Geophysical Research Abstracts Vol. 20, EGU2018-2284, 2018 EGU General Assembly 2018 © Author(s) 2017. CC Attribution 4.0 license.



Groundwater inputs drive spatial CO₂ dynamics in an Alpine headwater stream

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Inland waters are a key component of the global carbon cycle, not only transporting but also transforming organic carbon and ultimately emitting CO2 and CH4 to the atmosphere. Recent estimates indicate that up to 36% of the CO₂ evasion from streams and rivers originate from headwaters. However, the origin (that is, catchment-derived versus in-stream produced) of CO_2 emitted to the atmosphere is poorly understood to date. Data is particularly scarce for high-elevation headwater streams, which are predicted to be highly susceptible to climate change. Here we aimed to identify the spatial and seasonal variation of sources and drivers of streamwater CO₂ partial pressure (pCO₂) and to assess evasion fluxes from an Alpine headwater stream (Avançon, Switzerland). To this end, we sampled streamwater 50 to 80 m along the main stem (4.5 km) and its tributaries in winter, spring, summer and autumn. We found that most of the CO_2 in the streamwater originated from groundwater recharge, delivering CO_2 from carbonate bedrock weathering in the catchment. Deliveries of groundwater CO_2 (pCO₂ 3 - 4 times higher than in the streamwater) locally depleted streamwater δ 13C-DIC and the δ 13C-CO₂. Downstream from a major groundwater infiltration front, CO₂ evaded rapidly from the streamwater, which led to an isotopic enrichment of the δ 13C signatures owing to δ 13C fractionation. Within 400 m from the maximum groundwater infiltration front, streamwater pCO_2 decreased 20 to 50 % depending on the season. This rapid decrease in pCO₂ coincided with a notable increase in pH (by 1 to 5 %). We conclude that the downstream change in δ 13C-DIC was primarily driven downstream carbon export, CO₂ evasion and calcite precipitation. Streamwater CO₂ dynamics in the Avançon headwater catchment differs from previous studies on boreal and temperate systems. We suggest that this is because soil respiration and carbonate weathering contribute most to streamwater CO_2 , and that high gas transfer velocity accelerates CO_2 evasion to the atmosphere. Our results evoke greater CO₂ evasion fluxes than previously thought from high-elevation and high-slope streams (average slope of the Avançon headwater stream is 12.3%). We suggest that more efforts should be directed to include small and steep headwater streams into global carbon budgets, to better understand their role in the "boundless carbon cycle".