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A coupled O₂-CO₂ model to understand CO₂ source partitioning in flowing freshwaters

Jacob Diamond^{1,2} and Enrico Bertuzzo¹

¹University of Venice Ca' Foscari, Venice, Italy (jacob.diamond@unive.it)

²INRAe, RiverLy, France (jake.diamond@inrae.fr)

The freshwater riverine carbon budget has an unexplained imbalance ($\sim 1.5 \text{ Pg-C y}^{-1}$) between estimates of terrestrial C lateral imports and freshwater emissions. This imbalance may be resolved by investigating the source of freshwater CO₂ emissions. That is, what proportion of the excess CO₂ in rivers comes from lateral CO₂ inputs (external, allochthonous sources) versus from riverine respiration of organic matter (internal, autochthonous sources)? We address this question by developing a model to estimate the reach-scale dissolved inorganic carbon (DIC) mass balance using sub-daily time series of dissolved O₂ and CO₂. The approach extends the classical single station model for the estimation of stream metabolism based on O₂ observation by coupling the mass balance of DIC with the lateral input of water, O₂ and DIC, and the mass balance of total alkalinity. Here, we present the results of the model application to several study sites across varying discharge and carbonate chemistries. We further show the model's utility in estimating magnitudes of river metabolism, lateral DIC concentration, photosynthetic and respiratory quotients, and carbon flux to the atmosphere.