



Radiocarbon as a key constraint for prediction of river carbon biogeochemistry

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The lateral transport of riverine carbon is a key component of the global carbon cycle, yet several aspects are poorly understood. In particular, the magnitude and nature of carbon cycle responses in freshwater aquatic networks to on-going climate and environmental change remain unclear. Addressing this issue requires assessment of temporal changes in riverine carbon dynamics and identifying the underlying factors that influence the fate of transported carbon. For example, long-term observations of river chemistry from the Swiss National River Monitoring and Survey Program have revealed a steady increase in dissolved inorganic carbon (DIC) concentrations in the major four Swiss rivers (Rhine, Rhone, Ticino, and Inn) over the past ~50 years, yet the cause of this increase remains unclear. Potential contributors include increased DIC inputs from bedrock weathering, soil organic matter (OM) respiration or OM remineralization within aquatic systems. All of these processes are potentially accelerated with increasing temperatures due to global warming, but they have markedly different implications with respect to carbon cycling and ecosystem dynamics. While sensor monitoring and remote sensing approaches are invaluable for creating high-resolution spatially and temporally resolved data, distinguishing specific source components requires ancillary information. In this context, radiocarbon (¹⁴C) measurements obtained through coordinated sampling programs can serve as a powerful complementary constraint on carbon sources, turnover and transport times.

Switzerland provides a unique opportunity to use radiocarbon to assess carbon provenance in alpine streams and rivers, thanks to its high diversity of watersheds spanning strong climatic, elevational, lithological, ecological as well as anthropogenic gradients. This diversity is expressed in a wide range of ¹⁴C signatures for particulate organic carbon (POC; $\delta^{14}\text{C}$ values, -446‰ to -158‰), for dissolved organic carbon (DOC; -377‰ to -43‰) and DIC (-301‰ to -40‰). We argue carefully designed parallel field sampling of streams and rivers and subsequent measurement of

radiocarbon and ancillary geochemical parameters would aid in groundtruthing high-resolution sensor data. To illustrate the value of ^{14}C measurements, we present a multi-year ^{14}C time-series from the sub-alpine Sihl River system to highlight event- and seasonally-driven changes in the composition of riverine carbon POC, DOC, and DIC. We place these observations in the context of ^{14}C measurements on a broad range of Swiss river systems to further investigate overarching controls on fluvial carbon export from alpine and sub-alpine watersheds. Such information can help the design of targeted sampling and measurement programs to complement sensor measurements in order to develop a comprehensive understanding of changing river carbon biogeochemical dynamics.