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# Investigating a high resolution, stream chloride time series from the Biscuit Brook catchment, Catskills, NY

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**Summary** In conjunction with stream discharge, stream chloride ($Cl^-$) concentration has traditionally offered hydrologists a means to better understand internal catchment processes. Here we examine a 10 year, weekly stream $Cl^-$ concentration time series from the Biscuit Brook catchment, NY, United States. Using a two reservoir box model plus a snowmelt component, we replicate daily stream discharge reasonably well (Nash–Sutcliffe efficiency = 0.64) and capture general trends in the stream $Cl^-$ concentration ($R^2 = 0.36$ during nonfreezing conditions). Additionally, we find that both the observed and modeled stream $Cl^-$ concentration time series appear to be $1/f$ noise when analyzed spectrally. Differing from previously published explanations of $1/f$ noise in other catchments, we propose that $1/f$ noise in the $Cl^-$ concentration signal of Biscuit Brook may originate from a suite of watershed-scale processes affecting both water content and $Cl^-$ mass in the system and occurring at multiple time scales.


## Introduction

Due to its widespread presence in the environment and its presumed chemically conservative nature, chloride ($Cl^-$) is frequently used as a tracer to investigate catchment hydrologic response. For example, many studies have analyzed single storm events and used end-member mixing models to deduce the source and age of water contributing to streamflow (see Table 1 in review by Jones et al., 2006). Extending this traditional line of investigation, Kirchner et al. (2000) inferred the travel time distribution of stream water by analyzing a long, high resolution stream $Cl^-$ time series in frequency space for catchments in Plynlimon, Wales. Specifically, they observed that power spectra for the $Cl^-$ time series were inversely related to frequency (so called $1/f$ noise), a feature potentially explained by assuming long-tailed, power-law travel time distributions for $Cl^-$ moving laterally through the catchment (Kirchner et al., 2000). But, despite the apparent possibility of deducing catchment transport characteristics, no studies on other watersheds have adopted this approach. This lack of follow-up is most likely due to the dearth of lengthy, high resolution time series needed for such an analysis.

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To begin to fill this gap, we examine a 10 year, weekly stream $Cl^-$ concentration time series from the Biscuit Brook catchment, NY, United States. Our objectives are: (1) to consider the suitability of using a simple, bucket model to explain the Biscuit Brook $Cl^-$ time series, (2) to assess the power spectra of the observed and simulated $Cl^-$ time series, and (3) to offer possible explanations for the slope of the power spectra of the observed signal by way of comparison to the simulated signal.

## Catchment and data set

### Chemical and hydrometeorological drivers

Within the Biscuit Brook catchment, average annual precipitation, as measured at the National Atmospheric Deposition Network gage during the period of record (ID: NY68), is 136 cm. But, given that the gauge is at the lowest point in the catchment (622 m), supplemental precipitation data were taken from a National Weather Service gauge at Slide Mountain, NY (el. 808 m). Average annual potential evapotranspiration (PET) is 55 cm (before scaling by 0.7) based on an average of pan evaporation measurements from three stations located in Delhi, Stamford, and Walton, NY.

We used stream $Cl^-$ concentrations measured at the USGS gauge (ID: 01434025) approximately weekly (seven day intervals ±1 day) between January 1995 and October 2004. $Cl^-$ was analyzed by ion chromatography at the USGS lab in Troy, NY and reported to within 10% error (Brown et al., 1999). The margin of error in the chemical analysis is of particular importance given that stream $Cl^-$ concentration fluctuates within a narrow range – approximately 0.40–0.80 ppm – and meaningful, deterministic variations need to be distinguished from measurement error. Previous studies in which samples were collected on the order of hours instead of weeks have reported $Cl^-$ to remain nearly constant across individual hydrologic events in streams within the Northeast US (Evans et al., 1999), a perception likely based in part on the small degree of change relative to other ions. However, as seen from the 10 year, weekly observations (Fig. 1), deterministic changes do occur and are particularly apparent at longer time scales.

Chloride wet deposition and rainfall were measured at a station of the National Atmospheric Deposition Network (ID: NY68) located just outside the watershed. Stream $Cl^-$ concentrations are systematically higher than rain $Cl^-$ concentrations even when accounting for concentrating effects due to evaporation, an indication wet deposition is not the only $Cl^-$ source. Other researchers have noted that wet deposition underpredicts total $Cl^-$, and unmeasured sources such as dry deposition and cloud deposition can contribute up to 50% of the total $Cl^-$ load (Peters and Ratcliffe, 1998; Neal et al., 1988). Using the daily average Biscuit Brook streamflow ($0.30\ m^3\ s^{-1}$ or $0.27\ cm\ day^{-1}$) and average stream $Cl^-$ concentration (0.54 ppm) and assuming conservative behavior, the expected average $Cl^-$ rainfall concentration would be 0.38 ppm for the average daily precipitation of 0.37 cm for the 10 year record. However, the observed average rainfall $Cl^-$ concentration is only 0.15 ppm, requiring an adjustment by a factor of 2.5 to the $Cl^-$ concentration used in the model. Throughfall data measured in the adjacent Shelter Creek watershed corroborate the importance of dry and cloud deposition; limited measurements indicate the $Cl^-$ mass flux under a forest canopy was 1.4 times higher than from a clear-cut forest (Burns, personal correspondence, 2006), and we presume more extensive monitoring could reveal remaining missing inputs.

As an additional complication, recent research has suggested that $Cl^-$ may not actually behave as a conservative tracer. Using column experiments, Oberg and Sanden (2005) found that 20–50% of $Cl^-$ was transformed to chlorinated organic carbon in a carbon rich O-horizon. They postulated that this chlorinated organic carbon could be transported to deeper soil horizons where inorganic $Cl^-$ would be generated by mineralization. With this mineralization, $Cl^-$ flux would appear to be near steady state when looking only at the catchment signal (Lovett et al., 2005; Svensson et al., 2007), but up to 50% of the $Cl^-$ generation could be independent of the timing of $Cl^-$ entering by wet, dry, or cloud deposition. Measurements in the Catskills have found on average 36% carbon content in a 5 cm thick O-horizon (Johnson et al., 2000) while Oberg and Sanden (2005) uses soil cores with 72% carbon content in ~13.5 cm thick horizon, suggesting that there is less potential in the Catskills for transformation of $Cl^-$ to chlorinated organic carbon. However, to accommodate this possible steady state input in the model simulation, one could assume that a portion of the inputs not measured in wet deposition (although <50%) originates from a constant source.

### Catchment characteristics

Biscuit Brook is a 9.7 sq km. forested catchment located in the Catskill Mountains of Ulster Co., NY, approximately 120 miles from NY City (Fig. 2). The catchment is steep (mean slope ~25%) with hillslopes commonly terminating at the channel edge, thus leading to minimal riparian area and, consequently, limited saturation overland flow (Evans et al., 1999). Catchment elevation ranges from 622 m at the outlet to 1129 m at the highest ridge. A layer of glacial till 100–150 cm in depth is underlain by level, fractured bedrock. Based on the Ulster Co. soil survey (Tornes, 1979), the vast majority of this till layer is composed of a silt-loam rock outcrop complex that has minimal soil conductivity below approximately 40 cm. Additionally, observations within the adjacent Shelter Creek catchment indicate that a thin, highly conductive organic soil horizon (O-horizon) overlays less conductive mineral soil (Brown et al., 1999), conditions also assumed to exist in the Biscuit Brook catchment. Water content in the O-horizon has been found to fluctuate much more rapidly than water content in the mineral soil, suggesting rapid lateral transport in the O-horizon (Brown et al., 1999). Furthermore, bypass flow directly to the bedrock appears to occur since changes in water content in the mineral soil appear to lag changes in the groundwater table (Brown et al., 1999). Concentration-discharge plots for major solutes ( with the exception of $NO_3^-$ and acid neutralizing capacity) of 33 flow episodes in catchments within the Catskills display little or no hysteresis, corroborating the notion of a two-component system response (O-horizon and bedrock) in which each

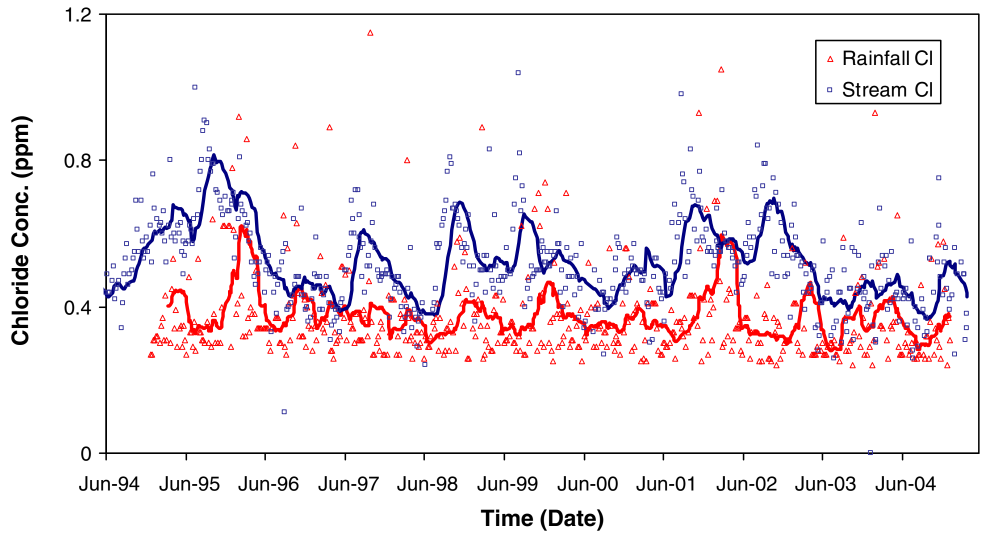


**Figure 1** Rainfall and streamflow chloride concentrations for Biscuit Brook, Ulster County, New York. The bold lines indicate 12 week moving averages. To account for inputs other than wet deposition, a concentration value of 0.23 ppm has been added to the observed rainfall concentration. This 0.23 ppm baseline concentration is the average increase per day needed to close the mass balance over the 10 year period of study.

component responds simultaneously during a hydrologic event (Evans et al., 1999). These prior observations of catchment response provide the basis for the structure of the simple, lumped hydrologic and chemical model for Biscuit Brook.

## Model description

The hydrologic and chloride mass balance models consists of two connected, well-mixed reservoirs plus a snowmelt component (see Fig. 3) run on a daily time step. We assume the two reservoirs operate semi-independently; the upper reservoir will discharge lateral flow without the lower reservoir saturating, but the lower reservoir is only recharged by flow from the upper reservoir. The general form follows from that of the so-called Birkenes model (Neal et al., 1988). Additionally, stream $Cl^-$ concentrations at Biscuit Brook do not appear to be the attenuated signal of rainfall $Cl^-$ concentrations (Fig. 1), a contrast to Plynlimon where the impulse-response relationship is starkly apparent (see Fig. 1c in Kirchner et al., 2001). With no obvious justification for applying a linear convolution to $Cl^-$ concentration, the model formulation provides a flexible and transparent basis from which to assess the dual role of discharge and mass flux in influencing concentration.

The water balance is illustrated in Fig. 3. $A$ and $B$ denote the storage in each reservoir (in cm), and $Q_A$ and $Q_B$ are daily losses (cm day$^{-1}$) from each reservoir occurring with recession rates of $R_A$ and $R_B$ (day$^{-1}$), respectively. Discharge only occurs if the water storage is above a minimum level ($A_{\min}$ or $B_{\min}$). If the storage is above a maximum in the $A$ reservoir, excess is routed directly out of the catchment from the $A$ reservoir (Excess$_A$ in cm day$^{-1}$).

Precip is daily precipitation (cm day$^{-1}$), ET is evapotranspiration (cm day$^{-1}$), and melt is snow melt (cm day$^{-1}$). ET occurs at the measured PET above soil field capacity (the same parameter value as $A_{\min}$) and decreases linearly to zero between $A_{\min}$ and the soiling wilting point (*WP*). Precip is a weighted average of the Biscuit Brook gauge record (75%) and the Slide Mountain gauge record (25%). To account for snow, when the mean daily ambient temperature is below 0 °C, all precipitation is snowfall. Snowfall is maintained in a separate store and returned to the system as melt. Melt is modeled using a temperature index method

$$\text{melt} = k_{\text{melt}} \cdot T, \quad T > 0\,^{\circ}\text{C} \tag{1}$$

where $k_{\text{melt}}$ is a melt coefficient (cm °C$^{-1}$ day$^{-1}$) and $T$ is the average daily temperature. The total discharge from the catchment (Fig. 3) is given as

$$Q_{\text{Stream}} = f_A Q_A + Q_B + \text{melt} + \text{Excess}_A \tag{2}$$

The $Cl^-$ mass balance closely follows the hydrologic balance except flux due to ET is excluded. In the upper reservoir,

$$\text{Cl}_A^t = \text{Cl}_A^{t-1} + 0.001 \cdot \text{Area} \cdot \Delta t(\text{C}_{\text{dep}} \cdot \text{Precip} + \text{C}_{\text{snow}} \cdot \text{melt}) - \text{Loss}_A^{t-1}\Delta t \tag{3}$$

where $\text{Cl}_A$ is chloride mass (mg) in the $A$ reservoir, $\text{C}_{\text{dep}}$ is the chloride concentration due to wet deposition and dry deposition mobilized by precipitation (mg L$^{-1}$), 0.001 is a conversion factor from cm$^3$ to L, Area is catchment area (cm$^2$), $\Delta t$ is 1 day, $\text{C}_{\text{snow}}$ is the chloride concentration (mg L$^{-1}$) in any accumulated snow, and $\text{Loss}_A$ (mg day$^{-1}$) is the $Cl^-$ mass flux from the $A$ reservoir. In calculating $\text{C}_{\text{snow}}$ we assume that $Cl^-$ becomes well-mixed in any existing accumulated snow layer. Also, note that $\text{C}_{\text{dep}}$ is assumed constant over the weekly intervals on which it is measured, but the actual mass input of $Cl^-$ on a given day will vary with precipitation. We calculate $\text{Loss}_A$ as

$$\text{Loss}_A = \frac{\text{Cl}_A}{A}(Q_A + \text{Excess}_A) \tag{4}$$

As shown in Eq. (4), we assume $Cl^-$ lost from $\text{Excess}_A$ consists of water well-mixed in the $A$ reservoir. Note, $\text{C}_{\text{dep}}$ is a combination of the reported wet deposition concentration

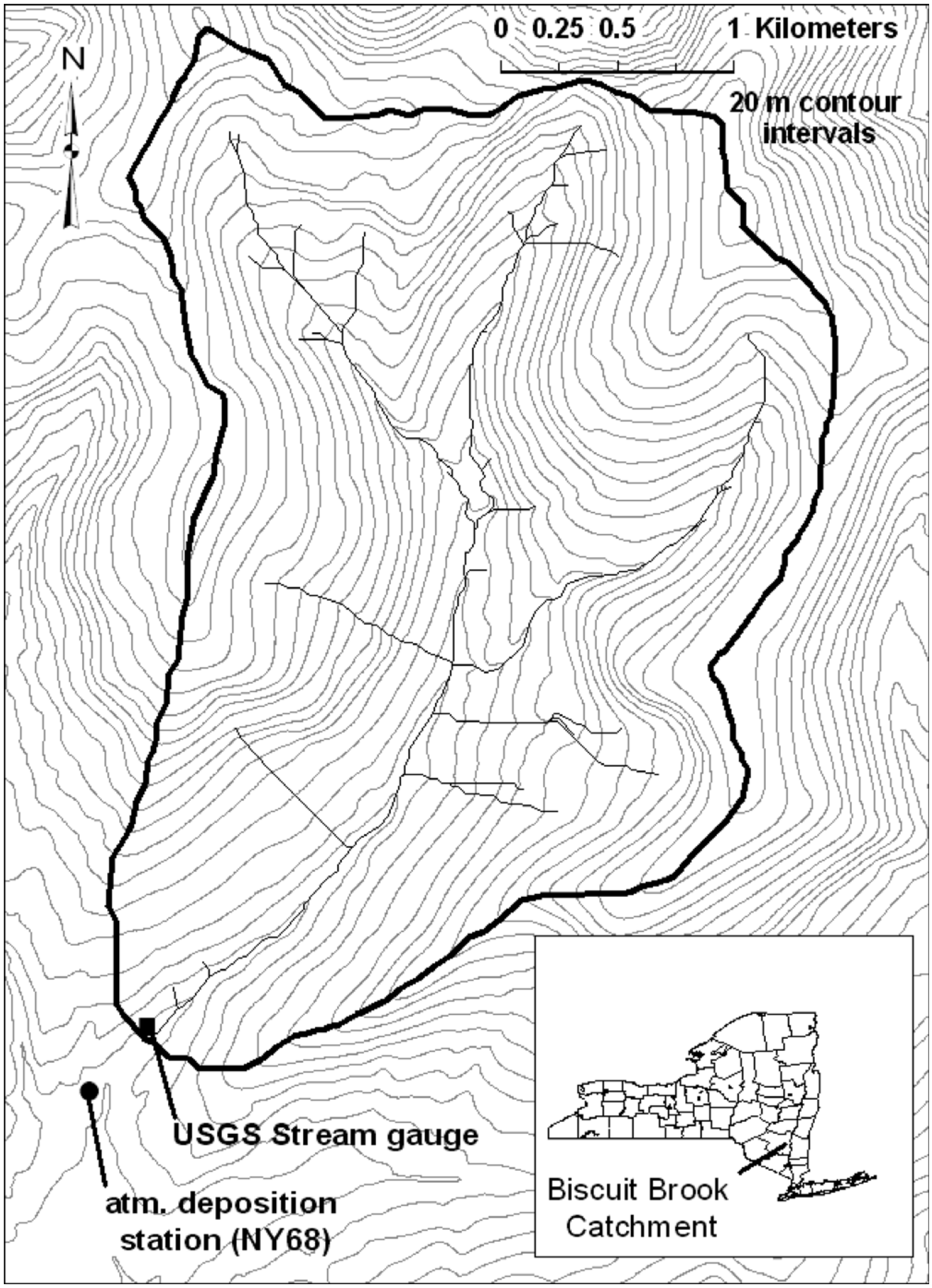


**Figure 2** Biscuit Brook catchment location and site topography.

for each week (mean of 0.15 ppm) plus a constant concentration of 0.19 ppm to account for dry and occult deposition (with the addition of $\text{Source}_{\text{deep}}$ below, the total input results in a daily average of 0.38 ppm).

In the lower reservoir,

$$\text{Cl}_B^t = \text{Source}_{\text{deep}}\Delta t + \text{Cl}_B^{t-1} + \frac{\text{Cl}_A^t}{A^t}(1 - f_A)Q_A^t\Delta t - \text{Loss}_B^{t-1}\Delta t \quad (5)$$

where $\text{Source}_{\text{deep}}$ ($1.4 \times 10^6$ mg day$^{-1}$) accounts for Cl$^-$ originating from the mineralization of chlorinated organic carbon. The magnitude of $\text{Source}_{\text{deep}}$ is 10% of the daily average Cl$^-$ load in the stream discharge, a rough approximation based on the limited findings of Oberg and Sanden (2005) in Sweden and the known lower organic matter content in the Biscuit Brook soils (as discussed above). Finally,

$$\text{Loss}_B = \frac{\text{Cl}_B}{B}Q_B \quad (6)$$

The modeled stream chloride concentration (mg L$^{-1}$) is calculated as

$$C_{\text{stream}} = \frac{f_A\frac{\text{Cl}_A}{A}Q_A + \frac{\text{Cl}_A}{A}\text{Excess}_A + \text{Loss}_B}{Q_{\text{Stream}} \cdot \text{Area} \cdot 0.001} \quad (7)$$

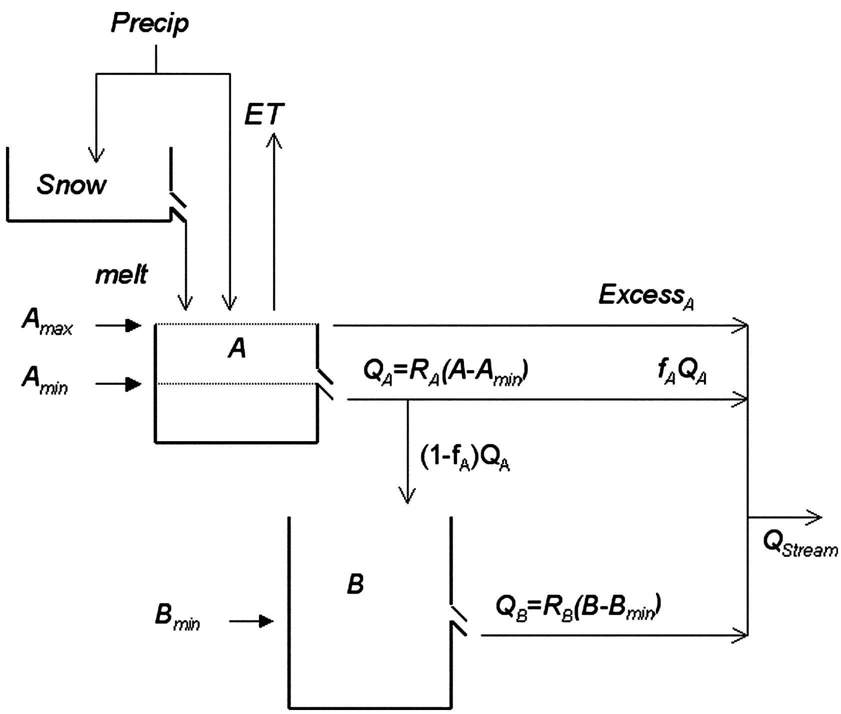


**Figure 3** Schematic of the hydrologic model. The $Cl^-$ model uses similar reservoirs but has no losses due to *ET*. $Cl^-$ fluxes between reservoirs are assumed to be the product of concentration of $Cl^-$ within the upstream reservoir and discharge from the reservoir.

## Results

### Model fit to discharge

The hydrologic model generally matches the behavior of the observed daily streamflow (Nash–Sutcliffe efficiency (NS) was 0.64 over the full 10 year record) despite several incidents where the single rainfall gage could not capture intense, localized rainfall within the catchment or nonuniform snowmelt complicated by large elevation differences (see Fig. 4). Dividing the record into periods with and without snow, NS was 0.71 during non-snow periods and 0.55 with snow. In an assessment of the daily rainfall-runoff response predicted from 19 different lumped models applied to different catchments, Perrin et al. (2001) found that the mean NS ranged between 0.57 and 0.68. Several alternate model formulations were tested, including requiring the *B* reservoir to saturate before any discharge occurred from the *A* reservoir, a formulation proposed previously by Evans et al. (1999) but never evaluated. This formulation

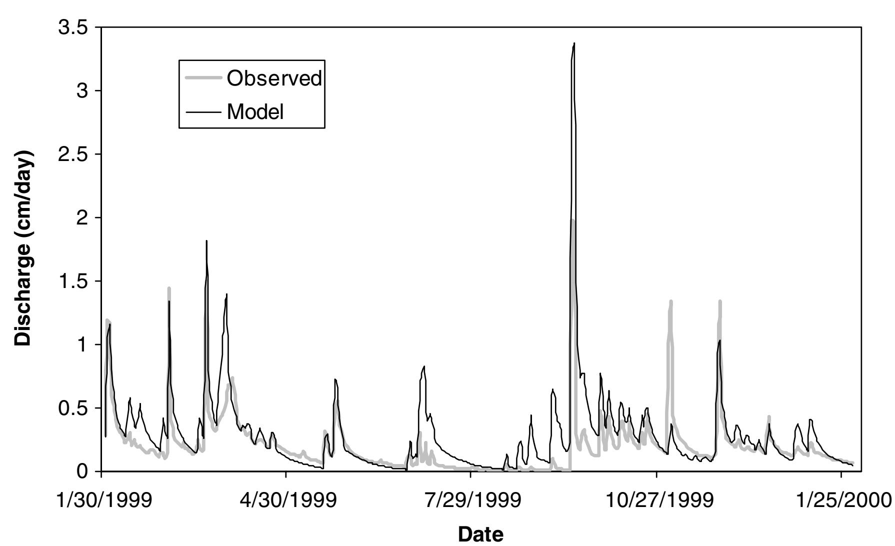


**Figure 4** Comparison of observed (solid line) and modeled (dashed line) streamflow for a representative time period. The Nash–Sutcliff efficiency is 0.64.

overdamped the stream discharge hydrograph leading — as did other model variations — to either no improvement in the results or outright physically unrealistic output.

Model parameters are summarized in Table 1. We did not try to optimize the parameter selection; parameters were simply manually adjusted to achieve a suitable and behaviorally reasonable fit to observed daily discharge. As will be discussed further later, the model exhibited a great deal of equifinality with multiple sets of parameters providing similar fits as based on Nash–Sutcliffe efficiency. Therefore, we generally tried to constrain our choice of parameters based on previously reported physical descriptions of the catchment. Assuming the upper ($A$) reservoir represents a shallow soil layer such as the O-horizon and the lower ($B$) reservoir entails a shallow groundwater layer, the parameters have a reasonable physical basis. The $A$ reservoir has a maximum capacity of 6 cm; for a soil with a porosity of 0.5, this implies a depth of 12 cm. $A_{\min}$ (conceptualized as a field capacity) is 4 cm, equivalent to a ~0.30 volumetric water content. With a recession coefficient of 0.40 day$^{-1}$, at the maximum soil moisture in the $A$ reservoir ($A_{\max} - A_{\min} = 2$ cm) the flux would be the same as Darcy flow at saturation with conductivity of 2200 cm day$^{-1}$, a hydraulic gradient of ~0.25, an approximate stream perimeter of 24 km, and the assumption that only 20% of the $A$ reservoir loss becomes streamflow (as dependent on $f_A$). The soil conductivity is similar to those reported for surface O-horizons by Chappell et al. (1990, 1991) while the gradient and stream perimeter were taken directly from catchment characteristics (Fig. 2). For the $B$ reservoir, an investigation of baseflow recession within a small Catskill catchment estimated an aquifer transmissivity of 2600 m$^2$ day$^{-1}$ and a gradient of $1.7 \times 10^{-3}$ (Vitvar et al., 2002) resulting in a recession coefficient within a factor of two of the $R_B$ value used in the model (Table 1). As an alternate estimate of $R_B$, we calculated the recession constant using the Brutsaert and Nieber (1977) recession analysis method on our 10 years of daily discharge data. Somewhat surprisingly, this method resulted in a baseflow recession constant of 0.07 days$^{-1}$, the exact value we settled on through our manual calibration. The soil melt constant, $k_{\text{melt}}$, was within the range of previously reported temperature index values used within the Northeastern US (Walter et al., 2005).

## Model fit to Cl$^-$ concentration

The Cl$^-$ concentration model replicated general trends (Fig. 5a) but exhibited greater variability in the modeled signal on a week-to-week basis than in the observed Cl$^-$ signal (Fig. 5b and c). Also, it is apparent the model worked better in conditions without snow; $R^2 = 0.36$ when the average daily temperature > 1 °C and $R^2 = 0.14$ when <1 °C. When snow is present, the model, in many cases, underpredicted Cl$^-$ concentration, consistent with observations by others of preferential ion elution within a snowpack. For instance, Iida et al. (2000) found that Cl$^-$ concentrations diminished to low levels approximately six weeks before the snowpack itself melted. While an $R^2$ of 0.36 certainly indicates we cannot fully explain the signal with our model, it is generally on par with reported efficiencies for other recently published stream chemistry models. In modeling stream Cl$^-$ in Plynlimon, Wales, Page et al. (2007) noted low NS efficiency values and used a composite likelihood measure to identify behavioral parameters sets. In modeling stream alkalinity, Welsch et al. (2006) reported a NS efficiency of 0.26.

Additionally, we note that the $R^2$ is based on the comparison of instantaneous grab samples on 512 dates to the corresponding simulated daily average for the date of the grab sample. However, event sampling in Biscuit Brook in the early 1990's has shown sizable fluctuations over intervals less than a day. For instance, on 7/22/91, Cl$^-$ concentrations started at 0.76 ppm, dipped to 0.65 ppm 8 min later, and returned to 0.73 ppm after an additional 35 min. Thus, particularly on days with precipitation, there is some inherent discrepancy between the grab sample and the simulated daily average.

Unlike attempts to model the Plynlimon, Wales system with a similar Birkenes type model formulation, we did not find that the stream Cl$^-$ signal was underdamped in comparison to the rainfall Cl$^-$ (Christopherson and Neal, 1990), and we actually observed several periods of strong volatility in the observed stream signal. Despite discrepancies between the model and observed signal at short-time scales, we also evaluated the overall time series structure by comparing spectral signals, similar to the approach used

**Table 1** Model parameters used for two reservoir Birkenes type model

| Parameter | Value | Justification |
|---|---|---|
| $R_A$ (day$^{-1}$) | 0.4 | Similar loss as Darcy flow in O-horizon with 25% slope and $K_{\text{sat}} = 2200$ cm day$^{-1}$ |
| $A_{\max}$ (cm) | 6 | Saturation of 12 cm thick O-horizon with 50% porosity (Rawls et al., 1993) |
| $A_{\min}$ (cm) | 4 | Field capacity of 12 cm thick O-horizon with 50% porosity (Rawls et al., 1993) |
| $f_A$ | 0.4 | Calibrated parameter; ranges from 0 to1 |
| $WP$ (cm) | 1 | Wilting point of 12 cm thick O-horizon with 50% porosity (Rawls et al., 1993) |
| $R_B$ (day$^{-1}$) | 0.07 | Similar loss as assuming aquifer transmissivity of 2600 m$^2$ day$^{-1}$ and a gradient of 1.7 e-3 (Vitvar et al., 2002); similar value also found using Brutsaert and Nieber (1977) recession flow analysis |
| $B_{\min}$ (cm) | 12 | Minimum water content for lateral flow in shallow aquifer |
| $k_{\text{melt}}$ (cm °C$^{-1}$ day$^{-1}$) | 0.3 | In the range of values (0.6 –1.7) fit to a temp index model for sites in Vermont and NY (Walter et al., 2005) |

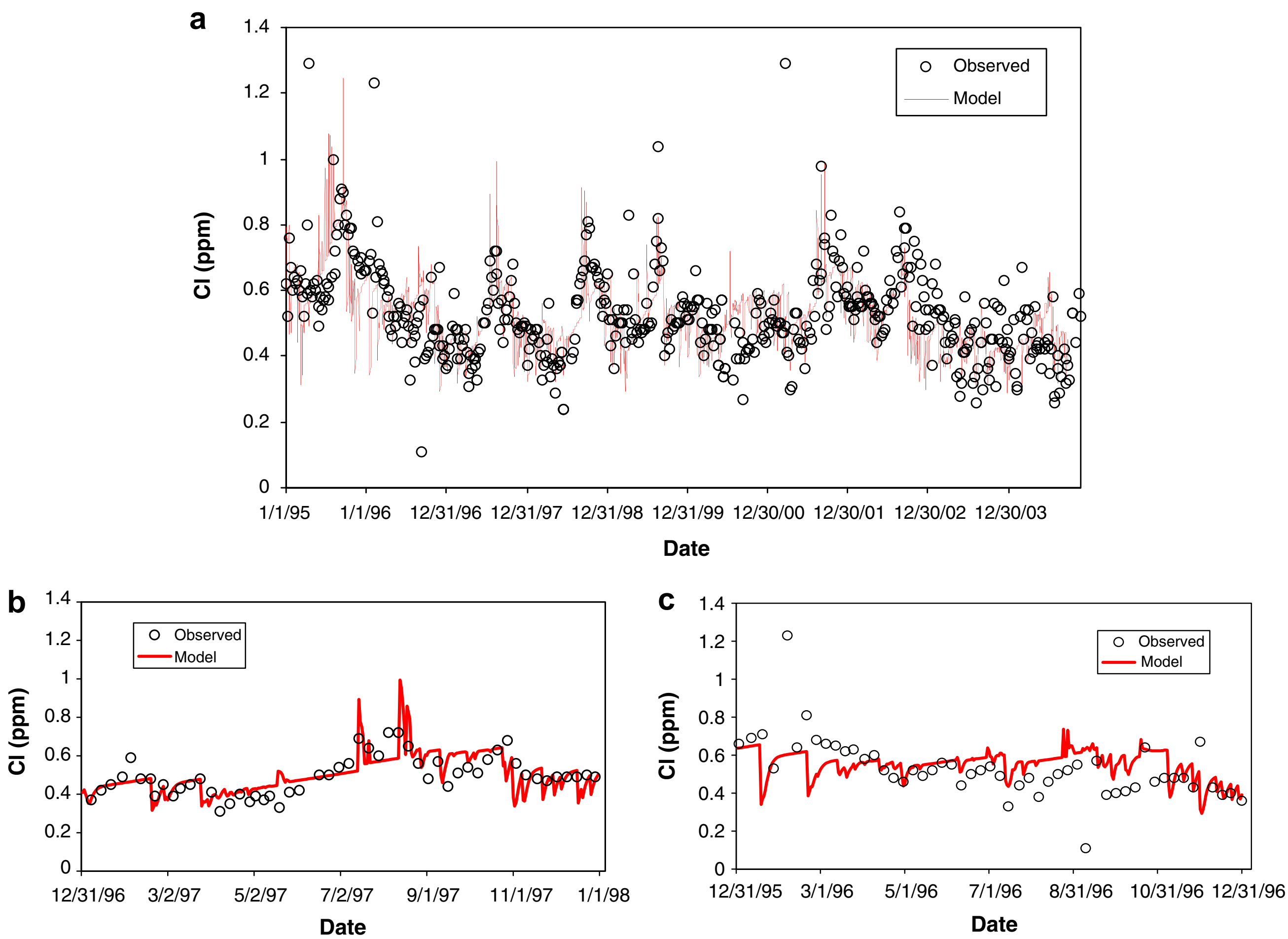


**Figure 5** Comparison of modeled (solid line) and observed stream $Cl^-$ concentrations (open circles). (a) Shows the fit over the 10 year record while (b) and (c) are subsamples intended to illustrate the discrepancies between the model and observed $Cl^-$ on a week-to-week basis.

by Kirchner et al. (2001) in which time series themselves were not explicitly modeled.

## Power spectrum of the $Cl^-$ signal

The power spectra of the observed streamflow $Cl^-$ concentration, rainfall $Cl^-$ concentration, and modeled stream $Cl^-$ concentration were computed using a fast Fourier transform (FFT) in Matlab (The Mathworks, Inc.); we used a weekly time interval for the observed values and a daily interval for the simulated values. Fundamentally, a Fourier analysis of a time series decomposes the signal into $N/2$ sine waves of differing wavelength where $N$ is the number of sample points in the series (Jenkins and Watts, 1968). A power spectrum plots the square of the amplitude of each of these sine waves versus the frequency of the respective wave (Jenkins and Watts, 1968) and is typically presented on log–log axis. The observed streamflow $Cl^-$ concentration time series (raw time series available at <http://ny.cf.er.usgs.gov/nyc.uno-ono.cfm>) included values at intervals less than one week as well as several missing values. Thus, values were excised to leave the standard sampling interval at $7 \pm 1$ day. Since measurements are instantaneous grab samples, any sample can be considered to be a representation of the average over a given day (recall the 0.10 ppm fluctuation in $Cl^-$ in less than an hour during the 7/22/91 event). Therefore, we still considered a sample shifted by one day a reasonable proxy for a representative concentration actually falling on the seven day interval. Furthermore, we linearly interpolated to fill missing values. One week gaps were filled on 11/14/95, 12/20/95, 6/10/97, 10/18/00, 7/03/01, 1/20/04, 2/25/04, 6/9/04, 8/5/04, 9/2/04, and 10/13/04. Four and five week gaps were filled on 6/15/98 and 6/21/00, respectively. The observed streamflow $Cl^-$ power spectra were processed (using the Matlab program of Kirchner, 2005) to remove aliasing at high frequencies, an artifact of the continuous, catchment signal exhibiting variability at a frequency higher than the sampling rate.

The slopes of the power spectra were determined by fitting a least squares line to power spectra filtered using a rectangular moving average window in log frequency space (log window size = 0.13 ). The weekly observed streamflow $Cl^-$ power spectrum had a slope of $0.98 \pm 0.27$ (95% confidence interval used here and throughout) while the daily modeled $Cl^-$ concentration power spectrum (Fig. 6) had a slope of $1.14 \pm 0.14$ on log–log axis over approximately two orders of magnitude. To date, there does not seem to be a consistent approach in the hydrologic literature to

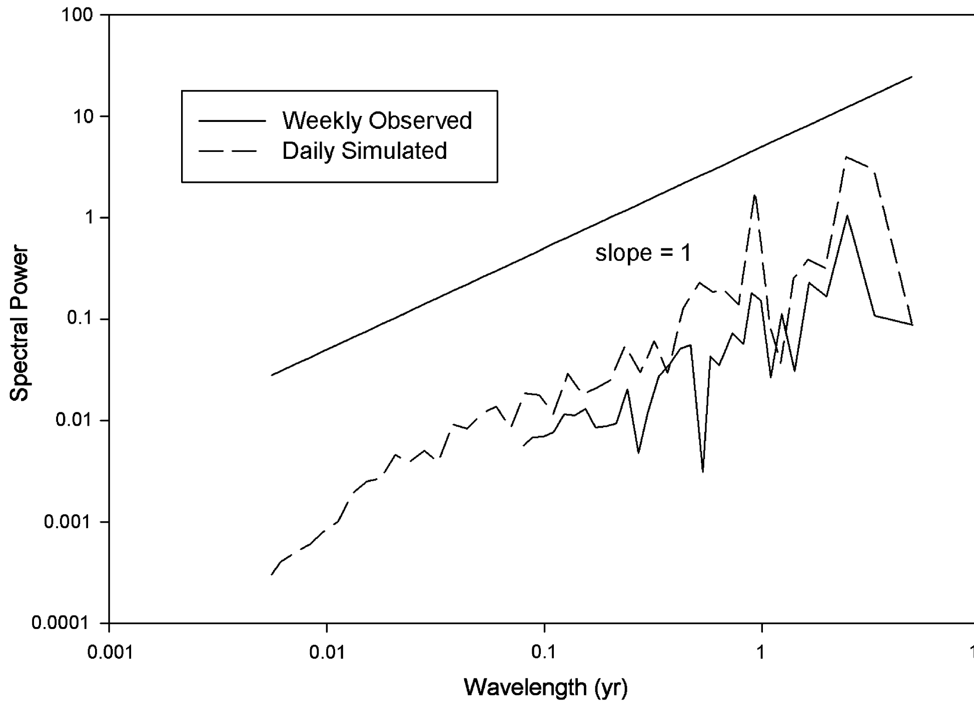


**Figure 6** Comparison of power spectra functions for observed and modeled stream $Cl^-$ concentration. The power spectra were averaged using a rectangular moving average window in log frequency space (width $\sim$0.13 in log space). The slope of the filtered spectra were determined using a linear least squares fit. Weekly observed slope = 0.98 ± 0.27 (95% confidence interval). Daily simulated slope = 1.14 ± 0.14.

determine power spectra and their slopes; Kirchner et al. (2000, 2001) leaves the method unstated, Kirchner (2005) implies that a best-fit line is applied to spectra averaged with a log frequency space window, and Page et al. (2007) use Welch's averaged periodogram method with a Hanning window. Welch's method divides the time series into overlapping sections, applies an FFT to each grouping, and averages power spectra from each group, a reasonable method when data is noisy with no apparent deterministic signal. Thus as a matter of comparison, when calculated with Welch's method using a Hamming window in Matlab, the weekly observed streamflow $Cl^-$ power spectrum had a slope of 1.12 ± 0.14 and the daily modeled $Cl^-$ concentration power spectrum had a slope of 1.33 ± 0.05, similar to the slopes found from applying an FFT and averaging the power spectra.

Despite the slope of the power spectrum not being exactly one, the literature has loosely classified $1/f$ noise as being within 1 ± 0.3 (Press, 1978) or 1 ± 0.5 (Gisiger, 2001; Wagenmakers et al., 2004). Within this range, the $Cl^-$ signals exhibit the standard characteristics of $1/f$ noise ( discussed further below). The weekly rainfall $Cl^-$ concentration time series was found to be white noise (slope = 0.31 ± 0.18), indicating little role in influencing the streamflow $Cl^-$ power spectra.

## Parameter sensitivity

The only parameter determined solely by way of calibration was $f_A$, but the model output was relatively insensitive to its manipulation (i.e. $f_A$ was increased from 0.4 to 0.8 with a decrease in the NS efficiency for discharge to 0.55 and a negligible change in model fit for $Cl^-$). As could be expected from an eight parameter model, the model exhibits a large degree of equifinality. While we have tried to constrain the model using physically justifiable parameters, we know from model experimentation that multiple parameters sets with values covering a broad range produce reasonable model simulations. However, even with varying parameter sets, we still consistently see a spectra slope of $\sim$1. For example, if we increase the soil depth in the $A$ reservoir to $A_{max}$ = 18 cm, $A_{min}$ = 12 cm, and $WP$ = 3 cm, summer $Cl^-$ $R^2$ = 0.39, winter $Cl^-$ $R^2$ = 0.19, discharge NS efficiency = 0.61, and the spectra slope = 1.20 ± 0.15. Thus, a slope near one in the spectra does not appear to be a curiosity arising from a very specific set of parameters but seems to be a more general outcome originating from a range of physically reasonable parameter sets.

## Alternate explanations of 1/*f* noise

For the Plynlimon catchment, Kirchner et al. (2000) postulated that a $1/f$ noise arose from a linear impulse-response process with a long-tailed travel time distribution. Kirchner et al. (2001) demonstrated that such a distribution could be generated by assuming that the outlet signal is the integration of rainfall tracers entering at all points along a hillslope and traveling different distances by an advective—dispersive process where the advective time scale was similar to the dispersive time scale. In the Biscuit Brook catchment, the power spectra of the observed stream $Cl^-$ still clearly suggest $1/f$ noise. However, with no obvious relation between the precipitation $Cl^-$ concentration and the stream $Cl^-$ concentration (consider Fig. 1 as well as the fact that a portion of the $Cl^-$ input is assumed constant in time) and the successful use of lumped, mixing-type models in Catskill watersheds ( Burns and Kendall, 2002; Brown et al., 1999; Evans et al., 1999), an alternate starting point for explaining $1/f$ noise may be justified. While prior explanations of $1/f$ noise in catchment hydrology have primarily considered the ability of specific mathematical functions to describe the long-tailed response function within the linear convolution (Scher et al., 2002; Kirchner et al., 2001), we start by considering more general characteristics of $1/f$ noise.

In particular, some insight can be gained by considering means of generating time signals using recursive models, a perspective considered in other fields when investigating $1/f$ noise (Hosking, 1984; Gisiger, 2001; Wagenmakers et al., 2004). For instance, a simple lag-1 autoregressive (AR1) model is a recursive model frequently used to generate synthetic streamflow (Box and Jenkins, 1976)

$$X_t = \phi_1 X_{t-1} + \varepsilon \tag{8}$$

where $X_t$ denotes some observation on time $t$, $\phi_1$ is the magnitude of dependence, and $\varepsilon$ is a random noise term (Box and Jenkins, 1976). Notably, an AR(1) model is the same as assuming a chemical tracer passes through a single well-mixed reservoir. For a $\phi_1$ of 0.60 and $\varepsilon$ drawn from a Gaussian distribution, we generated a 8,192 observation time series and determined its spectral density using an FFT (Fig. 7). This simple autoregressive model generates a power-law relationship between the power spectra and high frequencies before becoming a white noise signal at larger wavelengths. Summing the signal from multiple AR(1) processes in parallel — each with a different autoregression coefficient — generates a power-law relationship over a wider range of frequencies (slope ~1) (Fig. 7). Note though, only by manipulating the autoregression coefficients and the variance of the random input to each AR(1) process did we achieve a close fit to a slope of one. Thus, we see relatively simple recursive models can result in seemingly scale-invariant power spectra, albeit only with intentional manipulation.

As noted by Gisiger (2001), a $1/f$ noise inherently has a tendency towards exhibiting correlations at longer wavelengths as well as at shorter wavelengths, a condition approached by generating a signal from parallel AR models with differing magnitudes of regression coefficients. Naturally, there must be a balance in the magnitude of variations at each wavelength (albeit log-scaled) so that no one correlation length dominates. Others (Wagenmakers et al., 2004; Hosking, 1984) have noted that this balance in the correlations of the short and long wavelength processes can appear as relatively long periods of consistently low and high values, cyclical behavior that is ultimately stationary over a long enough interval. A quintessential display of this $1/f$ noise generating behavior is seen in the beat of a healthy heart; the rate shifts between several regional averages with localized variations centered around these more regional plateaus (for an illustration, see Pilgram and Kaplan, 1999).

Daily hydrologic time series in temperate regions will inherently include elements of this balance between the strength of long range and short range correlations. In particular, soil moisture deficit varies approximately sinusoidally across the hydrologic year, reflected as the degree

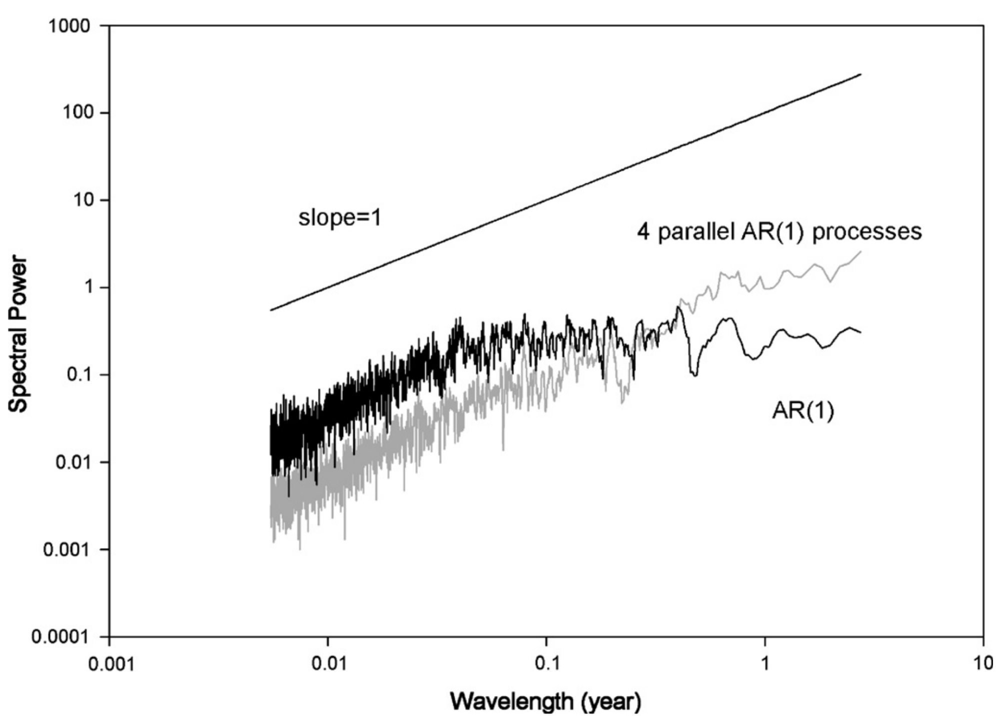


**Figure 7** Comparison of power spectra for an AR(1) model and four parallel AR(1) processes with different regression coefficients.

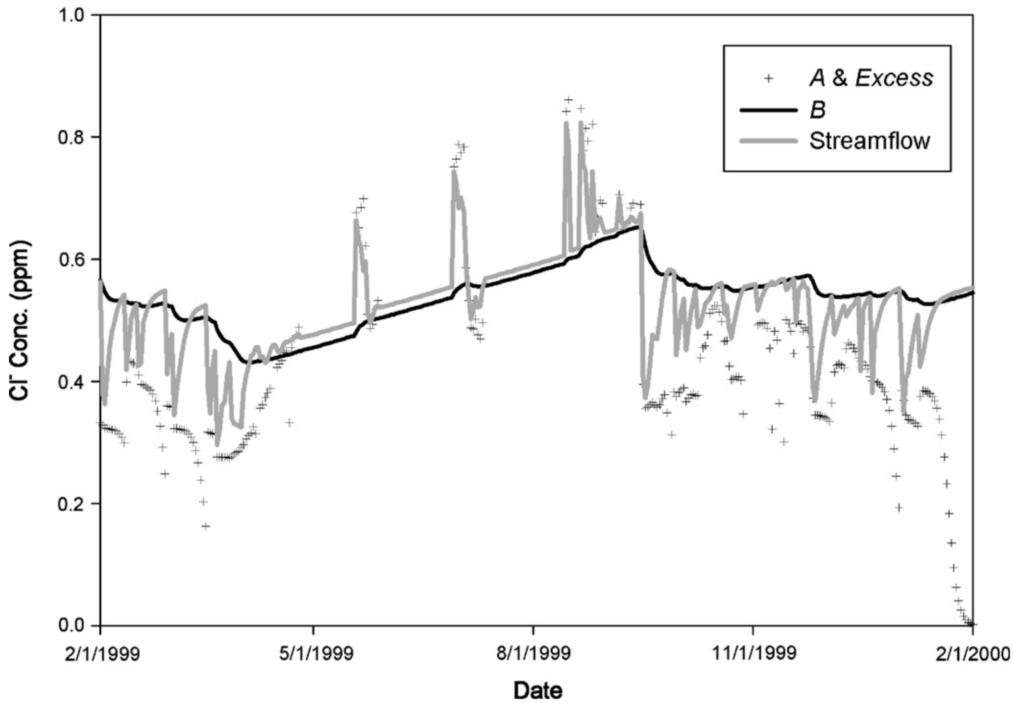


**Figure 8** Illustration of chloride concentration in discharge from the *A* component and Excess (plus symbols), the *B* component (black line), and the stream discharge (gray line).

of dilution-intensification acting on the system's $Cl^-$ flux. Then, within each year's wet and dry periods, there are still appreciable correlated fluctuations due to the short-memory system response to rainfall inputs. The only critical additional requirement is that the system has some low frequency components above a one year wavelength. These low frequency components may be due to some autocorrelation in $Cl^-$ inputs or meteorological fluxes. The model itself captures these essential features: (1) the rapid discharge and small volume in the *A* reservoir provides slightly damped (thus autocorrelated) response to inputs, (2) moisture deficits driven by differences in *ET* and precipitation reduce the mixing volume in the *A* reservoir and increase $Cl^-$ concentrations on an approximately annual period, (3) the larger mixing volume and slow discharge from the *B* reservoir provides a more highly damped response to inputs. Other processes, such as snow accumulation, likely play a role but in less readily identifiable ways. Fig. 8 illustrates the portion of the $Cl^-$ signal originating from either the *A* reservoir or Excess flow (runoff) and the *B* reservoir subcomponent. The figure gives a qualitative sense of how each subcomponent combines to generate a $1/f$ noise is the actual stream discharge.

Of particular interest is the ability of the model to generate near $1/f$ noise with little manipulation of parameters, especially in contrast to the parallel AR processes that needed to be fine tuned to achieve near $1/f$ noise. Researchers have shown that an exact $1/f$ power spectrum can be generated from integrated autoregressive moving average (ARIMA) models with fractional differencing (Hosking, 1984). Our model does not reduce to a form of an ARIMA model with fractional differencing but instead seems to be a collection of time-variant, non-linear relationships not easily reduced to well-studied systems. For instance, we can illustrate by looking at individual components. For $\text{Loss}_A$, substituting a mass balance expression for $Cl_A$ into Eq. (4) and putting in terms of $\text{Loss}_A$

$$\text{Loss}_A^t = \text{Loss}_A^{t-1}\left[\frac{(Q_A^t + \text{Excess}_A^t)\Delta t}{A^t}\left(\frac{A^{t-1}}{(Q_A^{t-1} + \text{Excess}_A^{t-1})\Delta t} - 1\right)\right] + \varepsilon \tag{9}$$

where $\varepsilon$ (mg day$^{-1}$) is a random input component due to $Cl^-$ in atmospheric deposition. From this form, we see that $\text{Loss}_A$ is similar to an AR(1) model but that the autoregression coefficient varies in time. The value $C_{\text{stream}}$ is of course a combination of four different time series, among which there is some dependency. Thus, while not readily teased out, this time-variant, non-linear model structure seems to be a robust mechanism for generating $1/f$ noise when applied to Biscuit Brook and is more complicated than parallel AR processes.

## Conclusions

Spectral analysis of a stream $Cl^-$ time series from the Biscuit Brook catchment revealed a power spectrum slope of approximately one. We reproduced power spectra with a similar slope using a simple, lumped hydrologic model. But, when considered in the time domain, the lumped model clearly did not capture all of the variation in the $Cl^-$ signal. Improvements in predicting the $Cl^-$ signal could arise from a better quantification of the timing of dry and cloud deposition inputs, a better understanding of biogeochemical

$Cl^-$ transformations, or the inclusion of small-scale transport processes such as delays due to $Cl^-$ front movement across the vadose zone (see for instance Labadia and Buttle, 1996). However, with the ability of the lumped model to generate $1/f$ noise in Biscuit Brook, there is the possibility that $1/f$ noise does not originate only from transport processes, as was postulated for Plynlimon (Kirchner et al., 2001). Instead, $1/f$ noise in the $Cl^-$ concentration signal may also originate from a mix of multiple watershed processes affecting both water volume and $Cl^-$ mass occurring at multiple time scales. In the case of the lumped model used at Biscuit Brook, longer range correlations in $Cl^-$ concentration appear to be driven by seasonal changes in catchment moisture deficit, snow accumulation and melt, and system storage while short-term correlations reflect the short-term memory inherent in the response of a shallow surface layer.

Overall, this investigation suggests $1/f$ noise could be a relatively ubiquitous feature arising for different reasons in different places. While others have not ruled out a range of possible mechanisms for generating $1/f$ noise (Kirchner et al., 2001), an emphasis has thus far been placed on in-catchment transport processes and the possibility of deducing catchment travel time distributions (Sivapalan, 2003; Kirchner, 2006). But, deducing hydrologic travel times may be complicated by lumped processes if these processes do have an influence on the $Cl^-$ signal. In further assessing lengthy, high resolution data sets exhibiting $1/f$ noise, we suggest the source of $1/f$ noise continue to be approached with an open mind.

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