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Quantifying new water fractions and water age distributions using ensemble hydrograph separation

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Catchment transit times are important controls on contaminant transport, weathering rates, and runoff chemistry. Recent theoretical studies have shown that catchment transit time distributions are nonstationary, reflecting the temporal variability in precipitation forcing, the structural heterogeneity of catchments themselves, and the nonlinearity of the mechanisms controlling storage and transport in the subsurface. The challenge of empirically estimating these nonstationary transit time distributions in real-world catchments, however, has only begun to be explored. Long, high-frequency tracer time series are now becoming available, creating new opportunities to study how rainfall becomes streamflow on timescales of minutes to days following the onset of precipitation. Here I show that the conventional formula used for hydrograph separation can be converted into an equivalent linear regression equation that quantifies the fraction of current rainfall in streamflow across ensembles of precipitation events. These ensembles can be selected to represent different discharge ranges, different precipitation intensities, or different levels of antecedent moisture, thus quantifying how the fraction of "new water" in streamflow varies with forcings such as these. I further show how this approach can be generalized to empirically determine the contributions of precipitation inputs to streamflow across a range of time lags. In this way the short-term tail of the transit time distribution can be directly quantified for an ensemble of precipitation events. Benchmark testing with a simple, nonlinear, nonstationary catchment model demonstrates that this approach quantitatively measures the short tail of the transit time distribution for a wide range of catchment response characteristics. In combination with reactive tracer time series, this approach can potentially be extended to measure short-term chemical reaction rates at the catchment scale. High-frequency tracer time series from several experimental catchments will be used to demonstrate the utility of the new approach outlined here.