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Geochemical and isotopic investigation of diurnal variations in a river system

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Groundwater-surface water exchange influences the ecological and biogeochemical processes occurring in river systems. Additionally, solar radiation impacts plant activity and water temperature over daily cycles. These influence the control by biological processes in the hyporheic zone on dissolved metal concentrations and nutrient availability, and by river thermodynamics and chemistry on the precipitation and dissolution of calcium carbonate. In order to more closely understand the evolution of these controls on dissolved species in river systems over daily cycles, better tools like high-frequency datasets and isotopic tracers are necessary. Here, we examine diurnal processes at a river flowing through an aquifer system located near Paris, France, using high-frequency sampling to examine major dissolved species and physico-chemical parameters during a period of baseflow. High-frequency data was acquired using a River Lab, a fully automated lab installed permanently at the study site and configured to measure all major dissolved species approximately every hour. Additionally, isotopic measurements ($^{87}Sr/^{86}Sr$, $d^{44/40}Ca$) were analyzed in samples collected hourly over 24 hours. We show that daily oscillations in river chemistry are not linked by straightforward relationships between solar energy, evapotranspiration and concentration, but also depend on hydrologic contributions. Data demonstrate significant and regular diurnal variations affecting major dissolved species and physico-chemical parameters in the stream; evapotranspiration only partially impacts river chemistry. Over the study period, some major dissolved species generally increase (Ca, Mg, SO_4^{2-}) while others remain chemostatic (Na, Cl, K). Isotopic data suggest a relative evolution of aquifer contribution to the river. The unsaturated nature of the lower confined aquifer suggests that diurnal variations depend on catchment lithology, and that the relative contribution of groundwater evolves over a single day, increasing in contribution when stream level is low. Multiple processes are at work in the river, including geophysical-dependent processes (hyporheic) and geochemical-dependent processes (calcium carbonate precipitation, nitrate chemistry). Exchange between groundwater and surface water under baseflow conditions provides enhanced detail on how river watershed systems dissipate solar energetic flux through a number of connected processes.