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Long-term, high-frequency water quality monitoring in an agricultural catchment: insights from spectral analysis

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The choice of sampling frequency is a key issue in the design and operation of environmental observatories. The choice of sampling frequency creates a spectral window (or temporal filter) that highlights some timescales and processes, and de-emphasizes others (1). New online measurement technologies can monitor surface water quality almost continuously, allowing the creation of very rich time series. The question of how best to analyze such detailed temporal datasets is an important issue in environmental monitoring.

In the present work, we studied water quality data from the AgrHys long-term hydrological observatory (located at Kervidy-Naizin, Western France) sampled at daily and 20-minute time scales. Manual sampling has provided 12 years of daily measurements of nitrate, dissolved organic carbon (DOC), chloride and sulfate (2), and 3 years of daily measurements of about 30 other solutes. In addition, a UV-spectrometry probe (Spectrolyser) provides one year of 20-minute measurements for nitrate and DOC.

Spectral analysis of the daily water quality time series reveals that our intensively farmed catchment exhibits universal $1/f$ scaling (power spectrum slope of -1) for a large number of solutes, confirming and extending the earlier discovery of universal $1/f$ scaling in the relatively pristine Plynlimon catchment (3). $1/f$ time series confound conventional methods for assessing the statistical significance of trends. Indeed, conventional methods assume that there is a clear separation of scales between the signal (the trend line) and the noise (the scatter around the line). This is not true for $1/f$ noise, since it overestimates the occurrence of significant trends. Our results raise the possibility that $1/f$ scaling is widespread in water quality time series, thus posing fundamental challenges to water quality trend analysis.

Power spectra of the 20-minute nitrate and DOC time series show $1/f$ scaling at frequencies below 1/day, consistent with the longer-term daily measurements. At higher frequencies, however, the spectra steepen to a slope of -2, indicating that at sub-daily time scales the concentration time series become relatively smooth. However, at time scales shorter than 2-3 hours, the spectra flatten to a slope near zero (white noise), reflecting analytical noise in the measurement probe. This result demonstrates that measuring water quality dynamics at high frequencies also requires high measurement precision, because as measurements are taken closer and closer together in time, the real-world differences that must be measured between adjacent measurements become smaller and smaller. Our results highlight the importance of quantifying the spectral properties of analytical noise in environmental measurements, to identify frequency ranges where measurements could be dominated by analytical noise instead of real-world signals.

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