

## **Carbon dioxide budgets in cave air and carbon in speleothems; insights from a shallow cave in Ireland**

Frank McDermott and Dominika Phillips

University College Dublin, UCD School of Earth Sciences, Dublin, Ireland (frank.mcdermott@ucd.ie)

The conventional view that hydrological inputs (e.g. drip-water degassing) comprise the dominant source of cave air CO<sub>2</sub> has been challenged by recent studies that emphasise the importance of direct advection of gaseous CO<sub>2</sub> from above and beneath cave voids (e.g. 'soil air' and 'ground air'). A better understanding of CO<sub>2</sub> gas budgets in caves is important, not only for the correct interpretation of  $\delta^{13}\text{C}$  values and <sup>14</sup>C activity data in speleothems, but also for an understanding of the wider role of karst in the global carbon cycle as a source or sink of atmospheric CO<sub>2</sub>. This study presents new results from a combined air-temperature and CO<sub>2</sub> monitoring programme at a small multi-chamber cave in SE Ireland (Ballynamindra cave, Co. Waterford), building on an earlier study at this cave (Baldini et al., 2006). Episodic, low-amplitude but temporally coherent diurnal-scale cave air temperature fluctuations detected almost simultaneously by a series of temperature loggers within the cave were used to detect air mass advection. The sequence and pattern of temperature fluctuations at different locations within the cave enabled the identification of discrete air-inflow and air-outflow events. These diurnal-scale events occur episodically throughout the year in the winter/ spring and summer/autumn temperature ventilation regimes of the cave. Importantly, changes in cave air *p*CO<sub>2</sub> values recorded by an infra-red logger located in the inner chamber a few metres from the back of the cave occur contemporaneously with the air-mass displacement events, and are consistent with direct advection of CO<sub>2</sub>-rich soil air via fractures in the subjacent cave roof and walls. In the winter regime, episodic diurnal-scale air outflow events draw CO<sub>2</sub>-rich air over the logger, resulting in short-lived pulses of air, typically containing c. 0.7% CO<sub>2</sub> (by volume), several times the ambient cave air CO<sub>2</sub> values at this site. Similar events occur during the summer/autumn thermal regime, but these reach higher CO<sub>2</sub> values (1-1.2%), similar to those measured previously in the overlying soil. Overall, the data confirm an important role for soil and/or ground air sources at this cave and indicate that the episodic CO<sub>2</sub> inputs are not controlled by drip-water inputs. Some recent studies have additionally argued that advected 'ground-air' is not only an important constituent of cave air, but also an important source of carbon in speleothems. This claim is critically evaluated here using <sup>14</sup>C activity measurements from actively growing zero-age soda-straw stalactites from the small inner chamber of the cave where the CO<sub>2</sub> monitoring was carried out. Surprisingly, soda-straws collected from within a few metres of each other in this inner chamber exhibit quite different <sup>14</sup>C activities (93-101 pMC), and are not identical as might be expected if complete carbon isotope exchange had occurred between the dissolved inorganic carbon and the cave atmosphere. The reasons for this will be discussed, drawing on the results of published kinetic models for degassing and isotope exchange. Overall, it is concluded that while the CO<sub>2</sub> budget of the air in Ballynamindra cave is dominated by directly advected soil air, water transported dissolved inorganic carbon (DIC) likely remains an important carbon source for its speleothems.

Baldini, J.U.L., Baldini, L.M., McDermott, F. and Clipson, N. (2006) Carbon dioxide sources, sinks, and spatial variability in shallow temperate zone caves: evidence from Ballynamindra Cave, Ireland. *Journal of Cave and Karst Studies*, 68, 4-11.