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SPATIAL AND TEMPORAL VARIATIONS IN THE DISSOLVED ORGANIC CARBON CONCENTRATIONS IN THE VADOSE KARST WATERS OF MARENGO CAVE, INDIANA

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In order to better understand the organic content of microbands in speleothems, seasonal variations in the organic concentrations of vadose drip waters were examined in relation to climatic and environmental variables. Seasonal variations in the organic concentrations of the vadose waters were observed by documenting the fluctuations of Dissolved Organic Carbon (DOC) and its corresponding fluorescence. Tracer dye tests established that the larger drips depositing calcite in Marengo Cave were fed by waters with a short residence time. A strong seasonal variation in DOC concentrations and natural fluorescence was detected at quickly responding sites. Slow, constant drip sites displayed a weaker seasonality. Further investigation is required to distinguish low fluorescing DOC and to determine if the same fluorophors identified in the vadose water can be identified in the organics trapped in the recipient calcite. The overall conclusions are that fluorescence is well correlated with DOC when the fluorescence range is high but it is not a strong indicator of DOC at low fluorescence values; that the value of fluorescence as a predictor of DOC may vary significantly with individual sampling sites; and that the highest fluorescence values occur in springtime and the weakest in summer and fall.

The organic content of microbands in speleothems is a promising but poorly understood field for paleoclimatic interpretation. Paleoclimatic studies of stalagmites and flowstones have included the isotopic records contained in the calcite of vadose-zone speleothems (Schwarcz 1986; Gascoyne 1992; Dorale *et al.* 1992, Baker *et al.* 1993). Many speleothems show varve-like submillimeter-scale color bands. Gascoyne (1977) and White (1981) determined that the color of such speleothems is chiefly due to the presence of variable amounts of clay or humic substances which coprecipitated or absorbed onto calcite surfaces from drip waters that passed through soil before entering the cave. Lauritzen *et al.* (1986) found that humic and fulvic acids are readily soluble and may be expected to enter speleothem feed waters preferentially during growing seasons. The two groups found in speleothems may be taken as indices of productivity in the overlying soil and plant cover and, therefore, as a proxy measure of paleoclimate (Lauritzen *et al*. 1986). Shopov *et al.* (1994) found a well-defined annual cycle in many vadose-zone speleothems that could be used to define the chronology of short-term events. This cycle is probably a response to hydrological events in the recharge to the cave. The most basic research on the response of organic material to climatic and environmental variables is still lacking. In this study, seasonal variations in the organic concentrations of vadose drip waters were examined in relation to climatic and environmental variables. The results will help to set up transfer functions for paleoenvironmental interpretation of organic content of speleothems, at least from Marengo Cave, Indiana.

Organic (humic) substances occluded in the calcite crystals of many vadose speleothems cause luminescence in UV light. This may produce varve-like bands parallel to growth, and visible color layers are often resolvable down to micrometer scales. Shopov (1987) and White and Brennan (1989) showed that the luminescence is caused by calcium salts of humic and fulvic acids along with some low-molecular-weight organic esters. Shopov (1987) provided the first indirect evidence that the banding may reflect paleoenvironmental parameters. By assuming that the finest bands were annual, 11 to 22 year cycles were demonstrated in some samples. It appears that some variable of the paleo-ecosystem caused variations in the amounts of clay or humic substances to be coprecipitated with, or adsorbed onto, calcite. The first step in order to understand this paleoenvironmental signal is to study the relationship of ecosystem parameters and organics in drip water today. In the study reported below, drip water sites were monitored over the spring and summer of 1995 in order (i) to characterize the organic matter in the vadose waters and its fluorescence, and (ii) to determine any seasonal variations in organic concentrations.

STUDY SITE

Southern Indiana today has a strongly seasonal climate with a mean annual precipitation of 1110 mm of which approximately 420 mm falls in winter, and a mean annual temperature of 13.4ºC with a typical annual range of -5° to 25.5°C. The topography of the region consists of hills, ridges, valleys and sinkholes. Marengo Cave, 50 km northwest of Louisville, Kentucky (Fig. 1) is situated beneath a mature forest producing significant amounts of organic matter, and has many active speleothems within easy access. The cave is located under a sandstone-capped ridge in the 152 m thick Middle Mississippian Limestone of the Blue River Group (which

Figure 1. Location of Marengo Cave, Indiana.

includes the St. Louis, Ste. Genevieve and Paoli Formations). Sampling sites were chosen from the upper cave, a simple low gradient river cave now abandoned by flowing water and truncated at both ends by breakdown (Fig. 2). The majority of the sampling sites were located at the two ends of the cave where the overlying bedrock is not very thick and decorations are profuse. The distribution of speleothems reflects the behavior of modern drips: the highest volume drips coincide with the highest volume of speleothems towards the cave ends (e.g., the Crock, Lions Cage), and the lower volume drips with the fewer speleothems of the cave center.

METHODS

The route of water flow from the forest floor to the cave drip sites (Fig. 2) was traced with eight dye tests in early May 1995 (Table 1). For each test an automatic water sampler operated for 24 hours after injection at the site deemed most likely to be the relevant drip point. Sampling was augmented by manual collection from 18 other possible sites for up to six weeks after injection. The results of the dye tracing provided the basis for subsequent drip water sampling.

Samples for DOC and fluorescence were collected from Tomtom, Crystal Palace, Lions Cage and the Crock (Fig. 2) on a weekly basis between February and October 1995, using Teflon tubing attached to the stalactite with copper wire and protecting the mouths of the 2.5 L collecting jugs with aluminum foil (folded to prevent the shiny, possibly organically contaminated side from coming into contact with the water).

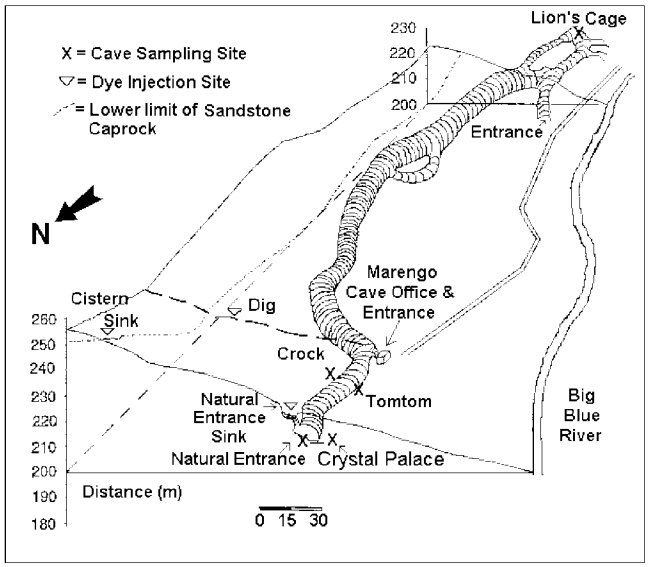

Figure 2. 3-D Model of Upper Marengo Cave, Indiana, a simple low gradient, abandoned river cave. Sites for injection and recovery of dye during the tracer dye tests.

A suite of smaller (200 mL) samples was collected daily, directly into Teflon bottles, from May to mid-June 1995 from 8 dripping stalactites, 8 drips into pools and 2 drips from fractures. Temperature and conductivity were measured *in situ*. The samples collected daily, directly into Teflon bottles, were analyzed for total fluorescence (on a Turner Fluorometer, with a blue filter) usually within a few hours of collection, at the cave site and, thus, at ambient cave temperature. The samples collected weekly, approximately a quarter of the total, were stored in a cold room and analyzed within 2 to 3 months of collection at McMaster University, Ontario, Canada. Ninety-nine samples representing the widest range of measured fluorescence (from 30 to 700 total fluorescence measured on a relative scale) were analyzed in McMaster University for Dissolved Organic Carbon (DOC) by syringe injection into a DC-180 DOHRMANN Carbon Analyzer. Each sample was acidified with HNO_3 to a pH of 2 and degassed with argon for 5 to 10 minutes in order to remove the dissolved inorganic carbon.

RESULTS

DYE TRACING

Dye traces showed both the underground water routes and the response times. Results are shown in Table 1. Flow rates may have been abnormally fast because May 1995 was an especially wet month with 284.2 mm of rain. In spite of the rain, water had to be added along with dye for most of the tests to flush it into the system. Only three of the tracer dye tests, all at the north end of the cave, were successful.

The peak of the dye injected at the Cistern appeared 7.5 hours later and 45 m lower, at the Natural Entrance. A second

Table 1. The results of the tracer dye tests - injection and recovery sites shown in Figure 2. All samples were analyzed with a Turner Systems Fluorometer, Model 10, using an orange filter for Rhodamine WT, Sulpho-Rhodamine B and Eosine, and a green filter for Fluorescein, Pyranine and Eosine.

Test No.	Date	Flow Rate (m/sec)	Injection Point	Recovery Point	Dye	Mass of Dye Injected/Recoverd	Weather Conditions	Water Added	Success/ Failure
1	8-May	$1.67*10^{-3}$	Cistern Sink	Natural Entrance	Rhodamine WT	1.74 g / 1.36g	Dry	Yes	Success
2	9-May	$1.67*10^{-2}$	Cistern	Natural Entrance	Fluorescein	2.57 g / 1.59 g	Rain Storm	No	Success
3	9-May	N/A	Natural Entrance Spring	Natural Entrance	Sulpho Rhodamine B	NA	Rain	Yes	Failure
4	10-May	$4.32*10^{-3}$	Gift Shop "Dig"	Crock	Eosine	60 g / 39.37 g	After Storm	No	Success
5	11-May	N/A	Bonaza Sink	No Recovery	Pyranine	N/A	Dry	Yes	Failure
6	11-May	N/A	Coral Sink	No Recovery	Sulpho Rhodamine B	N/A	Dry	Yes	Failure
7	11-May	N/A	Dig	No Recovery	Fluorescein	N/A	Dry	Yes	Failure
8	11-May	N/A	Nicks Sink	No Recovery	Sulpho Rhodamine B	N/A	Dry	Yes	Failure

injection at the same site during a storm event emerged in only 45 minutes. These fast flow rates (1.67 x 10^3 m/sec for the first test and 1.67 x 10^3 m/sec for the second) and the absence of any dye at the nearby site of Tomtom suggests a simple pipe connection. The other successful dye trace, from the Gift Shop "Dig" to The Crock was done shortly after a storm event and also showed a fast response rate (4.32 x 10^3 m/sec through 70 m of overburden) and a simple pipe connection.

The other tests were done during drier conditions and the added water to flush the dye in may have been insufficient. Although monitoring continued throughout the summer no traces of the dye were found. There is a possibility that the dye did emerge at some low elevation springs close to the injection points, but these were checked with only a few hand samples and the peak may have been missed.

The conclusion from the dye tests was that some of the larger drips (e.g. the Crock) are fed by waters that are underground for no more than a few hours to a few days, that the drip rate and volume responded quickly to surface water conditions, and that the route is usually a simple unbranched pipe connection. These sites also showed a large range of organic content and fluorescence and were classified as strongly responding sites. Other evidence indicates that some drips behave in a different way: for example, Tomtom showed no dye traces, and had a more consistent drip rate, volume and fluorescence than other sites. This suggests that the waters at Tomtom are well mixed and remain in the vadose zone longer. Slow flowing drips such as Tomtom also showed low values of organic content and fluorescence and were classified as weakly responding sites.

TOTAL FLUORESCENCE AND DISSOLVED ORGANIC CARBON (DOC) CONCENTRATION

For the analysis of total fluorescence and DOC concentration, it was expected that the majority of the fluorescence of vadose drip waters would come from dissolved organic carbon because particulate organics are filtered by the overburden through which the waters flow. The relationship between DOC and natural fluorescence was tested for all waters to see if fluorescence is a good predictor of DOC; the results, divided according to the time of collection, are shown in Figure 4. Work by Smart *et al.* (1976) has shown that the total organic carbon concentration in a range of polluted natural waters correlates linearly with fluorescence. The DOC concentration was expected to increase and peak throughout the summer and decline in the dry fall. To test this hypothesis, DOC and natural fluorescence were plotted against time. Only the strongly responding sites showed much seasonal change.

The spring waters (collected between March and mid-June 1995, Fig. 3) showed a statistically significant positive relationship of fluorescence and DOC (with an r^2 value of 0.617 and a one-tailed t value of 1.68, significant at the 0.05 level of probability). Spring waters, thus, show that the measured fluorescence of the waters was caused by the DOC; that fluorescence is simply and linearly proportional to the amount of DOC; and that the waters did not contain significant non-fluorescent DOC (the line begins close to the origin).

This trend did not continue in the summer waters (collected between mid-June and August 1995, Fig. 3). Although concentration of DOC increased to some extent during the summer months related to the increase in biological activity, fluorescence did not always increase, and no correlation between flu-

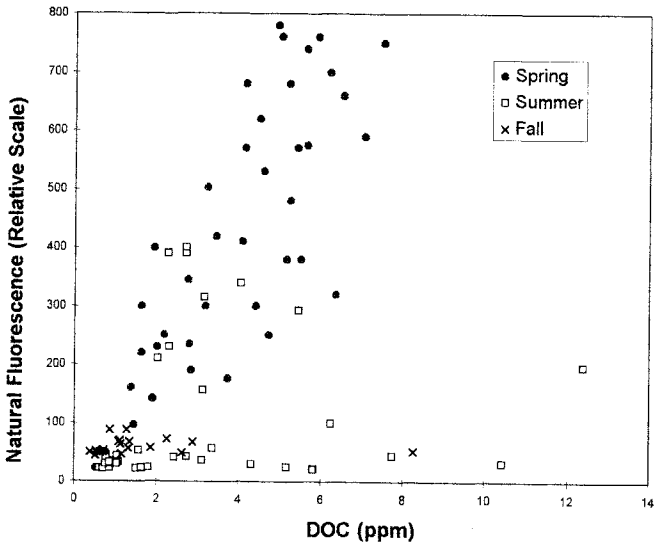

Figure 3. Total Natural Fluorescence vs. Dissolved Organic Carbon (DOC) Concentration (ppm) March - October, 1995 (Divided according to the time of collection).

orescence and DOC was found. The DOC must, therefore, be composed of mainly low-fluorescent organics, possibly due to long non-fluorescent carbon chains.

It was anticipated that the greatest fluorescence and DOC might reach the cave in summer with the greatest accumulation of organic matter on the forest floor. However, the highest values for fluorescence and DOC occurred in spring (rather than in summer or fall as expected). The fall waters (collected between September and October 1995, Fig. 3) showed a dramatic decrease in both concentration of DOC and fluorescence but with no apparent relationship between the two. The marked reduction in precipitation in the fall may have halted the transport of DOC to the cave site so that the organics remained in the upper soil layers. The high spring DOC and fluorescence values may result from a flushing out of organic material which accumulated and decomposed during the previous fall and winter.

CONCLUSIONS

(i) Spring waters showed the highest values for, and the strongest correlation between, fluorescence and DOC. These organics have probably been in storage in the soil over the winter and are well decayed into short length, high-fluorescent carbon chains. Spring waters, thus, behave as expected and support the basic working assumption for high resolution studies of speleothem fluorescent banding, that DOC concentration will be in simple proportion to fluorescence.

(ii) Fluorescence values fell sharply in summer and fall while DOC remained relatively high. These organics may be composed of less decayed, long length, low-fluorescent carbon chains. The absence of a correlation between fluorescence and DOC in the summer months, thus, contradicts the basic working assumption: low fluorescing bands may actually contain high levels of DOC.

(iii) Both fluorescence and DOC values were low during the fall. This may be related to a reduction in flow rate and flushing rate in the dry weather. The fall data probably represent the end of the annual cycle of soil organic flushing. Although no sampling was done in winter it is assumed that the vadose waters will probably freeze in the winter.

(iv) A strong seasonal effect was apparent only in the quickly responding sites with the fastest drip rates and fastest growing speleothems. Slow, constant drip sites exhibited a much weaker seasonality.

The overall conclusions are (i) that fluorescence is well correlated when the fluorescence range is high; (ii) that fluorescence is not a strong indicator of DOC at low fluorescence values; (iii) that the value of fluorescence as a predictor of DOC may vary significantly with individual sampling sites; (iv) that the highest fluorescence values occur in springtime and the weakest fluorescence occurs in summer and fall. The implications are that a speleothem with a high range of fluorescence is likely to show a strong paleoclimatic signature; that the highest fluorescing bands probably represent spring floods or storm activity; that the fastest growing speleothems are likely to show the clearest seasonal signal; that each speleothem may record paleo-ecosystem parameters in an individual way and each site should be tested before any environmental conclusions are drawn. This type of study has not been conducted elsewhere so it is not known to what extent Marengo Cave is typical and to what extent these conclusions can be applied to all caves and speleothems.

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