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## The When, Where and Why of $\mathbf{CO}_2$ outgassing fluxes from an Alpine stream network

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Headwater streams contribute substantially to  $CO_2$  outgassing to the atmosphere. However, regional and global estimates of  $CO_2$  outgassing fluxes from streams remain poorly constrained for several reasons. One of them relates to the temporal variability of streamwater  $pCO_2$  dynamics, which is rarely considered when extrapolating  $CO_2$  fluxes. A further limitation relates to our poor understanding of the gas transfer at the water/atmosphere interface in high-gradient streams. Elucidating these processes is key to understand the temporal and spatial dynamics of  $CO_2$  fluxes at the level of entire stream networks. Here we present data from a 3-years time series of diurnal measurements of  $pCO_2$  in the surface and hyporheic waters, and in the atmosphere of an Alpine headwater stream. Our results show how seasons, day-night shifts and fluctuations in discharge affect  $CO_2$  outgassing fluxes, and that nighttime outgassing was on average 1.8-times higher than day-time outgassing. Furthermore, based on repeated synoptic surveys in 148 streams in the same Alpine catchment we show how  $CO_2$  evasion rates change 1st and 5th-order streams. Our results suggest that small, first-order streams act as the predominant conduits for  $CO_2$  to the atmosphere in high-gradient streams, as they hold the highest potential for gas exchange combined with strong supersaturation of  $CO_2$ .