

Fluorescence intensity variations of speleothem-forming groundwaters: Implications for paleoclimate reconstruction

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Abstract. Groundwater discharges onto 16 speleothems and surface climate parameters have been measured in an oolitic limestone site in England. Groundwater recharge is demonstrated to lag behind periods of hydrologically effective precipitation by 30–50 days. With the exception of short periods of high rainfall intensity or quantity, summer rainfall has no effect on groundwater discharge onto the speleothems because of the development of a soil moisture deficit. The first groundwater fluorescence intensity increase was demonstrated to lag the autumn increase in groundwater discharge by 10–20 days, suggesting that the first groundwater comprises “old” stored groundwater, whereas later water derives from the overlying soil and has a high organic acid concentration. Despite the lags, the structure of autumn and winter moisture availability is reflected within the annual fluorescence intensity variations, suggesting that fluorescent organic acids, when trapped within speleothem calcite, may provide a proxy for past winter moisture variations for temperate latitudes.

1. Introduction

Fluorescence is the optical phenomena where excitation by a high-energy light source raises the energy levels of electrons within a molecule. These subsequently release this energy in the form of light; the emitted fluorescent light is at a longer wavelength than the excitation light. Fluorescence from organic material commonly comprises emission in the long wave ultraviolet (UV) and blue wavelengths (350–500 nm) after excitation by short or long wave UV light (200–400 nm). Fluorescence in natural waters is predominantly generated by organic and amino acids, which derive from decomposed plant and animal material in the soil zone. Several studies have investigated the fluorescence of these materials in soils, rivers, groundwater, and marine waters [Senesi *et al.*, 1991; Coble, 1996; Mobed *et al.*, 1996; A. Baker and D. Genty, Fluorescence wavelength and intensity variations of cave waters, submitted to *Journal of Hydrology*, 1998.] These studies have revealed the presence of several intensity peaks in the fluorescence spectrum but with a predominant organic acid peak in soil extracts and terrestrial waters at an excitation and emission wavelength pair of 290–350:400–480 nm, ascribed to a probable fulvic acid source. Results have suggested that organic acids from different sources (e.g., marine versus terrestrial [Coble, 1996]) as well as different types of organic acid (humic versus fulvic [Senesi *et al.*, 1991]) may be differentiated by their fluorescence properties. However, research has primarily considered varia-

tions in fluorescence wavelength as opposed to intensity variations.

To date few studies have investigated the fluorescence intensity variations of groundwater; exceptions have been those of Baker *et al.* [1997] and Baker and Barnes [1998], who have investigated the groundwater feeding stalagmites and flowstones at a cave site, principally at 3-week sampling intervals. Research presented in this paper was undertaken to answer some of the questions posed by these studies, in particular (1) to undertake a higher sampling frequency of groundwater fluorescence than previously obtained, for the duration of at least one annual hydrological cycle, in order to assess any climatic cause of winter fluorescence variability and (2) to undertake this sampling at multiple groundwater sources to assess the relationship between groundwater discharge and fluorescence properties and surface climate, in particular to assess whether different groundwater sources have different sensitivities to and lags with surface rainfall variations.

Therefore, fluorescence intensity variations of 16 groundwater sources sampled at frequencies of 10–20 days within one hydrological system are presented here for the period November 1996 to April 1998. The fluorescence intensity variations contained within the speleothems associated with the groundwater sources investigated here will be discussed in a future paper.

2. Site Description

The site chosen to investigate the fluorescence intensity variations of groundwaters was Brown's Folly Mine, Bathford, southwest England (51°23'W, 2°22'N; National Grid Refer-

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ence ST795660). This site is a former stone mine with over 5 km of passages that was abandoned in 1904 and is now part of a local nature reserve [Irwin and Jarrett, 1993; Price, 1984]. The mine is situated in the Bath Oolite, a local subdivision of the Great Oolite Series of the Jurassic limestone and was chosen as a sample site because of several advantages:

1. The mine is relatively easily accessible compared to equivalent cave sites, which facilitated the regular water-sampling program.

2. Stalagmites and flowstones have been forming within the mine since the time of abandonment; many of these deposits are known to contain annual fluorescence laminations preserved within them [Baker et al., 1998].

3. The hydrogeology of the Great Oolite is reasonably well studied. Smart [1977] demonstrated from dye tests that the karst aquifer comprises a range of flow pathways, from open fracture flow with extremely high hydraulic conductivity to fissure flow with low conductivity, and that considerable interaction between these end-members occurs. Rushton et al. [1992] confirm the presence of a rapid transfer component through observation of a rapid increase in river flows before aquifer storage is fully replenished, which is possibly due to a fissure system which is highly transmissive but has a low storage capacity. They argue that flow through this routing occurs whenever recharge exceeds 40 mm month⁻¹.

4. The site is overlain by a natural vegetation, secondary woodland, which has invaded the site since mine abandonment in 1904 and which is now part of a protected local nature reserve, and hence overlying soil and vegetation conditions can be assumed to have remained unchanged prior to and over the sampling program.

5. The mine is worked at a constant depth from the surface (5–15 m below surface). Previous research has suggested that the climate signal contained within fluorescence variations diminished with depth in the aquifer because of the mixing of waters with different residence time and the precipitation of organic acids in the upper sections of the aquifer through adsorption to the limestone or precipitation within speleothems [Shopov et al., 1994; Baker et al., 1996]. Therefore Brown's Folly Mine is at an ideal depth to test for a climate-groundwater fluorescence relationship.

6. The mine is both dissected by and adjacent to solutionally enlarged fissures that contain speleothem formations [Self, 1986, 1995]. Therefore should a groundwater fluorescence record be observed at Brown's Folly Mine, there is the potential to use this data to calibrate speleothem samples from these sites to reconstruct long palaeoclimate time series records.

Brown's Folly Mine is situated in a region of maritime temperate climate. Mean annual temperature at Bristol (22 km to the west) is 10.0°C, with a winter minimum of 3.9°C and summer maximum of 16.5°C. Mean annual precipitation is 842 mm; precipitation falls in all months, although with a winter maximum that is dominated by frontal rain. Summer rainfall comprises both frontal and convective rainfall. Snow lies typically fewer than 7 days in the year.

Sixteen drip waters were selected for analysis during reconnaissance trips in the summer of 1996, with the authors attempting to select a range of samples typical of all flow conditions at the site. Four samples were actively depositing flow stones from a single drip source (BFM-3, 3a, P, and N); all the other samples were depositing stalagmites. Sample locations are shown in Figure 1, together with the location of naturally forming gull rifts, which were bisected by the mine and which

represent natural vertical drainage routes through the Bath Oolite and overlying Jurassic deposits (predominantly brown shelly limestone and white oolite, with one clay band <1 m thick). Three speleothems were directly underneath the rifts and therefore probably directly hydrologically related (BFM-P, B, and F5). High-frequency sampling was commenced in the autumn of 1996 and maintained for that hydrological year. Additional funding permitted an extension of this sampling through the winter of the 1997–1998 hydrological year.

3. Methods

The 16 groundwater sampling sites were monitored at intervals of 10–20 days throughout the period November 1996 to April 1998. For the 1996–1997 hydrological year, sampling was maintained at 10-day intervals throughout the winter period, dropping to 20 days during the summer. Ten-day sampling was again maintained for the 1997–1998 hydrological year until January 1998, when sampling was reduced to a 20-day frequency owing to injury of one of the authors (N. J. M.). Discharge measurements were undertaken at all 16 sample sites throughout the sampling period by either of the following methods: (1) for groundwater sources with a drip discharge, by measuring the time between consecutive drips; (2) for groundwaters with a continuous flow source, by measuring the time taken to fill a flask of known volume. This was then converted to an equivalent rate in drips/s by assuming a constant drip volume of 0.15 cm³ [Baker et al., 1997]. Although drip volumes are not constant, the errors in making this assumption are significantly less than the seasonal variations in discharge at the site.

Drip water samples were collected in glass bottles with capacities of 30 to 125 mL. Bottles had been precleaned in dilute HCl, nonluminescent detergent and deionised water prior to sample collection. Water samples were filtered with Whatman GF/C glass microfibre filter papers (0.45 μm; preashed to 400°C) on return to the laboratory, and spilt into two fractions. One fraction was preserved with 1–3 drops of concentrated HNO₃ for trace element and major ion analysis (unpublished data); the other was frozen in glass bottles for between 1 week and 1 year prior to fluorescence analysis. The fluorescence intensity of the groundwater samples was determined using a Perkin-Elmer Luminescence Spectrophotometer LS-50B. The fluorescence peak attributed to fulviclike organic acids at excitation wavelength 300–340 nm and emission wavelength 400–440 nm was chosen for analysis, as it permits comparison with previously studied cave waters [Baker et al., 1997; Baker and Barnes, 1998] in which was utilized a fixed excitation source of 325 nm (HeCd laser). It is also in the range of fluorescence observable in speleothem samples with a mercury UV light source microscope. The Xenon source of the spectrophotometer had slits that were set at 5 nm for both excitation and emission. Excitation wavelengths were incremented from 290 to 350 nm at 2-nm steps; for each excitation wavelength, fluorescence emission was detected from 390 to 450 nm at 0.5-nm steps, and the maximum fluorescence intensity was recorded.

Fluorescence intensity was calibrated against blank water scans that were run every 5–15 analyses using distilled water, with the Raman peak of water at an excitation of 348 nm used both for calibration and as a test for machine stability. Raman emission at 395 nm averaged 14.9 ± 0.5 intensity units ($n = 31$) with no drift during the analytical period (January–April

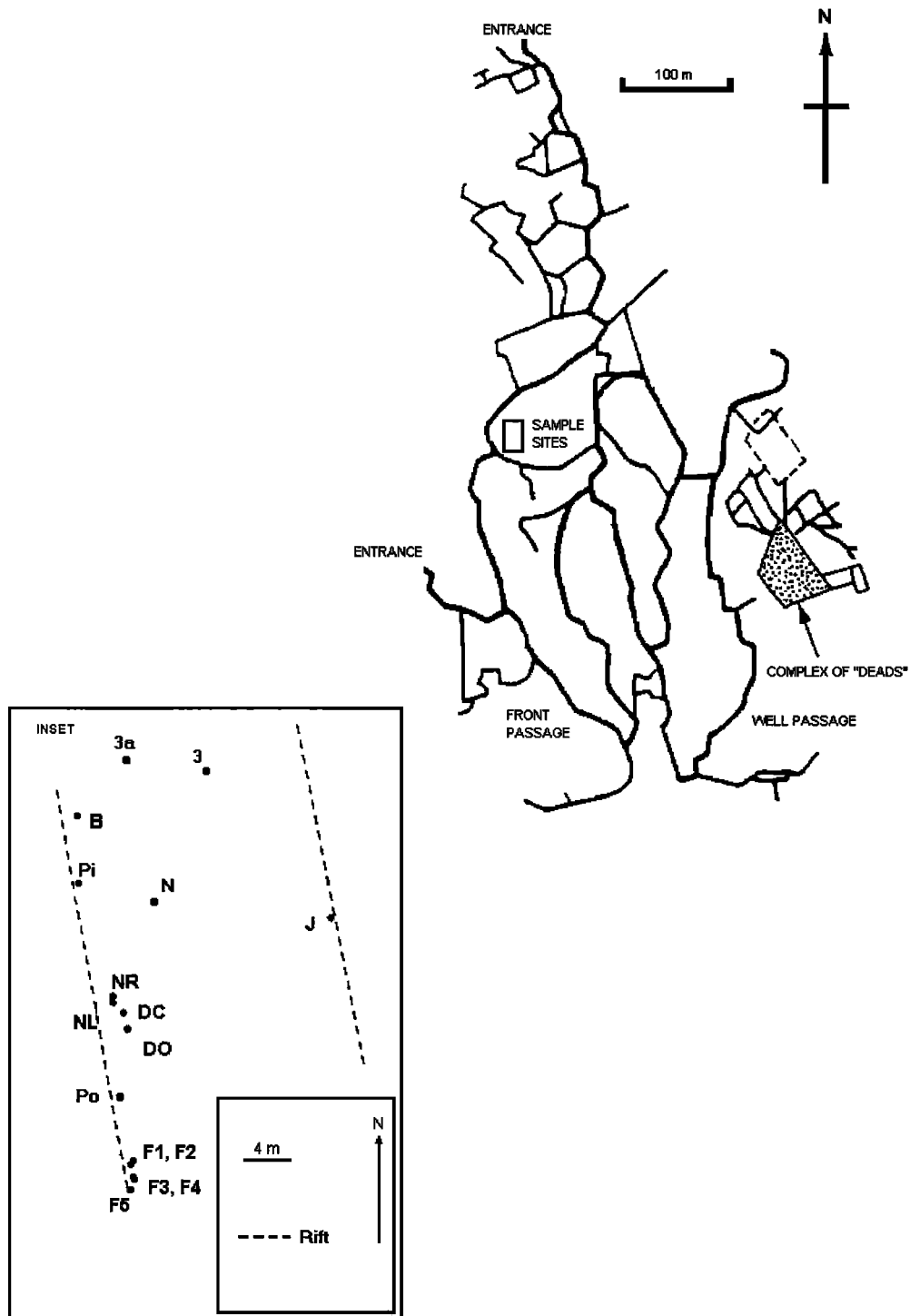


Figure 1. Survey of Brown's Folly Mine. Inset shows location of groundwater sample sites and of the gull rifts that focus groundwater recharge in this area.

1998). In addition, stability of the Raman peak was assessed for a 5-min period at the start of each day of data collection, and sample collection occurred only when the signal-to-noise ratio of the spectrophotometer was greater than 500:1.

Groundwater discharge and fluorescence data were compared to meteorological information gathered by the United Kingdom Meteorological Office's MORECS, version 2(c) rainfall and evaporation calculation system [Thompson *et al.*, 1981;

Hough *et al.*, 1995]. Using 150 national observation sites and 3000 calibration sites, site data for rainfall, sunshine, temperature, soil, and vegetation type are utilized to calculate the derived elements of actual and potential evaporation, soil moisture deficit, and hydrologically effective rainfall. Potential evaporation is calculated from a modified form of the Penman-Monteith equation (for detail see work by Hough *et al.*, [1995] and Ragab *et al.* [1997]). MORECS calculated evaporation, soil

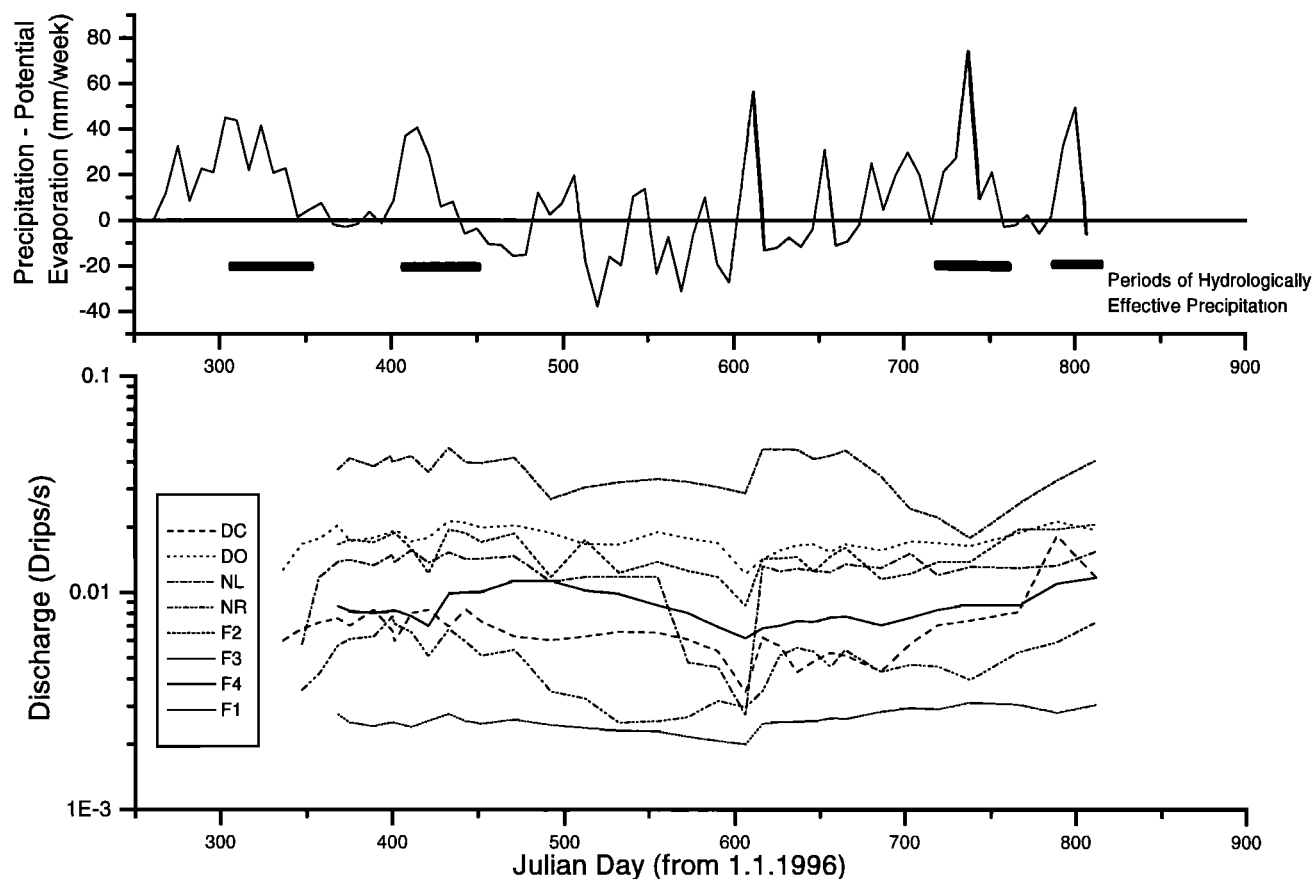


Figure 2. Precipitation–potential evapotranspiration and hydrologically effective rainfall as predicted by MORECS (top) and groundwater discharges for the eight slow-discharge, low-CV discharge sites (bottom).

moisture deficit, and hydrologically effective precipitation for the study area (MORECS grid square 157; deciduous woodland vegetation cover and median soil water capacity) were calculated daily and then averaged to give weekly output.

4. Results

4.1. Discharge Variability of the Sampling Sites

Between 30 and 38 discharge measurements were undertaken at intervals of 10–20 days for the 16 sample sites over the period November 1996 to April 1998. Field observations of the high-CV (coefficient of variation) sites ($CV > 100\%$) suggested that the sampling interval of 10–20 days might not be sufficient to detect all discharge events. It was therefore apparent that it would not be possible to undertake an analysis of the relationship among groundwater fluorescence, discharge, and surface climate variations at Brown's Folly for the high-discharge variability sites (Pi, B, N, 3, 3a, J, and Po), although future work utilizing automatic drip counters and waters samplers may be successful. Instead, research focused on the eight sites with a CV of discharge of $<50\%$, all of which were depositing stalagmite samples and for which a sampling interval of 10–20 days was sufficient to resolve discharge trends.

The discharge time series of the low-CV discharge sites is presented in Figure 2, together with two hydrological parameters that are most likely to affect groundwater discharge. P-PE (precipitation–potential evaporation) reflects the amount of water available to be held in the soil and ground-

water, and hydrologically effective precipitation (HEP) reflects the amount of moisture available for groundwater recharge after the soil moisture deficit (SMD) has been eliminated. Both parameters have been calculated using MORECS output; previous studies have suggested that the model overestimates the extent of summer SMD and thus HEP is underestimated [Ragab *et al.*, 1997]. All groundwater sources demonstrate a similar time series; increases in discharge at Julian days (JD) 330 and 610 (end of November 1996 and early September 1997) demonstrate a recharging of the limestone aquifer in late summer/autumn, with an intervening decline in drip discharge between JD 450 and 600 (end March 1997 to end August 1997). In the 1996–1997 hydrological year the first increase in discharge occurred ~30 days after the first increase in P-PE and HEP. In the 1997–1998 hydrological year, although the lag remained the same, the recharge occurred much earlier in the year, with precipitation in late August (JD 600–610) sufficient to recharge the aquifer (despite MORECS calculations suggesting that HEP would not occur). Rainfall during this week totalled 83.0 mm; with either the thin soil cover at the site (<20 cm brown earth) or macropore flow/flow through desiccation cracks being sufficient to recharge the limestone aquifer.

4.2. Comparison of Fluorescence, Discharge, and Climate Variations

4.2.1. All sites except F1. Fluorescence intensity variations for these seven sample sites are presented in Figure 3, together with weekly P-PE and periods of HEP. For all sites

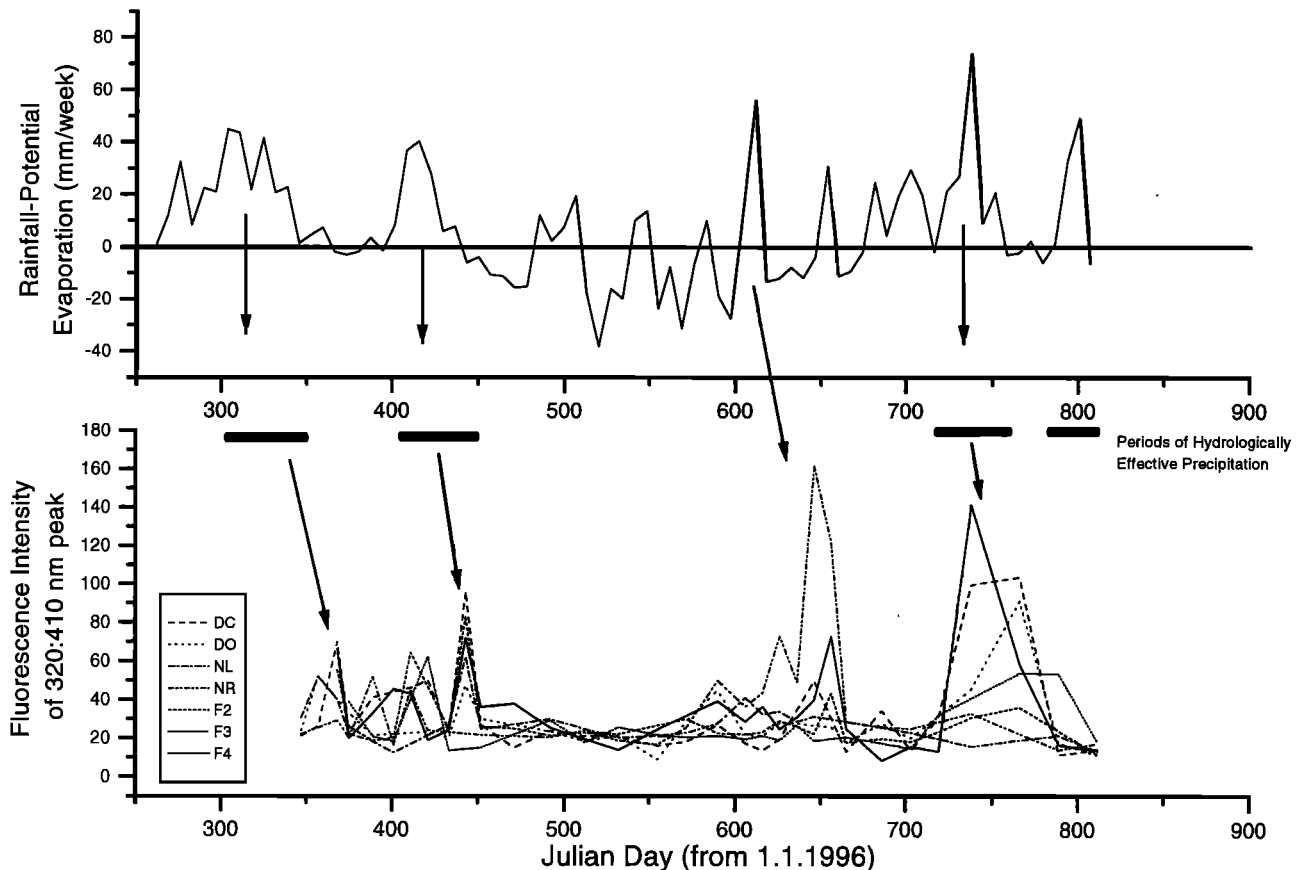


Figure 3. Precipitation–potential evapotranspiration and hydrologically effective rainfall as predicted by MORECS (top) and fluorescence intensity of the 320:410 nm wavelength pair for seven of the slow-discharge, low-CV discharge sites (bottom).

there is a baseline fluorescence of 15–20 units, superimposed on which are significant increases in fluorescence intensity which occur for periods of <10 days to 60 days. The baseline signal probably represents organic matter transported in the long residence time, fissure flow component of the groundwater. The fluorescence peaks, corresponding to flushes in fulvic-like organic acids from the overlying soil, probably transported via the short residence time, fissure flow network, range from a 2× increase to 10× increase on the baseline. This variability probably represents different flow paths of the water, which may lead to subtle differences in both the proportion of fissure and porous flow components as well as to subtle differences in lag time.

Comparison with Figure 2 demonstrates a very weak relationship between fluorescence and discharge, due to the low variability in the discharge record. The first fluorescence increase of the hydrological year, when compared to the timing of the autumn aquifer recharge, is observed to occur an additional 10–20 days after the first increase in discharge. This result suggests that the initial discharge increase is due to the flushing of old water that has had a longer residence time, probably resident in the fissure system since the previous spring.

Despite the weak relationship between fluorescence and discharge, a clear trend can be observed between fluorescence and P-PE and HEP. This is best observed for the 1996–1997 hydrological year, where two sustained periods of water excess

can be correlated with two fluorescence peaks. The relationship for the hydrological year 1997–1998 is more complex, as noted above, with the period of heavy rainfall in late August sufficient to flush organic materials through the aquifer to the speleothems. A second peak (or multiple peaks; 20-day sampling limits the resolution) can be observed commencing JD 720 (January 1998), correlating with a second, more sustained period of high P-PE and HEP.

4.2.2. Site F1. The one low CV discharge site that did not respond in a similar fashion to the other seven was BFM-F1. This site was distinguished from all the others by its continuous and relatively high discharges of 1 drip every 20–40 s for the complete hydrological year. Maintenance of such a high and continuous discharge suggests the presence of a significant reservoir of stored water, probably in a porous flow network. The presence of site F1 within 5 m of sites F2–F5, which demonstrate remarkably different hydrological responses, suggests the presence of at least two reservoirs of stored water in this vicinity with marked different flow routes.

The relationship between fluorescence intensity and climate parameters for site F1 is presented in Figure 4. No clear relationship is observed, which may be attributed to either of the following: (1) a decrease in fluorescence intensity in periods of high discharge. This may be attributed to a dilution of the predominantly storage-derived groundwater in times of high discharge, with the baseline fluorescence being 30–50 fluorescence units. (2) A lag of fluorescence intensity with periods of

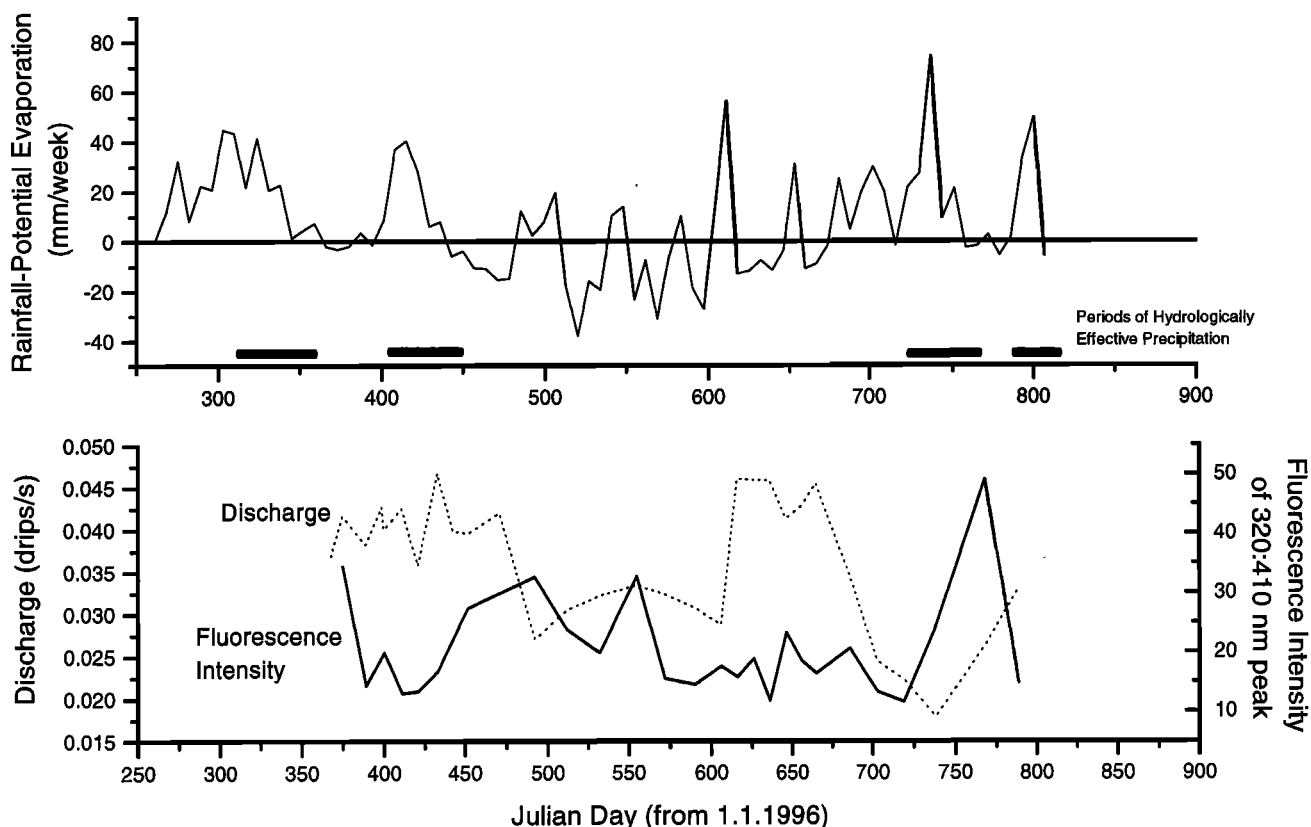


Figure 4. Precipitation–potential evapotranspiration and hydrologically effective rainfall as predicted by MORECS (top) and discharge and fluorescence intensity of the 320:410 nm wavelength pair for site F1 (bottom).

hydrologically effective precipitation with an additional lag of 20 days compared to the other sites at Brown's Folly, giving a total lag of 60–80 days. Again, this may be attributed to a greater proportion of long residence time, porous flow components in the groundwater at this site.

The sampling period of 18 months was not adequate to differentiate between the two processes, although the maintenance of a continuous flow at the site suggests that latter process is most likely.

5. Conclusions

All groundwater sample sites demonstrate groundwater fluxes that can be explained by a mixture of fissure (short residence time) and porous (long residence time) flow components. The maintenance of discharge throughout the hydrological year for sites with low discharge (<0.02 drips/s) and low CV ($<50\%$) suggests that these sites are dominated by the porous flow, relatively long residence time component. In contrast, many of the high-discharge (>0.02 drips/s), high-CV ($>50\%$) sites not studied here (P, 3, 3a, B, and J), all of which have a cessation of groundwater flow in most if not all summers, comprise predominantly fissure flow routings. One site, F1, maintains a high discharge all year; this suggests a porous flow groundwater flow route and because of its nearness to other sites with different hydrological characteristics, the presence of more than one groundwater reservoir.

The presence of one site, F1, that demonstrated clear fluorescence intensity variations but a complex response to surface rainfall, probably due to the longer groundwater residence time of the waters feeding this sample, confirms that the use of single stalagmite samples as high resolution palaeoclimate indicators is perilous. *Baker et al.* [1997] demonstrated from groundwater fluxes and fluorescence intensity variations in the Carboniferous limestone at Lower Cave, Bristol, that 1 in 6 samples exhibited a complex response to surface climate variations. Although no evidence of underflow behavior as observed in Lower Cave was found in this study, the presence of significantly different groundwater responses to surface rainfall within 5 m of each other confirms the necessity for caution. For the other seven samples a strong relationship between fluorescence intensity variations and periods of hydrologically effective precipitation was observed. The stalagmites associated with these groundwaters would therefore be expected to provide a record of palaeoclimate change for their deposition period over the last 100–150 years.

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