HYDROLOGICAL PROCESSES
Hydrol. Process. **22**, 3749–3758 (2008)

(www.interscience.wiley.com) DOI: 10.1002/hyp.6979

Temporal and spatial variations in the discharge and dissolved organic carbon of drip waters in Beijing Shihua Cave, China

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Abstract:

To detect the causal relationship between cave drip waters and stalagmite laminae, which have been used as a climate change proxy, three drip sites in Beijing Shihua Cave were monitored for discharge and dissolved organic carbon (DOC). Drip discharges and DOC were determined at 0 to 14-day intervals over the period 2004–2006. Drip discharges show two types of response to surface precipitation variations: (1) a rapid response; and (2) a time-lagged response. Intra-annual variability in drip discharge is significantly higher than inter-annual variability. The content of DOC in all drip waters varies inter- and intra-annually and has good correlation with drip water discharge at the rapid response sites. High DOC was observed in July and August in the three years observed. The flushing of soil organic matter is dependent upon the intensity of rain events. The DOC content of drip water increases sharply above a threshold rainfall intensity (>50 mm d^{-1}) and shows several pulses corresponding with intense rain events (>25 mm d^{-1}). The DOC content was lower and less variable during the dry period than during the rainy period. The shape of DOC peak also varies from year to year as it is influenced by the intensity and frequency of rainfall. The different drip sites show marked differences in DOC response, which are dominated by hydrological behaviour linked to the recharge of the soil and karst micro-fissure/porosity network. The results explain why not all stalagmite laminae are consistent with climate changes and suggest that the structure of the rainy season events could be preserved in speleothems. Copyright © 2008 John Wiley & Sons, Ltd.

KEY WORDS drip water; discharge; dissolved organic carbon; Shihua Cave; China; stalagmite lamina

Received 4 April 2007; Accepted 27 November 2007

INTRODUCTION

Dissolved organic matter (DOM) is an important constituent of soil and aquatic environments. DOM can not only change the properties of soil surfaces by inducing weathering (Raulund-Rasmussen *et al.*, 1998) and sorptive interactions (Murphy *et al.*, 1990), but also contributes to the mobilization and transport of metals (Pohlman and McColl, 1988), nutrients (Donald *et al.*, 1993), acidity (Guggenberger and Kaiser, 1998), and hazardous compounds (McCarthy and Zachara, 1989). DOM consists mainly of humic substances, a mixture of acidic organic compounds, formed by the partial decomposition of plant, microbial, and animal tissue (Aiken *et al.*, 1985; Hayes *et al.*, 1989). The production of DOM is oxidative and microbially driven (McKnight *et al.*, 1985), and it is sensitive to changes in climate, in particular to temperature and precipitation (Scott *et al.*, 1998). Production, however, is not the sole factor affecting the release of DOM, as adsorption onto soil particles (McKeague *et al.*, 1986; Kaiser *et al.*, 1996; Tipping *et al.*, 1999; Kaiser and Guggenberger, 2000) and soil water flow will exert some controlling effect upon export (Scott and Jones, 1998; Kaiser and Guggenberger, 2005). DOM is usually quantified in terms of its carbon content, which is referred to as dissolved organic carbon (DOC). Numerous studies of peat and forest ecosystems have shown that seasonal variations in the content of DOC in peat pools and soil leachates occur with concentration maxima in summer and autumn (McDowell and Likens, 1988; Tegen and Dorr, 1996; Scott and Jones, 1998; Hongve 1999; Tipping *et al.*, 1999; Kaiser *et al.*, 2001). Such seasonal variations indicate a dependence of DOC concentration on temperature and precipitation, and thus a potential sensitivity to climate and environment changes.

In karst areas, soil organic matter not only plays an important role in driving karst processes (Pan and Cao, 1999; Pan *et al.*, 2000), it is also transported by percolating waters from the soil into caves, where it may be trapped in speleothems, and in some cases cause the formation of luminescence laminae (Lauritzen *et al.*, 1986; White and Brennan, 1989; Baker *et al.*, 1993; Shopov *et al.*, 1994; van Beynen *et al.*, 2001). The organic matter in speleothems can record variations in the palaeoclimate and palaeoenvionment (Baker *et al.*, 1993, 1996, 1998, 1999a; McGarry and Baker, 2000; Charman *et al.*, 2001; Xie *et al.*, 2003). Studies on DOC in cave waters, therefore, can not only enhance the understanding of variation in the DOC of soil, but improve the reliability

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of interpretation of past records. Baker *et al.* (1993, 1999b) studied caves in England and found that most of the organic matter in drip waters reached the cave during late autumn-early winter, correlating with drip discharge. At Marengo Cave (Indiana, USA), however, cave waters yielded the highest organic matter levels in spring (Toth, 1998; van Beynen *et al.*, 2000). In Santana Cave, south-eastern Brazil, the annual maximum value for DOC systematically lags the rainiest period by 2–3 months, the peak in DOC content coinciding with more reduced conditions in the soil (Cruz *et al.*, 2005). These results suggest that the flush of organic matter in drip waters is strongly controlled by seasonal climate and in particular by precipitation. However, these previous studies used only a low sampling frequency, and therefore do not account for the dynamic process of organic matter in drip water responding to rainfall events over short time-scales. Fairchild *et al.* (2006) quantified relationships previously studied qualitatively, and showed that modelled fit to discharge improved greatly when daily rainfall data was used rather than weekly. Higher-resolution data may reveal close relationships that are obscured by less frequent sampling. Moreover, no studies on the mechanism of formation of stalagmite fluorescence laminae have been reported in monsoon climate zones.

This study is based on investigations of the relationship between surface precipitation and discharge and DOC content in drip waters at Shihua Cave, located in the East Asia monsoon zone. The study spans 3 hydrological years to investigate how responsive DOC content in drip water is in relation to rainfall on a short time-scale. In addition, Tan *et al.* (1999a, 2000) demonstrated that some stalagmite laminae in Shihua Cave are annual layers that are characterized by bi-optical variation in transparency and luminescence (bi-optical laminae are very thin dark layers that appears as bright bands when viewed with a UV-microscope. See website: http://www.gees.bham.ac.uk/collections/stalagmite-databank/search.asp). A recent study (Borsato *et al.*, 2007) demonstrated a close spatial association between a suite of trace elements known to be preferentially transported by aquatic colloids and the location of luminescent laminae in speleothems from Ernesto cave, NE Italy, which could give a reasonable explanation of how the bi-optical laminae formed. The study at Shihua Cave has shown when the bi-optical laminae form in the monsoonal zone.

Thickness variations in the annual layers of a stalagmite from Shihua Cave have been used to reconstruct the warm season (May to August) temperature over a 2650-year period (665BC to AD1985) (Tan *et al.*, 2003). However, this property is not always found in the stalagmite laminae from Shihua Cave. Another aim of this study is to understand the dynamic process controlling the concentration of DOC and discharge in drip waters in response to surface precipitation. The result will then be used to aid interpretation of the palaeohydrological signal of organic laminae preserved in speleothems, which could subsequently improve our knowledge of stalagmite lamina–climatology (Tan *et al.*, 2006).

SITE DESCRIPTION

The Shihua Cave (115°56′E, 39°47′N, 251 m above sea level at the entrance) is located in Baihua Hill, Fangshan county, about 50 km away from downtown Beijing. The Middle Ordovician carbonate rocks of the Maojiagou Formation, which mainly consists of limestone with some interlayered dolomite, house the Shihua Cave. This limestone strikes in an east–west direction and is inclined towards the south at about 30°. The thickness of the bedrock overlying the cave varies between 30 and 130 m. Coal layers are unevenly distributed above the bedrock. At present, the natural vegetation above the cave is dominated by shrubs, while persimmon and walnut trees are grown in the valley. The overlying soil is brown soil and its thickness varies from 0·6 to 1 m in the valley and 0 to 0·5 m on the hill slopes. The soil above the cave consists of a 5–15 cm humic layer that has a high content of total organic carbon (40–70 g kg^{-1}).

The cave has a multi-level and multi-branched structure. So far seven levels have been explored. The seventh level is underground river. The passage open to visitors (first to fourth levels) is about 2500 m long. There are numerous speleothems in this cave.

Within the East Asian monsoon zone, the Shihua Cave area typically has cold/dry winters and warm/wet summers. The East Asian monsoon is the major source of precipitation. In Beijing more than 70% of the total annual precipitation falls during the summer monsoon months (June to August), which are also the warmest months. According to the meteorological data, the dry period lasts for at least 8 months from October to May of the next year. From 1971–2000, the mean annual temperature was 12·3 °C while mean annual precipitation was 572 mm.

EXPERIMENTAL METHOD

To assess the spatial variation in drip rates throughout the cave, three sites (PL, SH, JG) were chosen from different localities along the cave passageways (Figure 1). Site PL is located on the first level, where cave air temperature ranges between 13 and 17·8 °C. JG is located at the exit on the second level with good ventilation, and more variable air temperature, ranging between 8·6 and 15·7 °C. Site SH is on the third level and has the narrowest air temperature range, from 13·6 to 16·5 °C. These three sampling points were selected to represent a range of associated speleothem forms (stalactites, soda straws etc.) and bedrock thicknesses (Table I).

The rainfall in the Shihua Cave area was measured by siphon rain gauge in 2004 and 2005, and automatically by tipping bucket rain gauges in 2006. The rainfall in the cave area was 587 mm and 591 mm in 2004 and 2005, respectively. In 2006, the rainfall data were

Table I. Characteristics of the three dripwater flows monitored

Sample site	Thickness of overlying bedrock (m)	Speleothem on the roof
PL	70	stalactite
SH	60	soda straws
JG	40	stalactite

obtained only from June to December (372 mm) because of the change of instruments. Discharge measurements were made at 0–14 day intervals throughout the period from December 2003 to December 2006. Drip rate was estimated by taking repeat counts of drips over 1 min or by determining the elapsed time between two drops and then taking the average.

From April 2004 to December 2006, 100 mL drip water samples were collected in 120 mL glass bottles that had been cleaned in dilute HCl and deionized water before sample collection. Water samples were quickly filtered through Whatman GF/F glass microfibre filters (0·70 µm pore size) and then kept at 4 °C on return to the laboratory. NPOC (non-purgeable organic carbon) was analysed as the concentration of DOC in drip water within a week using a Shimadzu-TOC-Vwp instrument (in the Resource and Environment College, Qinghua University in Beijing). The sample was acidified with phosphoric acid and sparged to eliminate the inorganic carbon (IC). The NPOC concentration is determined by measuring the carbon content of the sample after the IC is eliminated. The results are expressed as the mean of double or triplicate analyses with CV $\leq$2% (CV = coefficient of variation, that is percentage standard deviation of the mean). Some data measured within the rainy period of 2006 was discarded because CV >2%, resulting from instrument instability during automatic internal acidification.

RESULTS AND DISCUSSIONS

Inter- and intra-annual variation of discharge in drip waters

One of the most striking characteristics of the Shihua Cave time series is the marked seasonal variation in drip rate in response to seasonal variation in precipitation (Figure 2). This dependence is in agreement with previous studies (Baker *et al.*, 1997; Genty and Deflandre, 1998; Baker and Brunsden, 2003; Tooth and Fairchild, 2003). To account for the characteristics of the discharge curves, a superposition of at least two types of flow is necessary: a fast-flow component occurring via conduits (preferential flow) and a slow-flow via the network of fissures and porosity (diffuse flow). During dry periods, the frequency and amount of rainfall is low, so the drip flow is fed by diffuse flow from the soil or bedrock storage reservoir. During rainy periods, preferential flow through fractures or conduits dominated the discharge of drip water after storms (Tooth and Fairchild, 2003). Hence, the extent of the contribution of preferential flow can control how sensitive drip rates are in response to rainfall. This results in a high degree of spatial variation in discharge and in the nature of the drip rate response to rainfall at Shihua Cave, as also observed in drip water at other cave sites (Baker *et al.*, 1999b; Baker and Brunsden, 2003; Tooth and Fairchild, 2003). In terms of the time lag between precipitation and discharge, the three sites can be separated into two groups (adapted from Tooth and Fairchild, 2003):

Sites with rapid response. At the sites SH and JG (Figure 2), several abrupt peaks in drip rate occurred in response to important rain events during the rainy period. Compared with dry periods, the drip rate peak value was six–seven times higher at SH and >100 times higher at JG. The latter is the site with the thinner overlying bedrock. Over the rainy season the time lag

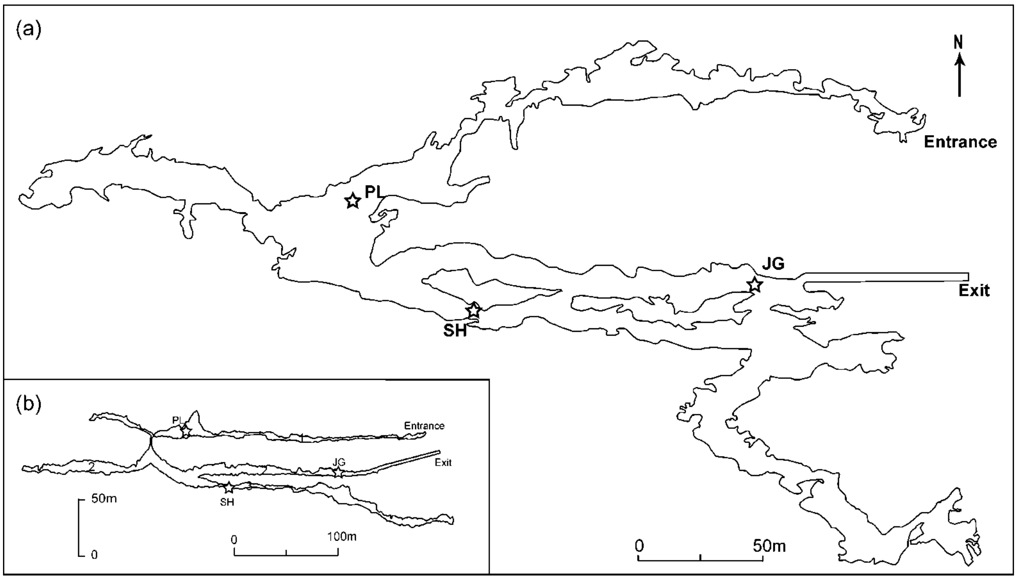

Figure 1. Plan view (a) and longitudinal profile (b) of Beijing Shihua Cave (adapted from Zheng M *et al.*, 2007). The hollow stars and capital letters indicate the sampled drip sites, and cave levels are numbered

DOI: 10.1002/hyp

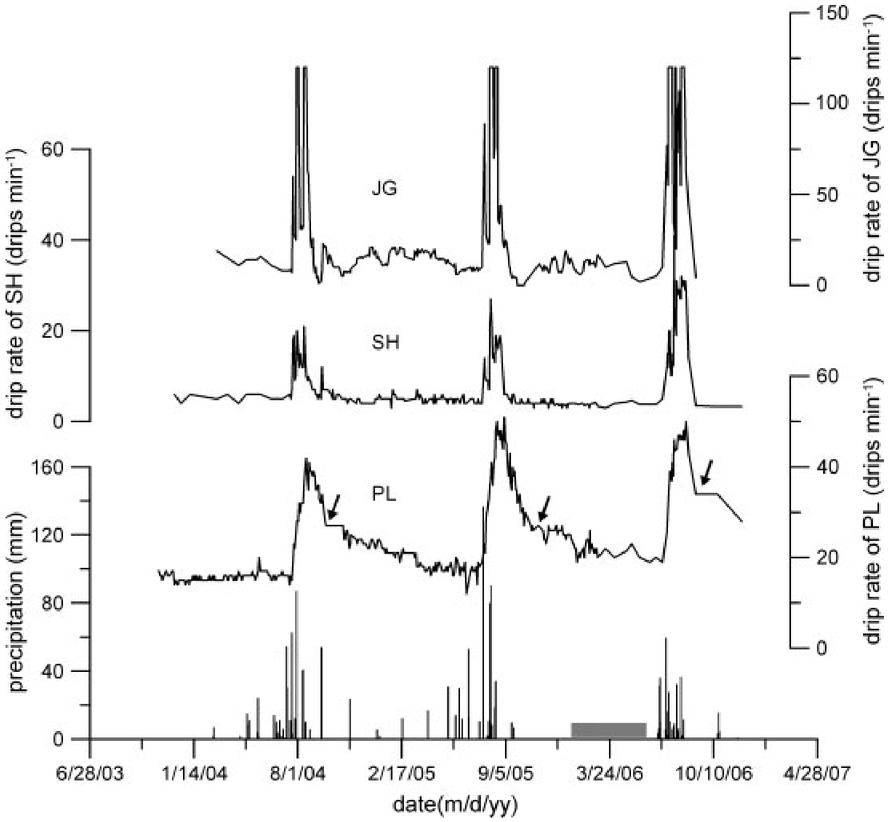

Figure 2. Comparison of drip rate at the three sites and amount of rainfall for the period between October 2003 and December 2006. (Arrows indicate three inflexions of discharge falloff curve at PL over three years). The rainfall data were not obtained from January to May in 2006 (shaded area)

also became shorter, from 2 days to several hours, as the amount and intensity of rain increased. This suggests that the extent of prior recharge to the soil and karst micro-fissure/porosity storage affects the response time of cave drips to precipitation (e.g. the rainwater first fills the soil pores and then infiltrates into the epikarst zone, and then the karst conduits) (Baker *et al*., 1997; Genty and Deflandre, 1998). It can also be observed that after rain storms the drip rates decreased immediately in the absence of further rainfall input. The discharge of SH and JG during dry periods was 4–5 drops min^{-1} and 1–20 drop min^{-1}, respectively. These low values indicate that the drip waters of JG and SH were recharged through large fissures and conduits dominantly during rainy periods and the extent of storage was limited. This also shows that new water cannot mix easily with the storage water in this type of drip site.

Response with associated time lag. At site PL, drip rate was higher (16–20 drops min^{-1}) during dry periods than at sites SH and JG. After some rain events, the PL drip rate increased gradually up to 50 drops min^{-1}, then fell to 25–28 drops min^{-1} for some time, before slowly returning to low values (Figure 2). There is also a time lag of 10–20 days between the rainfall maximum and the peak in drip rate at site PL. The general shape of the discharge curve during an entire hydrological year is very similar to the stalactite flow in the Père Noël cave, Belgium (Genty and Deflandre, 1998) with a steeply rising limb and much more gradual recession. The observed recession in drip rate represents a double-porosity system (Atkinson, 1977; Cronaton and Perrochet, 2002; White, 2002; Liedl *et al*., 2003) that is composed of a highly conductive low storage conduit network and a low-conductive high-storage rock matrix under variable boundary conditions. Site PL is thus characterized by a greater proportion of stored water than SH and JG, which contributes to the higher discharge during dry seasons. The storage reservoir may act as a buffer that allows new water to mix more easily with stored water during the rainy period.

In comparison with the seasonal variation, inter-annual variation of the discharge in drip waters was less obvious, which suggests that the flow paths did not change during the monitoring period.

It is obvious that cave drip water comes predominantly from rainwater. The hydrodynamic system and flow path are the main factors affecting the spatial variation in discharge, and this can influence the DOC content contained in this flow recharge.

Temporal and spatial variation of DOC in drip waters

Seasonal variation of DOC in drip water. Variations in the concentration of DOC for the three sites are presented in Figure 3. DOC concentration for the stalagmite drip waters ranged from 0·18 to 3·05 mg L^{-1}. At the three sites, DOC concentration shows similar temporal trends, with an increase in July–August (rainy season) during the monitoring period. During the dry period, DOC concentration was below 1·0 mg L^{-1} and exhibited little variation. In contrast, there were abrupt DOC peaks when the daily rain amount exceeded 50 mm (the rain events marked with hollow stars in Figure 3) during the rainy period. This suggests that the intensity of rain is an important factor controlling the flushing of soil organic matter.

This can be related to the characteristics of the monsoon climate with cold/dry winters and warm/wet summers. Every autumn, a large amount of leaf litter falls onto the soil contributing to soil organic matter (SOM). During the following 8-month dry period, SOM is decomposed by soil microorganisms, and there are also drastic changes such as drying and freezing of the soil (December to February of the next yrear). These can increase the release of organic matter with the hydrophilic fraction of SOM (Scott and Jones, 1998; Tipping *et al.*, 1999). Low precipitation during this period prevents the transport of DOC to the cave site so that the organics remain in the upper soil layers. A large amount of soil DOC produced in the dry season is therefore stored in the soil until the first intense rain events (>50 mm d^{-1}) of the rainy season flush the system, causing the observed sharp rises in concentration and flux of DOC in drip water. This sequence is similar to the observed variation in the DOC concentration in drainage water from soil systems, in which the higher DOC concentration occurs in summer following a dryer period (McDowell and Likens 1988; Tegen and Dorr, 1996; Scott and Jones, 1998; Hongve 1999; Tipping *et al.*, 1999; Kaiser *et al.*, 2001). Thus the variation of DOC content in drip waters reflects changes in the production and transport of DOC in soil, although some components, such as the hydrophobic fraction, could be absorbed or filtered when soil waters flow through bedrock.

Similar experiments measuring drip water luminescence over a hydrological year at Lower Cave, Bristol (Baker *et al.*, 1997) and the Brown's Folly Mine site (Baker *et al.*, 1999b), which are located in England under a maritime climate, also revealed an increase in DOC luminescence during the period of hydrologically effective precipitation in late autumn or early winter. In contrast, at Marengo Cave, located in Indiana, USA under a continental climate (Toth, 1998; van Beynen *et al.*, 2000) high fluorescent intensity and DOC are observed in the cave during spring, when rain causes the snow to melt and the soil to thaw out, generating a flush of organics from the soil to the cave. These observations confirm that an annual flush of organic substances from the soil during periods of hydrologically effective precipitation forms luminescent laminae preserved within speleothems. It can also be observed that seasonal dry/wet and cold/warm shifts in climate zones as diverse as those of China, England and USA can produce luminescent growth layers within stalagmites.

Annual variation of DOC in drip water. Besides seasonal change, Figure 3 also shows inter-annual variation in drip water. Inter-annual variation exhibits two aspects as follows:

The shape of the DOC concentration peak: In 2004, the DOC concentration in drip waters at the three sites

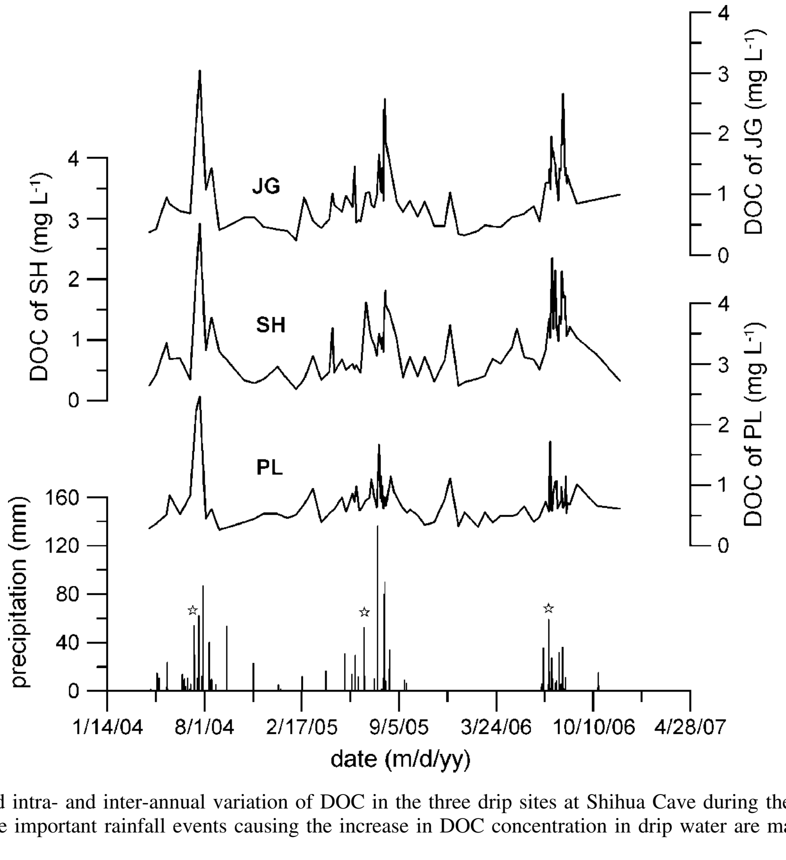

Figure 3. Rainfall amount and intra- and inter-annual variation of DOC in the three drip sites at Shihua Cave during the period between April 2003 and December 2006. The important rainfall events causing the increase in DOC concentration in drip water are marked with hollow stars

synchronously and abruptly increased (2·2–2·4 times higher than the mean value of 2004) after two continuous rainfall events (54·5 mm and 30·2 mm, respectively) at the beginning of the rainy period. DOC concentration reached its highest value (2·3–3 times higher than mean value of 2004) on 22 July. A single peak of DOC concentration occurred in 2004. However, during the rainy periods of 2005 and 2006, many peaks or sub-peaks in DOC concentration were observed after rain events. Taking the variation of DOC and drip rate in 2006 as an example, results show that DOC concentration increased, with a time lag of 2–7 days relative to the first heavy rain on 10 July (rain intensity: 59·6 mm d^{-1}, marked with a hollow star in Figure 4) and then quickly decreased. These peak values of DOC were 150–250% of their mean values for 2006. Similarly, during the rainy season of that year, other high intensity rain events (>25 mm d^{-1}) were also followed by peaks or sub-peaks in DOC (marked with solid stars in Figure 4). It is speculated that the single DOC peak in drip waters observed in 2004 was an artefact of the lower sampling frequency (1–2 week) used during that year, which was inadequate to capture the high frequency dynamics. In comparison, in 2005 and 2006, high-resolution sampling allowed observation of short time-scale variations. Baker *et al.*, (1999b) also observed double peaks of fluorescence intensity in autumn and winter. In their study, however, there were about 60–100 days between the two observed peaks. This may be ascribed to the duration of the rainy season and low sampling frequency. High-frequency monitoring has revealed differences among the complex multipeak structures of DOC in different hydrological systems (Figure 4).

The peak value of DOC concentration: During three years of monitoring, the peak values of DOC concentration at PL, SH and JG sites were highest in 2004 (2·47 mg L^{-1}, 2·93 mg L^{-1} and 3·05 mg L^{-1}, respectively). Next highest were the peaks of concentration of DOC in 2006 (1·72 mg L^{-1}, 2·35 mg L^{-1} and 2·66 mg L^{-1}, respectively). The peak DOC values were lowest at the three sites in 2005 (1·67 mg L^{-1}, 1·82 mg L^{-1} and 2·57 mg L^{-1}, respectively). It has been established that dilution by rainwater and water–rock–air interaction can

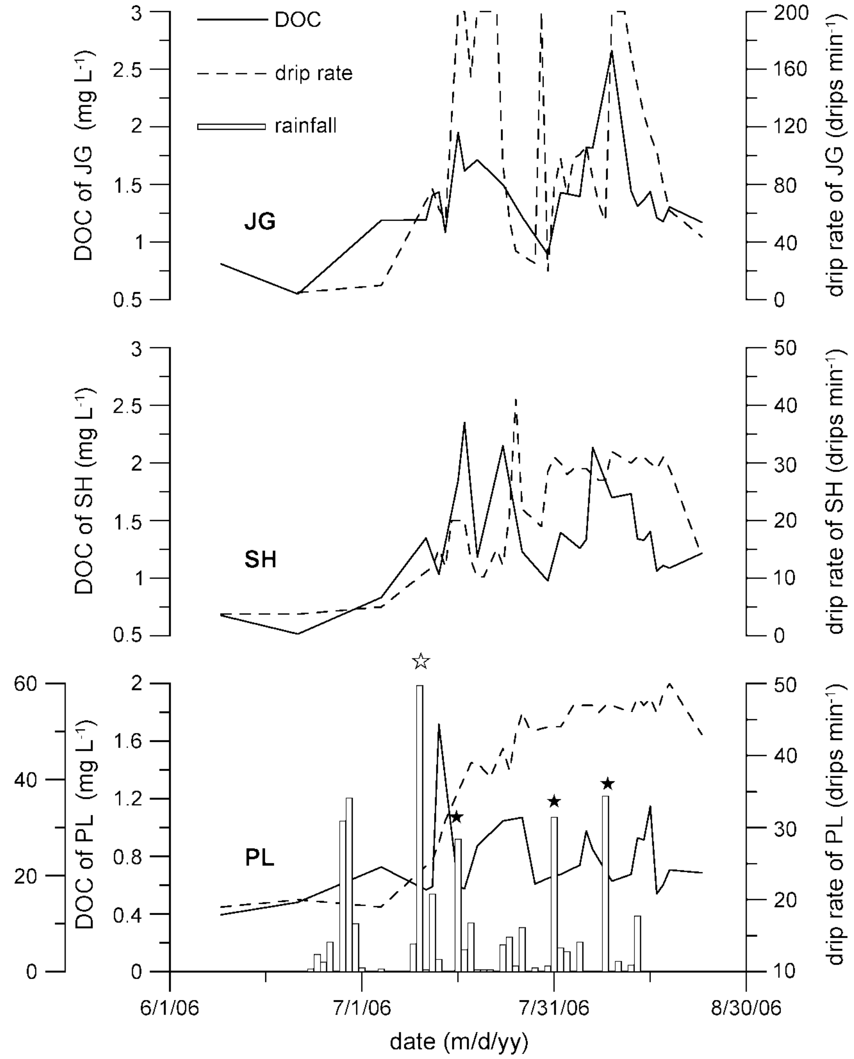

Figure 4. Daily rainfall and variations in DOC concentration and discharge of drip water from June to September 2006. The first intense rainfall event causing the increase of DOC is represented by the hollow star and other important rainfall events by solid stars

influence the hydrochemical nature of the conduit and fissure flow (Liu *et al.*, 2003). At the beginning of the rainy season in 2004, more than 10 rain events ($<$15 mm d^{-1}) occurred successively, but the discharge did not increase markedly. In this situation, the rainwater can be stored in the dry soil porosity or in bedrock fissures and has time to dissolve a large amount of soil organic matter (hydrophilic fraction) in the process of slow downward infiltration. Consequently, when the intensity of rainfall exceeded the threshold ($>$50 mm d^{-1}), storage water rich in DOC was flushed out by the input of fissure flow and the consequent increased hydraulic pressure (piston flow system). The dilution effect is decoupled owing to the absence of preferential flow. In contrast, high intensity and low frequency rain events, especially a heavy storm (136·6 mm) on 23 July 2005, resulted in the more obvious dilution effect in the rainy season of 2005. Therefore, the pattern of rain (frequency and intensity), and the effect this has on the availability of DOC in the soil are key controls of DOC concentration. These may differ significantly between years and with climate change. More detailed research on the cycling of dissolved organic matter in karstic soils must be conducted to evaluate these controls.

Spatial variation of DOC in drip water. From Figure 3, an obvious spatial variation in DOC concentration is observed between drip sites. The highest DOC values (mean peak value: 1·06 mg L^{-1}, $n = 92$; peak: 2·76 mg L^{-1}, $n = 3$) are observed in the drip water of JG located 40m beneath the surface, followed by SH site (mean peak value: 0·95 mg L^{-1}, $n = 91$; peak: 2·36 mg L^{-1}, $n = 3$) located 60m beneath the surface. The lowest DOC value (mean peak value: 0·73 mg L^{-1}, $n = 94$; peak: 1·95 mg L^{-1}, $n = 3$) was found at the PL site located 70 m beneath the surface. This was especially evident in 2005 and 2006. It is consistent with the observation of the variation of fluorescence intensity in drip water at Lower Cave and in stalagmites at GB cave, England (Baker *et al.*, 1996, 1997). This may be caused by the filtering and absorption effect of the soil and bedrock on organic matter as the percolation waters flow to the cave (Thurman, 1985; Jardine *et al.*, 1989). In particular, the hydrophobic humic acid is sensitive to absorption (van Beynen *et al.*, 2000). Therefore, the thinner the bedrock and the more rapid the response to rain in drip sites, the higher the peak of DOC concentration.

On the other hand, the correlation between drip rate and DOC content is different in the three sampling sites. At the rapid response drip sites SH and JG, soil preferential flow and conduit flow are the dominant processes, and high DOC concentration in drip water was transferred by the rapid flow. An exponential correlation between DOC and discharge have been observed at sites JG and SH during the rainy period. In contrast, at the PL site, no relationship was observed between discharge and DOC content during the rainy period (Figure 5). There are two possible explanations for this result: (1) the highest DOC peak every year is caused by the concentrated DOC waters flowing through the shortest flow paths. At the PL site with more rain input, there is more flow through more remote paths that combine and feed this site. This long residence component of the drip waters, however, may contain low DOC because losses during transport are increased. Hence, this type of water may dominate latter parts of the high discharge period. (2) At the beginning of the rainy season, the concentrated DOC water infiltrates into the epikarst storage reservoir. Later, some of the water is flushed into the cave by the hydraulic pressure resulting from continuing rain. With continuous rainfall, the water level of the epikarst reservoir becomes higher, resulting in the increase of discharge and a decrease in DOC concentration owing to dilution. The peak DOC concentrations therefore occur before the peak discharges at the PL site, and this may be termed the ‘reservoir effect’.

When compared with the drip rate (Figure 6), it is noticeable that the DOC peaks occurred with or before the discharge peaks in each of the three years of monitoring at Shihua Cave. This contrasts with some results obtained elsewhere. For example, there are 10–30 days and 2 months lag between discharge increase and luminescence increase at Brown’s Folly Mines, England (Baker *et al.*, 1999b) and at Grotte de Villars, Dordogne, France (Baker *et al.*, 2000), respectively. Aside from difference in the geology, depth of sample sites and extent of karstification between the caves (Baker *et al.*, 2000), another two reasons can be considered. (1) The caves are located in different climatic zones and are covered by different types of soil and vegetation, which influence

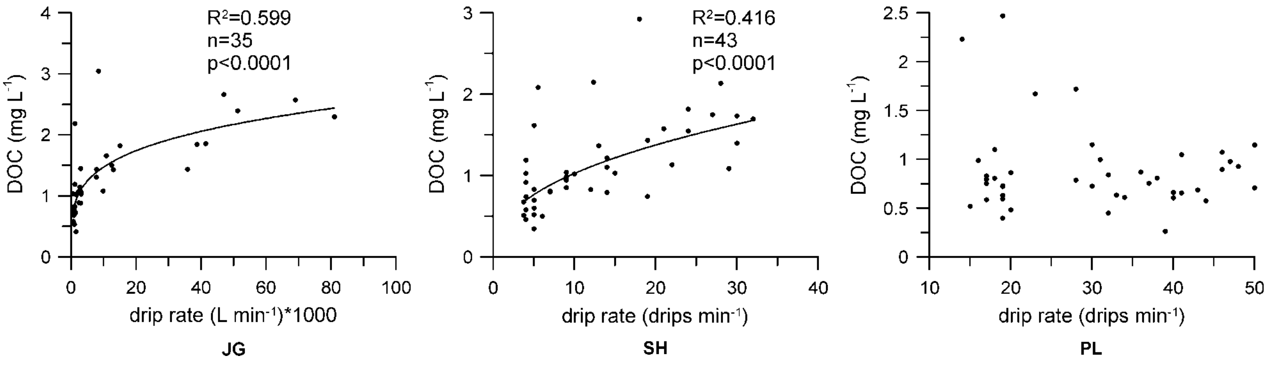

Figure 5. Correlation between discharges and DOC concentration in the rainy season (June–August)

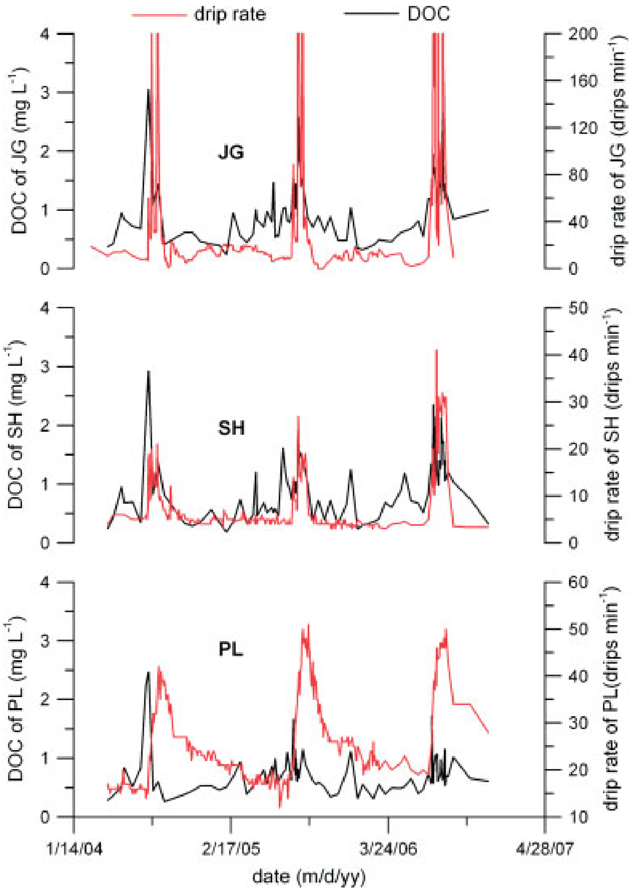

Figure 6. Comparison between the variation of DOC concentration and discharge

the quality and quantity of soil organic carbon and the nature of its transport. (2) The observations were based on different sampling frequencies.

Palaeoclimatic signal preserved by speleothems at Shihua Cave

The relationship between rainfall and DOC concentrations observed for three drip sites at Shihua Cave suggests that the annual structure of this signal preserved within cave speleothems has the potential to reconstruct palaeoprecipitation. This is because the sharp DOC peak in drip water during the rain period is thought to correspond with formation of the thin and dark layers within stalagmites, which are used to distinguish annual laminae. The variations in the shape of DOC peaks influenced by the frequency and intensity of rain can not only account for the diversity of stalagmite laminae, but also provides a better understanding of how organic acids in stalagmites can be used as a proxy record for palaeoprecipitation. One particular application of these results is that one may achieve cross-dating between different stalagmites in a cave according to the distinctive form of stalagmite laminae in extreme rainy years. Importantly, this study suggests that rainfall intensity rather than rainfall amount may be the threshold parameter for the flushing of DOC. In Shihua Cave, the first intense rain event (>50 mm d^{-1}) every year can be related to the formation of stalagmite laminae rich in organic matter. Moreover, the amount and frequency of rain that occurred before the threshold was passed can influence the height of the DOC peak by dilution or concentration. For example, high frequency and low intensity rainfall at the beginning of rain periods followed by a greater than threshold rain event has the potential to form clear and opaque layers in the cave speleothems (as in 2004 data). In addition, multiple intense rain events during the rainy period are likely to result in the formation of double or multiple laminae in a single year. This confirms the previous suggestion of Baker *et al.* (1999c) that double lamina can be generated by high intensity (>60 mm d^{-1}) and high quantity (>250 mm month^{-1}) precipitation in Pooles Cavern, England.

The spatial variation in karst hydrology influenced by thickness of bedrock, macro-or micro-fissure network feeding system, etc. provides clues to understanding how stalagmites respond to climate. A DOC peak occurred in the rapid response drip water every year, and consequently can be preserved in stalagmites as annual bands. However, it is a well known fact that annual banding is not observed in all stalagmite samples, and this may be because they are fed by more diffuse flow. Previous studies have mentioned mixing of groundwater in the aquifer, soil water residence characteristics, depth in the aquifer and the property of soil as a primary cause of the lack of banding preservation (Baker *et al*., 1993; 1996; Shopov *et al*., 1994; Tan *et al*., 1999b). But in addition, these studies of drip water DOC in Shihua Cave suggest that the pattern of rainfall can influence the formation and integrity of the annual record. Overall, caution must be exercised when reconstructing the palaeoclimate based on the thickness of laminae in stalagmites.

CONCLUSIONS

There are obvious inter- and intra-variations in the DOC of drip waters at Shihua Cave, located in the monsoon zone. High levels of DOC in drip water are present after the start of the rainy season in July and August. This may result in the formation of organic laminae within stalagmites. High resolution monitoring of the drip water dynamics indicates that the first intense rainfall (>50 mm d^{-1}) may be the critical threshold governing the rapid increase of drip water DOC concentration. In the same rainy season, other intense rain events (>25 mm d^{-1}) also trigger subsequent separate DOC peaks.

The intensity and frequency of rain is the main reason for short term inter-annual change in DOC concentration. A rainfall pattern consisting of high frequency and low intensity rainfall followed by an intense rain event has the potential to form the clear annual layers at Shihua Cave.

In addition, there are striking differences in the three drip sites investigated. There is a remarkable DOC peak in the rainy season every year at these sites responding rapidly to precipitation. Such peaks may be absent in sites with a time-lagged response to rainfall. The differences among the complex multipeak structures of DOC in different hydrological systems have been revealed by the high-frequency monitoring, although it is impossible to explain why these occur at present.

In conclusion, fluorescent laminae in stalagmites that are formed by organic matter variations may be formed during the rainy period in some drip sites in Shihua Cave, and have therefore the potential to record changes in past precipitation. However, as different sites in the cave show different variations in DOC, one must be cautious in selecting stalagmites to reconstruct the palaeoclimate.

ACKNOWLEDGEMENTS

We thank Andy Baker for his excellent comments and suggestions on the original draft. We thank the Administrative Committee of Shihua Cave for assistance, and Lianqing Li, Patrick Rioual and Xiaoguang Qin for their instructive discussions. Thanks to Ian Fairchild and an anonymous reviewer for their constructive suggestions. This work was supported by the National Basic Research Program of China (Grant No. 2006CB400503), the National Natural Science Foundation of China (Grant No. 40472091) and the Chinese Academy of Sciences (Grant No. KZCX2-YW-316).

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