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# Unravelling alkalinity and dissolved inorganic carbon dynamics in an alpine stream network

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Alkalinity in river ecosystems plays a crucial role in regulating carbon cycle across basin, regional, and global scales. Streamflow alkalinity acts as a pH buffer and drives the relative abundance of the different chemical forms of dissolved inorganic carbon (DIC), such as $CO_2$, bicarbonate and carbonate ions. Higher alkalinity supports greater carbon retention in non-gaseous forms, reducing atmospheric $CO_2$ emissions, while lower alkalinity weakens the buffering capacity, increasing water acidity and facilitating carbon loss to the atmosphere. Rivers, as dynamic links between terrestrial and marine environments, transport significant amounts of organic and inorganic carbon, making alkalinity a key driver of $CO_2$ exchange between rivers and the atmosphere.
Dissolved inorganic carbon (DIC) in stream networks can originate from allochthonous sources, such as catchment soil respiration and rock weathering, or from autochthonous processes driven by stream metabolism, i.e. the net ecosystem production (NEP), the balance between gross primary production and ecosystem respiration. As recent literature highlights, understanding the complex interplay among DIC, oxygen, and stream metabolism requires spatio-temporal characterization of alkalinity, which influences the different forms of DIC, its exchange with the atmosphere, and its biological availability.
This study contributes to this field by investigating the alkalinity dynamics in the Valfredda stream network, a 5 $km^2$ catchment in the Italian Alps characterized by pristine alpine conditions. Fed mostly by snowmelt, the Valfredda stream features cold, clear, oxygen-saturated waters with low nutrient concentrations. Its snowmelt-driven hydrology produces marked seasonal variations in flow rates and water temperatures, providing an ideal natural laboratory to study diverse conditions throughout the year.
Alkalinity was sampled at 12 locations within the river network approximately once a month. Additionally, daily sampling was conducted at the catchment outlet. Using a stream transport model based on a mass balance approach, we characterized the alkalinity concentration in the lateral discharge across different stream reaches. The combination of the model and the two datasets allowed investigating how alkalinity varied seasonally and spatially, revealing potential drivers such as land use, hydrology, or biogeochemical processes. At a selected stream reach, we combined alkalinity measurements with continuous monitoring of metabolic indicators: dissolved oxygen, pH, water and air temperature, and light intensity, using deployable sensors. By integrating data from discrete sampling and continuous monitoring, we quantified the DIC balance

at the scale of a single stream reach. Future work aims to extend this approach to the entire network.

These insights lay the groundwork for understanding the role of alkalinity in shaping river DIC balance and influencing $CO_2$ emissions. The comprehensive dataset will support the identification of seasonal trends and spatial patterns, offering a complete view of alkalinity dynamics within complex river network system.