Vadose Zone Journal

Air Carbon Dioxide Contents in the Vadose Zone of a Mediterranean Karst

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This study is based on in situ measurements of the soil and the vadose zone (<60 m) in a Mediterranean karst experimental site near Nerja Cave (a show cave in dolomite marbles in southern Spain). Air temperature, relative humidity, and CO_2 concentrations are the main variables measured, especially their variations with depth in a number of boreholes. The CO_2 content generally increases with depth. Our measurements indicate average vadose air CO_2 concentrations of nearly 40,000 μL L^{-1}, with a maximum of nearly 60,000 μL L^{-1}. In this context, the cave itself appears to be a vadose subsystem above the groundwater level, with significantly lower CO_2 concentrations (a few thousand microliters per liter maximum) due to its ventilation. The vadose air in the lower part of the boreholes also exhibits near-saturation humidity and a quite stable temperature around 21°C, similar to the conditions inside the cave. The measured vadose conditions were simulated by a reaction-path hydrogeochemical model that starts with the local rainwater composition and reproduces the chemistry of the cave drip water, particularly its high Mg^{2+} content. The soil cover, although very scarce, has a relatively high organic matter content. The $\delta^{13}C$-CO_2 data of the vadose air point to an origin of the gas mainly related to biological soil processes. This gas can diffuse or flow laterally, upward, or downward through karst conduits. Interactions between air masses of surface origin (relatively dry, with variable temperature and low CO_2 content) and typical vadose attributes (relatively high CO_2 content, near-saturated humidity and 21°C temperature) produce clear ascendant or descendant air fluxes inside the boreholes, especially those that cross significant karst voids.

Abbreviations: OM, organic matter; PVC, polyvinyl chloride.

The CO_2 partial pressure in both soil air and the unsaturated zone of carbonate aquifers is the master variable that controls the development of karstogenetic processes (Atkinson, 1977; White, 1988; Bourges et al., 2001; Appelo and Postma, 2005; Baldini et al., 2006). The CO_2 content of the soil air (epikarstic zone) can be up to two orders of magnitude greater than that of the open atmosphere (Atkinson, 1977; Troester and White, 1984; Keller and Bacon, 1998; Selker et al., 1999; Bourges et al., 2001; Walvoord et al., 2005; Benavente et al., 2006a,b). This increase is normally dependent on the soil biological activity, which in turn is controlled by temperature and water content.

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Some empirical expressions based on the average values of the local air temperature or the actual evapotranspiration have been proposed to estimate the average soil CO_2 content (Selker et al., 1999). The concentration of CO_2 is not always explained solely by a biogenic origin, however, so it is necessary to make direct measurements of the CO_2 content, considering its time evolution, variations with depth, and isotopic signature in the unsaturated or vadose zone of carbonate aquifers (Wood and Petraitis, 1984; Wood, 1985; Cerling et al., 1991; Clark and Fritz, 1997; Keller and Bacon, 1998; Hamada and Tanaka, 2001; Walvoord et al., 2005; Baldini et al., 2006; Vadillo et al., 2007).

This study is based on the results of experimental measurements conducted near Nerja Cave (Malaga province, southern Spain), <1 km from the Mediterranean shore (Fig. 1). Nerja Cave is an important show cave, visited by some 500,000 people each year, mostly during the summer months.

In a previous work, Cardenal et al. (1999) attempted to model the main hydrogeochemical processes that affect the local infiltration of rainwater through the epikarst and vadose zones to the cave roof. The subsurface flow was then modeled using a CO_2 partial pressure (P_{CO2}) of 3500 μL L^{-1}, similar to that successfully used in another aquifer to the east of Nerja, with carbonate materials of the same age and geologic context (Cardenal et al., 1994). The attempt failed to reproduce the Mg contents in the cave's drip water. To achieve this, higher P_{CO2} values must be entered into the model, a circumstance for which no direct confirmation was possible. Only indirect information based on equilibrium calculations of some nearby groundwater samples suggested this possibility (Andreo and Carrasco, 1993). A specific