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Disentangling lithological, climate and ecosystem controls on fluvial carbon export: The Engadin Valley as a natural laboratory

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Carbon exported by rivers draining mountainous catchments reflects the integral of myriad processes. The sensitivity of these processes to natural and anthropogenic forcing influences the role of inland aquatic corridors as sources or sinks of atmospheric carbon, however disentangling underlying processes and determining their response to forcing factors remains challenging.

In this study we examine geochemical characteristics of riverine dissolved and particulate phases in order to constrain the influence of lithology on carbon signatures exported from alpine watersheds. We sampled the Inn River and its tributaries in the Engadin valley in Graubünden, Switzerland. Bedrock in the upper Engadin is predominantly magmatic in origin, whereas the Lower Engadin is comprised of sedimentary rocks (dolomites, partially metamorphosed shales). We exploit this sharp geological contrast to constrain the influence of erosion and weathering of different lithologies on fluvial geochemistry. Samples collected seasonally and longitudinally along the axis of the Engadin valley were measured for dissolved inorganic carbon (DIC) isotopic composition, major ions, and rhenium concentrations in order to distinguish atmospheric, cryospheric, biospheric and lithospheric carbon sources.

We find a marked gradient in DIC $F^{14}C$ values along the ca. 120 km-long course of the Inn River with higher values (younger ^{14}C ages) in the Upper Engadin and lower values in the Lower Engadin, consistent with weathering of underlying bedrock supplying ^{14}C-depleted DIC (from carbonate minerals and/or petrogenic organic carbon). Historical ion data from a long-term river monitoring program suggest that the majority of weathering is driven by carbonic acid rather than sulfuric acid. Dissolved rhenium concentrations increase markedly downstream as sedimentary rocks increasingly dominate the geology. However, the inputs are highest from tributaries draining dolomite lithologies, and the dissolved rhenium source in the host rock remains unknown. Overall, ^{14}C-depleted DIC signatures were prevalent throughout the basin, even where sedimentary rocks are thought to be absent, suggesting additional sources of pre-aged carbon. Absolute values vary among seasons, with lowest DIC $F^{14}C$ values in winter and early spring, and highest values in summer. DIC $F^{14}C$ values also tend to converge with increasing discharge, indicating DIC contributions from remineralization of terrestrial biospheric carbon (soils).