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Spectral signatures of water quality from H+ to U: implications for trend analysis and change detection on timescales from days to decades.

Stream water quality varies across a wide range of timescales, under the influence of hydrological forcing, anthropogenic drivers, and in-catchment biogeochemical processes. This mixture of timescales and processes can complicate efforts to infer changes in anthropogenic drivers from water quality time series. Catchments also store and mix waters over a wide range of residence times, which may themselves vary with flow regime, further complicating efforts to understand water quality trends. The water quality data set from the Plynlimon catchments is a unique resource for exploring these issues. At Plynlimon, several small catchments have been sampled weekly for over 20 years, and two catchments have been sampled every seven hours for up to two years. Both the long-term and the high-frequency data sets have been analyzed for 45 analytes that span the periodic table, from H+ to U.

Here we show that these water quality time series exhibit fluctuations across all measurable time scales, and that they have a distinctive spectral signature. We show further that these time series are not self-averaging: that is, averages taken over longer and longer time periods do not converge to a stable mean, or do so very slowly. Such time series defy the Central Limit Theorem and the standard regimen of statistical tests that are based upon it. The implications of these findings for trend analysis and change detection will be discussed.