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Inorganic carbon budget for two headwater stream networks with contrasting climatic and geomorphic controls

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Accurately quantifying inorganic carbon dynamics in stream networks is essential for constraining estimates of catchment-scale carbon dioxide (CO_2) outgassing, identifying its sources (autochthonous vs. allochthonous), and assessing sensitivity to hydrological and geomorphological controls. However, most existing approaches rely on single-station measurements or simplified reach-scale models, neglecting transport processes, upstream–downstream connectivity, network topology, and spatial heterogeneity of lateral inputs. Here, we present a network-based sampling design coupled with a Bayesian modelling framework to estimate network-scale balances of dissolved inorganic carbon (DIC), alkalinity, pH, and dissolved oxygen (O_2).

We applied this framework to two headwater catchments with contrasting geology, climate, land cover, and hydrological regimes: Valfredda (5.3 km², north-eastern Italian Alps, Alpine climate) and Turbolo (6.9 km², southern Italy, Mediterranean climate). In both catchments, we conducted spatially distributed sampling of approximately 15 sites per network within a single day, measuring total alkalinity, dissolved CO_2, O_2, water temperature, pH, and discharge. Sampling was timed during periods of negligible gross primary production to minimize diel variability. This assumption was verified using continuous monitoring stations providing diel cycles of O_2, CO_2, and pH.

The framework models pixel-scale mass balances of DIC, O_2, and alkalinity by accounting for upstream and lateral inputs, in-stream production, atmospheric exchange, and downstream export. Instantaneous carbonate equilibrium is assumed to derive pH and CO_2 from alkalinity and DIC, allowing direct comparison with observations. Reaeration coefficients are estimated using empirical relationships based on hydraulic properties. The model enables the mapping of longitudinal biogeochemical patterns across entire stream networks and the derivation of network-scale carbon budgets.

The two catchments exhibit contrasting spatial dynamics. In the alpine Valfredda network, high headwater alkalinity associated with dolomitic lithology produces elevated initial DIC concentrations, while high turbulence promotes intense degassing, driving dissolved CO_2 concentrations toward atmospheric equilibrium downstream. In contrast, the Turbolo network is

characterized by heterogeneous lithology and dense vegetation, generating diffuse, carbon-rich lateral inputs that sustain elevated CO□ concentrations even in downstream reaches. In both systems, the model successfully reproduces observed spatial patterns, highlighting the importance of lateral inflows and network structure in shaping catchment-scale CO□ dynamics.

At the network scale, carbon flux magnitudes and dominant pathways differ markedly between catchments. Despite similar wetted channel areas (~7000 m² in Turbolo and ~8300 m² in Valfredda), Valfredda releases more than four times more CO□ per unit stream surface area (~1.45 vs. ~0.36 mol m□² d□¹), corresponding to total fluxes of ~12 000 and ~2500 mol d□¹, respectively. In Valfredda, CO□ evasion is sustained almost equally by lateral inputs and in-stream respiration, whereas in Turbolo it is dominated by lateral fluxes. Higher gas exchange rates and lower alkalinity in Valfredda favor rapid atmospheric CO□ release, while lower turbulence and higher alkalinity in Turbolo promote downstream DIC transport.

Overall, our results demonstrate that reliable estimates of riverine CO□ emissions require explicit representation of spatial structure, hydrological connectivity, and coupled biogeochemical processes across stream networks, providing a generalizable approach for scaling carbon fluxes from point measurements to entire catchments.