



## Daily variations of CO<sub>2</sub>, δ<sup>13</sup>CO<sub>2</sub> and CH<sub>4</sub> of cave air controlled by external weather conditions: example of rapid survey in Altamira cave (north of Spain)

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Altamira cave has been monitored since 1997, from which a multiyear registry of the main physical and chemical parameters has been obtained. As a low energy shallow cave, the exterior influence in its conditions is relatively high. Monitoring records allow us to differentiate two microclimatic seasons. During the cold, rainy season the system of macro and micro epikarstic fissures is almost permanently saturated with water making the host rock membrane impermeable. In contrast, during the warm, dry season the macro and micro epikarstic porous system is not water saturated and therefore acts as a connecting pathway between the outside and underground environments (Cuevza et al., 2011)

A 38 hours survey was carried out during the end of warm and dry season (September 2011). By using Cavity Ring-Down Spectroscopy CO<sub>2</sub>, δ<sup>13</sup>CO<sub>2</sub> and CH<sub>4</sub> variations inside the cave were have been obtained. As a result a daily cycle was obtained for each of these parameters. During the experience, internal and external atmosphere conditions were also monitored.

Exterior temperature reaches the maximum in 22.3°C around midday (13:00) and falls up to its minimum in 10.5 °C at night (03:00). Outer relative humidity shows the opposite pattern ranging between 69 and 97%. Inside, the cave air temperature remains constant about 14 °C. Temporal variation of CO<sub>2</sub> concentration shows a sinusoidal curve in which the maximum is reached around midday (11:48, 1950 ppm) and the minimum around midnight (00:30, 1471 ppm). <sup>222</sup>Rn increases its concentration during night and decreases during daytime showing a range between 2620 and 1606 Bq/m<sup>3</sup>. δ<sup>13</sup>CO<sub>2</sub> shows the opposite behavior ranging from -25 (at midday) to -22‰ (at midnight). Methane concentration varies with a very similar pattern to the isotope signal. Maximum value is reached during night and falls to 0 ppm early in the morning (8:30). Few hours after midday, the concentration begins to increase to reach the maximum again around midnight (23:17, 0.61 ppm).

Results indicate that the cavity presents its summer behavior in which it is still well communicated with the outer atmosphere, but two opposite patterns can be identified along a daily cycle. The nocturnal increase in CO<sub>2</sub> concentration, with low isotopic signal and CH<sub>4</sub> depletion points to a gas inlet with a mainly edaphic origin. Total and rapid CH<sub>4</sub>removing could be related to biochemical activity (Waring et al., 2009). On the contrary, CO<sub>2</sub> and <sup>222</sup>Rn depletion joined to a δ<sup>13</sup>CO<sub>2</sub> and CH<sub>4</sub> increase indicates an air inlet from outside atmosphere. During daytime, outer warmer air gets into the cave via the almost empty rock fracture system, during night soil porous system is closed by condensation cutting off communication with the outside atmosphere. Due to CO<sub>2</sub> gradient between the soil and air of the cave, soil CO<sub>2</sub> is forced by diffusion into the cavity increasing its concentration to 500 ppm in one day.

### References:

Cuevza, S., A. Fernandez-Cortes, D. Benavente, R. Serrano-Ortiz, A. S. Kowalski, and S. Sanchez-Moral (2011), Short-term CO<sub>2</sub>(g) exchange between a shallow karstic cavity and the external atmosphere during summer: Role of the surface soil layer, *Atmospheric Environment*, 45(7), 1418-1427.

Waring, C. L., D. W. T. Griffith, S. Wilson, and S. Hurry (2009), Cave atmosphere: A guide to calcification and a methane sink, *Geochimica et Cosmochimica Acta*, 73(13), A1419-A1419.