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Security of inorganic carbon delivery by rivers to estuaries and coasts

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Enhanced rock weathering (ERW) is being increasingly explored as an accelerated carbon dioxide removal (CDR) strategy, with sequestration potential estimated between ~0.35-2 Gt CO_2/yr by the year 2050 [1, 2]. Yet the stability of carbon storage along river transport pathways remains poorly constrained, particularly in downstream estuarine and coastal settings. Rapid mixing between seawater and river water in estuaries drives strong gradients in ionic strength, accompanied by a shift in the ratio of dissolved inorganic carbon (DIC) to total alkalinity (TA). These coupled changes modulate the carbonate speciation, carbonate saturation state and air-water CO_2 exchange, which could reduce the CDR efficiency.

We examine measurements of alkalinity transfer across the estuaries from global datasets (i.e., LOCATE, SNAPO-CO_2 etc.) and apply an equilibrium model that explores river water-seawater mixing in the absence of biological processes. Under baseline conditions, estuaries tend to act as a sink for atmospheric CO_2, depending on the river alkalinity. However, ERW driven alkalinity enrichment at the river endmember reduces the efficiency of CO_2 in-gassing and can potentially shift the estuarine mixing zone toward CO_2 degassing above a threshold alkalinity input (>~2.5 mM). Alkalinity-to-CO_2 conversion driven by secondary carbonate precipitation is found less favorable in the estuary compared to the river endmember. This implies an effective ceiling on the alkalinity, that can be transferred through estuaries, unless a substantial benthic exchange promotes alkalinity loss through localized carbonate precipitation. Furthermore, recent evidence for cation (Mg, Li) removal via authigenic clay formation in estuarine, and coastal delta settings suggests an additional pathway which could reduce CDR efficiency by consuming alkalinity and re-releasing CO_2 [3, 4]. Therefore, we aim to quantify secondary mineral formation kinetics and associated CO_2 exchange under different physicochemical conditions relevant to ERW application scenarios, to better constrain the security of inorganic carbon delivered by rivers to the coastal ocean.

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