8.18	2.14	26%	16	22.7	24.8	109%	18	$\times 2.78$
LC-4	14.2	2.94	21%	16	35.1	53.8	153%	18	$\times 2.47$
LC-5	5.24	0.61	12%	16	6.26	2.64	42%	18	$\times 1.19$
LC-6a	8.47	5.64	67%	16	30.6	24.0	79%	16	$\times 3.61$
LC-6b	dry		—	16	35.1	24.4	70%	18	

Table II. Cross-rank correlations on drip discharge data for Lower Cave, 1991–1992

	LC-1	LC-2	LC-3	LC-4	LC-5
All year					
LC-2	0.850				
LC-3	0.278	0.371			
LC-4	0.523	0.546	0.870		
LC-5	0.816	0.500	0.278	0.296	
LC-6a	0.729	0.826	0.801	0.866	0.483
Winter					
LC-2	0.786				
LC-3	0.536	0.036			
LC-4	0.464	0.107	0.857		
LC-5	0.821	0.429	0.571	0.357	
LC-6a	0.964	0.679	0.607	0.536	0.893
Summer					
LC-2	−0.457				
LC-3	−0.533	0.639			
LC-4	−0.344	0.074	0.800		
LC-5	0.714	0.029	0.000	0.050	
LC-6a	−0.445	0.679	0.979	0.828	0.142

winter drip discharge occurs between December and March (Julian days 334–420), and that this is 1–2 months after the first increase in precipitation. Lagged correlation coefficients between precipitation and drip discharge demonstrate statistically significant lags of between 24 and 30 days for all six sites (LC-1 to LC-6a; $0.54 < r < 0.67$; $n = 16$; statistically significant at a 95% confidence level).

Over the course of 1991–1992, only six of the seven sites were hydrologically active, with no discharge from LC-6b (Table I). LC-4 had a statistically higher discharge than all the other sites at a 95% confidence level, all other sites having statistically similar discharge characteristics (determined using Mann–Whitney *U* statistic). Most discharges were in the range expected for seepage flows (Figure 1). The coefficients of variation of discharge varied between 11.7 and 66.7%; there is no correlation between the coefficient of variation of discharge and discharge ($r = -0.063$). LC-5 had the lowest CV (coefficient of variation) and demonstrated little seasonal variation in discharge. Similar results have been observed for seepage flows by Smart and Friedrich (1987), explained by substantial storage maintained by seasonal recharge, yet only minor changes in the head driving flow. All of the drip sources remained hydrologically active for the whole year, with the exception of LC-6a, which was dry for the summer months. This is reflected in the high CV of this site, which falls outside the range of seepage flows of Smart and Friedrich (1987); see Figure 1. Instead,

Table III Cross-rank correlations on drip discharge data for Lower Cave, 1994–1995

	LC-1	LC-2	LC-3	LC-4	LC-5	LC-6a
All year						
LC-2	0.822					
LC-3	0.897	0.907				
LC-4	0.857	0.914	0.938			
LC-5	0.842	0.882	0.880	0.920		
LC-6a	0.819	0.963	0.930	0.951	0.865	
LC-6b	0.748	0.934	0.887	0.894	0.828	0.938
Winter						
LC-2	0.569					
LC-3	0.867	0.728				
LC-4	0.767		0.717			
LC-5	0.600	0.452	0.383	0.567		
LC-6	0.555	0.814	0.714	0.824	0.261	
LC-7	0.418	0.832	0.628	0.653	0.293	0.861
Summer						
LC-2	0.799					
LC-3	0.849	0.667				
LC-4	0.699	0.767	0.917			
LC-5	0.858	0.867	0.933	0.950		
LC-6a	0.860	0.900	0.850	0.883	0.950	
LC-6b	0.612	0.548	0.548	0.548	0.548	0.548

this has the discharge variability characteristics of subcutaneous flows yet at a lower discharge, and can be classified here as a seasonal drip.

The degree of cross-correlation between the individual sites show significant variation, both for annual and seasonal (summer and winter) data (Table II). Taking the year as a whole, most of the drips are correlated at a statistically significant level, the exception being LC-3, which is only weakly correlated with LC-1, LC-2 and LC-5, and the weak correlation between LC-4 and LC-5. LC-1 and LC-2 demonstrate the strongest correlation, suggesting a strong hydrological connection. When seasonal data are taken into consideration, the statistically significant cross-correlations persist in winter, but for most sites break down in the summer. This suggests that at this time the groundwater flow system for these sites is decoupled from the precipitation input, although significant variability in the cross-correlations demonstrates between-site variability with significant between-site differences in head or lag time to precipitation change.

Stalagmite Discharge Data 1994–1995

Drip discharge and precipitation data for 1994–1995 are presented in Figure 4, and data on the mean discharge and cross-correlations within the discharge data are given in Tables I and III, respectively.

In Figure 4 it is apparent that there is a rapid response to winter precipitation, an observation confirmed when the lagged correlation coefficients between precipitation and drip discharge are calculated. All sites demonstrate a lag between precipitation and discharge, with the best correlation with lags of the average total precipitation between 1–6 and 1–20 days ($0.618 < r < 0.799$; $n = 18$; all significant at a 95% confidence level).

Over the course of 1994–1995, all seven drip sources were hydrologically active (Table I). Mean discharges fell into three separate groups; LC-1 had a discharge that was statistically lower than all other sites; LC-5 had a statistically lower discharge than LC-2, -3, -4, -6a and -6b (Mann–Whitney U statistic). All sites remained hydrologically active throughout the year except LC-6b which only became active once the discharge through LC-6a exceeded $1.7 \times 10^{-6} \text{ l s}^{-1}$. Once active, the two sources were strongly linearly correlated

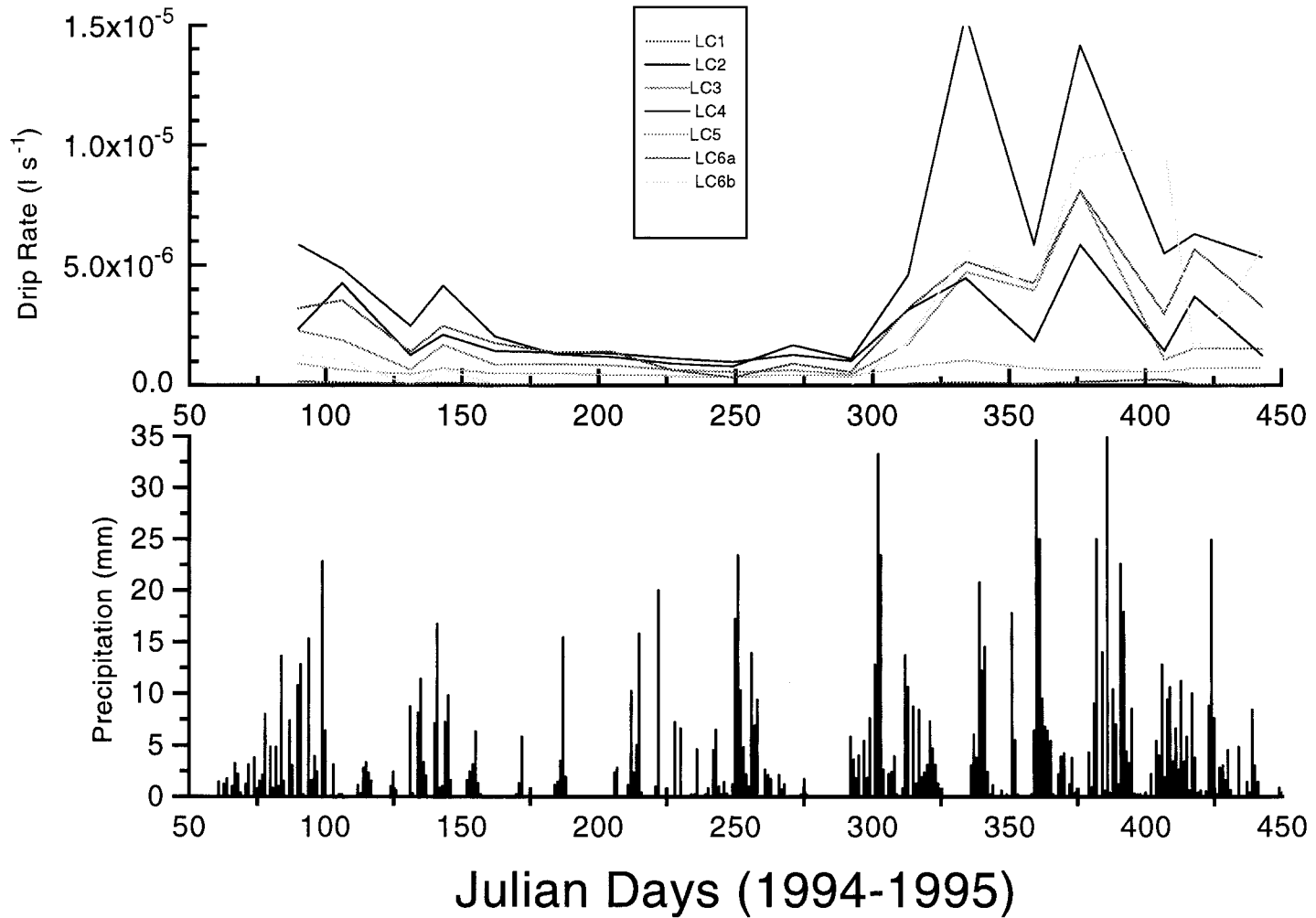


Figure 4. Daily precipitation for the period 1994-1995, together with the drip discharge for samples LC-1 to LC-6

Table IV. Relationship between mean annual discharge and degree of correlation of luminescence with discharge for Lower Cave, 1994–1995. The correlation coefficient is strongly correlated to the discharge ($r = 0.951$, $n = 5$)

Sample	Mean annual discharge ($\times 10^{-7} \text{ l s}^{-1}$)	Mean annual luminescence (units)	Correlation between discharge and luminescence	Significance level
LC-2	45.4 \pm 44.5	13.34 \pm 4.47	0.937 ($n = 16$)	99%
LC-3	18.5 \pm 20.5	12.12 \pm 1.25	0.538 ($n = 16$)	95%
LC-4	20.9 \pm 14.4	12.22 \pm 1.32	0.519 ($n = 15$)	95%
LC-5	5.8 \pm 1.9	10.62 \pm 1.55	-0.357 ($n = 15$)	None
LC-6	27.1 \pm 21.7	12.20 \pm 2.47	0.415 ($n = 16$)	90%

($r = 0.99$, $n = 10$, significant at a 99% confidence level), and demonstrate the presence of overflow characteristics at a low discharge and local scale. Coefficients of variation for all sites were high, ranging between 42 and 153%, with no relationship between the coefficient of variation of discharge and discharge ($r = 0.520$, $n = 7$, not statistically significant). The observed range of discharge and CV place all but LC-5 outside the range classifiable as 'seepage flows' in Figure 1.

Cross-correlations between the seven drip sites are presented in Table III. All sites are correlated at a statistically significant level throughout the year, although the relationship is weakest for LC-5 in winter. This suggests a different mode of operation of this site during the winter months compared with the other drips. This is confirmed by the data presented in Figure 4, which show very little seasonal variation in discharge at this site, as was also the case in 1991–1992.

Comparison of Discharge Records

Precipitation data for Bristol were provided from the Bristol Meteorological Office (National Grid Reference ST585727); the 10-year trend is presented in Figure 5. The 1991–1992 field cycle occurred after five years of below average precipitation (1.3–15.8% below the 12-year mean), whereas the 1994–1995 cycle followed three years of above average precipitation (4.9–23.9% above the 12-year mean). The response of the seven sites to the difference in long-term precipitation between 1991–1992 and 1994–1995 is presented in Table I. (Comparison with evapotranspiration was not undertaken owing to the large uncertainties associated with its determination.) Discharge at six of the seven sites increased with increasing precipitation, although this increase in discharge varied by between 119 and 278%. One site, LC-6b, went from being hydrologically inactive to having limited activity dependent on LC-6a. LC-6a went from being hydrologically inactive in summer in 1991–1992 to being active throughout the year in 1994–1995. One site (LC-1) decreased to 13.2% of its former discharge in 1994–1995. The variability of discharge also increased with increased annual precipitation. Differences in the lag time between precipitation and discharge are also noticeable; in 1991–1992 statistically significant lags occur at 24–30 days; in 1994–1995 these occur at between 1–6 and 1–20 days. The cross-correlations between the sites also vary between years; there are generally stronger correlations for annual data between sites in 1994–1995 compared with 1991–1992, and this persists for both summer and winter data. In 1991–1992, cross-correlations break down for the lower discharge summer period.

The variations in the hydrological response to precipitation change can be explained by the characteristics of karst aquifers (Figure 1). In particular, the variability of response between sites is typical of the variability of flow in the unsaturated zone. Changes in the hydrological connectivity, reflected in the loss of cross-correlations for many sites in the summer of 1992, demonstrates the importance of evaporative loss from the surface and the presence of a decoupling between the unsaturated zone and surface precipitation. The discontinuous cover at the site suggests that this evaporative loss may occur from the groundwater system as well as from soil moisture. Lag times between discharge and precipitation are long in comparison with an inlet feeding a flowstone at the site, which had a mean discharge in 1994–1995 of $5.4 \pm 7.0 \text{ l s}^{-1}$, and

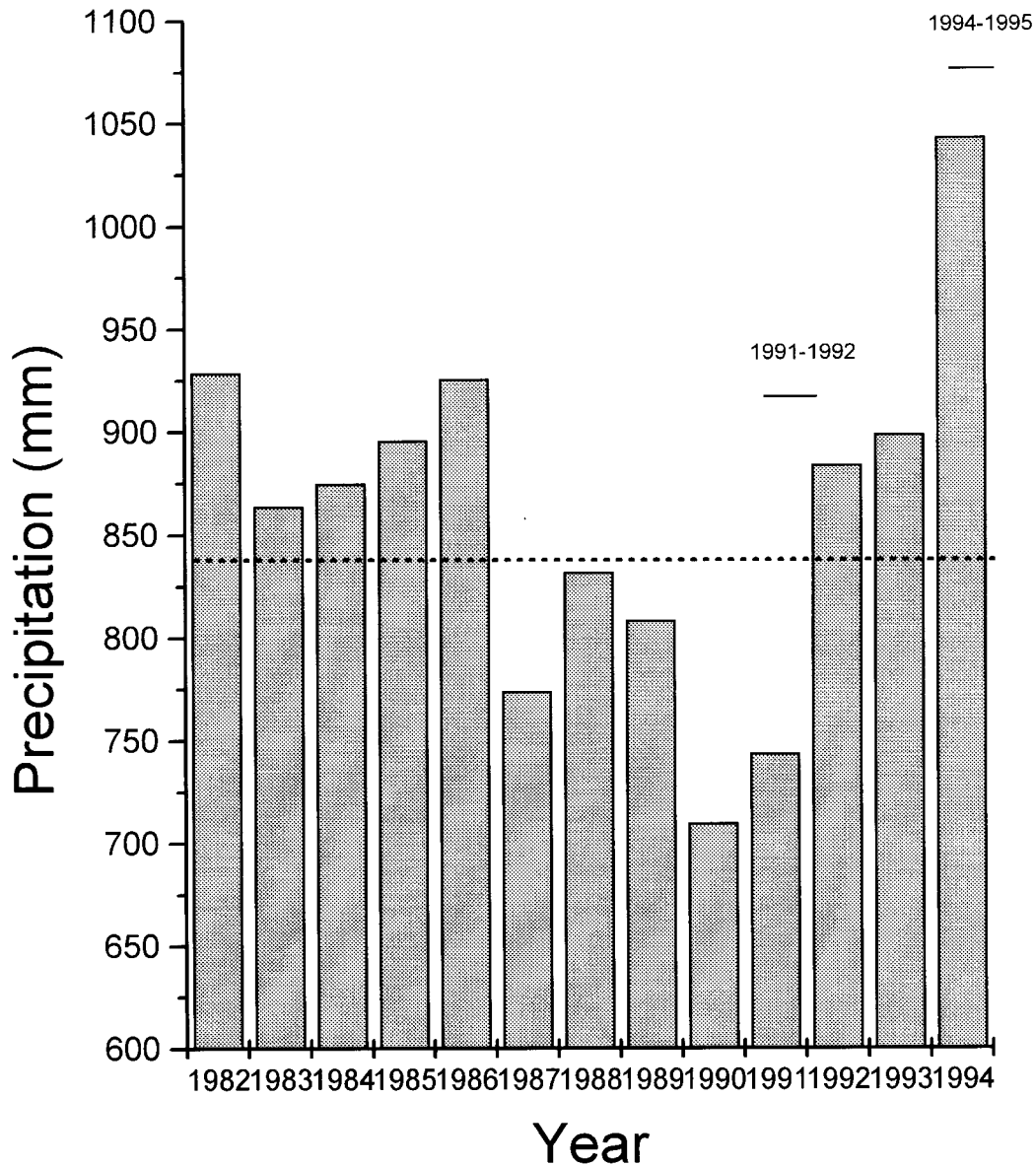


Figure 5. Annual precipitation for Bristol for the period 1982–1994. Mean annual precipitation is shown by the dashed line; sampling periods are also shown

a response to individual storm events of < 12 hours, yet these lags vary. In 1994–1995 the lag times are much shorter than 1991–1992, suggesting that lag times decrease with increased precipitation.

Comparison between the two years demonstrates the complexity of hydrological response to precipitation change in low discharge cave drips. In particular, the response of individual drips to both annual and long-term discharge is highly variable, with both underflow and overflow behaviour being present. It is suggested that in 1994–1995 the increased precipitation recharged the aquifer and filled a significant amount (if not all) of the available storage. This would lead to both rapid pulse flow in response to precipitation, which would

explain the high winter discharges, and more water to sustain discharge into the summer when evapotranspiration exceeds precipitation, which would explain the maintained cross-correlations. In addition, LC-1 decreased in discharge whereas all other samples increased, suggesting blocking or diversion of the flow path. Similar results have also been observed on a seasonal level for recently active seeps depositing flowstone samples (Baker, 1993) and for one site in G.B. Cave (Smart and Friedrich, 1987), but has not been demonstrated for low discharge drips. The nature of the transition from high to low discharge of LC-1 is not known; future studies of long-term, high frequency time-series data is needed to determine whether this occurred gradually or catastrophically.

Organic Matter Variations 1994–1995

Figure 6 presents the luminescence intensity data for sites LC-2 to LC-6 (samples were not obtained for LC-1 owing to the low discharge). To confirm that luminescence intensity reflects organic matter concentration, a random subsample of water samples from all the stalagmites was analysed for TOC. These results demonstrated the following relationship: $\text{TOC} = 3.57 + 3.45 \text{ LUM}$ ($n = 16$, $r = 0.63$), with the predicted and actual total organic carbon concentration for the stalagmite drip waters ranging from 0.5 to 2.0 mg l⁻¹. The strength of this relationship is weaker than that observed for peaty waters, and suggests that a significant fraction of the TOC is in a non-humic/fulvic acid form at the Lower Cave site, and that luminescence intensity reflects humic and fulvic acid concentration rather than total organic matter concentration.

Figure 6 demonstrates that humic and fulvic acid concentration increases in general at all sites from November to March (Julian days 330–420). This correlates with the winter maximum of discharge, as demonstrated in Figure 6 by the time-series plots of luminescence intensity and discharge. Hence it seems likely that: (1) when precipitation exceeds evapotranspiration, organic acids that have decomposed over the summer and autumn are washed into and through the karst groundwater system; and/or (2) surface organic matter production is continuous but the high molecular weight organic acids are only transportable through the karst aquifer when there is increased discharge. Winter increases in organic acids have also been inferred from observations of deposition of visible laminae in speleothem (Genty *et al.*, 1997a) and in stream sites (McDowell and Likens, 1988; Heikkinen, 1994). However, the relationship between discharge and luminescence/humic and fulvic acid concentration is not statistically significant for all sites (Table IV). In fact, there appears to be a relationship between the strength of the correlation and mean annual discharge ($r = 0.951$, $n = 5$), although further samples are required from other sites to determine whether this result is statistically significant. In particular, for the highest discharge site (LC-2), the double peak structure of winter discharge in 1994–1995 is reflected in the structure of the luminescence signal. Similar results have been demonstrated from a recently deposited, high discharge ($> 2.8 \times 10^{-3} \text{ l s}^{-1}$) stalagmite deposited in a Belgian tunnel (Genty *et al.*, 1997a).

CONCLUSIONS

Implications for Karst Aquifer Characteristics

The sites analysed in this study show only limited agreement with the 'seepage flow' characteristics as classified for low discharge feeds in G.B. Cave, Mendip Hills, by Smart and Friedrich (1987). Although the lag times to precipitation events are of a similar order of magnitude, most other flow characteristics were much more complex than previously recognized. In previous studies, intra-annual discharge data has been used to classify karst groundwater flow types. Here, the observed inter-annual variation (changes in discharge of $\times 0.13$ to $\times 7.05$ for a precipitation increase of 25%) is much greater than the intra-annual variation in discharge. Significantly, sites classified as 'seepage flows' under one year of data were reclassified as 'seasonal drips' in 1994–1995. Hence, several years of data under varying precipitation rates are required to classify groundwater drip flow.

In this study, the importance of complexities of flow are highlighted. Drip discharges demonstrated both typical 'seepage flow' characteristics, as well as overflow, underflow and seasonal dryness. The latter were

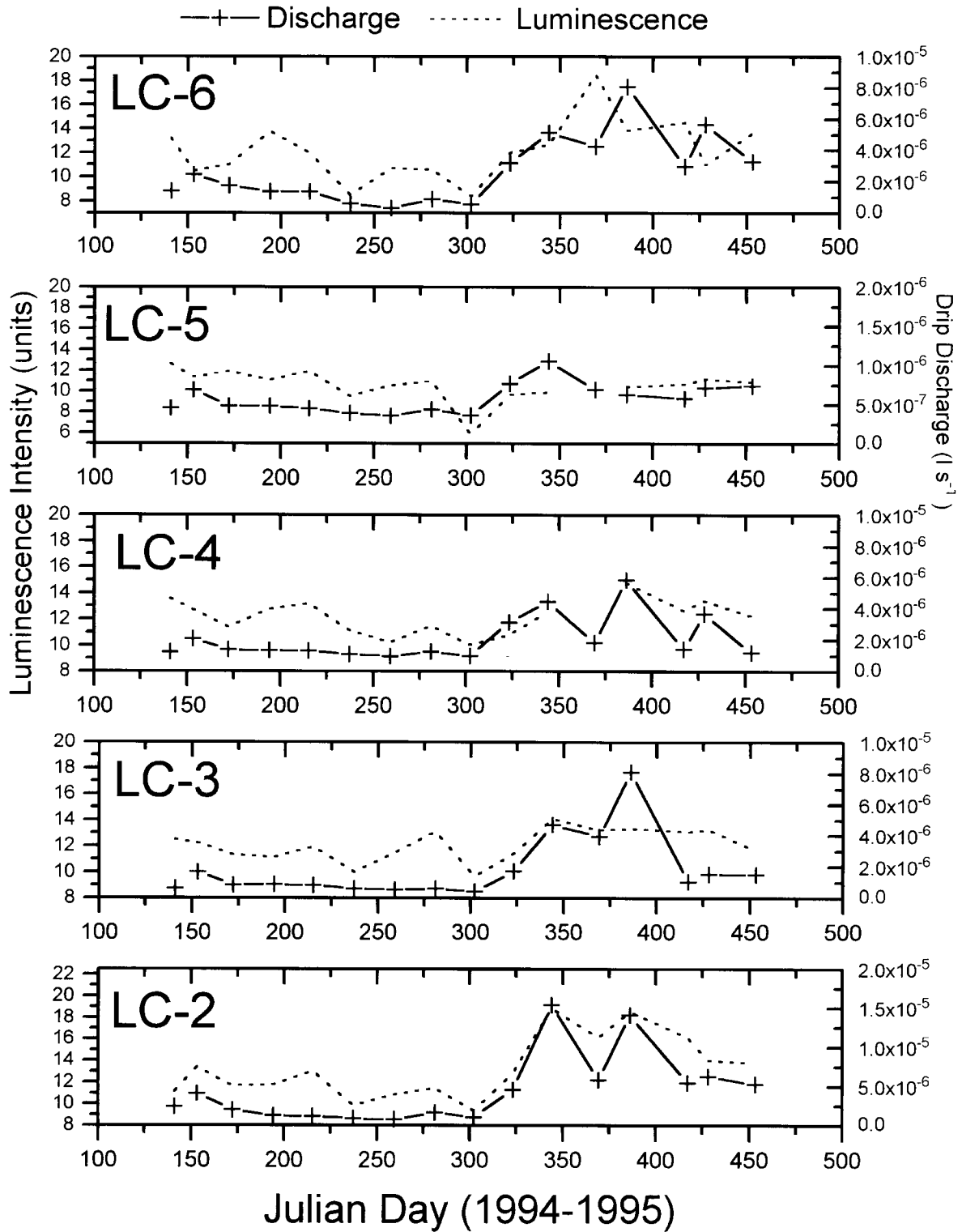


Figure 6. Time-series data for luminescence intensity and discharge for sites LC-2 to LC-6 for the period 1994–1995

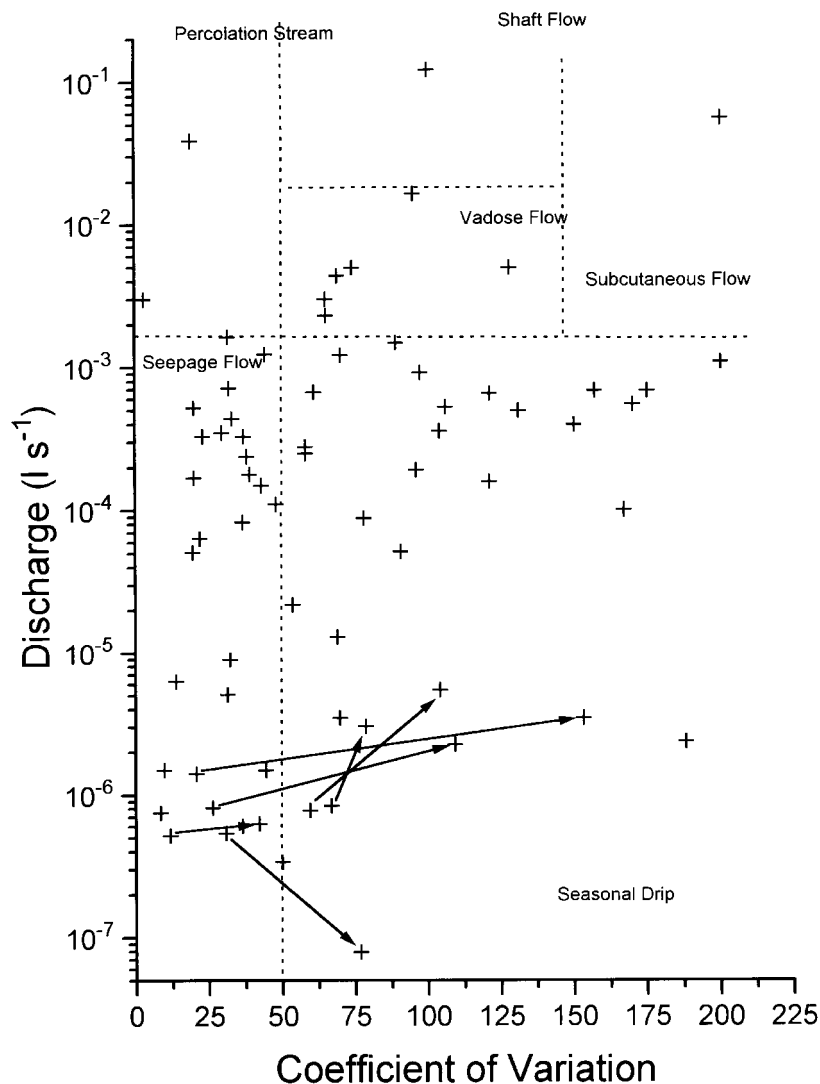


Figure 7. Relationship between discharge and the intra-annual variability of discharge for all cave sites in Carboniferous limestone in England. Intra-annual variability of the Lower Cave sites are labelled and linked by arrows demonstrating the interannual variation between 1991–1992 and 1994–1995.

characterized as seasonal drips; further studies are required in order to determine how frequently such drip characteristics are observed, and whether this frequency decreases with the depth in the unsaturated zone of the aquifer. In addition, no relationship was observed between discharge and the coefficient of variation of discharge; decreasing variability with decreasing discharge has been suggested by other workers (Smart and Friedrich, 1987). Figure 7 presents intra-annual discharge–discharge variability data for the sites analysed in this study, plus those from other work from British Carboniferous Limestone caves (Smart and Friedrich, 1987; Baker 1993; Pitty, 1966; 1974; Stenner, 1973). No correlation is present ($r = 0.03$) and it is again apparent that interannual variations in discharge and discharge variability are greater than between-site differences in intra-annual data, suggesting that further interannual data is required to obtain a precise picture of changing flow variability with discharge.

Implications for Palaeoenvironmental Reconstructions from Stalagmites

The results presented here demonstrate that palaeoenvironmental reconstructions using speleothem samples should ideally use multiple samples. The complexities of flow at even low discharge stalagmite drip feeds, including underflow and overflow behaviour and variable response of discharge to precipitation change, suggest that caution must be exercised when interpreting individual samples; similar cautions have been urged after analysing the growth patterns of mass spectrometrically dated Quaternary flowstone samples from Yorkshire (Baker *et al.*, 1996b). In particular, the complex response to precipitation change has specific implications for the environmental interpretation of growth rate variations and annual banding records.

Growth rate reconstruction. The growth rate of stalagmites has been demonstrated, in theory, to be dependent on the calcium concentration of the drip water, the water drip rate, the temperature, the thickness of the water film on the stalagmite cap and the carbon dioxide concentration in the cave air (Dreybrodt, 1980, 1981; 1988). Application of this theory has suggested that the water drip rate is not an important variable determining growth rate, with a doubling of drip rate generating only a 15% increase in growth rate (Baker *et al.*, 1995a). Variations in temperature and calcium concentration of the drip water are more important, although for recently deposited stalagmites where these variables are less likely to have varied, a correlation between growth rate and surface water excess has been observed (Genty and Quinif, 1996). The presence of seasonal cessation of one of the drip feeds in Lower Cave suggests that the reconstruction of palaeoenvironments from stalagmites may be more complex than previously observed. For example, a 50% decrease in growth rate may be a result of a seasonal drying of the drip source, whereas growth rate theory suggests that this could also be interpreted as a 4–7 °C fall in temperature.

Annual growth laminations. The relationship observed at Lower Cave for some sites suggests a potential signal between organic acid concentrations and annual lamination structure. This result confirms results observed within recently deposited stalagmites in the Godarville Tunnel, Belgium, for which the structure of the luminescence peak was observed to correlate with trends in the seasonal water excess (Genty *et al.*, 1997a). Data from Lower Cave suggest that this relationship is strongest for stalagmites with high drip discharges, although this relationship is derived from only five sites and further analyses need to be undertaken from different cave sites.

The presence of annual growth laminations also has implications for the interpretation of growth rate variations. Annual banding is not observed in all stalagmite samples; previous studies have quoted mixing of groundwater in the aquifer, soil water residence characteristics and depth in the aquifer as a primary cause of the lack of banding preservation (Baker *et al.*, 1993; 1996a; Shopov *et al.*, 1994). A seasonal cessation of the drip feed will lead to a lack of banding preservation, as the 'summer' component of the luminescence band will not be deposited. Hence, if a lack of growth banding correlates with a decrease in growth rate determined by other techniques (for example, uranium series dating), then it suggests that drip cessation is the cause and thus provides a limited palaeoclimate record.

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REFERENCES

- Atkinson, T. C. 1985. 'Present and future directions in karst hydrology', *Ann. Soc. Geol. Belg.*, **108**, 293–296.
- Baker, A. 1993. 'Speleothem growth rate and palaeoclimate', *PhD Thesis*, University of Bristol, UK.
- Baker, A., Smart, P. L., Edwards, R. L., and Richards, D. A. 1993. 'Annual growth banding in a cave stalagmite', *Nature*, **364**, 518–520.
- Baker, A., Smart, P. L., Barnes, W. L., Edwards, R. L., and Farrant, A. R. 1995a. 'The Hekla 3 volcanic eruption recorded in a Scottish speleothem?' *The Holocene*, **5**, 336–342.
- Baker, A., Smart, P. L., and Edwards, R. L. 1995b. 'Paleoclimate implications of mass spectrometric dating of a British flowstone', *Geology*, **23**, 309–312.
- Baker, A., Barnes, W. L., and Smart, P. L. 1996a. 'Speleothem luminescence intensity and spectral characteristics: signal calibration and a record of palaeovegetation change', *Chem. Geol.*, **130**, 65–76.
- Baker, A., Smart, P. L., and Edwards, W. L. 1996b. 'Mass spectrometric dating of flowstones from Stump Cross and Lancaster Hole, Yorkshire: palaeoclimate implications', *J. Quat. Sci.*, **11**, 107–114.
- Drew, D. P. 1970. 'The significance of percolation water in limestone catchments', *Groundwater*, **8**, 8–11.
- Dreybrodt, W. 1980. 'Deposition of calcite from thin films of natural calcareous solutions and the growth of speleothems', *Chem. Geol.*, **29**, 80–105.
- Dreybrodt, W. 1981. 'The kinetics of calcite precipitation from thin films of calcareous solutions and the growth of speleothems: revisited', *Chem. Geol.*, **32**, 237–245.
- Dreybrodt, W. 1988. *Processes in Karst System*, Springer Verlag, Berlin. 288 pp.
- Edwards, R. L., Chen, H. H., and Wasserberg, G. J. 1987. ' ^{238}U – ^{234}U – ^{230}Th systematic and the precise measurement of time over the last 500 000 years', *Earth Planet. Sci. Lett.*, **81**, 175–192.
- Genty, D. 1992. 'Les spéléothèmes du tunnel de Godarville (Belgique) — un exemple exceptionnel de concrétionnement moderne — intérêt pour l'étude de la cinétique de précipitation de la calcite et de sa relation avec les variations d'environnement', *Spéléochronos*, **4**, 3–29.
- Genty, D. 1993. 'Mise en évidence d'alternances saisonnières dans la structure interne des stalagmites. Intérêt pour la reconstitution des paléoenvironnements continentaux', *C. R. Acad. Sci. Paris*, **317** (Série II), 1229–1236.
- Genty, D. and Quinif, Y. 1996. 'Annually laminated sequences in the internal structure of some Belgian stalagmites — implications for palaeoclimate', *J. Sediment. Res.*, in press.
- Genty, D., Baker, A., and Barnes, W. L. 1997a. 'Comparison entre les lamines luminescente et les lamines visibles annuelles de stalagmites', *Comptes Rendus Acad. Sci.*, Paris, Submitted.
- Genty, D., Deflandre, G., and Quinif, Y. 1997b. 'Les, lamines de croissance des speleothemes: origine et intérêt paleoclimatique', *Ann. Soc. Geol. Belg.*, in press.
- Grieve, I. C. 1985. 'Determination of dissolved organic matter in streamwater using visible spectrophotometry', *Earth Surface Process. and Landf.*, **10**, 75–78.
- Gunn, J. 1981. 'Hydrological processes in karst depressions', *Z. Geomorphol., N. F.*, **25**, 313–331.
- Heikkinen, K. 1994. 'Organic matter, iron and nutrient transport and nature of dissolved organic matter in the drainage basin of a boreal humic river in northern Finland', *Sci. Total Environ.*, **152**, 81–89.
- McDowell, W. H. and Likens, G. E. 1988. 'Origin, composition, and flux of dissolved organic carbon in the Hubbard Brook Valley', *Ecol. Monogr.*, **58**, 177–195.
- Pitty, A. F. 1966. *An approach to the study of karst water*. University of Hull Occasional Papers in Geography, 5, UK.
- Pitty, A. F. 1974. 'Karst water studies in and around Ingleborough Cavern', in Waltham, A. C. (Ed.), *Limestone and Caves of North West England*. David and Charles, Newton Abbott. pp. 127–139.
- Railsback, L. B., Brook, G. A., Chen, J., Kalin, R., and Fleisher, C. J. 1994. 'Environmental controls on the petrology of a late Holocene speleothem from Botswana with annual layers of aragonite and calcite', *J. Sediment. Res.*, **A64**, 147–155.
- Shopov, Y. Y., Ford, D. C., and Schwarz, H. P. 1994. 'Luminescent microbanding in speleothems: high-resolution chronology and palaeoclimate', *Geology*, **22**, 407–410.
- Smart, P. L. and Friedrich, H. 1987. 'Water movement and storage in the unsaturated zone of a maturely karstified aquifer, Mendip Hills, England', *Proceedings, Conference on Environmental Problems in Karst Terrains and Their Solution, Bowling Green, Kentucky*. National Water Well Association. pp. 57–87.
- Stenner, 1973. 'A study of the hydrology of GB Cave, Charterhouse-on-Mendip', *Proc. UBSS*, **12**, 171–226.
- Williams, P. W. 1983. 'The role of the subcutaneous zone in karst hydrology', *J. Hydrol.*, **61**, 45–67.