SPECTRAL ANALYSIS OF CHEMICAL TIME SERIES FROM LONG-TERM CATCHMENT MONITORING STUDIES: HYDROCHEMICAL INSIGHTS AND DATA REQUIREMENTS

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Abstract. Hydrological and hydrochemical data from long-term monitoring stations are vital for inferring travel times and flowpaths of water, and transport of contaminants through catchments. Spectral analysis is particularly powerful for studying the hydrological and chemical dynamics of catchments across a wide range of time scales. Here, recent work is reviewed that illustrates how spectral analyses of long-term monitoring data can be used to infer the travel-time distribution of water through catchments, and to measure the chemical retardation of reactive solutes at the catchment scale. For spectral analysis, it is desirable to have data sets with high sampling frequency and long periods of coverage. Using two data sets, a 3-yr daily data series and a 17-yr weekly data series from the Hafren catchment at Plynlimon, Wales, we demonstrate that high-frequency sampling (e.g., daily or more frequent) is particularly useful for revealing the short-term chemical dynamics that most clearly reflect the interplay of subsurface chemical and hydrological processes. However, data sets that combine high-frequency sampling during storm events with low-frequency sampling between storms can cause spectral artifacts and must be treated with special care.

Keywords: catchments, hydrochemistry, Plynlimon, solute transport, spectral analysis, time series analysis, tracers

1. Introduction

Catchment studies are important for understanding water quality, contaminant transport, biogeochemical processes, and ecosystem responses to natural and anthropogenic disturbances (Černy *et al.*, 1995). It has been increasingly recognized that many catchment-level processes, such as soil responses to acid deposition and ecosystem responses to deforestation and forest fires, operate on timescales of decades or longer, and that observing these processes requires catchment monitoring programs spanning similar lengths of time. As a result, many monitoring programs have been set up, and their long-term time series of water and chemical fluxes not only record the history of ecosystem responses to disturbance, but also provide insight into the structure and function of ecosystem processes at the landscape scale

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(e.g., Church, 1997). For example, long-term data have enabled landscape-scale input-output budget calculations for various chemical species. Such calculations are essential for constraining rates of chemical weathering, biological uptake and release, and nutrient cycling at the catchment scale (e.g., Likens and Bormann, 1995). Further, these long-term data sets have made it possible to quantify temporal trends in major and trace element budgets. They also have provided understanding of catchment responses to various ecosystem disturbances, both natural and anthropogenic, including acid deposition, climate change, land use change (deforestation, agriculture), hurricanes and forest fires (e.g., Britton, 1991; Neal *et al.*, 1992; Kirchner and Lydersen, 1995; Wesselink *et al.*, 1995; Schaefer *et al.*, 2000). Long-term monitoring data also havebeen used to clarify subsurface flowpaths and reaction mechanisms, and to calibrate and test mathematical models of hydrological and geochemical processes (e.g., Hooper *et al.*, 1988; Kirchner, 1992; Kirchner *et al.*, 1992; Ferrier *et al.*, 1995).

In this contribution, we discuss spectral analysis as a little-explored use of long-term catchment monitoring data. We examine the utility of spectral methods in the context of long-term catchment studies at Plynlimon, mid-Wales (e.g., Reynolds *et al.*, 1986; Durand *et al.*, 1994; Neal *et al.*, 1997). We illustrate the importance of long-term data sets from research catchments like Plynlimon, and emphasize, using the Plynlimon data, the importance of both long-term coverage and high sampling frequency in catchment monitoring data sets.

2. Significance of Spectral Analysis for Catchment Studies

In a series of papers (Kirchner *et al.*, 2000a, 2001; Feng *et al.*, in review), we recently have used long-term monitoring data from Plynlimon to show how spectral analysis of naturally-occurring chemical tracers can be used to measure the travel-time distribution of water moving through a catchment, as well as the catchment-scale retardation factor for reactive solutes. In this section, we review the important contributions, emphasizing the value of time-series data sets and the utility of spectral methods. In the following section, we discuss desirable qualities of data sets for such analyses.

2.1. Catchment-scale travel-time distributions

Some fraction of the rain that falls on a catchment today will reach the stream today; some fraction will reach the stream tomorrow, some fraction the day after, and so forth. These timescales over which a catchment transmits precipitation to streamflow are quantified by its travel-time distribution, which is the probability distribution of the relative amounts of water reaching the stream after a given travel time through the catchment. The travel-time distribution is an important characteristic of a catchment because it determines how long it takes for the catchment to be flushed and, therefore, how long it would take for soluble contaminants to be cleaned up. Recently, Kirchner *et al.* (2000a) used long-term records of Cl^- in precipitation and stream water at Plynlimon to demonstrate how one can empirically determine a catchment's travel-time distribution from spectral analyses of passive tracer concentrations.

The Plynlimon catchments generally are covered with thin acid soils (podzols and gleys) that overlie fractured bedrock of slates and shales. Rainfall is typically about 2500 mm a^{-1} and evaporation plus transpiration amounts to 25 to 50% of the input, depending upon the type of vegetation cover. The available Cl^- data at Plynlimon include weekly measurements of precipitation and streamwater from mid-1983 to the present and daily measurements for three years (1994–1997) (Neal and Kirchner, 2000). This long sampling period, combined with three years of high-frequency data, was particularly useful for determining the travel-time distribution of the Plynlimon catchment (Kirchner *et al.*, 2000a).

For a chemical tracer that is supplied to the catchment entirely by rainfall, the concentration in the stream $c_S(t)$ at any time t will be the convolution of the travel-time distribution $h(\tau)$ and the rainfall concentration at all previous times $c_R(t-\tau)$, where τ is the lag time between rainfall and runoff:

$$c_s(t) = \int_0^{\infty} h(\tau) c_R(t - \tau) d\tau \tag{1}$$

Because the flow rate varies through time, Equation (1) is strictly valid when t and τ are expressed in terms of the cumulative flow through the catchment, rather than calendar time (Neimi, 1977; Rodhe *et al.*, 1996), but the mathematics are the same in either case (Neimi, 1977). The rainfall and stream Cl-time series can be used to constrain the travel-time distribution h(τ) by employing the convolution theorem, which states that the convolution in Equation (1) is equivalent to multiplying the Fourier transforms of each of its terms:

$$C_S(f) = H(f)\ C_R(f) \qquad \text{and} \qquad |C_S(f)|^2 = |H(f)|^2\ |C_R(f)|^2 \tag{2}$$

where f is frequency (cycles/time); $C_S(f)$, $H(f)$, and $C_R(f)$ are the Fourier transforms of $c_S(t)$, $h(\tau)$, and $c_R(t-\tau)$; and $|C_S(f)|^2$, $|H(f)|^2$, and $|C_R(f)|^2$ are their power spectra (Gelhar, 1993). This equation allows one to test alternative travel-time models $h(\tau)$ by calculating their power spectra $|H(f)|^2$, and testing whether they are consistent with the relationship between the input and output power spectra $|C_R(f)|^2$ and $|C_S(f)|^2$. Kirchner *et al.* (2000a) computed the power spectra of Cl^- in rainfall ($|C_R(f)|^2$) and Plynlimon streams ($|C_S(f)|^2$), and found that the spectral power of rainfall Cl^- scales roughly as white noise and the spectral power of stream Cl^- scales roughly as fractal $1/f$ noise (Figure 1), with spectral power increasing proportionally to wavelength. In addition, they showed that the

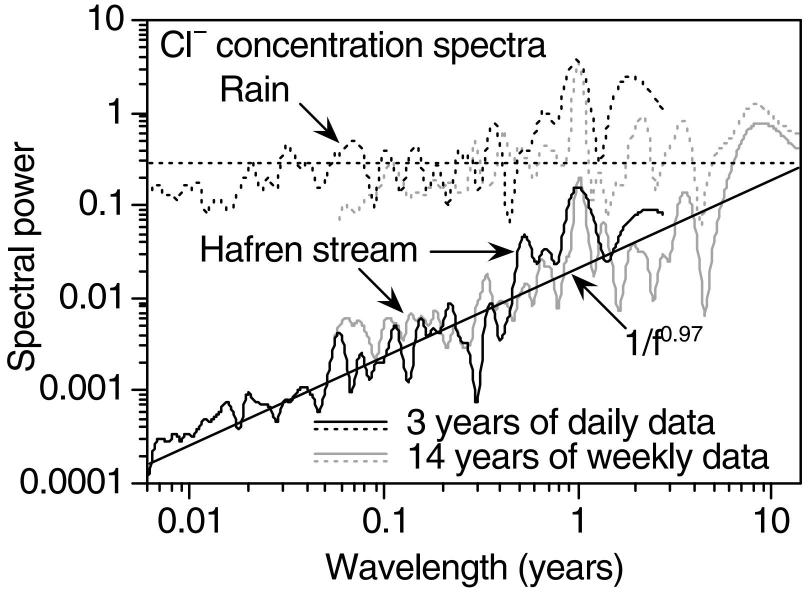

Figure 1. Power spectra of Cl^- variations in rainfall and Hafren stream water at Plynlimon, Wales.

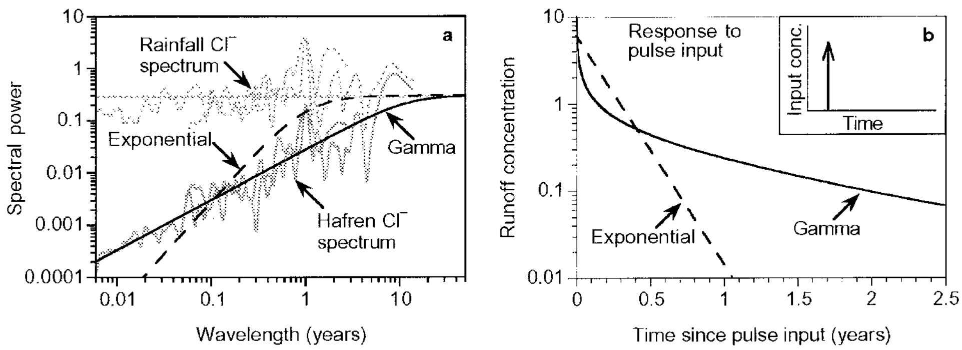

Figure 2. Comparison of two alternative travel-time distributions, their power spectra, and their consequences for contaminant transport. (a) Best-fit power spectra of the two distributions, superimposed on the rainfall and Hafren chloride concentration spectra. The gamma distribution is consistent with the observed power spectrum of Cl^- in Hafren streamflow, but the exponential distribution is not, showing that the catchment does not function as a homogeneous mixing tank. (b) Response of streamflow concentrations to a delta-function pulse input of contaminants. Compared to the exponential travel-time distribution, the gamma distribution would seem to remove the contaminant rapidly at the beginning. However, since the gamma distribution has a much longer tail than the exponential distribution, it sustains substantial contaminant concentrations for much longer time spans. The inset depicts the delta-function contaminant input.

Plynlimon Cl^- power spectra were consistent with a travel-time distribution that can be empirically approximated by the gamma distribution,

$$h(\tau) = \frac{\tau^{\alpha-1}}{\beta^{\alpha}\,\Gamma(\alpha)}\, e^{-\tau/\beta} \tag{3}$$

where β is a scale parameter and α ($\approx$0.5) is a shape parameter. Figure 2a shows that this gamma function closely reproduces the scaling of the Cl^- power spectra in stream water. In contrast, a conventional catchment 'box' model would predict an exponential distribution of travel times, which is inconsistent with the spectral scaling observed at Plynlimon (Figure 2a).

The inferred travel-time distribution has significant implications for contaminant transport through catchments. Figure 2b shows how a pulse input of a soluble contaminant is removed by natural flushing if the travel-time distribution is a gamma function versus an exponential function (see Catchment Models, below). Compared to the exponential distribution, the catchment having a gamma travel-time distribution would appear to flush out the contaminant quickly at first but then very slowly thereafter, delivering low-level contamination to the stream for a long time.

The $1/f$ scaling behavior of stream Cl^- is not unique to the Plynlimon catchments. A wide array of catchments, with substrates ranging from deeply fractured shales to glacially scoured gneisses, and with drainage areas ranging over three orders of magnitude, exhibit fractal tracer scaling similar to that shown in Figure 1 (Kirchner *et al.*, 2000b). By comparing the power spectra, and thus the travel-time distributions, from different catchments, it may be possible to determine how (or whether) the residence time of water is related to characteristics such as catchment geometry, hillslope gradient, soil depth, and substrate properties.

2.2. Catchment models

Empirical travel-time distributions, like those presented above, are even more useful for studying catchment transport processes if we know the mechanism(s) that generate them. This requires creating physical models that are consistent with the observed scaling in tracer fluctuations. The simplest catchment model is a 'box' or 'mixing tank' model, in which the catchment is viewed as a well-mixed water reservoir. In such a model, the travel-time distribution is an exponential function. However, as indicated in Figure 2a, this travel-time distribution is fundamentally inconsistent with the observed scaling of stream Cl^- at Plynlimon.

Kirchner *et al.* (2001) built a simple one-dimensional model in which spatially distributed rainfall tracer inputs advect and disperse with water flowing downhill. They showed that the power spectrum of the model tracer scales roughly as $1/f$ noise, as long as the Peclet number of the advection-dispersion system is of order 1 or smaller; that is, as long as the subsurface flow system is highly dispersive, with characteristic dispersion length scales on the order of the average hillslope

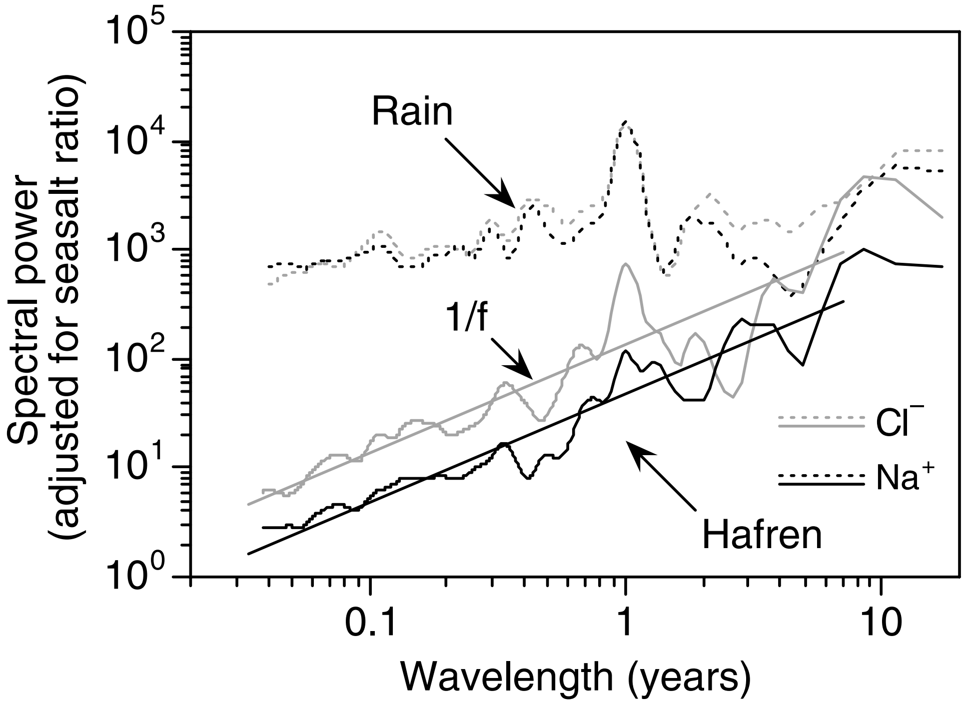

Figure 3. Power spectra of Na^+ and Cl^- in rainfall and Hafren stream at Plynlimon, Wales. The average retardation factor can be obtained from the vertical offset of the two spectra. In this case, the Na^+ retardation is 2.7 (Feng *et al.* (in press)).

length. This in turn implies that the subsurface flow is affected by large variations in conductivity, on all scales up to the hillslope scale itself, results that are in keeping with general field observations at Plynlimon (Neal, 1997).

Scher *et al.* (2002) have shown that a continuous-time random-walk (CTRW) model can also produce the $1/f$ scaling of the Cl^- spectrum and the corresponding travel-time distribution. We believe that there may be still other physical models that are consistent with the spectral tracer scaling that we have observed. Searching for these models will improve our understanding of subsurface flow routing and its consequences for physical, chemical and biological processes in catchments.

2.3. Quantifying reactive tracer transport using spectral analysis

Recently, we compared Na^+ and Cl^- time series in rainfall and stream water at Plynlimon (Neal and Kirchner, 2000), and used them to derive whole-catchment chemical retardation factors for Na^+ transport at four Plynlimon catchments (Feng *et al.* (in press)). At Plynlimon, both Na^+ and Cl^- are almost entirely derived from precipitation, and the flow weighted Na^+/Cl^- molar ratio in stream water is close to that of seasalt (0.86). When compared with stream Cl^-, stream Na^+ has a longer mean travel time and its fluctuations are more strongly damped in the stream relative to precipitation. This additional damping of Na^+ compared to Cl^- can be attributed to adsorption/desorption of Na^+ in the subsurface, most likely by cation exchange. The spectral power of both Na^+ and Cl^- scale as white noise in rainfall and as $1/f$ noise in streamwater. However, streamwater Na^+ has consistently lower spectral power than streamwater Cl^- across the range of wavelengths studied (e.g., Figure 3). From the vertical offset between the Cl^- and Na^+ spectra, we can calculate the whole-catchment chemical retardation factor for Na^+ (which equals 2.7 in this example). To our knowledge, whole-catchment retardation factors have never been reported before. This spectral method opens up new opportunities for studying and quantifying transport properties of reactive tracers.

These are a few examples showing the usefulness of spectral analyses for catchment studies. The long-term monitoring data at Plynlimon have made these studies possible. More studies at Plynlimon and similar studies for other catchments are yet to come. The spectral analysis methods reviewed here allow us to quantify hydrologically and geochemically important properties of catchments at catchment scale (such as their whole-catchment travel-time distributions and whole-catchment retardation factors). They thus provide new opportunities for determining whether these properties are shared among catchments generally, or whether they are specific to individual catchments with particular characteristics (substrates, geometries, soil types, climates, vegetation covers, etc.).

3. Data Sets for Spectral Analysis

For spectral analysis of time-series data, it is always desirable to have both long-term coverage and high sampling frequency. The importance of long-term catchment monitoring has been widely recognized in the scientific community (Church, 1997). Here, while acknowledging the importance of long-term data sets, we emphasize the utility of high-frequency sampling for revealing catchment behavior. This is because streams not only have a long chemical memory of precipitation, but also exhibit prompt responses to rainfall inputs.

Figure 4 shows three pairs of diagrams plotting the time series and power spectra of Cl^- concentrations in rainfall and stream water in the Hafren catchment at Plynlimon. From the top down, the figures show monthly, weekly and daily sampling frequencies. For all three sampling frequencies, the spectral power of stream Cl^- is consistently lower than the corresponding spectral power of rainfall Cl^-. In addition, these figures all suggest that high frequency rainfall variations are damped more in the stream water than low frequency variations are. With each increase in sampling frequency, one can see that this trend of greater damping at shorter wavelengths extends from monthly to weekly and to daily time scales.

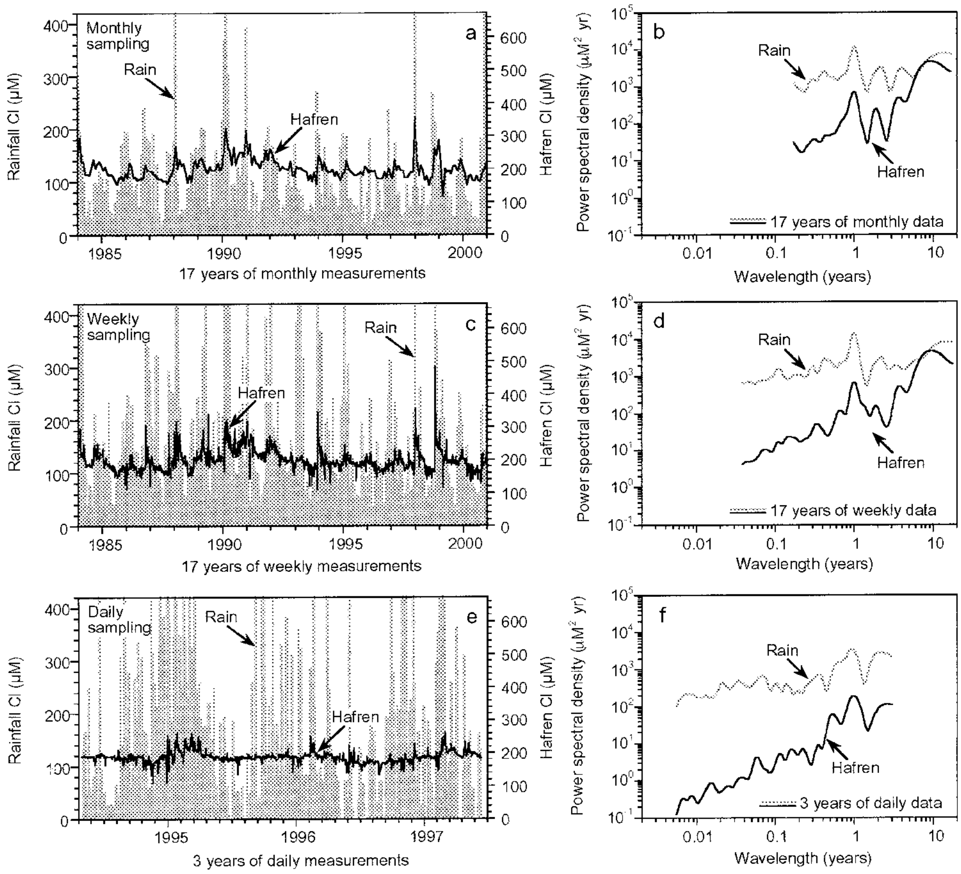

Figure 4. Time series and power spectra at monthly, weekly, and daily sampling frequencies for rainfall and stream Cl^- at the Hafren catchment. (a,b) Monthly measurements of Cl^- in rainfall and stream water, subsampled from a 17-yr data set of weekly measurements, and their corresponding power spectra. (c,d) Weekly measurements for 17 yr, and their corresponding power spectra. (e,f) Daily measurements for three years, and their corresponding power spectra. High-frequency sampling (e.g., daily data) more clearly shows short-wavelength features, better defining the $\sim 1/f$ scaling of stream spectra. Such high-frequency information is intrinsically missing in low-frequency data sets (e.g., monthly sampling, in this example).

This example demonstrates that the daily data set is particularly valuable for clarifying the $1/f$ spectral scaling of stream Cl^- at short wavelengths. One reason for this is that seasonal variations in Cl^- create an annual cycle with a strong spectral peak that dominates the spectrum at wavelengths near 1 yr. This strong annual peak makes it difficult to see the underlying $1/f$ scaling behavior unless the spectrum extends to wavelengths significantly shorter than 1 yr. The higher the sampling frequency, the farther the spectrum can be extended into the short-wavelength domain.

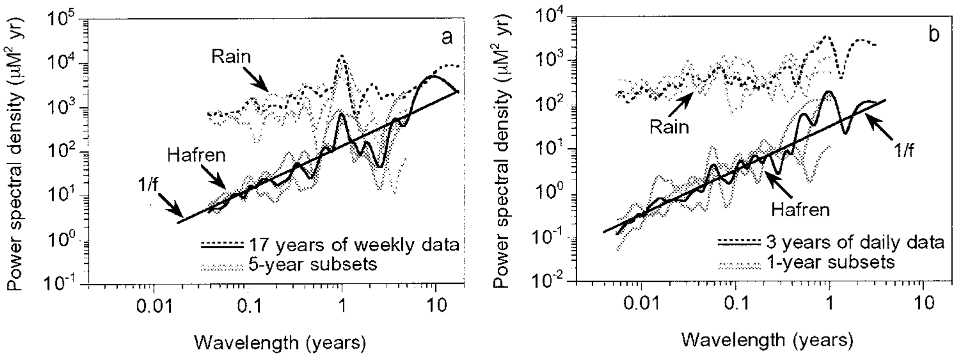

Figure 5. Comparison of power spectra of Cl^- data having different temporal lengths. (a) Comparison of the 17-yr weekly data set (black) with three 5-yr subsets (grey). (b) Comparison of the 3-yr daily data set (black) with three 1-yr subsets (grey). In both cases, the longer data set gives information at longer wavelengths than the short data sets. However, the daily data better define the $1/f$ scaling behavior of the spectra than weekly data regardless of the record length, because the daily data contain high-frequency information that is not present in the weekly data sets.

For a given sampling interval, one inevitably gets more information from a long data set than from a short one. Figure 5 illustrates two comparisons of spectra generated from long versus short data sets. Figure 5a shows the power spectra (solid lines) for 17 yr of weekly data in comparison to three 5-yr subsets (grey lines) from the same 17-yr data set. Of course, the 5-yr data sets cannot provide information for wavelengths longer than five years. Their spectra are also more variable than those from the 17-yr data set (particularly in the rainfall spectra), especially in the long-wavelength range near the annual peak and beyond it. This variability results from the fact that there are fewer cycles at these long wavelengths in the shorter data sets. For example, there are five annual cycles in the 5-yr data sets, but 17 in the 17-yr data set, so the longer data set can more accurately constrain the average spectral signature of the annual cycles in Cl^-.

Similar observations can be made from Figure 5b, in which the power spectra of the 3-yr daily time series are compared with those of three one-year subsets of the same data. Note, however, that even though the one-year data sets are three times shorter than the 3-yr data set, they are nevertheless helpful in constraining the spectral behavior at the short-wavelength end. The damping of stream Cl^- spectral power relative to that of rainfall Cl^- is more clearly shown from these data sets than from the weekly data sets (Figure 5a), and the $1/f$ scaling of stream Cl^- is better defined as well.

While stressing the importance of high-frequency sampling, we caution that if high-frequency data are only available for a relatively short window of time (as will usually be the case), the analysis may be biased if the catchment's behavior during that time window is unrepresentative. Hydrological conditions fluctuate significantly from year to year. Daily samples from a stormy year may lead to different

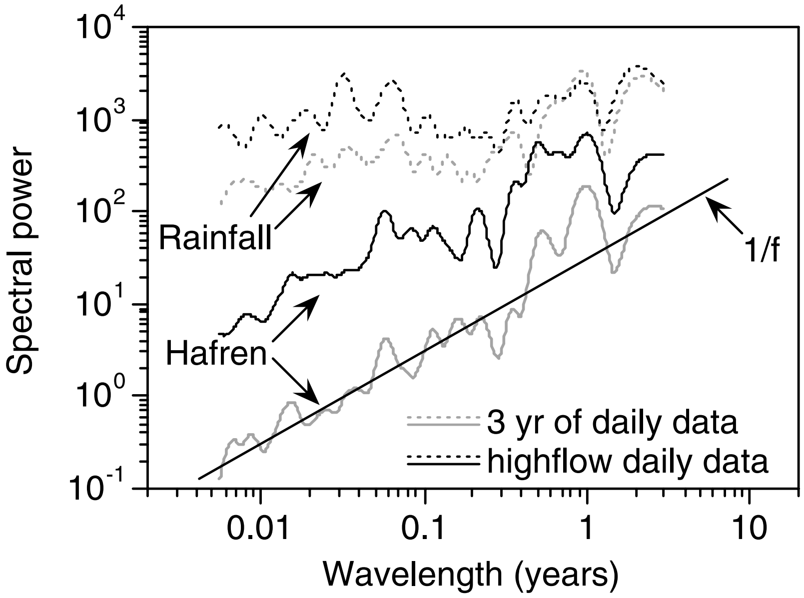

Figure 6. Spectral effects of sampling bias. A high flow data series is generated by subsampling the 20% of days in the 3-yr daily data with the highest stream flows. The power spectra from this highflow data set are compared with that of the complete 3-yr daily data set. The spectral power of stream Cl^- in the high-flow data is significantly higher than that in the complete data set, but both exhibit approximate $1/f$ scaling.

results than data sampled from a hydrologically calm year. Disturbances that affect catchment chemistry may contribute to this bias; examples are hurricanes, droughts, fire, ENSO events, etc. What this means in practice is that one should be careful when combining spectra from different data sets with different sampling frequencies, particularly when they cover different spans of time.

Many catchment data sets include long-term measurements taken regularly each week, with higher-frequency sampling during storm events. The recently-developed spectral analysis methods for unevenly-sampled data (Scargle, 1982; Foster, 1996) make it tempting to analyze such records, but caution is needed in interpreting the resulting spectra. The high-frequency sampling (and thus the short-wavelength characteristics of the spectrum) will be inherently biased toward the catchment's behavior during storm events, while the low-frequency regular sampling (and thus the long-wavelength part of the spectrum) will reflect the catchment's average behavior, of which storm events are just one component. Thus, the high-frequency data, and the short-wavelength end of the spectrum, will be unrepresentative of the average catchment behavior in the regular weekly data. The weekly monitoring data and the event data both contain useful information, but they cannot be uncritically combined.

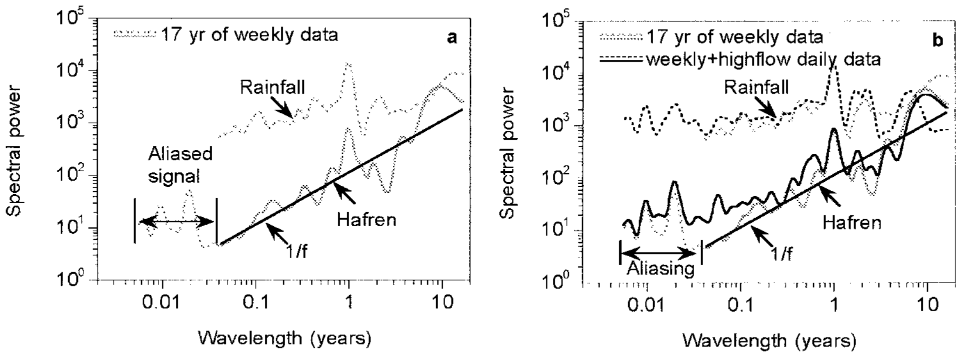

Figure 7. Spectral aliasing arising from analysis of time series combining regular weekly sampling with daily sampling during highflow periods. (a) Analyzing the weekly data at wavelengths shorter than the Nyquist limit (~ two weeks) generates marked spectral aliases. (b) These spectral aliases dominate the short-wavelength behavior of the combined weekly-plus-highflow-daily time series, obscuring the $1/f$ scaling that is observed in both the weekly and highflow daily time series when they are analyzed separately (see Figures 5a and 6).

To demonstrate this point, we generated a new data set by subsampling the existing 3-yr daily data set at Hafren, retaining only those points for days with the highest 20% of stream flows over the 3-yr period. This yields a data set covering only the high-flow periods (which are of course unevenly distributed through the three-year record). As Figure 6 shows, the spectral power of rainfall and streamflow Cl^- during these high-flow periods is substantially higher than in the continuous three-year data set. Thus, although event data contain useful information about catchment hydrochemical properties at high flow, it should not be misinterpreted as the average catchment behavior.

In addition to this sampling bias, spectral aliasing can substantially distort the power spectra of data sets that combine long periods of regular (or nearly regular) sampling with more frequent sampling during short episodes. Figure 7 demonstrates this aliasing effect. In Figure 7a, the weekly data from Hafren are intentionally analyzed down to wavelengths of only two days, corresponding to the conventional Nyquist limit for daily sampling. At wavelengths shorter than roughly 14 days (corresponding to the Nyquist limit for weekly sampling), the $1/f$ spectrum disappears and is replaced by a flat spectrum (white noise) punctuated by two peaks at wavelengths of 7 days and 3.5 days. These wavelengths correspond to the sampling frequency and its first harmonic; the peaks are aliases of the large low-frequency power in the signal. This spectral aliasing can persist, even if the time series contains higher-frequency sampling during brief episodes. We can demonstrate this aliasing effect by combining the long-term weekly data from Hafren with the high-flow subset of the daily sampling data. Figure 7b shows the spectrum of this combined time series. Note that the spectral aliasing of the weekly data dominates the short-wavelength end of the spectrum. Remember that the weekly data set and the highflow daily data set both exhibit $1/f$ scaling when they are analyzed

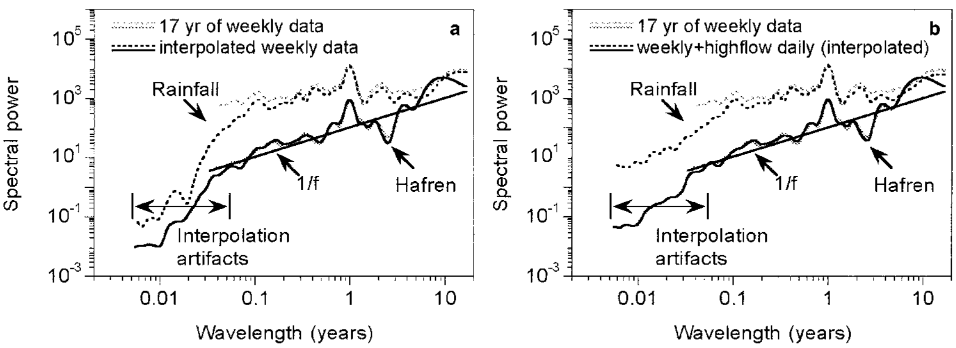

Figure 8. Spectral distortions arising from linear interpolation of time series combining regular weekly sampling with daily sampling during highflow periods. (a) Linear interpolation generates marked damping of spectral power at wavelengths shorter than the Nyquist limit for the original, un-interpolated data. (b) This interpolation artifact dominates the short-wavelength end of the spectrum even for time series that include high-frequency sampling during episodes.

separately, each over their appropriate ranges of wavelengths (see Figures 5a and 6). However, when the two time series are combined and analyzed together, the weekly data are analyzed beyond their Nyquist limit, resulting in spectral aliasing.

It is often assumed that chemical concentrations in stream water vary little between storms. It is therefore tempting to analyze records that mix long-term regular sampling with short-term episode sampling, by creating an evenly spaced high-frequency time series, using linear interpolation to bridge the gaps in the long-term regularly sampled data. We can test this approach using our combined weekly-plus-highflow data set, by interpolating between each of the real data to construct an evenly-sampled daily time series. At wavelengths shorter than the true sampling interval, linear interpolation will artificially reduce the spectral power, because the interpolated time series will be inherently less variable than the real, unsampled time series would be. As Figure 8a shows, interpolating between the weekly data to create a daily data set distorts the spectrum, artificially steepening it at short wavelengths. Including the highflow daily data in the interpolated time series reduces the interpolation artifact somewhat (see Figure 8b), but the short-wavelength end of the spectrum is still artificially steepened.

Great care must be taken when analyzing catchment data sets that combine long, regularly sampled records with shorter periods of high-frequency sampling during episodes. Here we have identified three types of distortions that can arise. First, the behavior during episodes may be atypical, generating bias (Figure 6). Second, the spectrum may be extended to wavelengths shorter than the Nyquist limit for the regularly sampled data, generating aliases (Figure 7). Finally, interpolating such records can produce artifactually low spectral power at short wavelengths (Figure 8). These distortions appear to be intrinsic to the time series themselves, as they appear with both of the widely used spectral analysis methods that are designed for unevenly sampled data (Scargle, 1982; Foster, 1996). It may be possible that at some specific combination of high-frequency episode sampling and low-frequency regular sampling, these three artifacts might offset one another. An undistorted spectrum might thus be obtained, but only through the sheer coincidence of the various distortions canceling each other out. A wiser approach, in our view, is to not merge the data sets in the first place, but instead analyze each of the different types of data separately, using spectral methods and wavelength ranges that are appropriate to each (as in Figures 1 and 4).

4. Conclusions

Spectral analyses of time series from long-term catchment monitoring stations are valuable for studying the hydrological and chemical dynamics of catchments across many time scales. Our recent work has demonstrated that travel-time distributions of water moving through catchments can be determined using spectral analysis of passive tracer concentrations in precipitation and in stream flow. By comparing the power spectra of passive and reactive tracers, it is possible to estimate chemical retardation factors for reactive solutes at the whole-catchment scale.

The ideal data set for spectral analysis would have a long temporal span (a decade or longer) and a relatively high sampling frequency (e.g., daily sampling); no such 'ideal' data set currently exists. High-frequency variations in rainfall and stream chemistry are particularly useful for understanding catchments' chemical response to precipitation at short time scales. At the Plynlimon catchments in Mid-Wales, three years of daily measurements reveal the spectral scaling behavior of stream Cl^- more clearly than 17 yr of weekly measurements. Higher-frequency sampling during storm events is common at many monitoring stations. However, these data should not be uncritically combined with regular monitoring data reflecting average catchment behavior, as spectral biases and aliasing can result.

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