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LETTER

Establishing fluvial silicon regimes and their stability across the Northern Hemisphere

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Scientific Significance Statement

Compared to other nutrients, silicon (Si) is understudied despite its importance for primary productivity, water quality, and global carbon sequestration. Understanding Si regimes—the seasonal patterns of Si concentrations—can help identify processes driving fluvial Si concentrations. Regimes describe the annual timing and magnitude of concentrations to identify hydrobiogeochemical, climate, and land use controls on Si concentrations. This article identifies the main Si concentration regimes from over 200 stream sites across the Northern Hemisphere. The results of our analysis indicate more variation in Si seasonality and stability than previously recognized both within and across ecosystems, highlighting the need to understand patterns and drivers related to intraannual and interannual variability in Si cycling.

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Author Contribution Statement: K.J., K.J.J., J.C., P.S., and A.S. designed the research. K.J., K.J.J., J.C., N.J.L., W.H.M.D., A.S., A.W., L.S., W.M.W., A.E.P., P.K., R.H., H.L., A.R., J.B.J., D.M.K., P.J., and P.S. provided data to the dataset. K.J., K.J.J., P.J., J.C., and L.S. harmonized and QA/QCed the dataset. K.J., K.J.J., and N.L. performed the analysis. P.S., K.J.J., W.H.M.D., A.S., and A.W. provided guidance and methodological ideas for analysis. K.J.J., J.C., W.H.M.D., A.S., A.W., L.S., W.M.W., A.E.P., P.K., R.H., H.L., A.R., J.B.J., D.M.K., P.J., and P.S. helped interpret results. K.J., K.J.J., and P.S. wrote the manuscript. J.C., N.J.L., W.H.M.D., A.S., A.W., L.S., W.M.W., A.E.P., P.K., R.H., H.L., A.R., J.B.J., D.M.K., P.J., and S.B. reviewed and edited the manuscript.

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Additional Supporting Information may be found in the online version of this article.

Abstract

Fluvial silicon (Si) plays a critical role in controlling primary production, water quality, and carbon sequestration through supporting freshwater and marine diatom communities. Geological, biogeochemical, and hydrological processes, as well as climate and land use, dictate the amount of Si exported by streams. Understanding Si regimes—the seasonal patterns of Si concentrations—can help identify processes driving Si export. We analyzed Si concentrations from over 200 stream sites across the Northern Hemisphere to establish distinct Si regimes and evaluated how often sites moved among regimes over their period of record. We observed five distinct regimes across diverse stream sites, with nearly 60% of sites exhibiting multiple regime types over time. Our results indicate greater spatial and interannual variability in Si seasonality than previously recognized and highlight the need to characterize the watershed and climate variables that affect Si cycling across diverse ecosystems.

Fluvial silicon (Si) plays a critical role in controlling primary productivity, ecosystem health, and carbon sequestration in freshwater, estuarine, and marine ecosystems (Conley et al. 1993; Buesseler 1998; Gregg and Rousseaux 2014). Si export supports diatom communities, which are responsible for ~20% of photosynthetically fixed CO_2 each year (Malviya et al. 2016). However, warming and land use change are altering how watersheds cycle Si. Warming increases the silicate weathering rate, which in turn increases Si exports (Deng et al. 2022). Additionally, urbanization may increase Si transport to streams (Carey and Fulweiler 2012; Maguire and Fulweiler 2016) whereas agricultural practices have been linked to reductions in Si export (Struyf et al. 2010). Shifts in Si concentrations with respect to other nutrients (i.e., nitrogen and phosphorus) may facilitate preferential growth of potentially harmful, non-silicious algae, with effects on water quality and ecosystem health (Conley et al. 1993; Turner et al. 2003). A recent synthesis of long-term trends in fluvial Si concentrations and loads from 60 streams showed that Si concentrations were changing, and that the timing of change during the year varied across and within biomes (Jankowski et al. 2023), indicating widespread changes in Si watershed processing may be occuring.

The seasonal pattern of stream water chemistry (i.e., its annual regime) reflects the integrated signal of climate, static watershed characteristics like lithology and terrestrial vegetation, and dynamic ecosystem processes such as instream and terrestrial primary productivity (Bernhardt et al. 2022; Bolotin et al. 2022). Recent efforts have characterized the fluvial regimes of major nutrient concentrations by evaluating the timing, magnitude, and rate of change in concentration peaks and troughs, which have provided powerful insights into controls on stream nutrient chemistry (Mattsson et al. 2015; Van Meter et al. 2020; Heiner et al. 2022). Previous work to understand stream Si seasonality has focused on temperate forest biomes, which are characterized by springtime concentration drawdowns driven by biological uptake with recovery throughout the summer and fall as uptake rates decline (Fulweiler and Nixon 2005; Carey and Fulweiler 2013) (Fig. 1a). Despite the importance of Si for freshwater and marine productivity, no published work has characterized Si regimes across biomes.

Existing work examining watershed cycling of Si has focused heavily on understanding hydrologic controls on Si concentrations. Concentration–discharge (CQ) relationships have shown that Si exhibits diluting (Carey et al. 2020), chemostatic (Godsey et al. 2009), and hysteretic (Hornberger et al. 2001) behavior, which indicates that fluvial Si concentrations are controlled by variable processes across landscapes. Little work has been done to assess drivers of different Si CQ patterns or to tie CQ behavior to seasonal variability in Si concentration.

A more complete understanding of Si regimes and their underlying drivers will provide insight into variability of Si regimes and help identify when and where Si concentrations may be changing most rapidly (Fig. 1b). Here, we take a step towards understanding the complex interactions that drive seasonal patterns of fluvial Si concentrations (i.e., regimes) by asking: 1) Are there distinct Si regimes among streams?; 2) Do streams show the same regime over their period of record?; and 3) How do climate, discharge, and source transport behavior influence regime pattern and stability (i.e., the tendency of a river to exhibit the same regime over time)? We hypothesize that rivers will exhibit distinct regimes (e.g., Bernhardt et al. 2022), that these regimes will cluster by climate zone (Li et al. 2022) and river size (Savoy et al. 2019), and that average CQ behavior (e.g., dilution and mobilization) will explain the timing of peaks and troughs (Minaudo et al. 2019). We further hypothesize that regimes will vary over time in response to interannual variability in discharge (Perdrial et al. 2014; Fazekas et al. 2021). To test these hypotheses and answer these questions, we analyzed data from 201 streams located across the Northern Hemisphere (Fig. 2a).

Methods

Data

We used dissolved Si concentration data sourced from published and/or publicly available datasets (Table S1; Johnson et al. 2023). Sites spanned eight climate zones between 18°N and 70°N. They varied in drainage area from < 1 km^2 to nearly 3 million km^2 and in mean stream discharge from < 0.01 cm to nearly 20,000 cm indicating a wide range in river size as

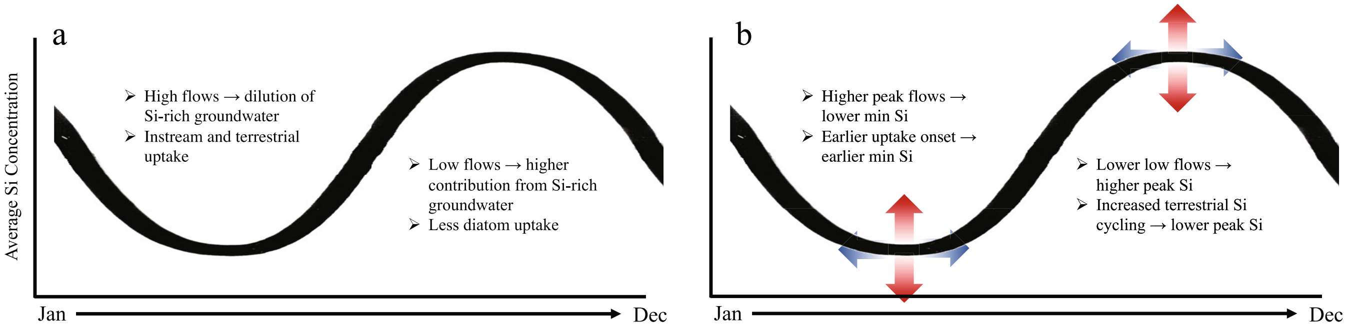

Fig. 1. (**a**) Conceptual model of factors influencing Si regime in temperate forests and (**b**) drivers that may lead to an unstable regime (movement in the blue arrow direction would lead to changes in timing of peaks and troughs, and movement in the red arrow direction would lead to dampening or exaggeration of regime variability).

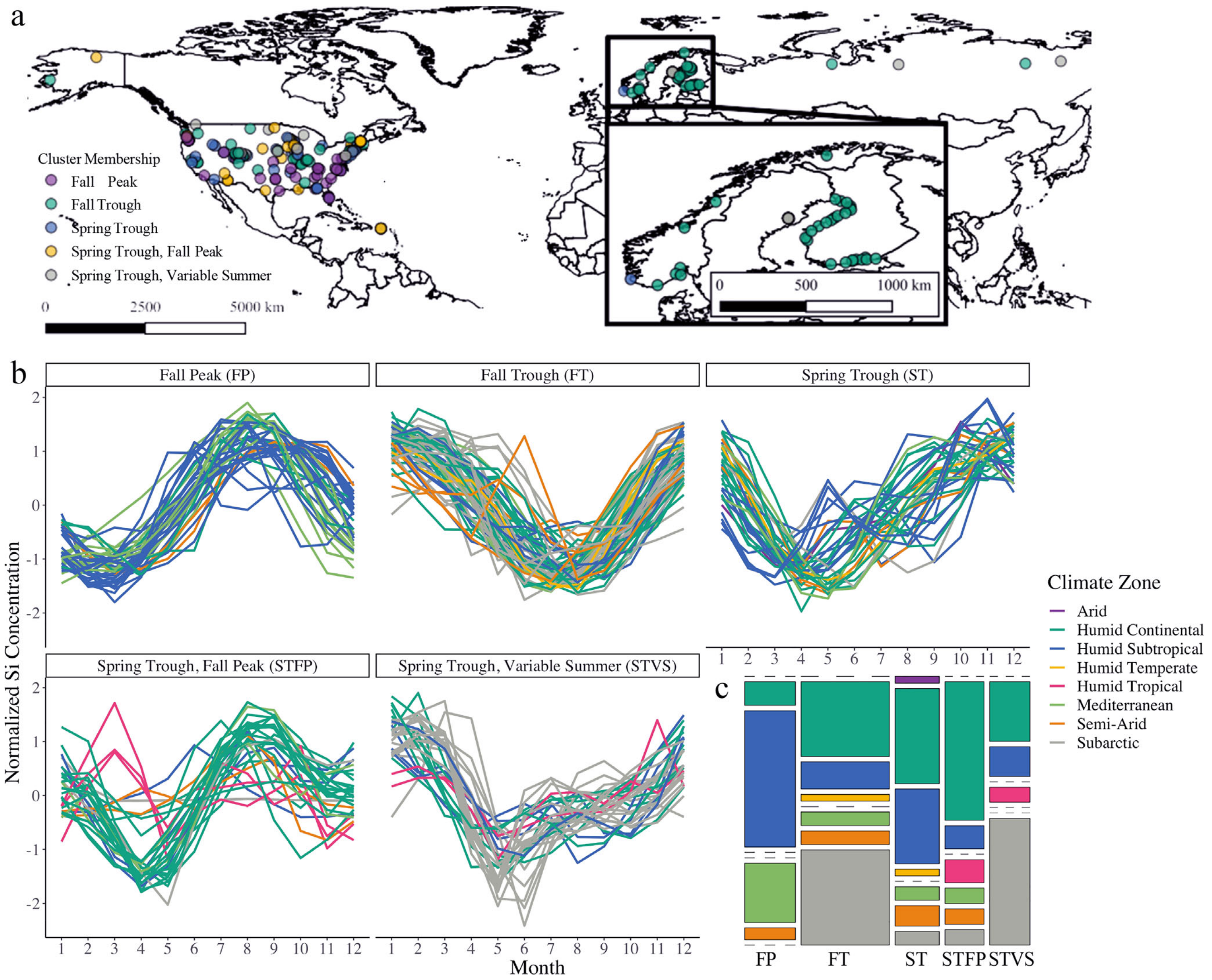

Fig. 2. (**a**) Map of sites, colored by cluster membership. (**b**) Five clusters formed from normalized average site regimes colored by climate, and (**c**) mosaic plot showing the distribution of climates across the five clusters. The width of each column of the mosaic plot indicates the relative number of sites in each cluster, and the colored bars within each column represent the proportion of each cluster that is made up of each climate.

discharge and drainage area are positively correlated with stream width (Frasson et al. 2019). We limited our analyses to perennial streams with at least 5 yr of Si measurements and continuous streamflow (Text S1).

Clustering of Si concentration

We used the weighted regressions on time, discharge, and season (WRTDS) model (Hirsch et al. 2010) to estimate flow normalized (FN) Si concentrations at each site (Text S1). Daily FN concentrations were aggregated to create monthly FN Si concentrations. WRTDS model performance was evaluated by examining the flux bias statistic and the relationship between measured and modeled Si concentrations on all sampled days (Hirsch and De Cicco 2015) (Fig. S3).

To establish distinct Si regimes, we *z*-score normalized average monthly FN Si concentrations for each stream (i.e., one time series per stream) and performed a clustering analysis on these time series. We used dynamic time warping (DTW) to quantify the distance between average Si concentration curves for all streams in the dataset (i.e., each stream's time series was compared to every other stream's time series). DTW allows time series that do not align 1:1 in time but have similar shapes to be clustered together (refer to Sakoe and Chiba 1978 for details). We allowed time series to vary by $+/-$ 1 month around each time step to calculate their DTW distance (i.e., warping windowing of 1 month; Ratanamahatana and Keogh 2005) and clustered the sites using a partitional clustering algorithm with a prototyping function that iteratively refines cluster membership until convergence criteria are met (i.e., DTW barycenter averaging; Petitjean et al. 2011). We tested 2–15 total clusters (Text S2).

Stability analysis

To evaluate variability in regime membership within a given site, we generated regimes for each stream for every year over its period of record. These stream-year time series were then assigned to a cluster group based on the smallest DTW distance between the time series and the centroid of the clusters generated above (Text S2).

We developed a stability metric (S) to evaluate variability in regime membership within a given site. S can be broken down into two metrics: 1) how often a site deviated from its modal cluster over its period of record (S_T; time stability) and 2) how many different clusters a site belonged to over its period of record (S_C; cluster stability). Time and cluster stability provide different insights into the controls on Si regime at a given site. For example, we would expect different processes to control regime stability in a site that switches between two clusters over its period of record compared to a site that switches between all five clusters, even if they have similar values of time stability. S_T can be calculated as:

$$S_T = \frac{y - y_{\text{in}}}{y} \quad (1)$$

where y is the number of years in the period of record and y_{in} is the number of years where the annual regime is the same as the site's modal regime. We determined the modal cluster for each site based on its stream-year cluster membership. S_T varies between 0 (most stable) and 1 (least stable). S_C can be calculated as:

$$S_C = 1 + \frac{C - C_S}{C} \quad (2)$$

where C is the number of clusters and C_S is the number of clusters a given site belongs to over its period of record. S_C varies between 1 (least stable) and 1.8 (most stable). These metrics are combined to calculate overall stability (S):

$$S = 1 - \frac{S_T}{S_C} \quad (3)$$

Overall stability ranges from 0 (least stable) to 1 (most stable). Differences in stability between climate zones and clusters were assessed using a one-way analysis of variance (ANOVA) test followed by the Tukey honestly significant difference (HSD) test at a 95% confidence level.

Drivers

We evaluated whether climate, Si concentration, discharge, and concentration–discharge (CQ) behavior explained cluster membership and stability. We classified sites into Koeppen-Geiger subgroup climate zones (hereafter referred to as climates) using the *kgc* R package (Bryant et al. 2017) (Table S2). Si concentrations and discharge were averaged across all available data into a median value for each stream.

We evaluated the CQ relationship at each site using log $C - \log Q$ slope (Eq. 4; Wymore et al. 2023). We calculated CQ slope from the raw concentration and discharge data. CQ relationships were analyzed using:

$$C = aQ^b \quad (4)$$

where a is a coefficient with units of concentration and b is an exponent that represents the slope of the log $C - \log Q$ relationship. Three dominant relationships can be inferred by the log $C - \log Q$ slope (Godsey et al. 2009): 1) chemostatic–insensitive relationship between C and Q (i.e., $b = 0$); 2) mobilization–positive relationship between C and Q (i.e., $b > 0.1$); and 3) dilution–negative relationship between C and Q (i.e., $b < 0.1$). CQ relationships can also be characterized as the ratio of the coefficients of variation (CV) of concentration and discharge (Eq. 5) (Thompson et al. 2011; Sullivan et al. 2019), where CV is defined as the standard deviation (σ) normalized by its mean (μ):

$$\frac{\mathrm{CV}_c}{\mathrm{CV}_Q} = \frac{\mu_Q \sigma_C}{\mu_C \sigma_Q} \tag{5}$$

CVs can be interpreted as chemostatic or chemodynamic behavior when streams exhibit low ($\mathrm{CV}_c/\mathrm{CV}_q \ll 1$) or large concentration variability ($\mathrm{CV}_c/\mathrm{CV}_q \geq 1$), respectively.

Results

Si regime clusters

We found five distinct cluster shapes that best explained the variability in Si concentration patterns (Fig. 2b) (Table S3). The cluster shapes were characterized by the timing of their minimum and maximum in the Northern Hemisphere: 1) fall peak, 2) fall trough, 3) spring trough, 4) spring trough-fall peak, and 5) spring trough-variable summer. The fall trough cluster contained the largest number of sites (68), whereas all other clusters contained between 30 and 40 sites. All clusters contained sites from at least four climates, and five of eight climates were found in at least three different clusters (Table S4).

Stability of cluster membership

There was a wide range (0.39–1.0) in overall cluster stability (S) across streams, and few significant differences in S between climate and clusters. The humid tropical climate was least stable (mean $S = 0.66$), whereas the Mediterranean, humid temperate, and subarctic climates were most stable ($S > 0.9$) (Fig. 3c,d). The fall trough cluster was most stable (mean $S = 0.93$), and the spring trough-variable summer cluster was least stable ($S = 0.80$). In general, clusters with spring drawdown behavior had lower S than those without spring drawdowns.

Association of cluster membership and stability with climate, discharge, and source-transport behavior

To identify drivers of cluster membership and stability, we assessed their relationships with climate, discharge, Si concentration, and CQ behavior. We found few significant differences in median Si concentration median Q among clusters (Fig. S1, Fig. S2a,b). We found no significant differentiation of CQ slope among clusters, and few significant differences in CVc/CVq values were found (Fig. S2c,d). All clusters exhibited a range of dilution, chemostatic, and mobilization behavior, with the strongest dilution observed in spring trough and fall trough clusters, and the strongest mobilization observed in fall trough and spring trough-variable summer clusters (Fig. 4). Although little direct relationship was found between climate and cluster, we did observe that climate emerged as a possible control of CQ behavior within a given cluster (Fig. 4).

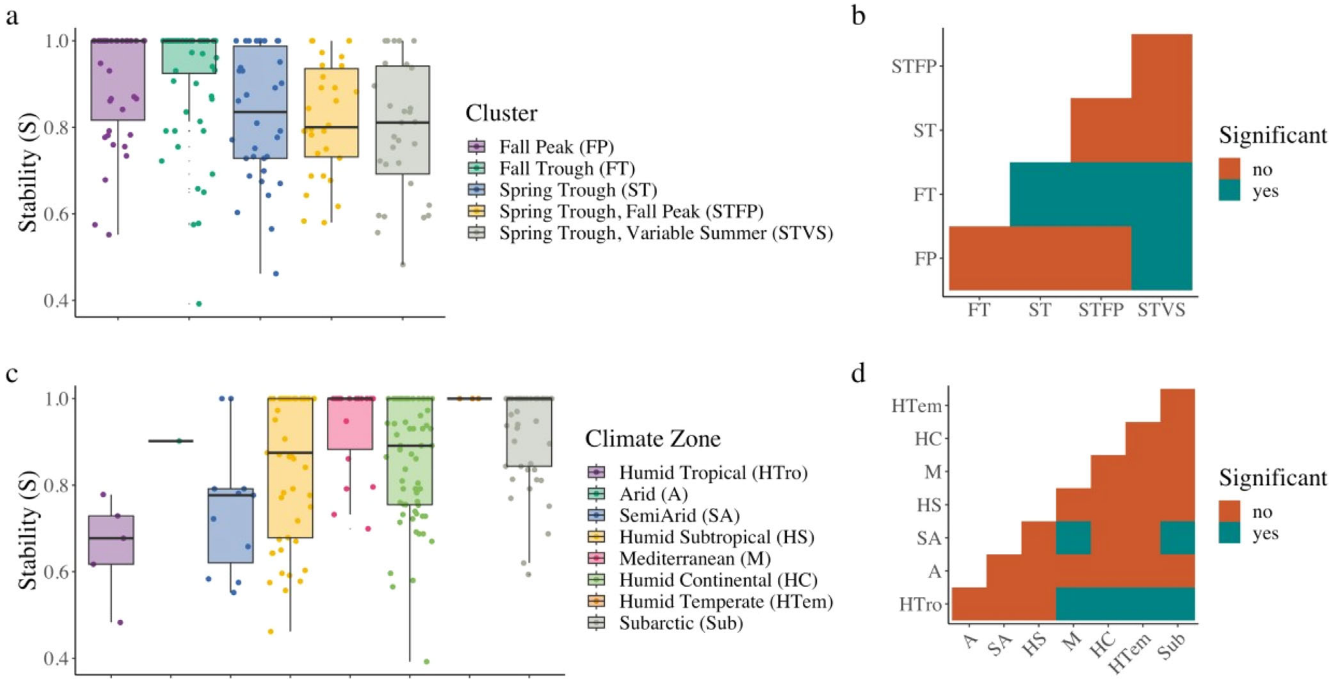

Fig. 3. Overall stability (S) by cluster (**a**) and climate (**c**). Stability ranges between 0 and 1, where a value of 1 means that, for a given site, the seasonality curve was in the same cluster over its period of record. Climates are plotted in order of high to low mean annual temperature. Lower and upper lines of boxplot box are quartile 1 and 3, respectively. The middle line is the median. Vertical lines indicate minimum and maximum, if < +/−1.5*interquartile range (IQR). Points outside +/−1.5*IQR are considered outliers and are plotted above/below vertical lines. Points show all sites associated with each cluster (a) or climate (c). Matrix of significant differences between clusters (**b**) and climates (**d**) (Tukey HSD, alpha = 0.05). Abbreviations in b and d are defined in legends of a and c.

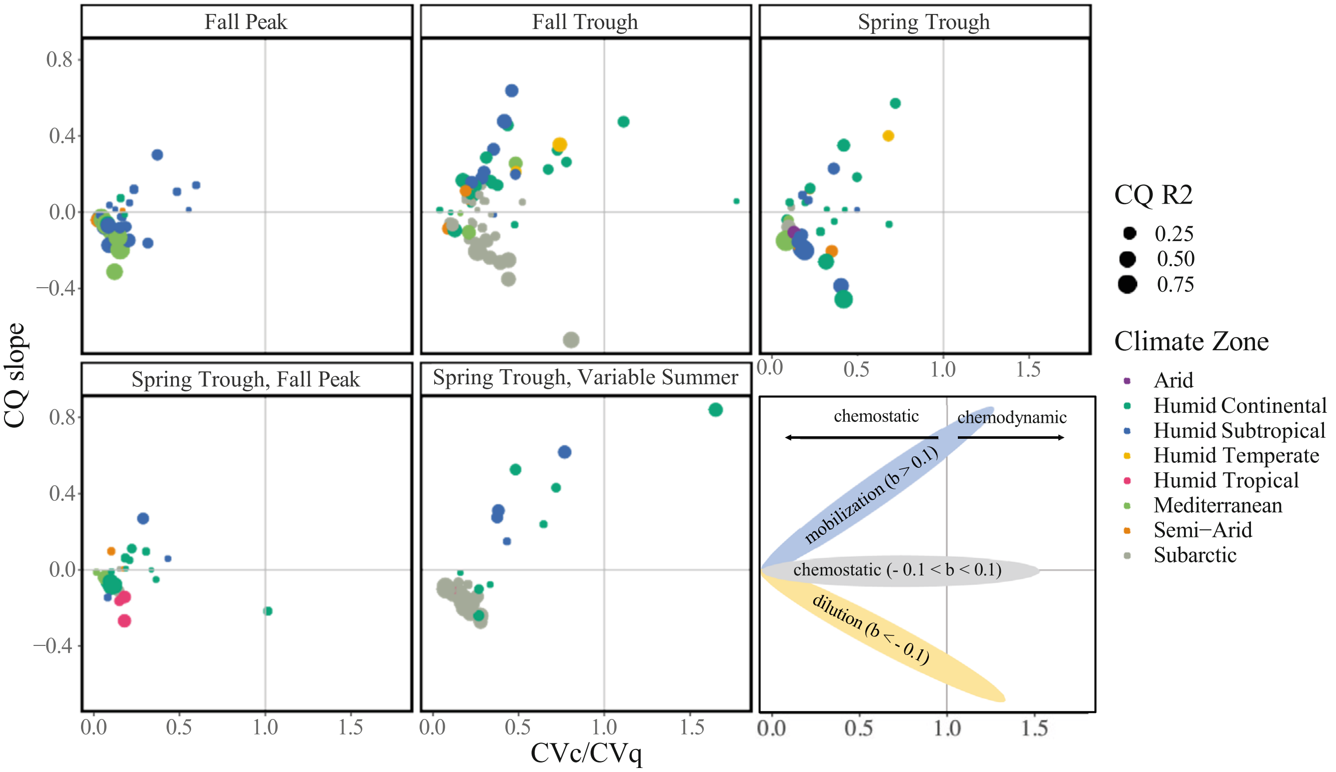

Fig. 4. CQ behavior (CQ slope on y-axis, CVc/CVq on x-axis) by cluster. Point color indicates climate, and size of point indicates coefficient of determination (R^2) of the CQ slope.

We found dilution behavior in the fall trough and spring trough-variable summer clusters were dominated by subarctic streams whereas dilution behavior in the fall peak cluster was dominated by Mediterranean streams. In the same clusters, mobilization behavior dominated humid continental and humid subtropical streams.

Discussion

Emergent regimes demonstrate variable Si seasonality across streams and over time

We found a great deal of variability in Si concentration regime across streams, with five main clusters capturing the range of behavior. Our conceptual model of the Si regime has been heavily informed by streams draining temperate forest basins, as those are systems where data availability is highest (Wall et al. 1998; Fulweiler and Nixon 2005; Carey and Fulweiler 2013). In these systems, spring declines in Si concentrations are driven primarily by diatom and terrestrial vegetation uptake, whereas fall peaks in Si concentrations occur due to lower biological activity and dissolution of fixed biogenic Si, a pattern that describes the spring trough cluster (Fig. 1a). Yet, our analysis of Si regimes across different biomes, including temperate forests, indicated that the humid continental climate (into which temperate forests fall) occurs in all five clusters indicating there is more regime variability even within a given climate than previous literature suggests. In addition, nearly 60% of streams showed some variability (stability < 1) in their regime, with over 20% of sites falling outside their modal behavior more than 25% of the time. Previous work describing biogeochemical regimes in rivers has focused primarily on describing “average conditions” (e.g., Bolotin et al. 2022); our work indicates that rivers exhibit multiple biogeochemical regimes. Our analyses indicate there is more variation in Si seasonality and stability than previously understood and point to a need to better understand intraannual and interannual Si dynamics across environmental gradients.

Climate and hydrochemical drivers of cluster membership and stability

We found that cluster membership was not clearly explained by a single factor. Clusters were comprised from sites representing at least four different climates (Table S4), and distributions of median discharge and Si concentration were similar among clusters (Fig. S1). All five clusters showed dilution and chemostatic CQ behavior similar to the variability reported in the literature (e.g., Godsey et al. 2009; Carey et al. 2020), but we also observed mobilization behavior, which has been less frequently reported. To date Si mobilization behavior has been linked to agriculture during high flows that increase connectivity between the landscape and stream (Sethna et al. 2022), which may explain the mobilization behavior observed at some of the analyzed sites. In contrast, we infer that snowmelt and distinct wet–dry seasonal cycles may drive the dilution behavior observed in subarctic and Mediterranean streams (Fig. 4). This indicates that although Si CQ may be related to climate and land use, it spans clusters indicating many CQ behaviors can give rise to similar regimes.

We hypothesize that differences among regimes likely arise from complex interactions between hydrologic and biologic processes and intraannual variability in solute transport behavior (Fig. 5). In diluting systems, spring troughs may be controlled by snowmelt (Fig. 5c–e; Carey et al. 2020), whereas fall peaks may be controlled by Si-rich baseflow (Fig. 5a,d; Benettin et al. 2015). However, in streams where winter flows are groundwater dominated, Si-rich baseflow may lead to a winter peak (Fig. 5b,c,e; Brooks et al. 2021). In contrast, in mobilizing streams peaks and troughs may arise due to variability in Si transport during the wet and dry season (Fig. 5a–c,e; Wollheim et al. 2018). Seasonal patterns in streams that exhibit chemostatic behavior may be more controlled by biologic processes, which, like hydrologic processes, can exhibit variable timing. Vegetative uptake of Si occurs during the growing season but can vary in timing and magnitude among species (Fig. 5c,d; Epstein 1994), and algal blooms can occur throughout the spring and summer (Fig. 5b–e; Wall et al. 1998). These controls on Si concentrations can co-occur, leading to exaggeration or dampening of individual signals.

When examining drivers of stability, we found that regimes characterized by a spring trough generally had lower stability. Many studies have noted that climate change leads to earlier onset of the growing season (e.g., Sommer and Lengfellner 2008; Monahan et al. 2016) and increased variability in the timing of spring onset (Menzel et al. 2006). Changes in the timing or rate of Si drawdown, or variability in summer and fall seasonality, may lead to movement between spring drawdown regimes and therefore lower stability. For example, a site with consistent snow melt pulse but variable summer Si uptake may fluctuate between spring trough and spring trough-variable summer. Understanding stability is important because predicting the timing of Si delivery to downstream communities may be more difficult in sites with unstable behavior. Our work indicates that the fall peak

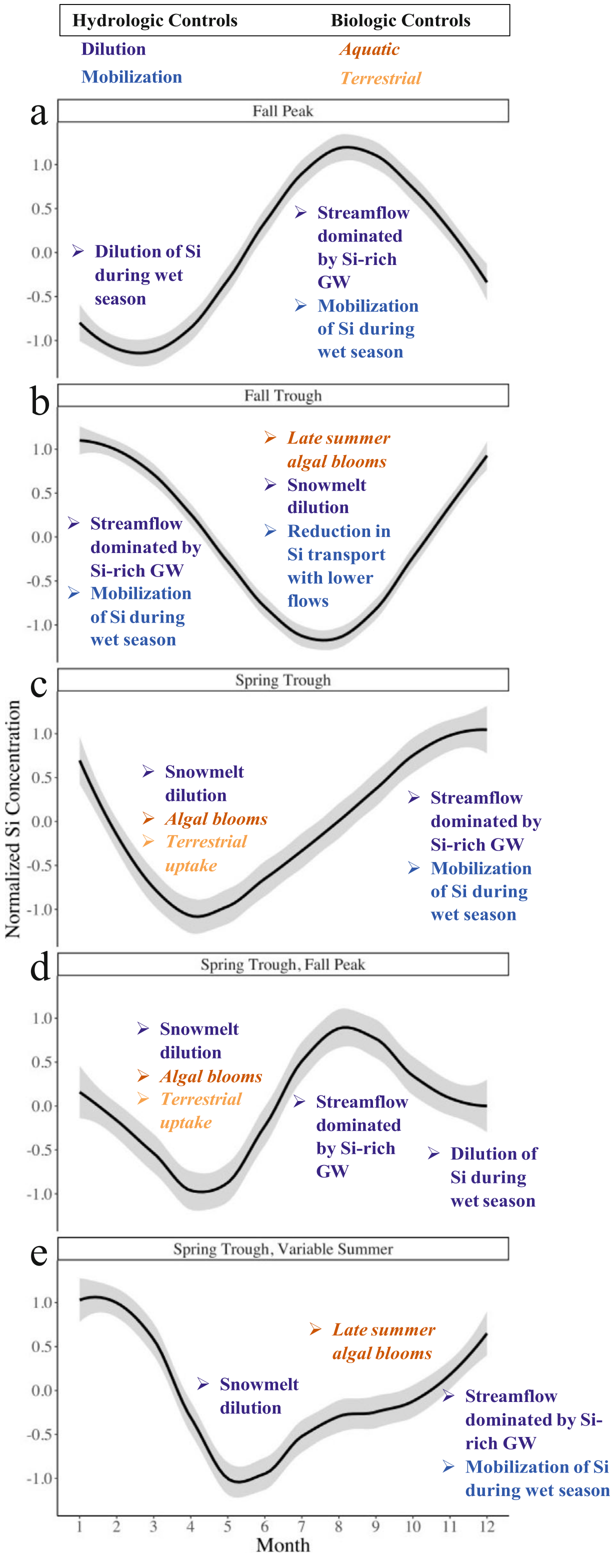

Fig. 5. Conceptual model of potential processes driving the patterns of the five Si regimes we observed. Average behaviors of all site seasonality curves are shown in black. Gray shading around the black lines represent error around the average regime shape (99% confidence interval). Non-italicized, blue text represents hydrologic processes that control Si concentrations, where dark blue represents dilution driven processes and royal blue represents mobilization driven processes. Italicized, orange text represents biologic processes that control Si concentrations, where light orange represent terrestrial processes and dark orange are aquatic processes. All sites are reflective of Northern Hemisphere seasonality.

and fall trough clusters and Mediterranean, subarctic, and humid temperate climates will be most consistent in Si export timing, whereas spring trough clusters and humid tropical or semiarid climates may exhibit more variable export timing.

Implications and limitations

Stability may be interpreted as an indicator of ecosystem resilience (Holling 1973), where sites with more stable regimes may be considered more resilient (i.e., able to withstand perturbations). Our work indicates that spring trough sites are less stable, possibly reflecting the impact of climate change on spring snowmelt and Si uptake processes. We observed that some sites show systematic shifts from one regime to another (e.g., directional), whereas other sites varied between all five regimes (e.g., chaotic). We hypothesize that these two behaviors should be interpreted differently. Sites that exhibit more directional instability (i.e., shift from one regime to another) may be interpreted as being driven by mechanistic processes (e.g., reduction in groundwater input, earlier snowmelt) (Spence et al. 2015; Foks et al. 2018; Zhi et al. 2020), whereas sites with chaotic instability (i.e., shift randomly among many regimes) may suggest that systems have weaker internal feedback mechanisms and thus shift rapidly in response to changes in external drivers (Dent et al. 2002), such as variable onset of Si uptake (Menzel et al. 2006), weather patterns (i.e., floods and droughts; Greenwood and Eimers 2023), or variability in stream-release schedules (Sawyer et al. 2009). Future work should be done to evaluate where directional and chaotic instability occur and evaluate mechanistic drivers of directional shifts.

Four additional considerations should be made to better understand Si regime behavior and its relationship to ecosystem resilience. First, regimes should be evaluated for ecological relevance. About 5% of our sites had an annual CVc < 0.1, indicating that variability in Si concentration was low (Fig. S5). At these sites, regimes may reflect amplified differences between the minimum and maximum Si concentrations due to *z*-score normalization, and therefore may not be ecologically significant. Second, Si regimes need to be related to other controlling factors including basin characteristics (e.g., basin slope and reservoir dynamics), climate (e.g., precipitation and temperature), and light availability. Third, processes that explain the behavior of Si regimes may be influenced by other nutrient cycles; thus, examining many nutrient regimes in tandem may be key to predicting aquatic productivity regimes and how they shift over time. Finally, the data used in this work represent streams primarily from North America and Europe, which are estimated to deliver only 16% of total global Si export to oceans (Dürr et al. 2011). Expanding our study of underrepresented regions and climates may elucidate other Si regimes not captured in this analysis.

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