

Interactive comment on “Atmospheric turbulence triggers pronounced diel pattern in karst carbonate geochemistry” by M. Roland et al.

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The authors gratefully acknowledge referee #1 for the constructive feedback that considerably improved the readability of this manuscript. We hereby provide a point-by-point response to the raised comments.

-Comment (1): p 5, 1st paragraph. The referee suggests discussing the belowground sources of CO₂ to explain the undersaturation of DIC in the soil solution at night.

-Response to comment (1): The mechanism addressed here is the role of the soil moisture content in the saturation state of DIC in the soil solution, regardless of possible belowground CO₂ sources. The addition of “pure” water at night causes the concentrations to drop, thus promoting carbonate dissolution. We believe this to be

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comprehensible from the concerned sentence: “In dry conditions, these daytime water losses are often compensated during the night, at least partly, by water vapor condensation or adsorption (Kosmas et al. 2001; Verhoef et al. 2006), causing undersaturation with respect to calcite that leads to the reverse reactions: dissolution of carbonates and CO₂ uptake.”

-Comment (2): p 5, last paragraph. The referee notes that the term “further” makes no sense here.

-Response to comment (2): The term is indeed superfluous and is removed from the revised manuscript.

-Comment (3): p 6, 2nd paragraph. “These rapid changes in underground CO₂ concentrations induce a strong carbonate disequilibrium and can thus be expected to interact with carbonate weathering rates.” The referee suggest to display the saturation index here, to demonstrate the magnitude of the disequilibrium of the carbonate reactions.

-Response to comment (3): The authors agree that the saturation index is an accurate parameter to quantify the carbonate disequilibrium. However, it is difficult to show this parameter without going into the details of carbonate weathering kinetics, which we would prefer to avoid in the main text. The values of the saturation index are shown in Discussion Figure 1 (Fig. D1), for a week in the beginning of the ventilation season in 2009. Displaying the modeled pCO₂ values was also considered, but as we observed a small time lag in the diurnal pattern of the measured and modeled pCO₂ values, we decided not to show these results for more clarity.

-Comment (4): The referee requests a more detailed discussion of the individual parameters prescribing the CO₂ efflux due to ventilation in equation (Eq. 2).

-Response to comment (4): The ventilation equation is indeed an important element of this manuscript. However, the focus of this work is on the effect of ventilation on

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Karst geochemistry rather than on the quantification of ventilation itself. Our ventilation model works well for the training set, because it was structured and parameterized to fit the observations, but worked more poorly when tested on independent data sets. The site specific parameters, such as the maximum water content and the minimum friction velocity for enabling ventilation were derived empirically; these values are displayed in the manuscript. Initially, we hoped to optimize and especially validate this ventilation model, but we rapidly learned that the drivers are not fully understood yet. Furthermore, this would require detailed insight in the three-dimensional structure of the Karst system to estimate macropore-interconnectivity and the presence of caves and cracks that serve as preferential CO₂ outflows. Our main aim was to test whether and how carbonate geochemistry is affected during and after ventilation events. Rather than attempting to model these ventilation events, one alternative could have been to simply extract (in the WITCH model) a given amount of CO₂ from the topsoil and see how this affects weathering rates. However, in this case, we would have completely uncoupled the WITCH model results from the eddy flux observations at the site. Using this equation we do capture days when ventilation occurs, although we are often a few hours early. We therefore opted to use the modeled ventilation flux provided that the associated uncertainties are clearly stated, and focus on its impact on carbonate weathering rather than its magnitude and drivers. We hope the referee can accept this approach.

-Comment (5): p 10, 1st paragraph. The referee proposes to move forward the clarification of the ambiguity about the sink-source behavior of carbonate weathering and precipitation.

-Response to comment (5): It is indeed more logical to explain this ambiguity in the beginning of the paper. In the revised manuscript we have moved the concerned paragraph to the introduction section.

-Comment (6): p 13, 2nd paragraph. The referee suggests mentioning the need for an additional CO₂ source in the model simulations earlier in the manuscript.

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-Response to comment (6): We agree that this information is quite essential and should be given at an earlier stage. In the revised manuscript, we therefore describe the deep CO₂ source together with the biological CO₂ production in the materials and methods section, as follows: "Half hourly meteorological data (see auxiliary material: A1.3 Measurements) from 2009 were used to force the model, these include: the soil water content (which defines the volumetric size of each reservoir and the fraction of the total reactive mineral surface that is available for weathering), rainfall, soil temperature and inputs of CO₂ from biological production. The latter was estimated by means of a Q10 function using the nighttime CO₂ fluxes from eddy covariance measurements during biologically active periods when geochemical fluxes were negligible. This production was prescribed only in the two upper layers (soil) and was assumed to be zero during the drought period, during which all plants are senescent and CO₂ efflux was typically zero in the absence of high turbulence. The measured daytime effluxes in this season could therefore not be attributed to respiration, making this the appropriate period to study ventilation. In order to reproduce the observed CO₂ concentrations in both the upper and deeper layers, we encountered the need to also include very little (0.1 $\mu\text{mol m}^{-2}\text{s}^{-1}$) but continuous CO₂ production in one of the deeper layers in the model. Possible sources of this deep CO₂ production in the Karst system are treated in the discussion below." The topic is then treated more in-depth in the discussion as it was in the previous version of the manuscript.

-Response to technical comments: The referee further suggests a few very helpful typographical and other small changes, which are all taken up in the revised manuscript. This includes mentioning the relevance for semi-arid areas in the abstract.

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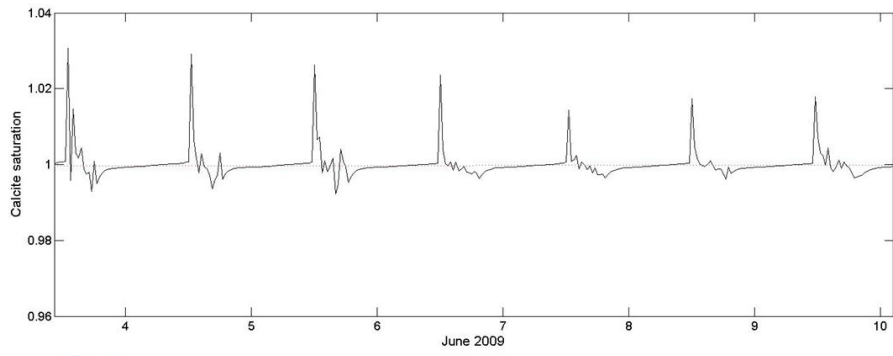


Fig. D1

Fig. 1.

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