Hydrological Processes
Hydrol. Process. **12**, 1447–1459 (1998)

Comparison of the luminescence properties of waters depositing flowstone and stalagmites at Lower Cave, Bristol

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Abstract:

Discharge and luminescence properties of waters feeding a flowstone in Lower Cave, Bristol, were measured at both three weekly and 30 minute sampling intervals within rainfall events over the period April 1994–April 1995 and July–December 1995, respectively. Results are compared with the discharge and luminescence of lower ($<0{\cdot}01$ ml s^{-1}) discharge waters supplying five stalagmites in the cave (Baker *et al.*, 1997). When sampled at three weekly intervals, the flowstone waters exhibit a statistically significant relationship between discharge and luminescence intensity ($r = 0{\cdot}75$), with luminescence maxima in late autumn and early winter. When compared with the stalagmite waters, the flowstone waters have a higher luminescence intensity at 420 nm (28 ± 11 vs. 12 ± 1 luminescence units) and a higher wavelength of maximum luminescence intensity (430 ± 2 vs. 419 ± 1 nm). The relationship between discharge and luminescence is weaker for the flowstone than for the fastest dripping stalagmite waters ($r = 0{\cdot}75$ vs. $r = 0{\cdot}85$), suggesting that hysteresis and other non-linear effects on the luminescent fraction in the waters may be important under higher flow regimes ($>0{\cdot}01$ ml s^{-1}) feeding flowstones. When 30 minute sampling results are considered, dilution and hysteresis effects can be observed in the discharge–luminescence relationship, both on an intra-event basis and over the winter as a whole. Exhaustion of organic matter within the karst groundwater system over the hydrological year may also be important. A very rapid flux of luminescent organic matter in early autumn generates a non-linear, order of magnitude change in water luminescence intensity. Flowstone water luminescence properties can be interpreted as having: (1) higher concentrations of luminescent organic matter compared with stalagmites (from luminescence intensity data); (2) a greater proportion of humic acid in relation to fulvic acid (from luminescence wavelength data); (3) a more rapid response to surface rainfall events; and (4) a consequently greater proportion of non-linear responses to surface rainfall variations. These results are considered in terms of the utility of the analysis of luminescence variations in solid samples of stalagmites and flowstones in aiding the reconstruction of past rainfall variations, and it is suggested that stalagmites are more useful than flowstones. © 1998 John Wiley & Sons, Ltd.

KEY WORDS stalagmite; flowstone; luminescence intensity; luminescence wavelength; discharge

INTRODUCTION

Recent research has highlighted potentially important climate signals contained within the luminescence properties of cave speleothems (secondary calcium carbonate deposits such as stalagmites, flowstones and stalactites). The spectral properties of the luminescence of these deposits suggest that they are primarily

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CCC 0885–6087/98/091447–13$17·50

Received 7 August 1997
Accepted 18 September 1997

derived from soil humic and fulvic acids (Senesi *et al.*, 1991), which derive from the overlying soil and are subsequently transported into the speleothem calcite by karst groundwaters. Humic and fulvic acids are defined by their solubility in acid solutions and thus their definition does not necessarily relate to their chemical structure, although typically soil humic acid has a weight of 20 000–100 000 daltons (Hayes *et al.*, 1989) and soil fulvic acid is lighter (700–3000 daltons; Hayes *et al.*, 1989). Studies of the luminescence intensity of speleothems that were deposited over the last 400 000 years have suggested that luminescence variations occur over both the annual time-scale (owing to seasonal fluxes in luminescent organic matter; Baker *et al.*, 1993, 1996; Genty, 1993; Genty and Quinif, 1996), over 1–10 year cycles (owing to El Niño and monsoonal effects on precipitation regimes; Ming *et al.*, 1997), over 11 to 100–200 year cycles (related, in an as yet poorly understood manner, to possible variations in solar output; Shopov *et al.*, 1994; Baker *et al.*, 1996; Genty and Quinif, 1996) and over the 10^3 time-scales (related to long-term vegetation changes; Shopov *et al.*, 1994; Baker *et al.*, 1996). These signals all superimpose upon one another to yield a complex palaeoclimate which requires calibration against the many climate variables that may affect soil organic matter production and breakdown (temperature, soil moisture, precipitation; Anderson, 1973; Grieve, 1990, 1994; Schindler *et al.*, 1992; Christ and David, 1996). For the long-term (10^3 year) trends, such calibration is difficult because of the paucity of climate analogues preserved in the geological record. However, calibration and modelling of processes on the $<10^2$ year time-scale is possible and has been the focus of recent research.

Recent calibration studies have demonstrated a remarkable correlation between surface precipitation and/or soil moisture excess on the one hand and stalagmite luminescence intensity variations on the other. Genty (1993) and Genty *et al.* (1997) demonstrate that the widths of annual luminescent and visible laminations are both correlated to soil moisture excess for several stalagmites in Belgium that were deposited over the last 30 years and which have been calibrated against local meteorological records. Recent results have demonstrated that the widths of annual luminescent laminations in a Chinese stalagmite show a very strong relationship with monsoon rainfall variations, both when calibrated against meteorological records as well as against documentary records for the last 500 years (Ming *et al.*, 1997). As well as variations in the width of annual laminae, Genty *et al.* (1997) demonstrated that for one stalagmite, the structure of the luminescence intensity peak, which is deposited into the stalagmites in early winter, is strongly correlated to the structure of winter rainfall variability over the last 30 years. In a study that involved three weekly sampling of the variations of drip water luminescence feeding five stalagmites in a British cave system, Baker *et al.* (1997) demonstrated that there is indeed a correlation between the luminescence intensity and the discharge on to the stalagmite, and that this correlation between luminescence intensity and discharge improved with increasing drip discharge. The authors also noted that individual stalagmites respond in a complex manner to surface precipitation change, each having a different proportion of associated groundwater storage flow, and some exhibiting overflow and underflow behaviour typical of karst waters, as observed by Smart and Friedrich (1987).

Previous research has highlighted several areas in the luminescence–discharge relationship that require further critical analysis. In particular, the contention that the correlation between luminescence intensity and discharge improves with increased discharge has important implications for the reconstruction of past rainfall variations. As flowstones are deposited underneath waterfalls or cascades, or at the base of rivulets or streams, which have comparatively high discharge compared with drip fed stalagmites, it has been suggested that flowstones should yield more precise records. Until now, this relationship has been derived from only five stalagmites with a discharge of less than $0{\cdot}01$ ml s^{-1} (Baker *et al.*, 1997). In addition, the highest resolution calibration studies have involved three weekly field sampling of waters; such a resolution may be obscuring still higher frequency variations in luminescence fluxes, which are especially important if one is to consider high discharge samples, which may provide a high resolution record of climate change. With a typical growth rate of 10–1000 μm yr^{-1} (Dreybrodt, 1988; Baker and Smart, 1995) and luminescence excitation by UV laser with a resolution of <1 μm, a theoretical reconstruction of past climate events at a resolution of 8 hours to 5 weeks is possible. As well as considering variations in luminescence intensity, seasonal and long-term variations in other luminescence properties, such as the wavelength of the maximum luminescence intensity, need to be examined. Studies of soil extracts suggest that fulvic acids have a more intense luminescence and shorter wavelength of luminescence than the humic acids (Senesi *et al.*, 1991), because of the higher molecular weight of humic acids as well as the presence of linearly condensed aromatic ring systems bearing electron-withdrawing substituents such as carbonyl and carbonyl groups. Fulvic acids, by contrast, may comprise a greater proportion of electron-donating substituents, such as hydroxyl, methoxyl and amino groups, which can enhance luminescence by increasing the transition probability between the singlet and ground state (Senesi *et al.*, 1991). The relative proportions of the two acid types in the waters may provide important hydrochemical or environmental information.

The research presented here critically addresses the issues described above. Water from one flowstone sampling point at Lower Cave, Bristol, was analysed for variations in luminescent properties over the period April 1994–April 1995 (three week sampling interval) and June 1995–December 1995 (30 minute sampling during rainfall events), and comparisons were made with results from five stalagmite sampling sites (sampled at a three week sampling interval) from the same cave system that were studied from April 1994 to April 1995 (Baker *et al.*, 1997).

SITE DESCRIPTION

Lower Cave, Bristol (51°27′N, 02°36′W; National Grid Reference ST 566732) is an 18 m long cave in Lower Carboniferous Limestone. Full site descriptions have been presented previously (Baker *et al.*, 1997; see, especially, Figure 2 therein). The flowstone analysed in this study is situated as the furthest extent of the cave, and comprises a *c.* 5 m long, 90 mm thick deposit. Waters feeding the flowstone derive from a <20 cm fissure at the back of the cave which has been smoke-traced to the surface, 10 m upslope (Speleological Group, Rodway School, 1973). The flowstone comprises part of a once beautiful grotto which has since been vandalized (Figure 1); a detritally corrected U–Th date on the base of the flowstone yields $6{\cdot}9 \pm 2{\cdot}5$ ka (Baker, 1993) and suggests that it has been deposited over the majority of the Holocene time period.

EXPERIMENTAL METHOD

The hydrological characteristics of the water flowing over the flowstone and feeding the stalagmite samples were sampled at a three weekly interval over the period April 1994–April 1995. Subsequent to the 1994–1995 sampling period, higher resolution sampling was undertaken within individual storm events to determine if significant variations in discharge or luminescence occurred on a <three week time-scale. Water samples were thus collected at 30 minute frequency on 7 and 10 September 1995 and 20, 21 and 22 December 1995. Water samples were collected from the base of the flowstone and on top of the stalagmites in either 15 or 30 ml glass bottles, and were frozen for subsequent laser analysis. Luminescence was excited with a UV He–Cd laser operating at 325 nm. The luminescence signal was focused on to the entrance slits of a scanning monochromator and recorded by a photomultiplier. The luminescence intensity of each sample was recorded at 5 nm intervals between 350 and 600 nm, thus building up a luminescence spectrum. Data were logged by computer for future analysis. The Raman peak of triple-distilled, deionized water at 365 nm was used to calibrate the laser intensity and collection efficiency between analyses, and the luminescence intensity calculated by integrating the total luminescence between 350 and 600 nm after subtraction of the Raman peak (Figure 2a). Discharge was calculated as the time taken between drips and converted to ml s^{-1} by assuming a constant volume of $0{\cdot}15$ cm^3 per drip (Baker and Smart, 1995).

RESULTS AND INTERPRETATION

Comparison of flowstone and stalagmite luminescence intensity (3 week sampling frequency)

Between 15 and 16 water samples were collected at each drip site over the period 1994–1995; the discharge and luminescence results for the flowstone are presented in Figure 2, and discharge, luminescence intensity

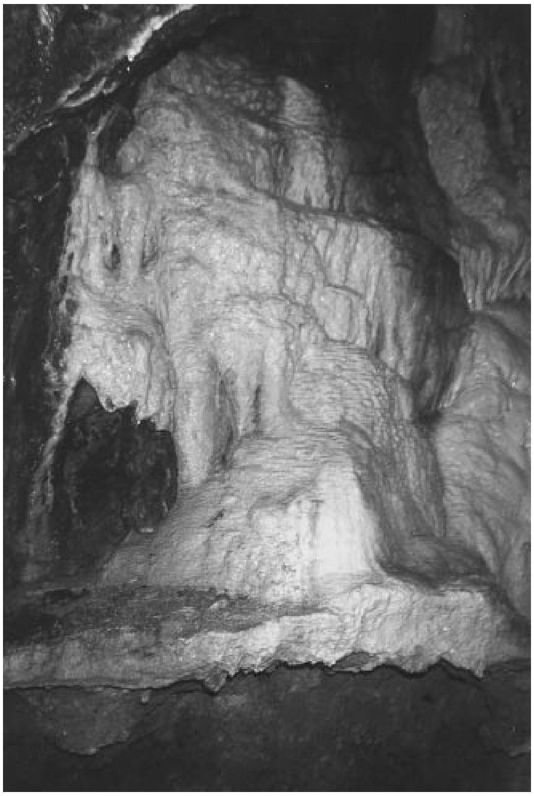

Figure 1. Photograph of the Lower Cave flowstone. Total height is 2 m, water flows from top centre to bottom centre of the field of view before flowing over the end of the truncated basal flowstone deposit

and wavelength results for all samples are given in Table I. The data in Table I demonstrate that the mean flowstone luminescence is significantly higher than that reported for the stalagmites in the cave over the same time period, although the coefficient of variation of luminescence for the flowstone (40·3%) is significantly greater than that for the stalagmite samples (15·4 ± 4·6%). These findings may be interpreted in several ways.

1. Waters supplying the flowstone have a higher discharge than the stalagmites and thus have a greater capacity to transport the high molecular weight organic acids. The weight of solid humic acids is several orders of magnitude greater than that of fulvic acids, and this relationship is maintained in solution

Table I. Hydrological and luminescence data for the waters feeding the flowstone and five stalagmites from Lower Cave for three weekly sampling, April 1994 to April 1995. All data are mean and 1 sigma standard deviation

	n	Discharge (ml s^{-1})	Luminescence intensity (units)	Wavelength of luminescence maxima (nm)	Coefficient of correlation between discharge and luminescence
Flowstone	15	0·020 ± 0·026	27·97 ± 11·28	430·63 ± 1·92	0·75
Stal-2	16	0·0023 ± 0·0024	13·34 ± 2·85	420·47 ± 1·67	0·85
Stal-3	16	0·00096 ± 0·0010	12·12 ± 1·25	419·31 ± 1·88	0·57
Stal-4	15	0·0015 ± 0·0023	12·22 ± 1·33	419·39 ± 1·62	0·54
Stal-5	15	0·00025 ± 0·00013	10·62 ± 1·55	418·28 ± 2·18	0·07
Stal-6	16	0·0013 ± 0·0010	12·20 ± 2·48	419·15 ± 1·45	0·47

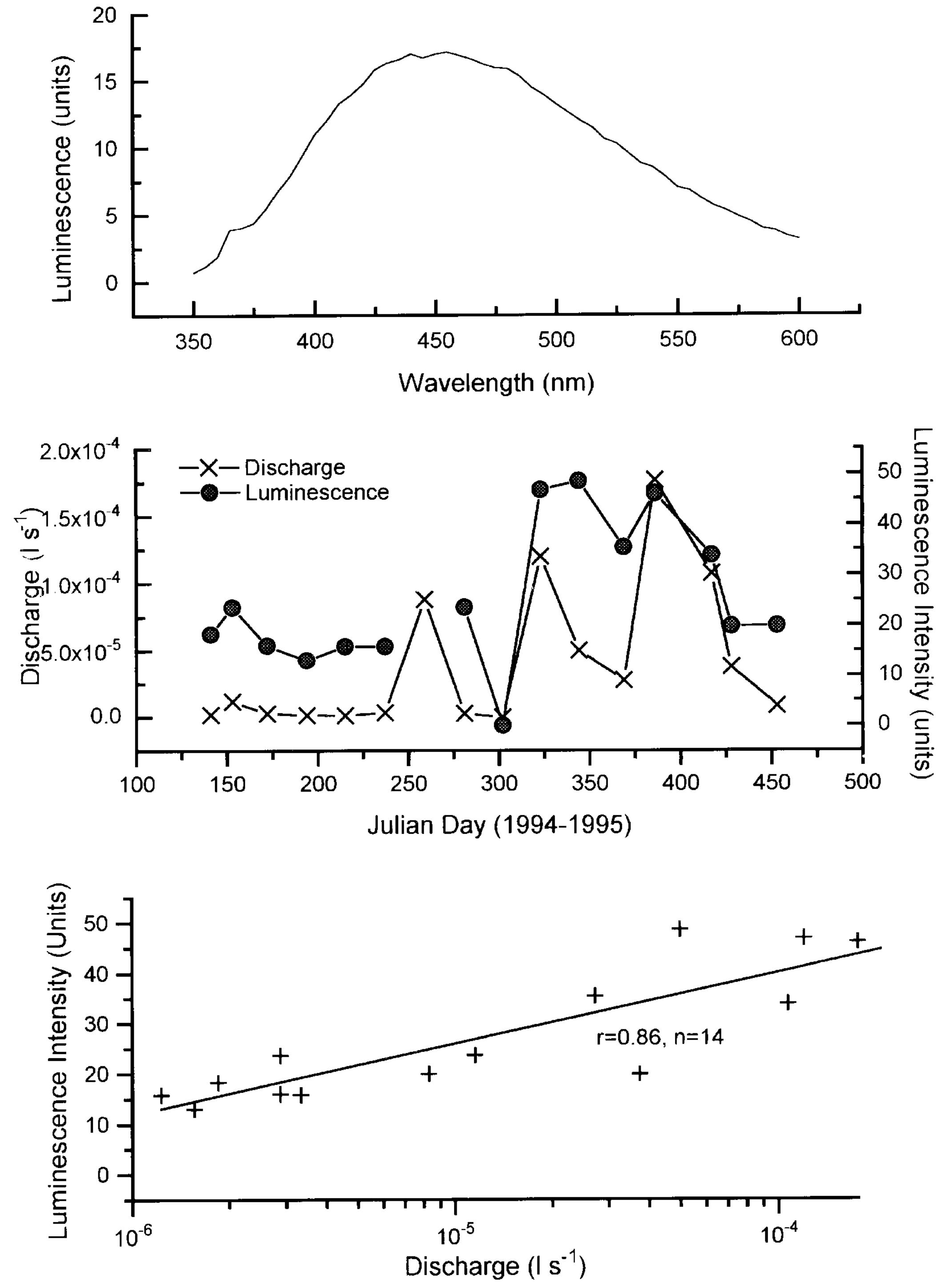

Figure 2. (a) Typical luminescence emission spectra for excitation at 325 nm for waters feeding the Lower Cave flowstone; luminescence intensity is calculated for all samples from the area under the curve between 350 and 600 nm after subtraction of the 365 nm Raman peak. (b) Luminescence and discharge for the Lower Cave flowstone for three weekly samples in 1994–1995. One luminescence data point is missing owing to sample loss. (c) Correlation between log discharge and luminescence intensity for three weekly sampling for the Lower Cave flowstone

although the weight of both acid types is significantly lower (1000–3000 daltons; Hayes *et al*., 1989) and humic acids are only 1–3 times heavier than fulvic acids.

2. That fissure width limits the transport of the organic acids. It may be hypothesized that the groundwater flow route of the waters feeding the higher discharge flowstone has a significantly wider fissure, which permits the transport of greater quantities of organic acids than that supplying the stalagmites. Typical fissure widths within karst aquifers have been calculated to be in the range 10–1000 μm (Dreybrodt, 1988; Palmer, 1991), which is significantly larger than the width of humic and fulvic acids (which have a maximum radius of gyration of 1–25 nm when solvated and are much smaller in solid form; Hayes *et al*., 1989). Baker *et al*. (1996) report an exponential decline in the luminescence of stalagmites with depth underground in one cave system, suggesting that this is due to limits in luminescent organic matter transport, which may be a result of the decreasing fissure width as one passes from the fractured subcutaneous zone to the saturated zone (Williams, 1983).
3. A different pH of waters supplying the flowstone compared with those supplying the stalagmites. Luminescence intensity of humic and fulvic acids has been demonstrated to be pH sensitive (Jones and Indig, 1996) with increasing pH generating a decrease in luminescence intensity associated with chemophores that emit in the shorter wavelengths (<450 nm) at the expense of those emitting in the longer wavelengths (>450 nm). However, these effects were most dramatic at a pH of 2–6, whereas between a pH of 7 and 8·5, the range typical of karst waters that are supersaturated with respect to calcium carbonate, little pH influence on luminescence is noticeable (Jones and Indig, 1996). Point samples of pH of the water supplying both the flowstone and the stalagmites were randomly sampled throughout the study period using a Camlab pH Boy 501© probe ($\pm 0{\cdot}1$ pH unit reproducibility; 0·1 ml sample size) and a slight difference was determined [flowstone pH $= 8{\cdot}1 \pm 0{\cdot}2$ ($n = 9$); stalagmite pH $= 7{\cdot}7 \pm 0{\cdot}3$ ($n = 12$)], confirming that the waters are within the typical range and therefore that pH is not likely to explain variations in luminescence intensity.
4. A higher calcium ion concentration in the waters feeding the stalagmites compared with those feeding the flowstone. Calcium ions in solution are known to complex with the free electrons within the organic acids (Higgo *et al*., 1993), which may prevent them from luminescing (Saar and Weber, 1980). However, because of the slow discharge of the waters supplying the stalagmites, collection of a sufficient sample size to determine the calcium ion concentration was not possible before significant degassing had occurred. Because calcium supersaturated waters have a concentration of *c*. 80–200 mg l^{-1} in British karst waters, and organic matter concentrations are two order of magnitudes smaller, it may be expected that in karst waters all available binding sites in the humic and fulvic acids are occupied by calcium ions. Thus, the quenching effects of calcium with the humic and fulvic acids may be considered to be complete, and thus any relative differences in calcium ion concentration between stalagmites and the flowstone at Lower Cave are likely to be of negligible importance.
5. A greater proportion of fulvic acids compared with humic acids in the waters feeding the flowstone compared with the waters supplying the stalagmites. Fulvic acids typically have a longer luminescence intensity than humic acids (Senesi *et al*., 1991), but also have a shorter wavelength of luminescence maxima, and thus this hypothesis can be tested by investigating the wavelength of the luminescence maxima (see below).

Comparison of the wavelength of maximum luminescence of flowstone and stalagmite waters (3 week sampling frequency)

Table I demonstrates that the waters feeding the one flowstone at Lower Cave have a significantly higher wavelength of maximum luminescence intensity than those supplying the five stalagmites at the site. This suggests that hypothesis (5) above is not likely, as fulvic acids have a lower wavelength of maximum luminescence intensity compared with humic acids. A long wavelength of luminescence intensity maxima must thus equate to a greater proportion of humic acid in the waters feeding the flowstone, which may be caused by factors (1) and/or (2) above, as well as two other possible mechanisms.

1. A shorter groundwater residence time for the flowstone waters, which may mean that a less complete breakdown of the organic acids may occur before the waters reach the flowstone, compared with those reaching the stalagmites. High resolution sampling of waters supplying the flowstone suggests a lag time of less than three hours between discharge increasing and rainfall events (see next section); the lag time for stalagmites at the sites is 20–40 days (Baker *et al.*, 1997). However, fulvic and humic acids take tens to hundreds of years to be broken down by microbial action (Frimmel and Christman, 1988), and hence the groundwater residence times for the stalagmites and the flowstone are insignificant over this time-scale.

2. Heterogeneous soil cover differing between that overlying the stalagmites and that overlying the flowstone. However, analysis of five soil cores taken from six locations overlying the cave reveal no difference between samples, with just a thin 1–5 cm humic layer existing at all locations, and thus this factor can be considered unlikely.

Correlation between discharge and luminescence

Figure 2b demonstrates a good relationship between luminescence and discharge over the period 1994–1995, with a higher luminescence intensity in winter as exhibited by the stalagmites at the site (Baker *et al.*, 1997). Discharge and luminescence intensity are correlated (Figure 2c; correlation between luminescence intensity and log discharge $= 0{\cdot}86$; between luminescence intensity and discharge $= 0{\cdot}75$, $n = 14$; statistically significant at 95% confidence level). This result suggests that at low discharges, an increase in discharge increases the organic matter transport capacity of the water, after which, with increasing discharge, there is a threshold where other factors such as dilution effects become important and the correlation between discharge and luminescence weakens. The importance of the latter can be elucidated by high resolution sampling of the flowstone waters at high discharges. Comparison with the correlation between discharge and luminescence form the stalagmites from the site demonstrates that the correlation is worse than that for the fastest flow stalagmite at the site ($r = 0{\cdot}85$, Table I), despite discharge being an order of magnitude higher ($>0{\cdot}01$ ml s^{-1}).

High frequency sampling

Sampling at 30 minute frequency was undertaken on 7 and 10 September and 20, 21 and 22 December 1995. Figure 3 presents hourly rainfall totals recorded at the 2 km distant Bristol Meteorological Office (National Grid Reference ST585727), as well as the half-hourly discharge and luminescence variations. High frequency sampling reveals events that would have been missed on a three weekly sampling interval. In particular, flowstone luminescence intensity variation exhibits an order of magnitude increase during the first rainfall events of autumn (7 and 10 September) following two dry months. The high resolution sampling undertaken during 20–22 December exhibited no such increase, and the luminescence is of the same order of magnitude as that determined under three weekly sampling.

At an intra-event level, it can be observed that the luminescence–discharge relationship is not always maintained. On 7 September, the correlation is very strong, whilst on 10 September there is a strong dilution effect at the start of the discharge peak and hysteresis within the storm as a whole. Later events in December show similar effects. Within the September sampling as a whole, a linear correlation between discharge and luminescence is observed, this is also true for December, although for this time period it is similar to the relationship observed for the three weekly sampling interval (Figure 4). Dilution and hysteresis effects become subsumed within the two correlations, although with a significant order of magnitude threshold being passed in early autumn.

High resolution sampling also revealed considerably greater variations in the wavelength of the luminescence maxima than that observed at the three weekly sampling frequency (Figure 5). The wavelength of luminescence maxima was observed to be highest in December and most variable in September. No

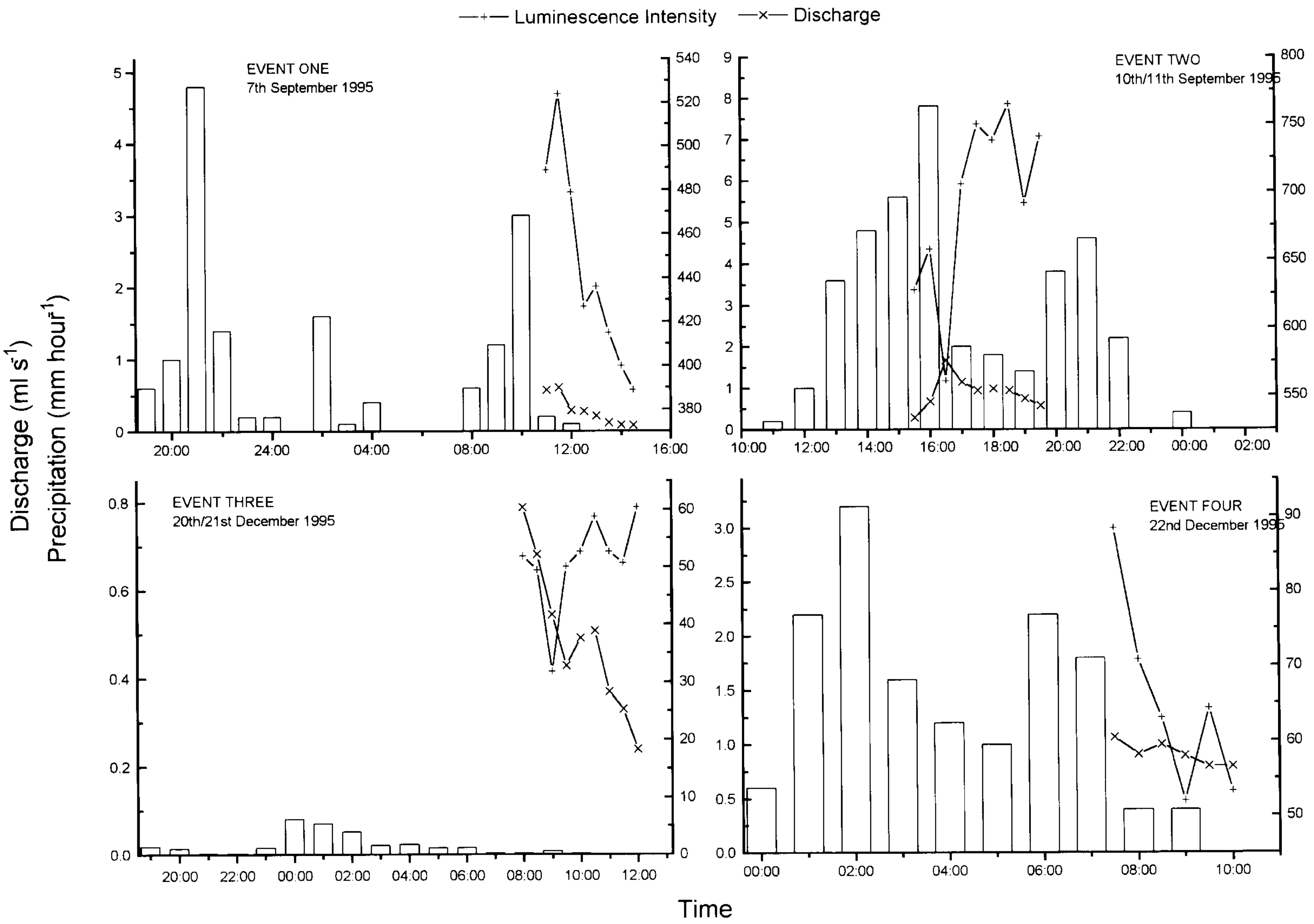

Figure 3. Hourly rainfall, flowstone discharge and luminescence intensity for four rainfall events, (a) 7 September, (b) 10 September, (c) 20 December and (d) 22 December 1995

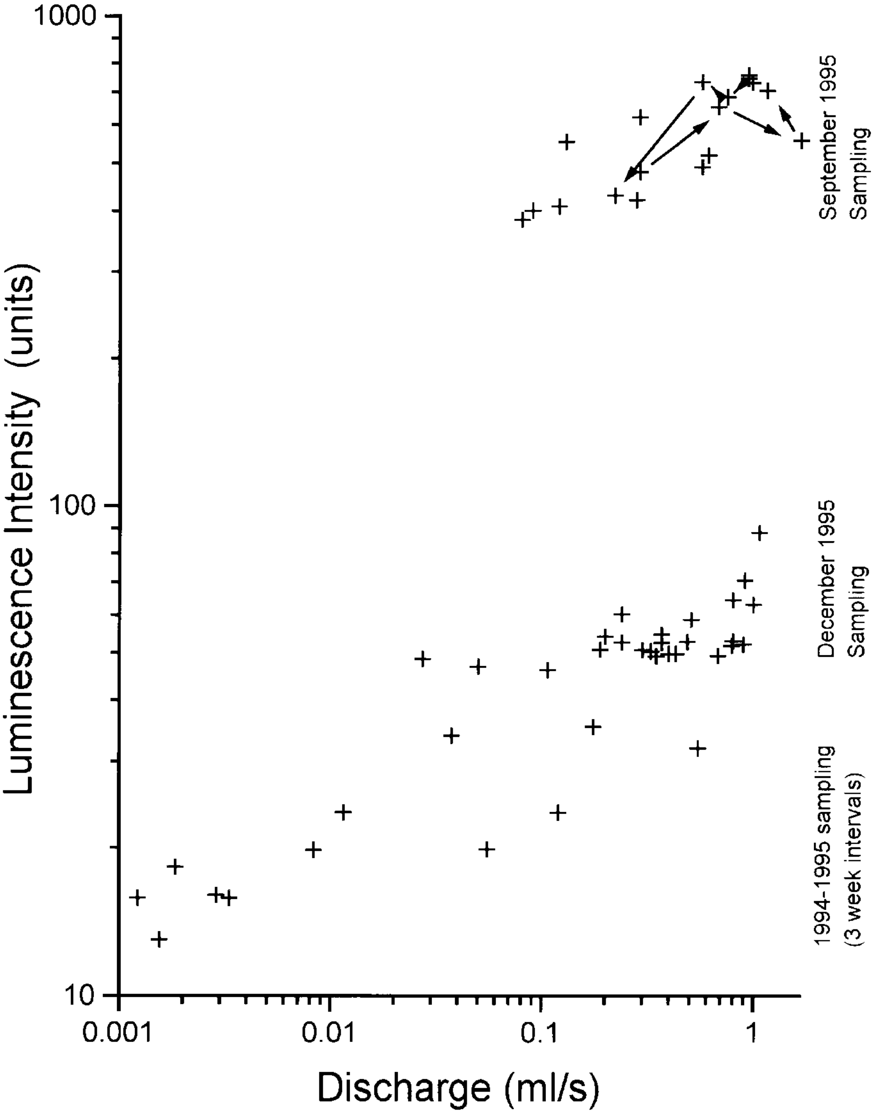

Figure 4. Relationship between discharge and luminescence intensity for three weekly sampling and 30 minute frequency storm sampling for the Lower Cave flowstone. The hysteresis within the 7 September event is shown

significant correlation exists between the wavelength of luminescence maxima and discharge or luminescence intensity. These results suggest that the September waters have a component with a greater mix of humic and fulvic acids; these may represent fractions that have been mobilized over a wide range of geochemical conditions over the months of May–August. The December luminescence signal comprises a greater proportion of humic material and is less variable, suggesting that a more uniform organic fraction has been mobilized over a shorter time period.

DISCUSSION

Relationship between discharge and luminescence for flowstones and stalagmites

The results presented above suggest that the combination of the increased luminescence intensity and longer wavelength of maximum luminescence experienced by waters feeding the flowstone, in comparison

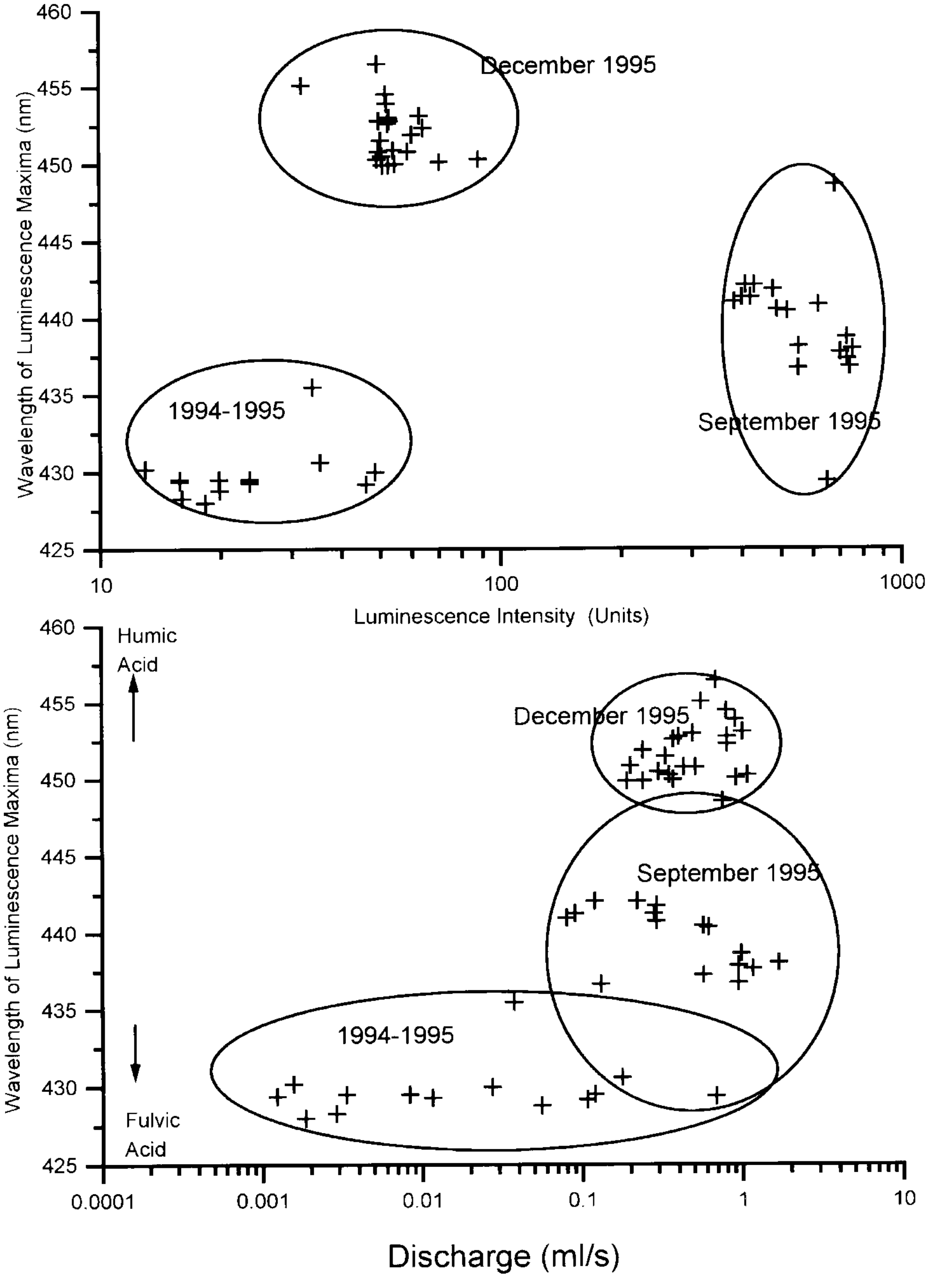

Figure 5. Relationship between (a) luminescence intensity and wavelength of maximum luminescence and (b) discharge and wavelength of maximum luminescence, for the Lower Cave flowstone. For comparison, mean stalagmite wavelength of luminescence maxima = 416·3 ± 0·9 nm and mean discharge = 0·003 ± 0·002 ml s^{-1}

with the waters feeding the stalagmites, is due to an increase in total luminescent organic matter, which has a greater proportion of humic matter than fulvic matter compared with the stalagmite waters. Of the possible causes of this difference in water luminescence properties, only two are possible; a wider fissure width or a higher discharge, or a combination of both factors. Both these factors enable a greater quantity of both total

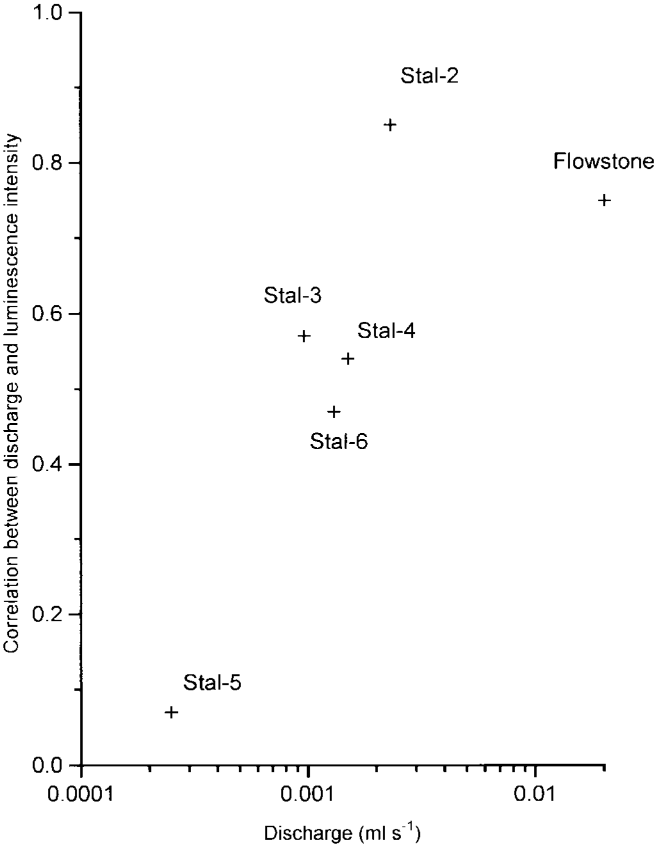

Figure 6. Relationship between discharge and the discharge–luminescence correlation for all samples at Lower Cave. Discharge variabilities are not shown for clarity but have coefficients of variation from 50–150%

and high molecular weight organic acids to be transported in the karst groundwaters. However, further research into other flowstone feed waters, as well as improved organic matter categorization, is needed to identify the relative importance of these two factors.

Figure 6 demonstrates the relationship between discharge and the correlation coefficient associated with the relationship between discharge and luminescence for the five stalagmites and one flowstone at Lower Cave for three weekly sampling intervals. For the five stalagmites, which have discharges up to 0·01 ml s^{-1}, it is apparent that increased discharge increases the transport of organic acids, whereas after this the relationship weakens. This may be caused by dilution and other non-linear effects at high discharge (see the next section).

High frequency sampling suggests that events of <1 day may generate significant changes in luminescence intensity, and these may be preserved within flowstone samples. Such events are less likely to be found in stalagmite samples, which have a lagged response to surface precipitation changes of between 1 and 60 days (Pitty, 1966, 1968, 1971; Baker *et al.*, 1997). Hence, for the reconstruction of past rainfall variations, high discharge stalagmite samples appear to be of more value than flowstones, because the relationship between discharge and luminescence is stronger. However, three weekly sampling of stalagmite waters may not be of adequate temporal resolution to resolve all events for all stalagmite samples, and with a theoretical laser resolution of <1 day, it is important that calibration studies match this resolution, either by utilizing high resolution sampling for a short time period during the hydrological year, or by the installation of automatic drip counters and water samplers.

Dilution, hysteresis and exhaustion

The high resolution sampling interval utilized here has demonstrated the importance of dilution and hysteresis effects in the transport of organic matter within the karst groundwater. Dilution and hysteresis were observed within individual storms (for example, Figure 3b), and it can be considered likely that the latter effect occurs at a larger scale throughout the winter hydrological cycle, with less organic matter mobilized for the equivalent discharge in late winter. In theory, a gradual exhaustion of organic matter within the soil–groundwater system may also be expected to be observed over the winter to spring period; however, the three weekly sampling undertaken in this study was not of sufficient resolution to confirm this. Dilution, hysteresis and exhaustion have all been observed elsewhere in the hydrological cycle, both within karst waters (karst springs hydrographs; Jakucs, 1959; Hess and White, 1993; Blavoux *et al.*, 1992) and surface streams [in the flux of organic matter; in Figure 2 of Grieve (1990)], solutes (Stott and Burt, 1997) and sediment (Hasnain, 1996), and so should not be unexpected in the cave environment.

CONCLUSIONS

Sampling at three weekly intervals can miss important events for high discharge flowstone samples, although this resolution is probably adequate for most stalagmite feed waters, which have a significant lag time between surface rainfall events and discharge. For flowstone feed waters, more frequent sampling is required. Discharge data may be collected using automatic drip counters or tipping bucket gauges, but automatic luminescence data is more difficult to sample in the cave environment owing to the high relative humidity (99–100%), which is likely to destroy any *in situ* laser equipment, although the stability of humic and fulvic acids suggests the possibility of automatic sampling in the cave and subsequent preservation by freezing.

The wavelength of the luminescence intensity maxima can provide useful information on the nature of luminescent organic matter in cave waters, in particular in terms of distinguishing the relative importance of humic and fulvic acid components. In addition, the recent development of synchronous scan spectra and excitation–emission matrices (EEM) (Matthews *et al.*, 1996; Mobed *et al.*, 1996) may yield additional environmental information; both techniques involve changing both the excitation wavelength and emission wavelength to identify multiple excitation peaks within the humic and fulvic acids, which may correlate with changes in hydrochemistry, climate or environment. Further research is required to implement EEM techniques at high resolution over the whole seasonal cycle, as well as investigating its potential for use on fossil stalagmites to elucidate past variations in organic matter flux and type.

The results presented here suggest that stalagmites are likely to be better than flowstones in the preservation of palaeoprecipitation data, providing their drip discharge is relatively high ($>0{\cdot}002$ ml s^{-1}) and their groundwater residence time is short (<1 month). Most stalagmite feed waters do not suffer from dilution effects, and any hysteresis is buffered by the groundwater residence time. Future research needs to undertake high resolution monitoring of high discharge stalagmite feed waters to confirm the reproducibility of the discharge–luminescence relationship for different geologies and soil covers.

ACKNOWLEDGEMENTS

Thanks are extended to Jon Bawdon for collecting samples, Dominique Genty and Natalie Mockler for comments on an early draft of the manuscript, and to the Royal Society and the University of Exeter for funding. The raw data presented here can be accessed on http://www.ex.ac.uk/~abaker/stalag.html.

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