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## Analyses of tracer time series to decompose the watershed response across a spectrum of spatio-temporal scales

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The different processes affecting the transport and fate of solutes in watersheds are often difficult to quantify, partly because the governing mechanisms responsible for the transport dynamics span over a wide range of temporal and spatial scales. Here we propose a novel methodology to evaluate the watershed solute response using a distributed solute transport model with spatially variable parameters. The model is applied to a network of surface and sub-surface transport pathways representing the watershed scale. By transforming the watershed response from the time domain into the frequency domain closed-form solutions of the transport problem were used to derive formal expressions of the power spectral response. This spectral decomposition attributes the watershed solute response in specific intervals of frequencies to governing processes and spatial regions within the watershed.

The spectral decomposition methodology was evaluated using chloride and sodium concentration time series extracted from a set of high-frequency long-term hydrochemical data collected by the Centre for Ecology and Hydrology (CEH) in the Upper Hafren Watershed, Wales. In our analyses we observed a systematic smoothing of the solute concentration in the output signal compared with the input signal. Further, we linked the damping of the concentration fluctuations to the watershed dispersion mechanisms in selected frequency intervals reflecting various environments responsible for the damping.

In the Upper Hafren Watershed, we found frequency-dependencies of some of the key model parameters affecting the transport and dispersion of solutes, which can be interpreted such that different pathways contributed to the concentration fluctuations at different frequencies. Thus, the evaluation indicates that environments with different transport characteristics dominate the watershed solute response at different temporal scales. The specific findings include typical transit time of chloride ranging from approximately one week for the fluctuations with shortest periods (predominantly surface water and shallow ground water transport) to two years for the longest ones (predominantly deeper ground water transport). Moreover, the retardation of sodium compared to the chloride transport increased from being negligible for short period fluctuations to almost a factor three for the longest ones.