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Environmental factors controlling transient and seasonal changes of trace gases within shallow vadose zone

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Shallow vadose environments below soil, mainly caves, show significant seasonal and even daily variations in gas composition of ground air, which involves the exchange of large amounts of gases, e.g. greenhouse gases (GHGs) as CO_2 or CH4, with the lower troposphere. To understand better the role of caves as a sink or depot of GHGs, geochemical tracing of air (atmosphere, soil and ground air) was performed at Rull cave (southeast Spain) by monitoring CH4, CO_2 and the stable carbon isotopic delta13C[CO_2] using cavity ring-down spectroscopy (CRDS). A comprehensive microclimatic monitoring of exterior and cave atmosphere was simultaneously conducted to GHGs-tracking, including factors as temperature, barometric pressure, relative humidity and concentration of CO_2 and 222Rn. The analysis of the measured data allows understanding outgassing and isolation processes taking place in the karst cavity. Annual patterns of gases behaviour can be distinguished, depending on the prevailing relationship between outer atmosphere, indoor atmosphere and soil system. Cave air temperature fluctuates around 15.7 ºC and relative humidity remains higher than 96% the whole annual cycle. The mean concentration of 222Rn is 1584 Bq m-3 while CO_2 remains 1921 ppm. When external temperature is higher of indoor temperature (April-October), the highest levels of both trace gases are reached, while levels drop to its lowest values in the coldest months. Preliminary results obtained show an annual variation in concentration of CO_2 inside the cave between 3300 ppm and 900 ppm, whereas corresponding isotopic signal delta13CO_2 varies between -24‰ and -21‰The results have been studied by Keeling model that approximates the isotopic signal of the source contribution in a resulting air mix. The values registered inside the cave were represented joined to results for exterior air (average values round 410 ppm of CO_2 and -9 ‰ for delta13C). Value obtained is -27‰ pointing to a high influence of the soil produced CO_2 (with a characteristic signal of -27‰ for C3 plants) in the cave atmosphere. The lowest levels of CO_2 coincide with the highest of delta13C pointing to an input of exterior air during the degassing stage. Regarding the CH4 concentration inside the cave, higher values (0.3 ppm average concentration) are observed during outgassing stage than the isolation period (CH4 mean value of 0 ppm), confirming a major connection with the exterior atmosphere (average value of methane 1.8 ppm) during outgassing stage. By introducing wavelet analysis on obtained time series filtered signal of raw data show strong dependencies between trace gases and studied parameters. For instance, values of coherence between relative humidity and CO_2 or 222Rn concentration are higher than 0.9. Results show that gas patterns dependence on relative humidity, atmospheric pressure and temperatures (indoor and outdoor) prevails throughout a year, determining the outgassing and isolation periods identified by statistical analyses. The measured of delta13C and CH4 concentration became a useful tool to understand processes affecting cave air and driving parameters variations inside the cave. Moreover, combining wavelet analysis, statistics and resemblance techniques, seasonal and transient behaviour of gases exchange can be highlighted in subterranean sites as Rull Cave.