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Vadose zone air as a biogenic source of methane in Nerja Cave system (South of Spain)

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Subterranean air in karst cavities has often low methane contents in comparison to atmosphere and so karst systems have been considered a sink of atmospheric methane. Methane-oxidizing bacteria have been hypothesized as responsible for CH₄ depletion in many caves around the world, although ionization radiation was also proposed as possible mechanism for this process. We measured CO₂ and CH₄ concentration and their C isotopic composition ($\delta^{13}\text{C-CO}_2$ and $\delta^{13}\text{C-CH}_4$) over 2 years within the Nerja cave system (South Spain) and in 9 boreholes drilled into the vadose zone (Triassic carbonate aquifer) surrounding the cave. According to $\delta^{13}\text{C-CO}_2$ and $\delta^{13}\text{C-CH}_4$ vadose zone of this karst system is a source of biogenic methane, produced both by acetate fermentation and CO₂ reduction. Biogenic and atmospheric methane flows (along fractures from the vadose zone, and through ventilation, respectively) into the cave, where it is oxidized by methanotrophic bacteria that we detected on soil samples into the cave.