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## Measured temporal variations of CO<sub>2</sub> concentration and atmospheric emissions in a hydropeaking-impacted river

Giulio Dolcetti<sup>1</sup>, Sebastiano Piccolroaz<sup>1</sup>, Maria Cristina Bruno<sup>2</sup>, Elisa Calamita<sup>3</sup>, Stefano Larsen<sup>2</sup>, Guido Zolezzi<sup>1</sup>, and Annunziato Siviglia<sup>1</sup>

<sup>1</sup>Department of Civil, Environmental and Mechanical Engineering, University of Trento, Trento, Italy ([giulio.dolcetti@unitn.it](mailto:giulio.dolcetti@unitn.it))

<sup>2</sup>Research and Innovation Centre, Fondazione Edmund Mach, San Michele all'Adige, Italy

<sup>3</sup>Department Surface Waters - Research and Management, Eawag, Dübendorf, Switzerland

Rivers are increasingly recognised as active players in the global carbon cycle. They are able to transport, transform, and exchange organic matter, and can emit considerable fluxes of greenhouse gases (e.g., CO<sub>2</sub>) into the atmosphere, with a magnitude comparable to the global carbon input to the oceans. However, the quantification of these processes is still affected by considerable uncertainties, driven by an incomplete understanding of the interplay between physical, geochemical, and biological parameters, and by a lack of spatially and temporally resolved high-quality data. For instance, and despite a potentially strong impact on kilometres of rivers worldwide, the effects of hydropeaking on riverine CO<sub>2</sub> emissions have been almost completely neglected until recently (Calamita et al., *Unaccounted CO<sub>2</sub> leaks downstream of a large tropical hydroelectric reservoir*, PNAS 2020). As a contribution to filling this knowledge gap, we present the results of a field-measurement campaign performed in a single-thread Alpine river (River Noce, Italy) during multiple hydropeaking events. Data of water-dissolved CO<sub>2</sub>, water temperature, and flow discharge, were collected sub-hourly both downstream and upstream of the outlets of a hydropower plant, revealing a complex pattern of variation in time at both locations. Water released from the hydropower plant during hydropeaking had oversaturated CO<sub>2</sub> concentrations relative to the atmosphere, in close agreement with water samples collected in the hypolimnion of the upstream reservoir. Higher flow rates during hydropeaking events were associated with higher rates of gas exchange through the water-air interface. Higher exchange rates and higher CO<sub>2</sub> concentrations in water during hydropeaking events enhanced CO<sub>2</sub> fluxes, as confirmed by measurements with a floating CO<sub>2</sub> flux chamber. Meanwhile, the CO<sub>2</sub> concentration upstream of the outlets displayed strong diel fluctuations around the atmospheric equilibrium concentration, which were likely driven by primary production within the residual flow during the day. It is shown that the residual flow can have a previously unacknowledged added value as a CO<sub>2</sub> sink during the day, fueled by its biological activity. Hydropower releases bypassed the residual flow and discharged hypolimnetic water oversaturated with CO<sub>2</sub> at high flow rates during hydropeaking, offsetting CO<sub>2</sub> concentration and fluxes downstream of the outlets and increasing emissions on average. These results highlight the ubiquity of hydropeaking impacts also with respect to greenhouse gas emissions. They illustrate the complexity of the riverine carbon cycle and demonstrate the importance of temporally and spatially-resolved data for the accurate

assessment of the riverine carbon balance.