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Examining diurnal dissolved inorganic carbon dynamics at the river-groundwater interface

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Hydrologic and biological interactions within the Critical Zone are driven by the impact of solar energy and climate on energy and mass transfer within the system. Daily cycles of photosynthesis and respiration influence dissolved inorganic carbon (DIC) dynamics in a catchment system, impacting diurnal geochemical patterns. High frequency data collection provides increased detail of geochemical variation in rivers, making geochemical tools another indicator of river-groundwater interactions. Here, we investigate daily geochemical changes using a dataset collected during a period of baseflow at a small, carbonate-rich catchment ~70 km east of Paris, France with the goal of understanding how river-groundwater interactions influence DIC dynamics. Major cations (Ca^{+2}, Mg^{+2}, K^{+}, Na^{+}) and anions (Cl^{-}, SO_4^{-2}, NO_3^{-}) were acquired approximately every hour via a RiverLab, a fully automated 'lab in the field' installed at the study site. Data demonstrate regular diurnal variations affecting physico-chemical parameters (pH, river temperature, river discharge) and major dissolved species. Through a geochemical model using PHREEQC and R software, we show that daily oscillations of Ca^{+2} in the river are influenced by both hydrologic mixing and input of CO_2 to the aqueous system. Precipitation of secondary carbonate in the river varies diurnally. Solar energy input likely influences DIC dynamics by impacting evapotranspiration and photosynthesis/respiration cycles. We quantify potential DIC inputs to the catchment, such as soil respiration, carbonate supersaturation in the carbonate-rich aquifer system, dissolution of carbonate due to HNO_3 input from agricultural activity, riparian zone respiration, and respiration within the river. In conclusion, river-groundwater interactions are multi-faceted and depend on geophysical processes (e.g., hydrologic mixing, transport), geochemical interactions (e.g., DIC chemistry and speciation), and biological activity (e.g., respiration). Using high frequency datasets to examine river-groundwater exchange under baseflow conditions offers increased sight into how carbonate-rich catchment systems dissipate solar energetic flux through these processes.