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Diurnal cycles in water quality across the periodic table

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Diurnal cycles in water quality can provide important clues to the processes that regulate aquatic chemistry, but they often are masked by longer-term, larger-amplitude variability, making their detection and quantification difficult. Here I outline methods that can detect diurnal cycles even when they are massively obscured by statistically ill-behaved noise. I demonstrate these methods using high-frequency water quality data from the Plylimon catchment in mid-Wales (Neal et al., 2013; Kirchner and Neal, 2013).

Several aspects combine to make the Plynlimon data set unique worldwide. Collected at 7-hour intervals, the Plynlimon data set is much more densely sampled than typical long-term weekly or monthly water quality data. This 7-hour sampling was also continued for two years, much longer than typical intensive sampling campaigns, and the resulting time series encompass a wide range of climatic and hydrological conditions. Furthermore, each sample was analyzed for a wide range of solutes with diverse sources in the natural environment. However, the 7-hour sampling frequency is both coarse and irregular in comparison to diurnal cycles, making their detection and quantification difficult.

Nonetheless, the methods outlined here enable detection of statistically significant diurnal cycles in over 30 solutes at Plynlimon, including alkali metals (Li, Na, K, Rb, and Cs), alkaline earths (Be, Mg, Ca, Sr, and Ba), transition metals (Al, Ti, Mn, Fe, Co, Ni, Zn, Mo, Cd, and Pb), nonmetals (B, NO_3, Si, As, and Se), lanthanides and actinides (La, Ce, Pr, and U), as well as total dissolved nitrogen (TDN), dissolved organic carbon (DOC), Gran alkalinity, pH, and electrical conductivity. These solutes span every row of the periodic table, and more than six orders of magnitude in concentration.

Many of these diurnal cycles are subtle, representing only a few percent, at most, of the total variance in the concentration time series. Nonetheless they are diagnostically useful, because their amplitude and phase contain important clues to the mechanisms controlling these solutes in streamwater. The amplitudes of these cycles vary seasonally, and from wet to dry conditions; the phases are typically much more consistent over time. Under low-flow conditions, the diurnal cycle phases of different elements vary systematically with their electronic structure, as reflected in their placement in the periodic table. Potential mechanisms for this surprising pattern will be discussed.

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