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Modeling river hydrochemistry through dynamic travel time distributions

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Characterizing the age of streamflows represents a key issue for the prediction of solute turnover in river basins. However, tracking the age of water fluxes in stochastic dynamic systems like watersheds requires the use of appropriate mathematical tools that allows for a coherent description of the aging, mixing and release of water and solute inputs. Here, we propose the use of methods derived from the time-variant theory of travel time distributions to interpret tracer measurements and model catchment functioning under different hydrologic conditions. Water and solute particles traveling through a catchment are seen as a dynamic population where individuals get older while they move within a catchment, until they eventually reach the sampling point, where a mixture of different ages is simultaneously represented. The temporal variability of fluxes and storages, and the age selection (and removal) operated by output fluxes are explicitly accounted for, providing a robust mathematical framework for the interpretation and the prediction of the chemical response of rivers. We present applications to highly monitored watersheds in diverse regions of the world. Our results show that the long-term dynamics of different solutes are controlled by the catchment's transitions across a gradient of humidity states - that imply changes in the ages stored and released by the system accordingly. The model allows inferences about the chemical memory of catchments and gives insights on the interaction between shallow and deep catchment storages, with implications for the understanding of nutrient and pollutant loading persistence in rivers.