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Seasonal synchronicity and multi-decadal stability of headwater biogeochemistry in the northern temperate zone

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Abstract Temporal patterns in chemistry of headwater streams reflect responses of water and elemental cycles to perturbations occurring at local to global scales. We evaluated multi-scale temporal patterns in up to 32 y of monthly observations of stream chemistry (ammonium, calcium, dissolved organic carbon, nitrate, total dissolved phosphorus, and sulfate) in 22 reference catchments within the northern temperate zone of North America. Multivariate autoregressive state-space (MARSS) models were applied to quantify patterns at multi-decadal, seasonal, and shorter intervals during a period that encompassed warming climate, seasonal changes in precipitation, and regional declines in atmospheric deposition. Significant long-term trends in solute concentrations within a subset of the catchments were consistent with recovery from atmospheric deposition (e.g., calcium, nitrate, sulfate) and increased precipitation (e.g., dissolved organic carbon). Lack of evidence for multi-decadal trends in

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most catchments suggests resilience of northern temperate ecosystems or that subtle net effects of simultaneous changes in climate and disturbance regimes do not result in directional trends. Synchronous seasonal oscillations of solute concentrations occurred across many catchments, reflecting shared climate and biotic drivers of seasonality within the northern temperate zone. Despite shared patterns among catchments at a seasonal scale, multi-scale temporal patterns were statistically distinct among even adjacent headwater catchments, implying that local attributes of headwater catchments modify the signals imparted by atmospheric phenomena and regional disturbances. To effectively characterize hydrologic and biogeochemical responses to changing climate and disturbance regimes, catchment monitoring programs could include multiple streams with contributing areas that encompass regional heterogeneity in vegetation, topography, and elevation. Overall, detection of long-term patterns and trends requires monitoring multiple catchments at a frequency that captures periodic variation (e.g., seasonality) and a duration encompassing the perturbations of interest.

Keywords Headwater streams · Long-term trends · Multivariate autoregressive state-space models · Seasonality · Synchrony · Time series

Introduction

Chemistry of headwater streams reflects integrated signals resulting from hydrologic, ecological, and biogeochemical processes in streams and contributing terrestrial ecosystems. Records of stream chemistry can therefore reflect short-term responses to weather or disturbance events and longer-term patterns caused by climate or press disturbances (e.g., Bormann and Likens 1967; Eimers et al. 2008; Argerich et al. 2013; Laudon et al. 2021). Thus, in addition to assessing water quality, long-term monitoring of headwater catchments can provide mechanistic understanding needed to forecast responses to environmental policies, land cover and land use, and global change. However, the expense of long-term monitoring programs prompts justification for their design and continued operation (Hewlett et al. 1969; Lovett et al. 2007; Rosi et al. 2023). Novel approaches for analysis of patterns and trends in time series could enhance the value of monitoring by reliably detecting and quantifying patterns across multiple spatial and temporal scales.

Catchment monitoring programs have now accumulated several decades of observations that encompass changes in the disturbance regime, including ongoing anthropogenic effects, and potential recovery from disturbances. Patterns and trends in stream chemistry are apparent at decadal scales owing to press disturbances such as declining atmospheric deposition of nitrogen and sulfur (Likens et al. 1996; Webster et al. 2021b; Templer et al. 2022) and warming climate (De Wit et al. 2008; Baron et al. 2009). Monitoring programs have also captured long-term trajectories of recovery from press and pulse disturbances (e.g., clear-cutting or land use/management; Likens et al. 1970; Kreiling and Houser 2016; Lajtha and Jones 2018; Stets et al. 2020; Webster et al. 2022b). However, patterns in solute concentrations that might serve as signals of disturbance or recovery are embedded within time series that also contain variation at shorter time scales. For example, seasonality in temperature, precipitation, or primary production influence mobilization, transport, and retention of solutes within catchments resulting in periodic variation in solute concentrations (Clark et al. 2004; Dawson et al. 2008; Halliday et al. 2012). In contrast, stochastic variation in solute chemistry resulting from events such as storms, insect outbreaks, fires, or drought can cause departures from seasonal oscillations or long-term trends (Mikkelson et al. 2013; Murphy et al. 2018; Tiwari et al. 2022). Data analyses designed to capture patterns at multiple

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temporal scales can therefore best characterize temporal variation and avoid misattributing patterns that might be obscured by phenomena occurring at other time scales.

Environmental perturbations can also induce shared temporal patterns across multiple spatial scales, such as among adjacent catchments, within regions, or across continents. Owing to their broad spatial extent, atmospheric attributes including temperature, precipitation, and deposition of acidic pollutants can cause temporal synchrony (i.e., coherence, including consistently lagged relationships; Seybold et al. 2022) in solute dynamics among catchments at regional to continental scales. For example, long-term declines in concentrations of nitrate and base cations resulting from declining atmospheric deposition are observed in streams across regional to global extents (Likens et al. 1996; Templer et al. 2022; De Wit et al. 2023). Similarly, synchronous solute exports occur at regional to continental spatial scales due to recurring patterns in precipitation and temperature at seasonal to decadal timescales (e.g., Pacific Decadal Oscillation; Smits et al. 2019; Morison et al. 2022). In contrast, local or spatially heterogeneous perturbations (e.g., fire, storms) cause asynchrony among catchments of the same region (Mast and Clow 2008). Contrasting temporal patterns also arise among adjacent catchments because local attributes including topography, geology, glacial history, vegetation, or land use can mute or amplify the effects of larger-scale drivers (Houlton et al. 2003; Clark et al. 2004; Yao et al. 2011).

One goal of monitoring headwater catchments is to quantify the effects of multi-scale drivers on ecosystem processes in streams and their catchments. Analyses targeting a focal spatial or temporal scale, such as estimating and attributing long-term trends, have revealed responses of catchments to characteristic drivers. However, processes occurring at longer or shorter frequencies can interfere with signal detection. For example, temporal autocorrelation of discharge and solute chemistry arises due to short-term periodicity (e.g., diurnal or seasonal oscillations), water residence time distributions, and/or in-channel biogeochemical reactivity (Kirchner et al. 2000; Hensley et al. 2018). Presence of temporal autocorrelation and periodic patterns can result in anti-conservative behavior of statistical approaches commonly applied to detect trends, such as the Mann–Kendall test and Sen’s slope estimate (Kendall 1938; Mann 1945; Sen 1968; Yue et al. 2002; Hamed 2008; Sagarika et al. 2014; Serinaldi et al. 2018). Modeling approaches that can accommodate temporal autocorrelation and patterns at multiple spatial and temporal scales could improve understanding of catchment processes, decrease uncertainty in predictions, and improve the design and maintenance of monitoring networks.

We applied multivariate autoregressive state-space models (MARSS) to quantify long-term trends in solute chemistry of headwater streams. The objectives of the analysis were to: (1) estimate long-term trends in solute concentrations, (2) determine the spatial scales of temporal synchrony in solute concentrations, and (3) compare trends estimated by MARSS models to estimates from other statistical approaches. Models were fit to 18–32 years of monthly, flow-weighted solute concentrations in 22 forested reference catchments from eight long-term monitoring networks across the northern temperate zone in North America. In addition to climate warming, catchments included in the study have received increased annual or extreme precipitation, and declining atmospheric deposition of sulfur and nitrogen (Peters et al. 2013; Kunkel et al. 2020; Templer et al. 2022). We used MARSS models to quantify long-term trends and seasonal oscillations in solute chemistry while accounting for temporal autocorrelation, avoiding potential sources of error common to other statistical methods for estimating temporal trends (Fig. 1). We also assessed data support for shared temporal patterns at multiple spatial scales, including continental, ecoregion, and observatory scales (i.e., among headwater catchments within a river basin; Fig. 2). We expected that broad-scale climate or atmospheric deposition phenomena would generate synchronous temporal patterns at continental or ecoregional extents. Finally, we compared multidecadal trends estimated by the state-space models with those estimated by the widely applied, non-parametric seasonal Kendall test.

Methods

Study sites and data sources

We modeled temporal patterns in solute concentrations of 22 headwater streams (contributing areas:

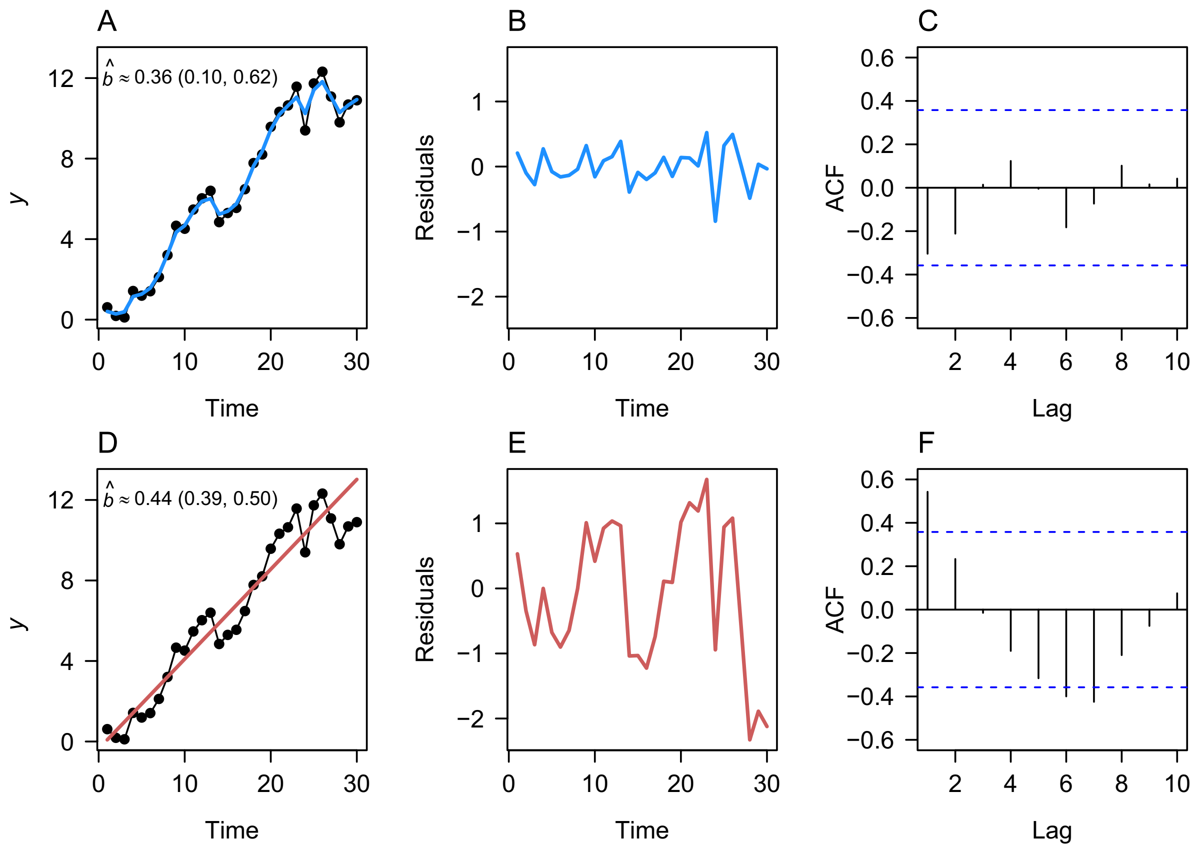

Fig. 1 Illustration of two methods for estimating the temporal trend (i.e., bias) in a simulated time series. Data were simulated with a temporal trend of 0.3. In **A**, the bias is estimated by a MARSS model as in Eq. 3b, which results in smaller model residuals **B** with no significant autocorrelation apparent in **C**, where dotted horizontal lines represent 95% CIs. In **D**, the bias is estimated via Sen's slope, which results in larger model residuals **E** relative to (B) and significant autocorrelation **F** in the residuals. Also note that the estimated bias ($\hat{b}$) for (A) is much closer to the true simulated value of 0.3 and the 95% confidence bounds include the true value. In (D), however, the estimated bias is much larger than the true value and the 95% confidence interval, while smaller, does not contain the true value

0.05–1.9 km^2) distributed among eight catchment observatories in the northern temperate zone of North America (Fig. 3, Table S1). All sites were reference catchments with no experimental manipulations of land cover or chemistry. Observations of discharge and solute chemistry encompassed a maximum extent of water years 1986–2019 and time series of less than 18 years were not included to maintain comparability across sites and solutes (see time series depicted in Figs. 4 & S1-5). Times series were generally of the same length among catchments within an observatory for each solute, though there were exceptions (e.g., HBR, Fig. S1). Further details about the sites and monitoring programs are provided elsewhere (Emmerton et al. 2018; Leach et al. 2020; Campbell et al. 2021; Sebestyen et al. 2021; Webster et al. 2021a; Johnson et al. 2021; Patel et al. 2021; James et al. 2022; Shanley et al. 2022).

We analyzed volume-weighted mean concentrations of ammonium (NH_4^+), calcium (Ca^{2+}), dissolved organic carbon (DOC), nitrate (NO_3^-), sulfate (SO_4^{2-}) and total dissolved phosphorus (TDP). We focused on volume-weighted mean concentrations for three reasons. First, volume-weighted concentrations minimize bias in trends that might be caused by under- or over-sampling periods of high relative to low flows, an issue affecting solute concentrations that are correlated with discharge (Eimers

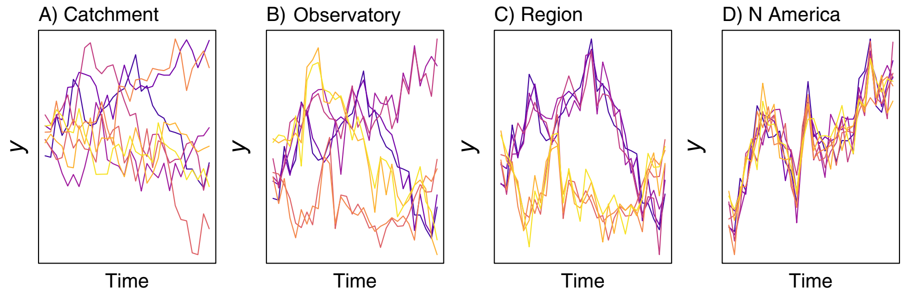

Fig. 2 Examples of state processes considered in this study to characterize the spatial scale of temporal synchrony. Panels depict state processes at four spatial scales for eight simulated time series, where each line color represents a single headwater catchment. Unique state processes at the catchment level **A** occur when the time series in each headwater stream is an observation of a unique state. Observatory-level state processes **B** reflect shared temporal patterns among streams co-located within the same observatory site, which in turn contrast with temporal patterns at other observatories. Similarly, **C** represents ecoregional states, reflected in shared patterns among all catchments within each ecoregion. In contrast, **D** depicts all catchments as observations of a single shared state at the continental (N America) state

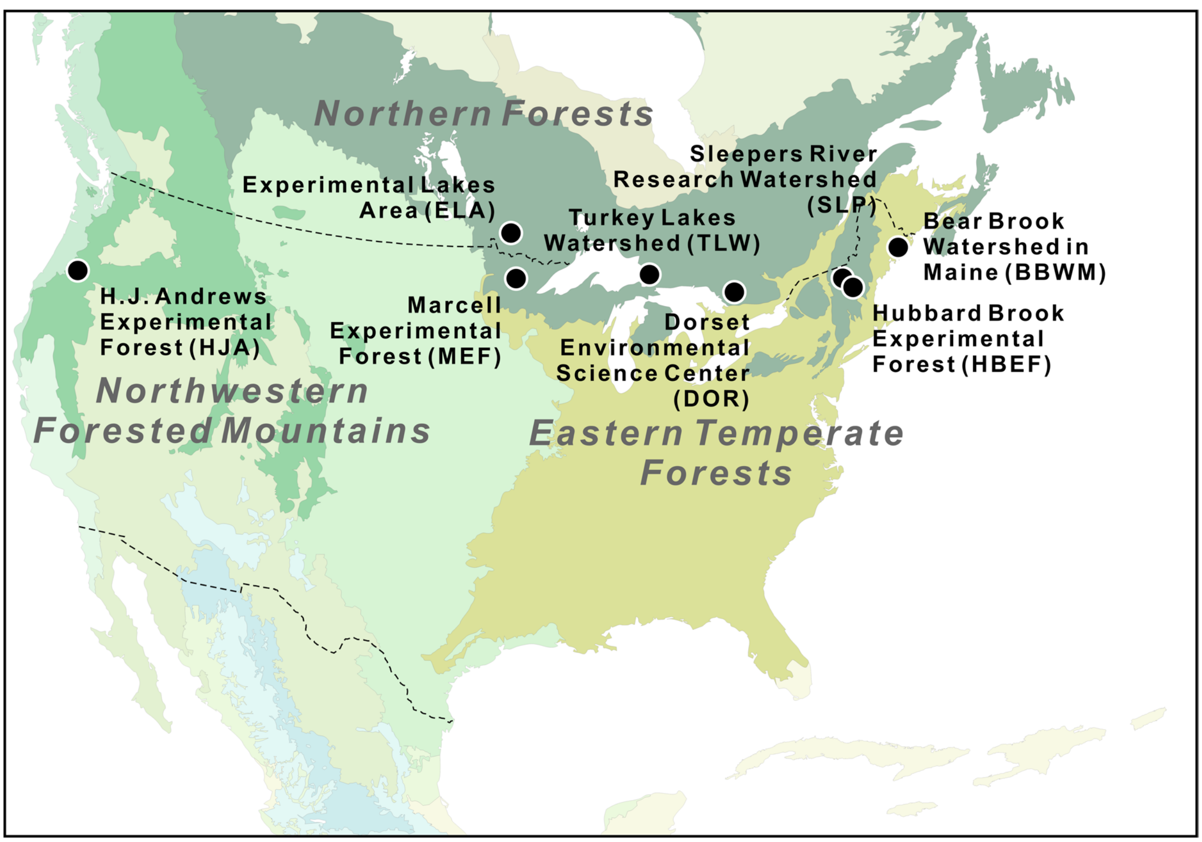

Fig. 3 Observatories located in temperate forests of North America. Time series of stream chemistry were collected in 1–5 headwater streams within each observatory. Colored background shading represents Level I ecoregions (https://www.epa.gov/eco-research/ecoregions-north-america). MARSS models were compared at four spatial scales to represent shared states at continental, ecoregion, and observatory extents, or unique states across all individual catchments

et al. 2008). Second, trend estimates derived from volume-weighted concentrations permit comparison with trends estimated by other statistical approaches for many of the same observatories included here. Finally, some observatories, including HJA, conduct flow-proportional sampling and instantaneous observations of time-averaged concentrations are not available.

Observations of discharge and solute concentrations at daily to biweekly frequency were aggregated to monthly intervals as volume-weighted concentrations following Eq. 1:

$$\frac{\sum_1^n \left(c_i * t_i * q_i\right)}{\sum_1^n \left(t_i * q_i\right)} \tag{1}$$

where n is the number of observed concentration values within 30 days, t_i is the number of days between observations of concentration, c_i is the measured solute concentration during each interval, and q_i is the observed stream discharge corresponding to each observation of solute concentration. Monthly means were assigned NA if the time between observations, t, was greater than 30 days. Data were typically missing at random, except ELA and MEF, where observations were missing for 2–4 months each winter due to ice cover.

We applied the analytical detection limits reported by each monitoring program and did not further analyze solutes for which more than 50% of the observations were less than the detection limit. At MEF, total organic carbon concentration was considered as equivalent to DOC concentration because particulate organic carbon was not detectable (Sebestyen et al. 2021). At HBEF, phosphate concentrations were considered as equivalent to TDP because dissolved organic phosphorus was negligible (Hobbie and Likens 1973; Buso et al. 2000).

Statistical analyses

We quantified multi-decadal trends, seasonality, stochastic variation, and spatial coherence in temporal patterns of solute concentrations using multivariate autoregressive state-space (MARSS) models. State-space models have been applied in ecological and limnological studies (e.g., Ives et al. 2003; Ohlberger et al. 2018) and increasingly to detect long-term, seasonal, or finer-scale patterns in catchment biogeochemistry (Smits et al. 2019; Webster et al. 2022a; Elmstrom et al. 2024). Here we use MARSS models to quantify temporal patterns at multiple scales using observations from long-term monitoring programs and evaluate synchrony of multi-scale temporal patterns at headwater to continental spatial scales.

State-space models consist of two parts described by two linear models: (1) a process model designed to capture the true, but unobserved state of nature (i.e., temporal dynamics resulting from natural processes), and (2) an observation model to map the observed data onto the true states (Harvey 1990). State processes were modeled as autocorrelated time series of the true, but unobserved, log-transformed volume-weighted concentration of each solute using one of two forms of a random walk,

$$x_t = x_{t-1} + w_t \tag{2a}$$

$$x_t = x_{t-1} + u + w_t \tag{2b}$$

where x_t is the log-concentration of a solute at time t, u is the bias (tendency to increase or decrease; referred to as "trend" for comparison with other statistical approaches), and w_t is a normally distributed error with mean zero and variance q. We evaluated data support for the inclusion of the bias term in Eq. 2b using AICc as a metric to compare models with and without this term (Eq. 2a & b) and by evaluating bootstrapped 95% confidence intervals (CIs) around the bias term for overlap with zero. Estimating the bias term after accounting for temporal autocorrelation avoids misattributing variance, which is responsible for anti-conservative behavior of other common approaches applied to estimate temporal trends (Fig. 1).

We examined coherence in temporal patterns of solute concentrations at multiple spatial extents using multi-model inference. To identify the spatial scale at which patterns were most temporally coherent for each solute, we used AICc as a metric to evaluate data support for models with state processes shared among: (1) headwater catchments within each of eight *observatories*, (2) within *ecoregions*, (3) a single *North American* pattern, and 4) unique states in all headwater *catchments* (Figs. 2 & 3). These comparisons were designed to evaluate the relative contributions of potential drivers of temporal patterns, including large-scale atmospheric phenomena, regional climate and vegetation, and local-scale attributes. Comparing headwater streams aggregated at the four hierarchical spatial scales entailed expanding the univariate random walk models in Eq. 2 to multivariate forms:

$$\mathbf{x}_t = \mathbf{x}_{t-1} + \mathbf{w}_t \tag{3a}$$

$$\mathbf{x}_t = \mathbf{x}_{t-1} + \mathbf{u} + \mathbf{w}_t \tag{3b}$$

where $\mathbf{x}_t$ is a $p \times 1$ vector of log-concentrations of a solute for p different states of nature. When the observed data are assumed to represent measurements of unique states at the catchment level, p equals the total number of catchments with available time series data (max = 22). As the spatial organization is aggregated to increasingly larger scales, p decreases such that it equals one at the broadest spatial extent ("North American scale"). The $p \times 1$ vector $\mathbf{u}$ in Eq. 3b contains the bias term for each of the unique states. In these models, the process errors $\mathbf{w}_t$ are assumed to be drawn from a multivariate normal distribution with a mean vector of $\mathbf{0}$ and covariance matrix $\mathbf{Q}$. We assumed that each state had its own unique variance with no covariance among states, such that $\mathbf{Q}$ is a diagonal matrix with variance terms along the diagonal and 0's elsewhere.

The monthly resolution of the data required estimation of nonlinear seasonal patterns that could otherwise obscure upward or downward trends over long time periods. Thus, we included two dummy covariates consisting of discrete sine and cosine transforms to estimate seasonality, such that:

$$\mathbf{x}_t = \mathbf{x}_{t-1} + \mathbf{C}\mathbf{c}_t + \mathbf{w}_t \tag{4a}$$

$$\mathbf{x}_t = \mathbf{x}_{t-1} + \mathbf{u} + \mathbf{C}\mathbf{c}_t + \mathbf{w}_t \tag{4b}$$

where $\mathbf{c}_t$ is a 2×1 vector of discrete sine and cosine values at time t, and $\mathbf{C}$ is a $p \times 2$ matrix of coefficients quantifying effects of the dummy covariates, which characterize the amplitude of seasonal variation. We report significance of the sine and cosine terms determined by evaluating bootstrapped 95% confidence intervals (CIs) around the corresponding $\mathbf{C}$ terms.

To map the times series from each of the individual catchments onto each state representing varying spatial extents, we used a so-called observation model:

$$\mathbf{y}_t = \mathbf{Z}\mathbf{x}_t + \mathbf{v}_t \tag{5}$$

where $\mathbf{y}_t$ is an $n \times 1$ vector of the measured log-transformed and mean-centered concentration of a solute at time t for each of the n catchments, and $\mathbf{Z}$ is an $n \times p$ matrix of 1's and 0's, which matches each measurement (row) to its hypothesized state (column). That is, at the smallest spatial extent where each catchment is considered a unique state, $p = n$ and $\mathbf{Z}$ is an $n \times n$ identity matrix with 1's down the diagonal and 0's elsewhere. At the other extreme, when all catchments are thought to represent a single North American pattern, $p = 1$ and $\mathbf{Z}$ is an $n \times 1$ column vector of all 1's. Because the actual solute data arise from an imperfect sampling scheme and analytical error, we allowed for non-zero differences between the observations ($\mathbf{y}$) and true states ($\mathbf{x}$) with an additional $n \times 1$ vector of observation errors ($\mathbf{v}_t$). Due to similar sampling and analytical methods among the observatories, we assumed that these observation errors were independent and identically distributed, with a mean vector of $\mathbf{0}$ and diagonal covariance matrix, $\mathbf{R}$. We compared AICc values to evaluate the relative data support for each of eight models fit to each solute (i.e., four states representing spatial extent of shared temporal patterns, with and without bias terms). We fit the MARSS models using the *MARSS* package (Holmes et al. 2021) for R software (R Core Team, 2020).

Finally, we compared long-term trends estimated by MARSS models (bias term, u) with trends estimated by the seasonal Kendall test (Kendall 1938; Hirsch et al. 1982). Non-parametric tests of temporal trends have been widely applied to estimate long-term trends in hydrologic and biogeochemical time series, including many of the datasets included in this study (e.g., Eimers et al. 2008; Navrátil et al. 2010; Argerich et al. 2013; O'Brien et al. 2013; Garmo et al. 2014; Webster et al. 2021b; Templer et al. 2022). Though many previous studies applied the Mann–Kendall (Mann 1945) and Sen's slope (Sen 1968) approaches as originally proposed, here we applied the seasonal Kendall test with correction for autocorrelation to facilitate comparison with trends estimated by MARSS models (Hirsch et al. 1982). The seasonal Kendall test is based on the sum of differences between pairs of points at all lag separations for each month, with significance determined by comparing the ratio of this sum to its variance (adjusted for covariance among months within the same year following Hirsch et al. [1982]) with a Z distribution. The long-term trend is estimated as the median slope of all possible pairs of observations within each month, with a 95% confidence interval containing the inner 95% of estimated slopes. We checked for heterogeneity in the sign of trends among months (Van Belle and Hughes 1984) and do not report trends for streams or solutes yielding significant seasonal heterogeneity. We applied these non-parametric tests to log-transformed and mean-centered solute concentrations using the *EnvStats* package in R (Millard 2013).

Results

Temporal patterns in monthly volume-weighted mean solute concentrations (Figs. 4, S1-4) were statistically distinct among headwater catchments for all solutes (Table 1). That is, compared to models

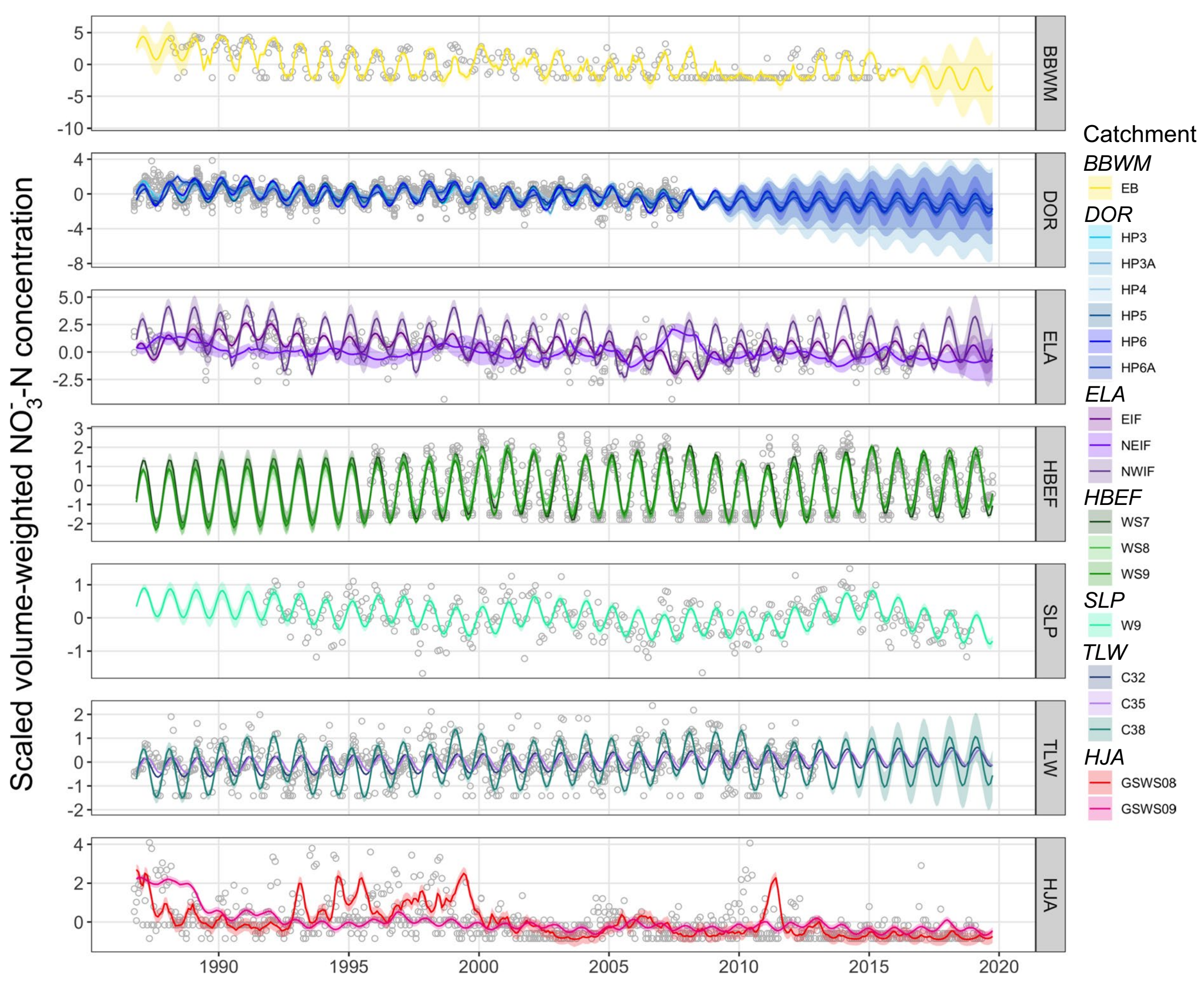

Fig. 4 MARSS models fitted to observed time series of nitrate concentration in streams of each observatory. Model fits reflect unique states at the catchment level and include a bias (temporal trend) term. Colored lines and shading represent model fits and 95% confidence intervals for each catchment, respectively, and gray points depict observations. Streams lacking visible shading are due to confidence intervals narrower than lines representing model fits. All models were fitted to the time period of water years 1986–2019 and increasing uncertainty of modeled estimates occurs in the absence of observations. Model fits to remaining solutes are shown in Supplemental Figs. 1–5. BBWM = Bear Brook Watershed; DOR = Dorset Environmental Science Center; ELA = Experimental Lakes Area; HBEF = Hubbard Brook Experimental Forest; HJA = H.J. Andrews Experimental Forest; MEF = Marcell Experimental Forest; SLP = Sleepers River Research Watershed; TLW = Turkey Lakes Watershed

incorporating shared state processes at observatory, ecoregion, or continental scales, models with unique state processes at the catchment scale were better supported by observations (ΔAICc ≥ 263; Table 1). This finding was robust to exclusion of observatories that included a single catchment (Table S2). Therefore, all subsequent discussion addresses results of models representing a unique state process in each headwater catchment (as in Fig. 2a).

Concentration of each solute varied seasonally in some or all catchments, indicated by confidence intervals around estimated coefficients of sine and

Table 1 Data support for MARSS models varying in spatial scale of shared state processes and inclusion of a bias (trend) term. Values reflect difference in Akaike's Information Criterion adjusted for small sample size (ΔAICc) between each model and the model with lowest AICc value for each solute. Bolded values indicate the model form that was best supported by the data for each solute

Model	Calcium	DOC	Ammonium	Nitrate	TDP	Sulfate
Catchment states	**0**	**0**	**0**	7.4	**0**	**0**
Catchment states + bias	23	13	22	**0**	25	35
Observatory states	701	395	263	4317	305	305
Observatory states + bias	711	409	275	4306	310	311
Regional states	2615	1249	1286	7567	702	978
Regional states + bias	2606	1249	1291	7554	704	980
Continental state	3307	1546	2370	7831	702	1334
Continental state + bias	3309	1548	2372	7833	704	1336

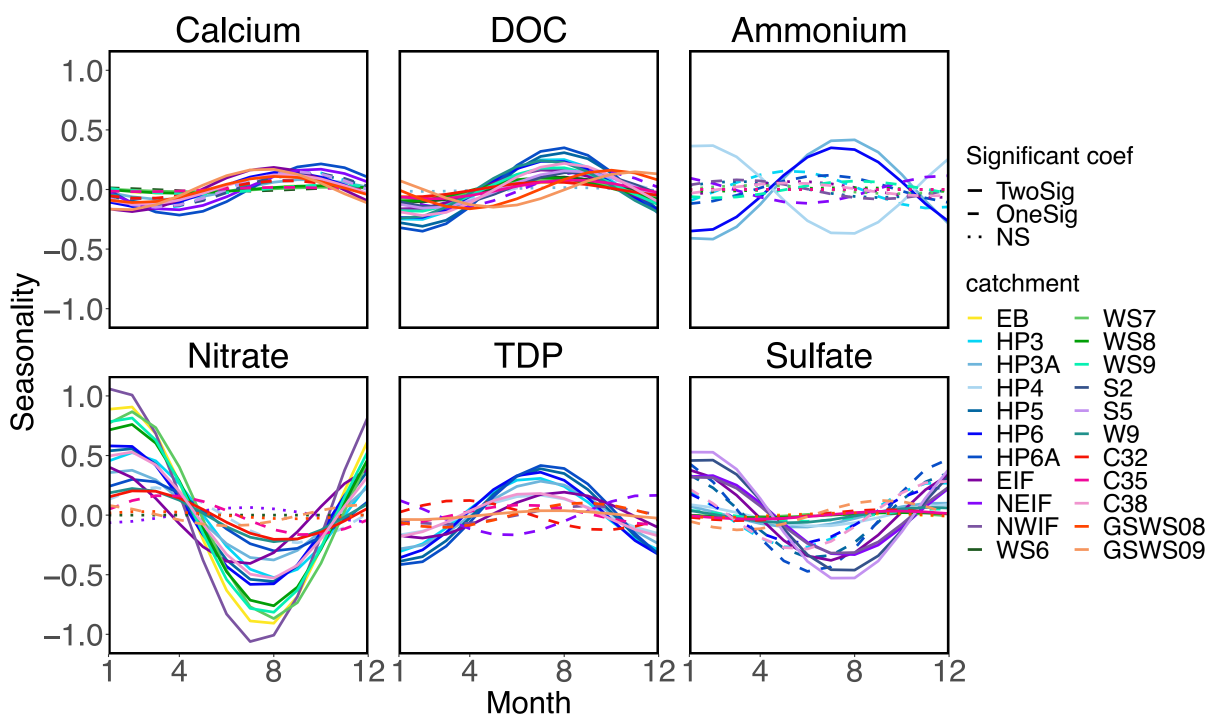

Fig. 5 Model-predicted effects of seasonality in solute concentrations for each stream. Non-linear seasonal patterns were estimated using sine and cosine transforms applied to time series of volume-weighted mean solute concentrations (**C** terms in Eqn. 4a & b). Line type indicates whether the 95% CIs for both sine and cosine seasonality coefficients excluded zero (TwoSig, solid lines), only one term was significant (OneSig, dashed lined), or neither excluded zero (NS, dotted lines). Predictions reflect model fits from models with a unique state process for each catchment and include a bias term

cosine terms that did not include zero (Fig. 5). Here we report on seasonality estimated by models including separate states at the catchment level. Significant seasonal variation in Ca^{2+} and TDP concentrations occurred in all catchments. Dissolved organic C was seasonal in all but one of the 22 catchments analyzed. Two catchments were aseasonal in NO_3^- and SO_4^{2-} concentrations, whereas a quarter of the catchments were aseasonal in NH_4^+ concentration. On average, the amplitude of seasonal variation was greatest for NO_3^- concentration, which peaked in winter or early spring and was lowest in summer. Dissolved organic C reached maximum concentration during summer in most catchments but peaked in autumn for catchments at HJA. Peak concentration of SO_4^{2-} tended to occur in winter and Ca^{2+} concentration peaked in summer–autumn. Seasonal oscillations of NH_4^+ and TDP varied in timing and amplitude across catchments and indicated asynchrony even among catchments within the same observatory. For example, whereas TDP reached maximum concentration during summer in most streams, a single catchment within each of TLW and ELA peaked in early spring and winter, respectively. Similarly, timing of peak NH_4^+ concentration contrasted across adjacent catchments monitored at DOR. Finally, though significant, the amplitudes of oscillations in both SO_4^{2-} and Ca^{2+} concentrations were muted in catchments at HBEF compared to the other observatories.

For all solutes except NO_3^-, models lacking a bias term (u) were more strongly supported than models that included bias (Table 1). Thus, across all catchments, concentrations of most solutes did not consistently increase or decrease during the period of record. Although data did not support inclusion of bias terms across all catchments, we present bias coefficients estimated by the state-space models for comparison with other catchments and analytical approaches. We detected significant trends (i.e., 95% CI of bias term not overlapping zero) in only 16% of long-term (up to 32 years) records of solute concentrations (Fig. 6). Significant trends typically occurred in only a subset of catchments monitored within an observatory (Fig. 6). Positive bias terms for DOC occurred in one or more catchments within four monitoring observatories: DOR, HBEF, HJA, and MEF. Ammonium concentration declined in one catchment at ELA. Sulfate concentration declined at BBWM and in three of four catchments at HBEF. Calcium concentration

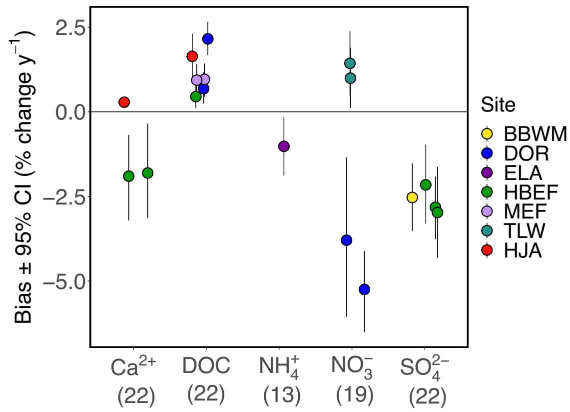

Fig. 6 Significant trends in solute concentrations. Values reflect the bias term (u) estimated by MARSS models with unique states for each catchment. Error bars are bootstrapped 95% CIs. For clarity, only significant bias terms are shown. Total number of catchments analyzed for each solute is shown on the horizontal axis. Bias terms were not significant for TDP concentrations. BBWM = Bear Brook Watershed; DOR = Dorset Environmental Science Center; ELA = Experimental Lakes Area; HBEF = Hubbard Brook Experimental Forest; HJA = H.J. Andrews Experimental Forest; MEF = Marcell Experimental Forest; SLP = Sleepers River Research Watershed; TLW = Turkey Lakes Watershed

declined in two catchments at HBEF but increased in one catchment at HJA. Nitrate concentration declined in two catchments at DOR and increased in two catchments at TLW. There were no significant long-term trends in TDP concentrations.

There was little agreement in trend detection between the seasonal Kendall test and the MARSS models (Fig. 7). The seasonal Kendall approach detected a significant trend in 20 time series whereas MARSS detected a significant long-term trend in 18 of 112 total time series with sufficient data to support analysis. The seasonal Kendall test yielded heterogeneous trends by month in 27% of the solute*catchment combinations that had sufficiently continuous time series to support the test and results of the Kendall test are not further reported for these time series. Both tests yielded significant estimates of trend for only five of the same time series, most of which were sulfate and were generally characterized by strong long-term trends and lower relative seasonal variation. The trend effects varied < 1–12% between the trends estimated as significant by both approaches (Fig. 7).

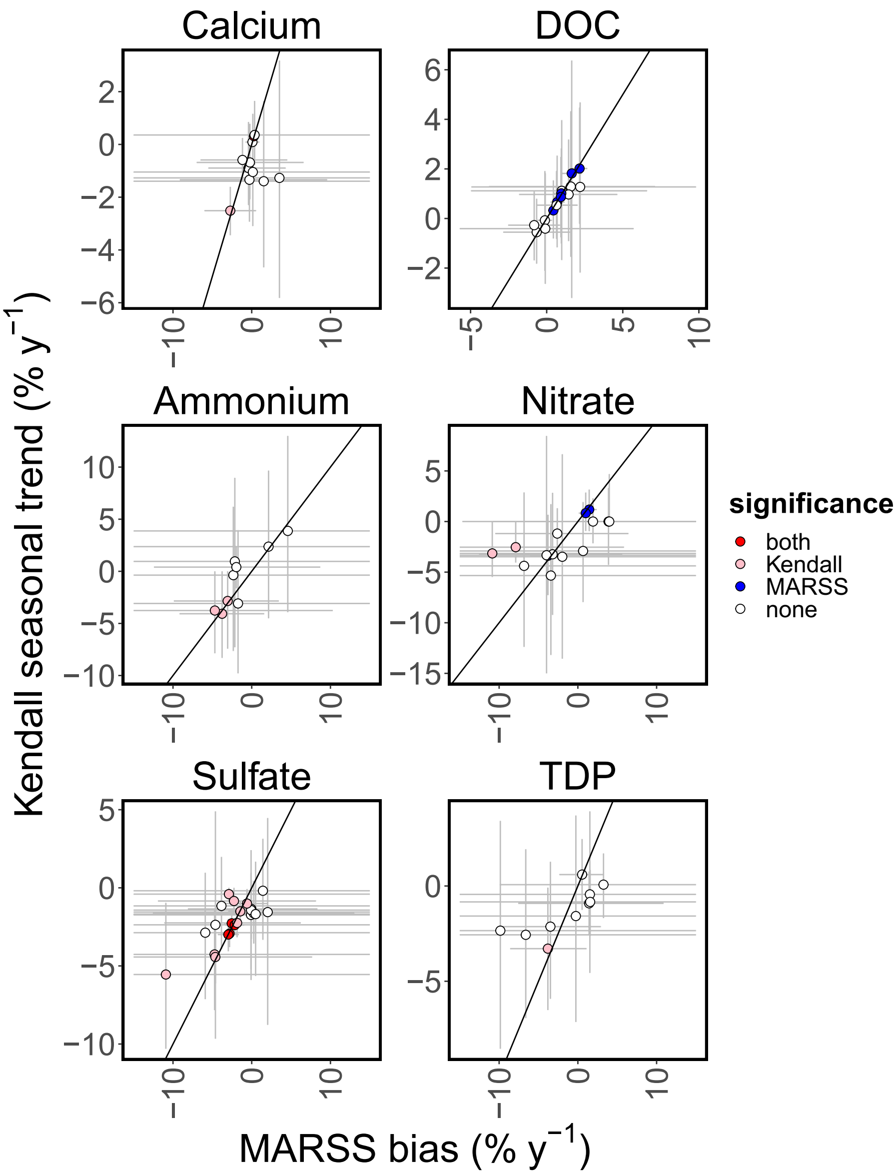

Fig. 7 Long-term trends in flow-weighted solute concentrations estimated by MARSS models and the seasonal Kendall test. Error bars represent 95% CIs, symbols mask CIs when uncertainty is low, and error bars were censored at -15 and 15 to facilitate visualization. Symbol color represents significance of the long-term trend estimated by each of the two modeling approaches. The 1:1 line is shown in black. Data are omitted for catchments and solutes that indicated heterogeneous long-term trends among months following the seasonal Kendall test

Discussion

Temporal patterns in biogeochemistry of headwater catchments can reflect the effects of phenomena occurring at multiple spatial and temporal scales. We applied multivariate autoregressive state-space models to extract patterns resulting from global change and responses of catchment and instream processes that are encoded in long-term records of solute concentrations at nested spatial and temporal scales. Using this statistical approach, we showed that temporal patterns differed significantly across even neighboring headwater catchments (Table 1, Fig. 3), implying that large-scale patterns in disturbance and climate were filtered through local catchment attributes to generate unique temporal patterns in biogeochemistry for each catchment. Significant long-term trends consistent with recovery from atmospheric deposition or increased precipitation were detected in some catchments (Fig. 6). Yet, the analysis also indicated that commonly applied approaches for analyzing temporal trends might overestimate significant long-term patterns (Fig. 7). We found limited evidence for multi-decadal trends in most catchments despite concurrent warming climate, increased total and extreme precipitation, and reduced atmospheric deposition of sulfur and nitrogen across the study area (Kunkel et al. 2020; Templer et al. 2022). Multiple mechanisms might have contributed to long-term stability in catchment biogeochemistry, including resilience of ecosystems to changing climate and disturbance regimes, presence of both disturbance and recovery effects within the time series, and limited net effects of multiple sequential or concurrent disturbances on biogeochemical cycles over multi-decadal time scales.

Spatial heterogeneity among catchments

Data support for unique state processes (i.e., temporal dynamics resulting from natural processes) at the headwater catchment scale (Table 1) indicated widespread temporal asynchrony, even among adjacent catchments. Thus, local heterogeneity obscured the potential synchronizing effects of broader-scale drivers, such as regional- or continental-scale patterns in climate or declining atmospheric deposition. Heterogeneity among neighboring catchments implies that capturing regional patterns, including responses to regional- or larger-scale disturbances, requires monitoring of multiple headwater catchments within an observatory, because local attributes contribute to distinct patterns in hydrology and biogeochemistry in addition to patterns shared across broader scales (Argerich et al. 2013). For example, catchment slope influences water residence time and biogeochemistry at the catchment scale (Creed et al. 2008; Creed and Beall 2009; Harms et al. 2016) resulting in opposing long-term trends in DOC concentration in adjacent upland and lowland catchments (Fork et al. 2020). Similarly, differences in elevation and aspect among catchments influence soil, vegetation, and atmospheric deposition, which in turn affect the timing and magnitude of solute export (Lawrence et al. 1999; Clark et al. 2004; Hinckley et al. 2014; Webster et al. 2021b). The state-space modeling approach was similarly used to identify contrasting temporal patterns in aquatic production among adjacent reaches of a large river, suggesting that heterogeneity in stream-riparian attributes can also generate local-scale variation (Jankowski et al. 2021).

Seasonality

Though the MARSS models indicated that each stream had unique long-term temporal patterns in stream solute concentrations, the synchronized seasonal component of temporal variation across many headwater streams implied that common mechanisms contribute to seasonality across these North American temperate catchments. Biotic uptake in the catchment or stream likely contributed to significant seasonal variation in NO_3^-, with peak concentration during periods of relative biotic dormancy in winter and lowest concentration during summer (Fig. 5; Goodale et al. 2009; Halliday et al. 2012). Similarly, seasonality of SO_4^{2-} concentration also suggests biological constraints on sulfur cycling, though supply of SO_4^{2-} in excess of biological demand might have contributed to the smaller amplitude of seasonal oscillations compared to NO_3^-. Maximum annual concentration of DOC in summer, or in autumn at HJA, suggests contributions of terrestrial primary production coincident with hydrologic flushing of DOC (Dittman et al. 2007; Dawson et al. 2008; Lajtha and Jones 2018; Wu and Yao 2024). Calcium concentration also peaked during summer or autumn in all catchments, potentially reflecting diminished dilution of mineral inputs from bedrock weathering during low flows in summer and throughfall enhanced by senescing foliage in autumn (Navrátil et al. 2010; Halliday et al. 2012). Aseasonal and asynchronous seasonal patterns in NH_4^+ and TDP concentrations may be attributed to biotic or abiotic drawdown of these nutrients to near analytical detection limits.

Long-term trends in catchment biogeochemistry

Long-term trends in solute concentrations were consistent with multi-decadal changes in atmospheric deposition and climate (Fig. 6). Within observatories historically subject to high rates of deposition (e.g., BBWM, DOR, and HBEF; Templer et al. 2022), significant declines in NH_4^+, NO_3^-, and SO_4^{2-} concentrations of streams likely resulted from reduced atmospheric deposition. The simultaneous decline in Ca^{2+} concentration at HBEF is likely due to reduced leaching of base cations from apatite as acid deposition subsided and to uptake of calcium by relatively rapidly growing deciduous forests (Likens et al. 1998, 2021; Lawrence et al. 1999; Huntington 2005).

The increases in DOC concentration detected at DOR and HBEF may be due to increasing production or solubility of DOC under less acidic conditions (Evans et al. 2006; Kang et al. 2018; Monteith et al. 2023; Wu and Yao 2024). However, we also observed similar rates of DOC increase in a catchment at HJA and in both catchments at MEF even though historic rates of acidic deposition at these observatories were at least five-fold less than at the northeastern observatories (NADP Program Office, Wisconsin State Laboratory of Hygiene 2022). Two alternative mechanisms might have caused increased DOC concentration in streams: (1) increased decomposition and leaching of organic matter under wetter or warmer conditions (Freeman et al. 2001; Eimers et al. 2008; Huntington and Shanley 2022) or (2) increased DOC production due to stimulation of primary production by increased atmospheric CO_2 (Freeman et al. 2004). Finally, positive trends in Ca^{2+} concentration in a catchment at HJA and in NO_3^- of two catchments at TLW are counter to expectations of recovery from acid deposition and might instead result from increased precipitation or warming effects on weathering and nutrient transformations (De Wit et al. 2008; Baron et al. 2009; Lucas et al. 2013). The observed changes in solute exports resulting from long-term increases in precipitation at the study sites are ecologically significant, influencing productivity of receiving ecosystems, including lakes (Sherbo et al. 2023).

Despite long-term increase in temperature and precipitation and declining atmospheric deposition (Deser et al. 2016; Kunkel et al. 2020; Templer et al. 2022), most catchments showed few or no long-term trends in solute concentrations over 2–3 decades (i.e., non-significant bias term; Table 1, Fig. 6). Relative stability in solute concentrations is consistent with limited evidence for long-term change in stream discharge in many of the study catchments (Campbell et al. 2011; Parker et al. 2009; Kim et al. 2010; Argerich et al. 2013; Crampe et al. 2021; Webster et al. 2021b; Huntington and Shanley 2022), or declining flows, particularly during summer in some catchments (AND, DOR; Yao et al. 2016; Ward et al. 2020). Lack of trends in stream hydrology and chemistry might indicate resilience of northern ecosystems to long-term changes in climate and atmospheric deposition (Emmerton et al. 2018). However, several processes could dampen trends or impede trend detection. We would expect no overall trend if multiple disturbances had contrasting effects on biogeochemical cycles during the same time period. Additionally, opposing sequential patterns such as increasing NO_3^- export due to atmospheric deposition followed by recovery to pre-perturbation conditions would not result in a significant long-term trend. Periodic variation in climate, such as the Pacific Decadal Oscillation, would also obscure detection of long-term trends. Finally, it is also possible that three decades is insufficient to detect slow rates of change relative to the temporal variation present at shorter frequencies (Argerich et al. 2013).

Previously researchers have applied the Mann–Kendall test and Sen's slope estimator to evaluate multi-decadal trends in volume-weighted solute concentrations in the same or similar datasets and have reported more trends than detected by the MARSS approach (Navrátil et al. 2010; Argerich et al. 2013; Fuss et al. 2015; Webster et al. 2021b; Rodríguez-Cardona et al. 2022). Because the Mann–Kendall test and Sen's slope do not account for temporal autocorrelation or other sources of variation in addition to long-term trend, those approaches estimate trends that are less accurate (i.e., less likely to estimate the true trend) with inflated precision (i.e., narrower confidence intervals) compared to MARSS models (Fig. 1). Temporal autocorrelation is present at multiple scales in time series of stream chemistry (Kirchner and Neal 2013; Hensley et al. 2018) and inflates the variance of the Mann–Kendall test statistic (Yue et al. 2002), resulting in trend estimates that can be biased high and overconfident (Fig. 1). "Prewhitening" approaches have been used to remove temporal autocorrelation (Yue and Wang 2002) and the seasonal version of the tests, such as applied here, were developed to address seasonal autocorrelation (Hirsch et al. 1982). However, these approaches can increase Type I errors, lack power, produce biased estimates of trends, or fail in the presence of seasonally heterogeneous trends and missing data (Collaud Coen et al. 2020). Importantly, trend detection differs between previous application of the Mann–Kendall approach to similar time series as analyzed here because the MARSS models parse environmental (i.e., process; Eq. 3a & b) from sampling (i.e., observation; Eq. 5) errors, whereas the Mann–Kendall and Sen's slope methods address only observation error. Finally, state-space models such as MARSS offer the advantage of simultaneous analysis of multiple time series, which generates more accurate parameter estimates and can uncover spatial scales of synchronous temporal patterns.

Implications for catchment monitoring programs

Observatories of headwater catchments were established to understand and better predict hydrologic and biogeochemical patterns and to detect responses to changing disturbance regimes, including climate and management activities (e.g., Grimm 1987; Jeffries et al. 1988; Baron et al. 2009; Webster et al. 2016; Aguilera and Melack 2018; Lajtha and Jones 2018; Likens et al. 2021; Tiwari et al. 2022). Ultimately, observations from these catchments have supported changes in environmental policy (e.g., Likens 2010) and will continue to inform environmental stewardship under shifting baselines caused by climate warming and other anthropogenic pressures. Despite the outsized value of long-term monitoring and research, funding limitations have resulted in decommissioning or rescoping of catchment monitoring programs, including some of those analyzed here (Hughes et al. 2017). We can build on the intrinsic value of long-term monitoring to reduce uncertainty in predicted catchment responses to change by adopting analysis approaches such as MARSS models to decompose variation at multiple temporal and spatial scales, explicitly incorporate observation errors, and attribute multi-scale patterns to ambient and anthropogenic drivers. We emphasize that accurate detection and characterization of temporal patterns at multiple scales requires long-term records that encompass the multi-scale temporal variation inherent to an ecosystem and its disturbance regime (Harms et al. 2021).

State-space analysis of long-term headwater observations at nested spatial scales might inform design and maintenance of environmental observatories. Differing non-seasonal patterns among adjacent headwater catchments (Table 1) indicate that monitoring a single catchment is insufficient if the goal is to characterize regional responses to disturbances. Regional patterns can only be reliably detected from observations in multiple headwater catchments that adequately represent the spatial heterogeneity of the region. However, monitoring a smaller number of catchments could adequately describe effects of large-scale temporal variation in climate, evidenced by shared seasonal patterns at the observatory scale and across many catchments at a continental scale (Fig. 5). Similarly, a comparison of the HBEF observatory to other monitoring sites within the northeastern US found that HBR effectively matched larger-scale trends in recovery of stream chemistry from acid deposition, but differed in absolute solute concentrations because its topography, geology, and climate were less representative of the region (Fahey et al. 2015). Selection of catchments for characterizing seasonality of biogeochemical cycles might also consider land use, which moderates synchrony in stream nutrient concentrations (Van Meter et al. 2020). Regardless of the focal scale of analysis, the value of catchment monitoring is enhanced by maintaining continuous time series because long-term records are more likely to encompass perturbations and possible recovery, and therefore support analyses that might detect catchment responses (Rosi et al. 2023).

Conclusions

Accurately extracting and attributing multi-scale temporal patterns within long-term records of stream chemistry can contribute to realizing the value of monitoring programs. Using MARSS models to quantify seasonality and long-term trends in solute concentrations at multiple scales, we detected shared seasonal patterns across much of the northern temperate region that are likely explained by seasonality in biotic uptake of solutes and hydrologic regimes (Fig. 5). However, synchronous seasonal patterns were embedded within longer-term variation that was heterogeneous among headwater catchments. Local spatial heterogeneity in long-term patterns despite regional-scale changes to environmental policy and rapidly changing climate (Fig. 6) highlighted how cross-scale interactions (sensu Heffernan et al. 2014) might complicate detection of ecosystem responses to environmental change. Such heterogeneity motivates maintenance of monitoring networks (i.e., multiple catchments within multiple observatories) that allow researchers and managers to parse local and regional-scale drivers of terrestrial and freshwater ecosystem change. For example, subsequent research could compare neighboring catchments to identify potential sources of resilience that contributed to absence of long-term trends in some catchments but not others.

Further time series models could also incorporate covariate effects to test hypothesized drivers of temporal variation including rates of atmospheric deposition, precipitation and/or discharge, and net primary production. Given time series of sufficient duration and frequency, additional modeling approaches could capture non-stationary patterns (e.g., dynamic linear models) expected under climate change, such as changing seasonality or shifting importance of drivers (Halliday et al. 2012; Johnson et al. 2024). Importantly, long-term records are required to support analyses that can detect and characterize multi-faceted effects of global change on catchment processes.

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Author contributions The study was designed by TKH, JH, MDS, and IC. Data preparation was contributed by all authors. Data analyses were performed by TKH, JH, and MDS. The first draft of the manuscript was written by TKH and all authors edited previous versions of the manuscript. All authors read and approved the final manuscript.

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Data availability Data are available from long-term research sites: BBWM, https://doi.org/10.6073/pasta/04d5e1c0533b1e60537530f726876952; DOR, https://data.ontario.ca/dataset?q=inland%2Bwater*;* ELA, https://www.iisd.org/ela/; HJA, https://doi.org/10.6073/pasta/bb935444378d112d9189556fd22a441d, https://doi.org/10.6073/pasta/0066d6b04e736af5f234d95d97ee84f3; HBEF, https://doi.org/10.6073/pasta/3f608226a1ed499e8fa3cd188e70757c, https://doi.org/10.6073/pasta/bbb8d5a6503d15c1d75b7de9775cb7a2, https://doi.org/10.6073/pasta/f8441200f77e2172af16e73ecc7ff25a, https://doi.org/10.6073/pasta/e6a8c2280faac6abf53fd25513d57c8f; MEF, https://doi.org/10.6073/pasta/a47f5019f2ce2aff6cbca0e555939950; SLP, https://doi.org/10.5066/P9380HQG; and TLW, https://open.canada.ca/data/en/dataset/f2ac0ae9-dd2f-4a70-b059-f8a49d9f5982. Synthesized data and code generating analyses are available at https://github.com/mdscheuerell/bgc_meta.

Declarations

Competing interests The authors have no relevant financial or non-financial interests to disclose.

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