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Long-Term Changes in Concentration and Yield of Riverine Dissolved Silicon From the Poles to the Tropics

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Key Points:

- Dissolved silicon concentration and yield changed over time in rivers across biomes
- Watershed biogeochemistry played an equal or greater role than river flow regimes in driving these changes
- Long-term changes in dissolved silicon showed seasonal differences in timing and magnitude across biomes

Supporting Information:

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

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Abstract

Riverine exports of silicon (Si) influence global carbon cycling through the growth of marine diatoms, which account for ∼25% of global primary production. Climate change will likely alter river Si exports in biome-specific ways due to interacting shifts in chemical weathering rates, hydrologic connectivity, and metabolic processes in aquatic and terrestrial systems. Nonetheless, factors driving long-term changes in Si exports remain unexplored at local, regional, and global scales. We evaluated how concentrations and yields of dissolved Si (DSi) changed over the last several decades of rapid climate warming using long-term data sets from 60 rivers and streams spanning the globe (e.g., Antarctic, tropical, temperate, boreal, alpine, Arctic systems). We show that widespread changes in river DSi concentration and yield have occurred, with the most substantial shifts occurring in alpine and polar regions. The magnitude and direction of trends varied within and among biomes, were most strongly associated with differences in land cover, and were often independent of changes in river discharge. These findings indicate that there are likely diverse mechanisms driving change in river Si biogeochemistry that span the land-water interface, which may include glacial melt, changes in terrestrial vegetation, and river productivity. Finally, trends were often stronger in months outside of the growing season, particularly in temperate and boreal systems, demonstrating a potentially important role of shifting seasonality for the flux of Si from rivers. Our results have implications for the timing and magnitude of silica processing in rivers and its delivery to global oceans.

Plain Language Summary

Silicon (Si) is an important nutrient for algae in freshwater and marine ecosystems and plays a fundamental role in the global carbon cycle. Dissolved Si (DSi), the bio-available form, is primarily derived from rock weathering, although many biogeochemical and hydrologic processes occurring across the land-ocean continuum control the flux of Si to coastal systems. Rivers are the main supplier of Si to the global oceans, with the flux often assumed to be unperturbed by human activities. Here, we present the first examination of multi-decadal shifts in river DSi concentrations and loads, synthesizing results from 60 sites that span nine biome types. We found widespread evidence for change in river DSi concentrations and loads in recent decades, with the largest increases occurring in alpine and polar regions. Changes were associated largely with shifts in watershed processing of DSi rather than changes in river flow regimes. The timing and magnitude of change varied according to the seasonality of temperature and precipitation across biomes. These results indicate that DSi concentration and loads are shifting over decadal timescales and are senstive to changing phenology, climate, and land use across multiple biomes.

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1. Introduction

Fluvial ecosystems transport and transform material along the land-ocean continuum, including weathering products that play critical roles in biogeochemical cycles. In the case of silicon (Si), a major weathering product, the global network of streams and rivers delivers >80% of annual Si loads to marine ecosystems (Tréguer & De La Rocha, 2013). This annual flux of Si drives global carbon (C) cycling by supporting marine diatom growth. Marine diatoms account for roughly 50% of net primary productivity in the ocean (Rousseaux & Gregg, 2013) and ~40% of the C deposited in marine benthos (Buesseler, 1998; Tréguer et al., 1995, 2018). Limitation of Si in coastal and freshwater ecosystems is typically defined by its ratio with nitrogen (N) and phosphorus (P) (Si: $N < 1$ and Si: $P < 16$), which can lead to a shift in phytoplankton species assemblages where non-siliceous species tend to outcompete diatoms (Anderson et al., 2002; Conley et al., 1993; Officer & Ryther, 1980). Such shifts in the autotrophic community have repercussions up the food chain, often with deleterious effects on marine and freshwater ecosystems. Non-siliceous algae tend to be a lower quality food source, export less C to deeper waters, and are more often associated with harmful algal blooms compared to diatoms (Guo et al., 2016; Turner et al., 2008; Wurtsbaugh et al., 2019). As such, Si supplies in marine and freshwater ecosystems exert global-scale controls on aquatic ecosystem function and C cycling.

The amount of Si exported by rivers is dictated by a variety of biogeochemical and hydrologic factors (Figure 1; Cornelis et al., 2010) operating across multiple time scales ranging from 10^0 to 10^6 years. Due to the abundance of mineral Si in the lithosphere (in the form of silicon dioxide (SiO_2); Meybeck et al., 1988; West et al., 2005; White & Blum, 1995), chemical weathering is a first order control on fluxes of Si from land to sea. The mobilization of this lithogenic Si is further influenced by regional erosion rates, basin slope, streamflow, flow path distribution, and the nature of the pedogenic pool (Asano et al., 2003; Frey et al., 2007; Gaillardet et al., 1999; Hilley & Porder, 2008; Meybeck et al., 1988). More precipitation of secondary clay minerals will result in greater Si retention along the land-sea continuum, altering rates of export (Cornelis et al., 2010). Terrestrial vegetation also regulates Si availability and flux, operating as both a source and sink of Si (Alexandre et al., 1997; Carey & Fulweiler, 2012a; Conley, 2002; Cornelis et al., 2011). Vegetative uptake has been estimated at 83 Tmol Si yr^{-1}, or roughly one-third of the total Si taken up by diatoms (Carey & Fulweiler, 2012b). Similar to diatoms, terrestrial vegetation incorporates Si into tissue, forming biogenic Si (BSi). Rates of plant Si uptake vary greatly across species (Epstein, 1994, 1999), resulting in a large degree of spatial heterogeneity in the role terrestrial plant communities play in modulating Si exports resulting from differences in land cover types within and across biomes (Carey & Fulweiler, 2012b; Conley, 2002; Cornelis et al., 2010). Terrestrial vegetation can also serve as a source of Si through the production of acidic root exudates that stimulate silicate weathering and dissolution, or through release of organic compounds that mobilize mineral Si (De Tombeur et al., 2021; Drever, 1994). Moreover, rates of BSi dissolution from plant derived organic matter degradation can be orders of magnitude faster than rates of mineral silicate weathering (Cornelis et al., 2011; Fraysse et al., 2009; Van Cappellen, 2003), resulting in a large fraction of Si being cycled through plant biomass before exported to river networks (Alexandre et al., 1997; Derry et al., 2005; Pokrovsky et al., 2013).

In-stream ecological processes, such as freshwater diatom blooms, also influence Si exports by drawing down river Si concentrations (Admiraal et al., 1990; Garnier et al., 1995). Other factors, such as N and P concentrations, light availability, invertebrate grazing, animal activity, and water residence time dictate in-stream primary productivity, diatom abundance, and Si fluxes (Conley et al., 2000; Fulweiler & Nixon, 2005; Humborg et al., 2000; Savoy & Harvey, 2021; Schoelynck et al., 2019). For example, increased water residence time in river basins can lead to the drawdown of Si through facilitating greater biotic uptake or sedimentation (Carey et al., 2019). Thus, hydro-physical and biogeochemical conditions within rivers themselves will dictate the flux of Si downstream.

Multiple processes across and within river basins exert control over fluxes of Si along the land-ocean continuum. How these processes are responding to long-term anthropogenic-driven perturbations across space and time, however, remains unknown. Compared to our knowledge of other major river solutes, such as C, N, or P (Griffiths et al., 2012; Holmes et al., 2000; Howarth, 2008; Raymond & Oh, 2007; Raymond et al., 2008), we have limited understanding of how global change is altering river Si fluxes, especially at the global scale. Regionally specific field investigations point towards potentially large shifts in river Si fluxes as a result of climate change. Increases in Si fluxes have been observed in streams of the high Arctic in areas with high rates of permafrost thaw and increased active layer depth, which was related to increases in rates of chemical weathering and soil-water interactions (Carey et al., 2020; Frey & McClelland, 2009). In temperate forested ecosystems,

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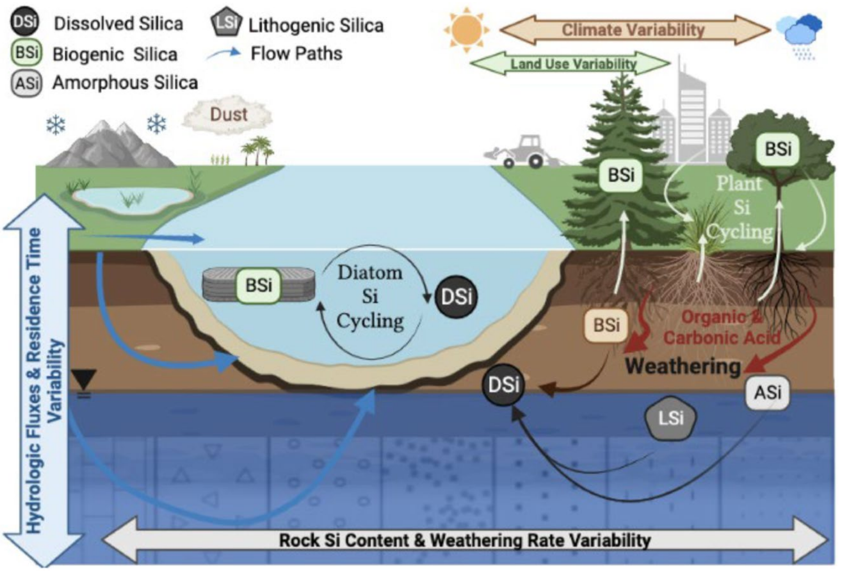

Figure 1. Conceptual figure of the terrestrial and aquatic controls on riverine dissolved silicon (DSi) concentrations and yields. Silica derived from geogenic processes occurs either through the breakdown of rock or soil at a specific site or through the input and eventual breakdown of dust. DSi can be taken up through biotic processes (e.g., vegetation or diatoms) or precipitated as amorphous silica. DSi is transported from land to streams across various hydrologic flow paths. The interaction of the processes and their control on DSi concentrations and fluxes is dependent on the type of underlying lithology, land cover, land use, and climate. Double headed arrows in the figure indicate a wide range of variability of a given process.

long-term warming experiments have resulted in faster internal Si cycling between vegetation and soil solution (Gewirtzman et al., 2019). Tighter terrestrial Si cycling thus reduces the Si available for hydrologic transport into adjacent river ecosystems and reduces net exports. Except for a handful of studies, it remains unclear how factors such as shifting land cover and climate conditions will alter Si flux from terrestrial to aquatic ecosystems across biomes over time.

To address this knowledge gap, we evaluated trends over 15–54 years in riverine dissolved Si (DSi) across 60 rivers representing distinct biomes ranging from tropical to polar latitudes. Specifically, we addressed the following questions: (a) Are river Si concentrations and yields changing over time across biomes?, (b) Are hydrometeorological, geological, or biogeochemical processes associated with changes in Si concentrations and yields across biomes? and (c) When during the year do we observe the greatest change in Si concentrations and yields within and across biomes? We hypothesized that we would observe the largest changes in streams located in the alpine and polar regions as a result of rapid warming, glacial melt and altered hydrologic cycles, and new substrate exposure via permafrost thaw. In addition, we hypothesized that seasonal changes would vary among biomes and highlight potential climate, terrestrial vegetation, or river-specific mechanisms driving change in DSi cycling. Finally, we hypothesized that shifts in the flow regime would be a major driver of changes in DSi concentration and yield.

2. Methods

2.1. Site Description and Data Synthesis

Our data set includes published or public data sets for 60 rivers from 11 long-term research areas, primarily located in North America, but including streams in the Caribbean, several large pan-Arctic rivers and small streams in eastern Antarctica (Figure 2; Tables S1 and S2 in Supporting Information S1). The streams and rivers in this compiled data set cover nine distinct biomes (Figure 2), which included Arctic tundra, alpine tundra, polar desert, the Arctic-boreal transition, temperate coniferous forest, temperate deciduous forest, temperate grassland, tropical rainforest, and tropical seasonal forest/savanna. The large Arctic-boreal transition rivers in this study were considered to represent a transitional but distinct biome type from the Arctic tundra. Although they have a large portion of their watersheds underlain by permafrost similar to the Arctic tundra stream, they drain large regions

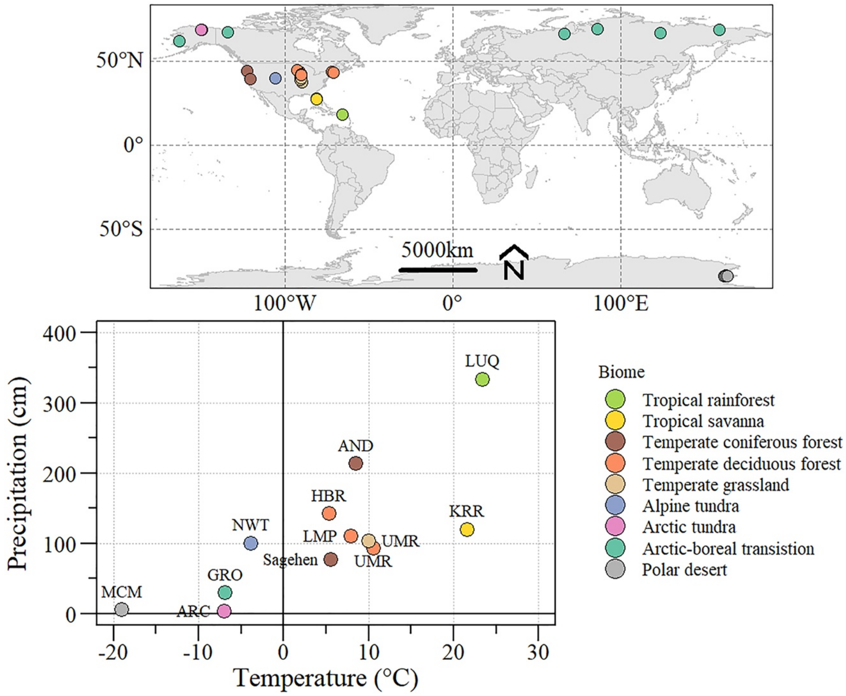

Figure 2. (Top panel) Location of rivers included in this study. Points are colored by biome. (Bottom panel) Mean annual temperature and precipitation for each of the long-term research stations from where river data were collected. AND = HJ Andrews Experimental Forest, ARC = Toolik Lake Arctic LTER, GRO = Great Rivers Observatory, HBR = Hubbard Brook Experimental Forest, KRR = Kissimmee River, LMP = Lamprey River Hydrologic Observatory, LUQ = Luquillo Experimental Forest, MCM = McMurdo Dry Valleys LTER, NWT = Niwot Ridge LTER, Sagehen = Sagehen Experimental Forest, UMR = Upper Mississippi River System.

that encompass both boreal forest and Arctic tundra. The data sets included in our study came from streams and rivers that ranged in size from small glacial headwater streams to some of the world's largest rivers (drainage area range: 0.1–2,950,000 km^2; mean annual discharge range 0.003–19,501 $m^3 s^{-1}$; Table S2 in Supporting Information S1) and have diverse land cover, land use and climate conditions (Figure 3). We subsequently refer to streams and rivers simply as "sites" to address this large range in their size.

We limited our analyses to data sets that had at least 15 years of continuous daily discharge data, were not missing more than 4 years of DSi concentration data, and included four or more observations per year that were distributed across seasons. The mean concentration record length was 26 years but ranged from 15 to 54 years except in the Arctic tundra where we included a stream with a shorter record because it was the only Arctic stream with available data (Table S2 in Supporting Information S1). Discharge records started several years prior to concentration records as required for the load modeling approach described below. Given the rarity of studies of long-term change in river Si, and that record length did not have a significant effect on the magnitude of the trend, all available data for each site were left in the analysis (Figure S1 in Supporting Information S1). These different time scales require different interpretation, so we have noted that where applicable throughout the text.

2.2. Evaluating Trends in Concentration and Flux

We used the Weighted Regression on Time, Discharge, and Season (WRTDS) model to estimate daily concentrations and fluxes over the period of record for each river (Hirsch et al., 2010) using the *Exploration and Graphics for RivEr Trends* package in R (Hirsch & De Cicco, 2015; Hirsch et al., 2018). The WRTDS model generates four values for evaluation: modeled DSi concentration and flux as well as flow-normalized concentration and flow-normalized flux. We subsequently calculated area-normalized DSi fluxes and flow-normalized fluxes (i.e., DSi yields) to enable a more direct comparison of how much DSi is exported per unit area across watersheds. Streamflow conditions can strongly influence annual mean concentration and flux; therefore, WRTDS generates "flow-normalized" concentrations and load by integrating the C-Q relationship over the observed

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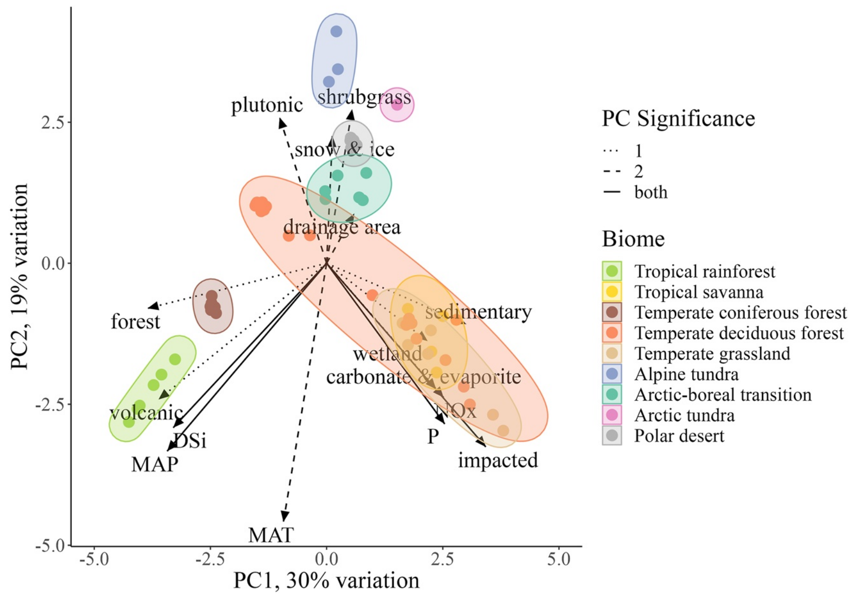

Figure 3. Influence of multiple watershed characteristics in differentiating sites. Principal components analysis shows the distribution of watershed characteristics that differentiated rivers included in the study. Only variables that are significantly related to one or both axes are shown. Watershed characteristics that were significantly related to the first axis (dotted line), second axis (dashed line), or both (solid line) are plotted. Points are individual rivers and ellipses encircle all rivers from a particular biome. MAP = mean annual precipitation, MAT = mean annual temperature, and P = phosphorus.

probability distribution of stream discharge over the period of record (Choquette et al., 2019). This approach removes the effect of year-to-year variations in streamflow, such as high- or low-streamflow conditions that are largely driven by variable weather and which can be particularly influential at the start or end of a record, to provide flow-normalized values that show gradual change over time (Hirsch et al., 2010; Rumsey et al., 2021). See Text S1 in Supporting Information S1 for more information on the WRTDS model and flow-normalization. When reporting overall mean DSi concentration and yield values for each site in the data set (Figure 4), we used WRTDS modeled concentration and yield rather than discrete measured observations as they better represent conditions over a full annual cycle. When evaluating long-term trends, we used flow-normalized DSi concentration and yield so that we could assess changes over time not due to year to year variability in discharge. We statistically evaluated trends in absolute and percent change in flow-normalized concentration and yield using the

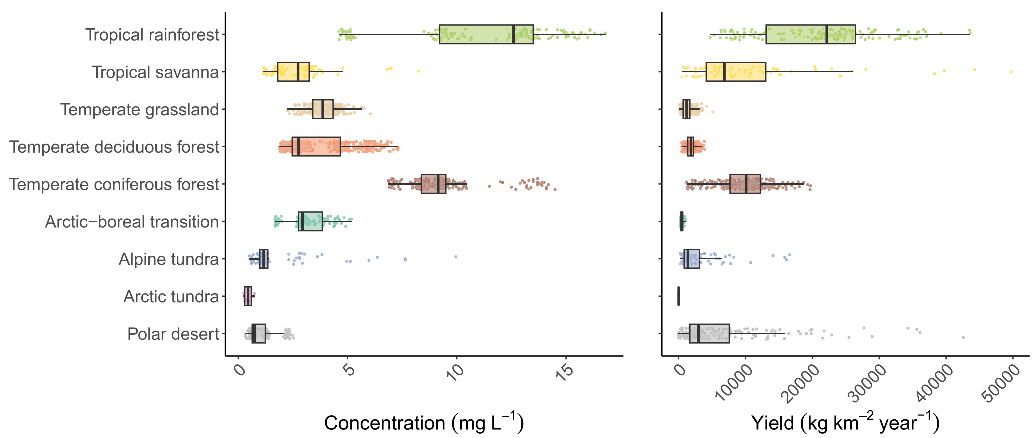

Figure 4. Distribution of annual mean dissolved silicon (DSi) concentrations and yields across biomes. Bold line in the center of the box is the median value; upper and lower ends of the boxes are 75th and 25th percentiles of the interquartile range, respectively; ends of the whiskers 1.5 times above the 75th percentile or below the 25th percentile of the interquartile range. Some site-year combinations from the polar desert streams had yields >50,000 kg km^{-2} yr^{-1}, but axis was shortened to better show variability across all biomes.

EGRETci package (Hirsch et al., 2015). EGRETci uses a flexible trend estimation approach that does not assume the trend to be linear and evaluates its likelihood and uncertainty through a block bootstrapping method (Hirsch et al., 2015). We normalized the trend estimates to the number of years in the period of record for each site. We report both absolute and percent change, as the latter allows us to consider the magnitude of change in concentration and yield on the same scale (Hirsch & De Cicco, 2015). We considered trends significant if they had 70% likelihood or greater (as described by Hirsch et al. (2015)). Finally, we statistically evaluated long-term trends in annual mean discharge using a Mann-Kendall non-parametric trend test (Helsel et al., 2020) and calculated Sen's slope, which is an estimate of the median slope among all pairs of sample points, using the *trend* package in R (Pohlert, 2018). Mann-Kendall trends were considered significant at a p-value of ≤ 0.05.

2.3. Potential Drivers of Change

An additional aim of this synthesis was parsing the potential long-term drivers of change in DSi concentrations and exports. To facilitate intra- and inter-biome comparisons in the drivers of DSi export, we used two approaches. First, we evaluated whether there were site-specific factors, independent of biome, that were associated with changing DSi concentration and yield, including watershed land use/land cover (LULC), lithology, drainage area, average climate (mean annual precipitation and mean annual temperature), and average river nutrient concentrations (inorganic N, P; refer to Text S1 in Supporting Information S1 for description of data used in these analysis). We compared five independent multiple regression models that included predictors from each of these five categories to assess their relative explanatory power for trends in DSi concentration and yield. We removed highly correlated predictors prior to their inclusion in each model and evaluated variable inflation factor (VIF) scores (variables with VIF > 4) were removed from the models and models were re-run. Predictors were transformed to meet normality assumptions and standardized prior to analysis to facilitate comparison of regression coefficients across predictors that varied greatly in scale. We compared models using AIC_c and report the adjusted coefficient of determination (R^2) of each model.

Second, we used an adaptation of the WRTDS model to assess whether changes in long-term concentration and yield resulted from a changing streamflow regime or shifts in watershed biogeochemical processing (Choquette et al., 2019; Murphy & Sprague, 2019; Rumsey et al., 2021). WRTDS generates this information by comparing two models, one in which the distribution of annual flows (i.e., the flow regime) is allowed to change over the period of record and the other in which it was held constant. WRTDS then estimates the portion of the overall trend explained by shifts in the flow regime alone (difference between the trends generated by the two models) versus proportion of the trend explained by changes in "watershed biogeochemical processes" (model 2; Rumsey et al., 2021). For instance, changes in concentration or yield mainly driven by changes in the flow regime (i.e., "flow regime trend") reflect shifts in the hydrologic system, such as changes in the quantity and timing of surface or groundwater flow. In contrast, trends driven by changes in watershed biogeochemistry (i.e., "biogeochemistry trend") reflect changes in DSi source dynamics (e.g., weathering rates, terrestrial uptake, river uptake) or management activities (Murphy & Sprague 2019; Rumsey et al., 2021). Although not completely independent, partitioning drivers into these broad conceptual categories provided a coarse estimate of the nature of the factors in the "hydrologic and source supply system" driving the trend in DSi (Choquette et al., 2019; Murphy & Sprague, 2019). Streamflow is often considered a central driver of changes in river DSi; thus, this approach allowed us to independently assess its relative role and whether its effect was additive or opposing from changes in source dynamics.

To quantify the relative role of changes in the streamflow regime versus biogeochemical processing in affecting concentration and yield trends, we assigned sites to these three broad categories using a ratio of the flow regime and biogeochemistry trend components: biogeochemistry-dominated, flow regime-dominated, or a mixture of both. To do so, we calculated a ratio of the absolute value of the two trend components: abs(flow regime trend)/abs(biogeochemistry trend). A ratio of 1 would mean that both components contributed equally to the trend. To evaluate which component dominated the trend, we set threshold ratios of <0.5 for trends dominated by biogeochemistry, >1.5 for trends dominated by the flow regime, and 0.5 to 1.5 as indicating a mixture of both. We also display all values on a continuous scale in Figure 7. Finally, we assessed whether the effect of the flow regime and biogeochemistry had additive or opposing effects on the overall trend using the trend direction information (e.g., positive effect of flow change but negative effect of biogeochemical change). For these analyses, we only considered sites that had significant changes in the long-term trend in concentration or yield.

2.4. Seasonality of Change

To quantify seasonal differences among sites and biomes, we used monthly mean temperature and precipitation data to calculate annual ranges and a seasonality index (Tian et al., 2016; Van Meter et al., 2020; Walsh & Lawler, 1981) (Table S3 in Supporting Information S1). More detailed methods on monthly temperature and precipitation data and calculation of the seasonality index are provided in Texts S2 and S3 of the Supporting Information S1, respectively. To evaluate how seasonal variation in the magnitude and direction of trends in concentration and yield aligned with these seasonal patterns across biomes, we estimated monthly long-term trends for each site using the non-parametric Sen's slope estimator (Helsel et al., 2020; *trend* package in R). Trends were considered significant at $p < 0.05$. We were not able to assess seasonal change in polar desert streams because they were only flowing December and January each year, so we excluded them from this analysis.

3. Results

The rivers in this synthesis represented a wide range of mean annual DSi concentrations and yields (Figure 4). The global mean concentration across all sites was 4.72 mg Si L^{-1} (median concentration = 3.22 mg Si L^{-1}) and ranged from 0.47 to 15.3 mg Si L^{-1}. The highest concentrations were observed in tropical rainforest streams in Puerto Rico and a coniferous forest catchment in California (Table S4 in Supporting Information S1). The tropical rainforest streams also exhibited the greatest range in concentration. The lowest concentrations were observed in polar desert and Arctic tundra streams, with similarly low variation in concentration. Mean annual yield across all sites was 6,136 kg Si yr^{-1} km^{-2} (median annual yield = 2,041 kg Si yr^{-1} km^{-2}) ranging from 18.0 to 47,000 kg Si yr^{-1} km^{-2}. The smallest yield was observed in a small Arctic tundra stream and the largest yields were observed in tropical savanna, tropical rainforest, and small polar desert streams in Antarctica. The greatest range in yield was exhibited by the tropical savanna and polar desert streams.

3.1. Long-Term Trends in Annual Mean Discharge

Changes over time in annual mean discharge were significant at eight sites (13%), all of which increased over time (Table S5 in Supporting Information S1). Where changes in discharge occurred, they did not necessarily change uniformly across all streams within a given region or biome. Specifically, annual mean discharge significantly increased at four polar desert sites, three temperate deciduous forest sites, and one tropical rainforest site. There were marginally significant upward trends ($p < 0.10$) in annual mean discharge at eight additional sites, which included one additional polar desert stream, one Arctic-boreal transition, one tropical savanna, and one temperate deciduous forest site.

3.2. Long-Term Trends in Concentration and Yield

We found significant changes in DSi concentration over time in 48 of 60 sites (80%), with changes ranging from −0.05 to 0.21 mg L^{-1} $year^{-1}$ (−1.5%–10.8% per year; Table 1, Figure 5). Sites where no significant change in concentration occurred were primarily in tropical rainforest streams and temperate coniferous forest streams (Figure 6). Of the sites with significant long-term changes in concentration, there was a nearly equal distribution of increases and decreases, but more sites had increasing ($n = 25$) than decreasing concentrations ($n = 23$; Figures 5 and 6). The most substantial increases in concentrations occurred at small headwater streams in polar and alpine sites, specifically the alpine and Arctic streams, which had increases ranging from 3.45% to 10.8% per year since the 1980s for alpine streams and during the early 2000s for the Arctic tundra stream (Figure 5). More modest increases in DSi concentrations were observed across a range of biomes, including temperate deciduous forest streams in the northeastern United States, tropical savanna sites, and sites in the temperate forest and grassland biomes in the upper midwestern United States. Decreases in concentration were distributed across biomes but most common among sites in the polar desert and Arctic-boreal transition biomes, with five of six Arctic-boreal rivers and four of eight polar desert streams showing significant decreases in concentration. Decreases were also common among temperate grassland sites in Midwestern US that had agricultural influence in their watersheds. Finally, although there were some general patterns in concentration change among biomes, only the alpine tundra biome had uniform trends among all sites within a single biome, indicating that trends within other biomes likely reflected complex local watershed factors in addition to long-term regional climate shifts.

Compared to concentration changes, a similar proportion of sites showed significant change in DSi yield over time ($n = 49$; 82% of sites). The mean change per year in yield among all rivers was 14.3 kg ha^{-1} yr^{-1} (range = −8

Table 1
Mean and Standard Deviation of Dissolved Silicon (DSi) Concentration and Yield Among All Sites (N) Within a Given Biome

Biome	*N*	Median ± SD concentration change (mg L^{-1})	Median ± SD concentration change (%)	Median ± SD yield change (kg km^{-2} y^{-1})	Median ± SD yield change (%)
Alpine tundra	3	0.71 ± 2.8	134.0 ± 95.1	654 ± 4,016	36.3 ± 58.6
Arctic tundra	1	0.45	166.0	13.7	121.63
Arctic-boreal transition	6	−0.26 ± 0.34	−8.4 ± 6.9	−21.2 ± 40.1	−2.9 ± 8.2
Polar desert	8	−0.06 ± 0.11	−6.1 ± 11.8	115 ± 1,571	4.3 ± 16.2
Temperate coniferous forest	8	0.05 ± 0.2	0.57 ± 2.2	−568 ± 719.4	−5.8 ± 7.7
Temperate deciduous forest	16	0.27 ± 0.33	7.9 ± 9.3	230 ± 206.7	16.5 ± 12.4
Temperate grassland	8	−0.39 ± 0.72	−9.1 ± 19.2	48.5 ± 137.7	5.1 ± 10.3
Tropical rainforest	6	−0.18 ± 0.41	−2.5 ± 3.1	426 ± 2,269	1.1 ± 8.9
Tropical savanna	4	0.06 ± 0.41	0.89 ± 17.2	490 ± 248.3	6.8 ± 7.6

Note. Reported as the absolute or percent (%) change in concentration or yield across the full period of record for each site. (mg L^{-1} = milligrams per liter; kg km^{-2} y^{-1} = kilograms of DSi per square kilometer per year).

7–330 kg DSi ha^{-1} yr^{-1}). Most sites had increasing (n = 37; 62% of sites) rather than decreasing DSi yield (n = 12; 20% of sites). The magnitude of percent (or relative) changes in DSi yield among biomes generally mirrored patterns in concentration, with the largest changes occurring in polar and alpine sites. The greatest relative increases in yield were observed in small alpine and Arctic streams (0.80%–7.33% per year), whereas

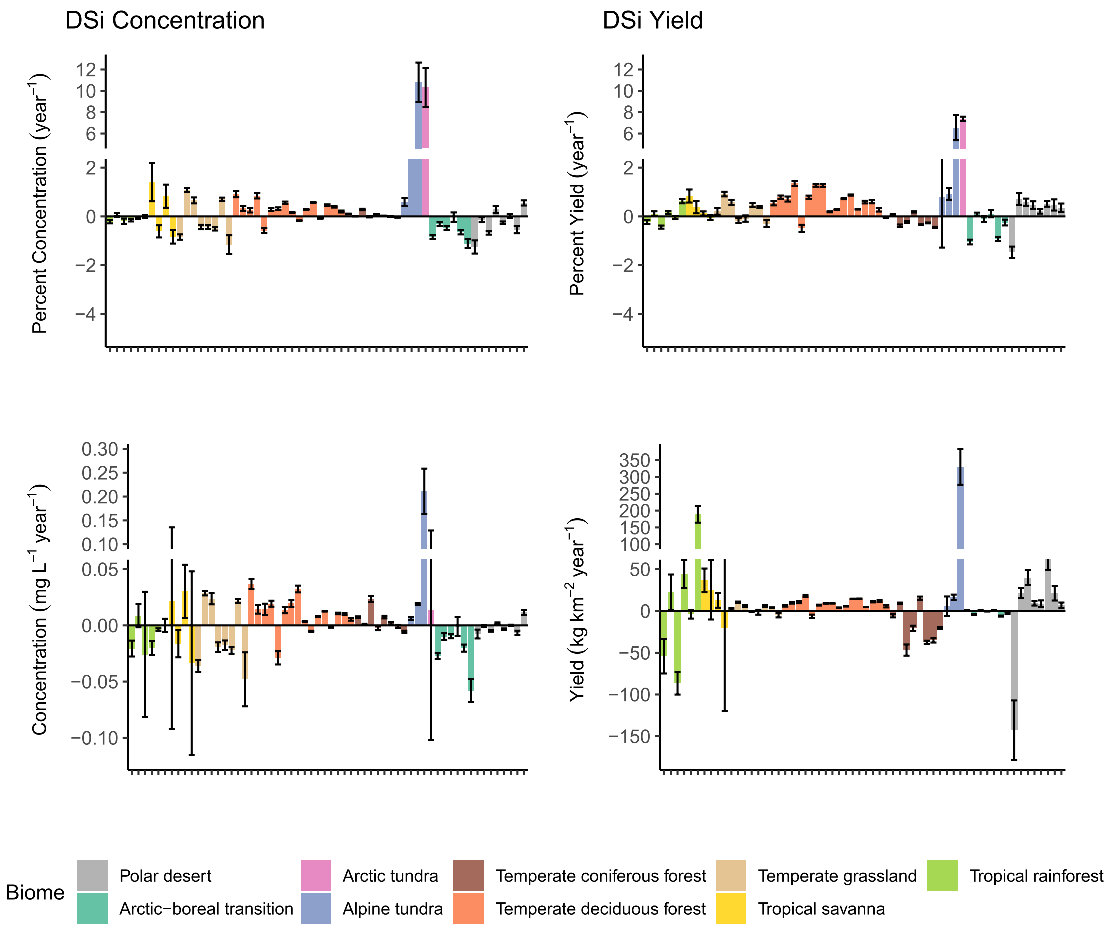

Figure 5. Changes in dissolved silicon (DSi) concentration and yield shown as (a) percent change in concentration per year, (b) percent change in yield per year, (c) absolute concentration change per year, and (d) absolute change per year. Bars are individual sites and are colored by biome. Error bars are 95% confidence intervals of bootstrapped trend estimates.

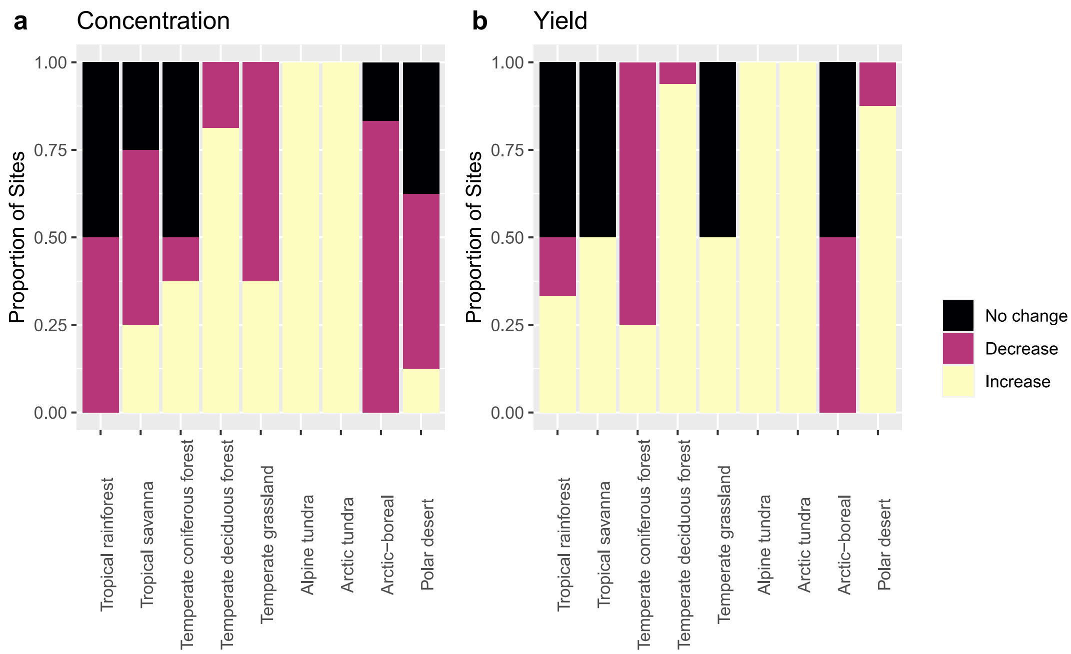

Figure 6. Proportion of sites with increasing, decreasing, and no change in dissolved silicon (DSi) (a) concentration and (b) yield by biome.

two Arctic-boreal rivers and one polar desert stream displayed the largest relative decreases in yield over time (−1.5% to −0.92% per year). Sites with no significant change in yield were mainly tropical rainforest and coniferous rainforest sites, but also included some temperate and tropical grassland sites. Patterns in absolute yield change differed somewhat from relative change, however, with large absolute yield increases occurring across a broader range of biomes. The greatest absolute yield increase was again at the highest elevation alpine tundra site, but the next greatest increases were observed in tropical rainforest and tropical savanna sites and the greatest absolute decreases occurred at tropical rainforest and temperate coniferous forest sites. Tropical rainforest and temperate coniferous forest had the smallest relative changes in yield over time but had the highest DSi concentrations among sites in our study (Figure 4), indicating that small changes in concentration in these high Si, high precipitation systems have important implications for DSi yields.

Finally, several sites had diverging trends in concentration and yield. For example, in polar desert streams, nearly uniformly increasing yields were observed, despite decreasing concentrations at 50% of sites. Such a response was due to increasing discharge at most of these sites (Table S5 in Supporting Information S1), although the concentration-discharge relationship decreased for most streams over time (Figure S3 in Supporting Information S1), indicating that processes affecting concentration decreases occurred predominantly under low flow conditions (Gooseff et al., 2017; Hirsch & De Cicco, 2015). Additionally, in coniferous forest streams, yields predominantly decreased, although most sites had either no change or upward trends in concentration. Given that there was no significant change in discharge at these sites (Table S5 in Supporting Information S1), this suggests that concentrations decreased proportionally more at higher flows.

3.3. Potential Drivers of Long-Term Change

LULC had the greatest effect on DSi trends across sites for both concentration ($R^2 = 0.42$) and yield ($R^2 = 0.30$; Table 2). When evaluating the effects of specific predictors included in the LULC model, percent shrubgrass and percent open water were the most influential variables (Table S6 in Supporting Information S1), with positive and negative effects on the trends, respectively. Percent forest cover had a significant but smaller negative effect on the trends in DSi, but percent watershed impact had no effect. After LULC, lithology was the next best model for both concentration and yield but did not explain much variation in DSi trends across sites in either case ($R^2 < 0.1$; Table 2).

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Table 2
Results of Multiple Regression Analyses Evaluating the Effects of Site Specific Variables on Trends in Dissolved Silicon (DSi) Concentration and Yield

Response variable	Category	Model terms	AIC_c	ΔAIC_c	R^2
Concentration					
	Land Use/Land Cover	Percent forest, shrubgrass, open water, impacted	223.8	0	0.42
	Lithology	Percent volcanic, sedimentary, carbonate, metamorphic, plutonic	251.2	27.4	0.08
	Geomorphology	Drainage area	251.9	28.1	0.01
	Climate	Mean annual temperature, mean annual precipitation, latitude	253.0	29.2	0.02
	Trophic status	phosphate, nitrate	254.2	30.4	−0.01
Yield					
	Land Use/Land Cover	Percent forest, shrubgrass, open water, impacted	188.8	0	0.30
	Lithology	Percent volcanic, sedimentary, carbonate, metamorphic, plutonic	206.9	18.1	0.07
	Geomorphology	Drainage area	207.3	18.5	0.00
	Trophic status	phosphate, nitrate	208.9	20.1	−0.02
	Climate	Mean annual temperature, mean annual precipitation, latitude	209.2	20.4	0.00

Note. Models for each category of variables were run individually. Model were compared via Akaike's Information Criterion (AICc) and the coefficient of determination (R^2). Land use/land cover and lithology variables are all percent of the watershed for each site.

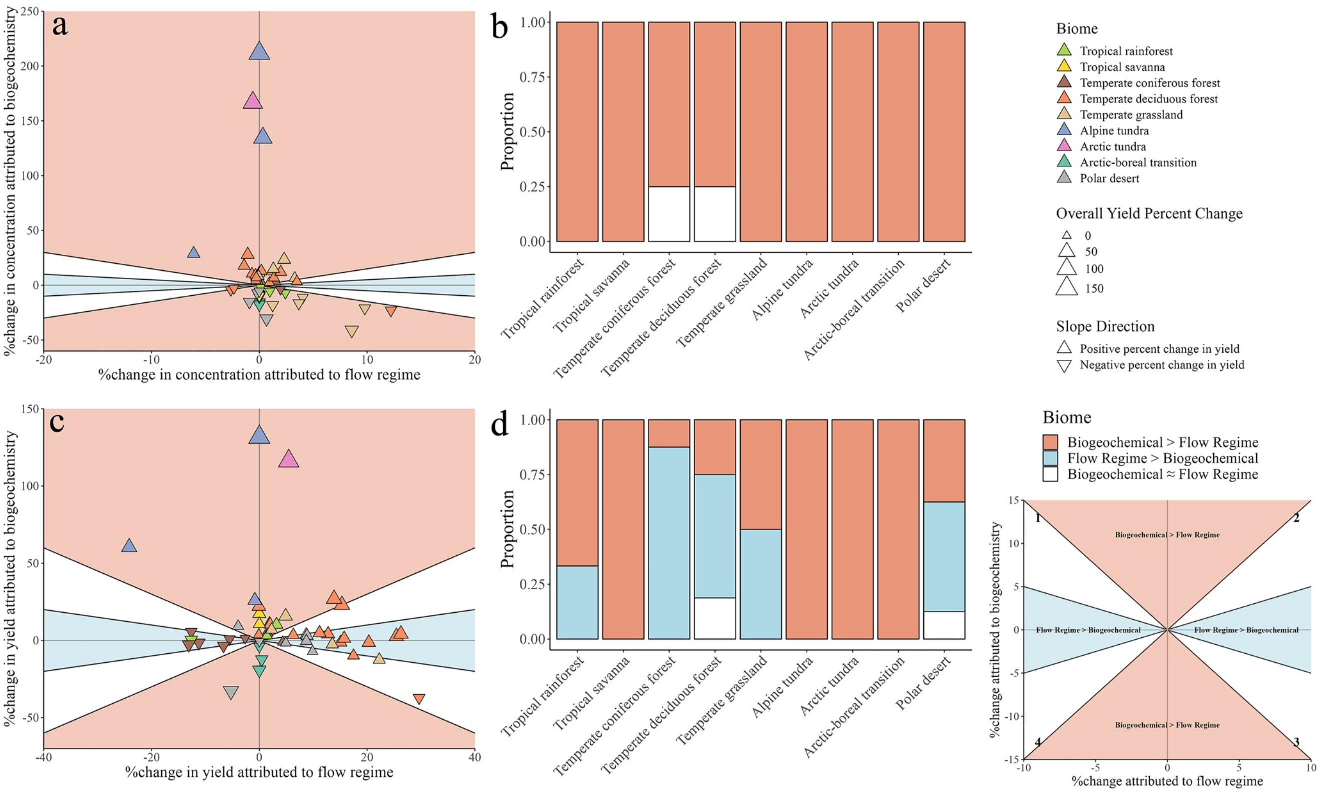

Figure 7. Proposed mechanisms for driving overall trends in dissolved silicon (DSi) in (a/b) concentration and (c/d) yield across all biomes and sites. The location of the points on the quadrant figures (a and c) indicates the proportional contribution of changes in watershed biogeochemical processing (position on *y*-axis) and the flow regime (position on *x*-axis) to the overall trend. Sites were assigned to categories based on the ratio of the proportional contribution of the flow regime to biogeochemistry to the overall trend. Blue color indicates a change in the flow regime > biogeochemistry (ratio > 1.5), orange indicates change in the biogeochemistry > flow regime (ratio < 0.5), and no color indicates change in the flow regime approximately equaled that of the biogeochemistry (0.5 < ratio < 1.5). Points are colored by biome, upward/downward triangles indicate the direction of the overall trend, and the size of the point indicates the percent change. Note that scales are different between *x* and *y* axes. Panels (b and d) show the proportion of rivers within each biome that fell into each of the categories. Only sites with significant overall trends in concentration or yield were included in this figure.

Results from the WRTDS model supported these findings, indicating that long-term change in DSi concentration was related more to watershed processes (changing watershed biogeochemistry) than a changing stream flow regime at most sites (Figure 7). Of sites with significant long-term changes in DSi concentration, 42 sites (88%) had a dominant effect of watershed biogeochemistry, zero sites had a dominance of a changing flow regime, and six sites (12%) had a mixture of both (Figures 7a and 7b). Only sites in temperate biomes had an influence of both biogeochemical and flow regime change on DSi concentration trends. Changing watershed biogeochemistry was the dominant component of the trend at all other sites, including all the sites in alpine and polar regions (Arctic tundra, Arctic-boreal transition, polar desert, and alpine tundra) and all tropical sites (ratio < 0.5; Figures 7a and 7d). More streams had opposing ($n = 23$, 55%) effects of watershed biogeochemistry and the flow regime than additive ($n = 18$, 43%) on the overall trend (note: percentages exclude streams where one component had zero contribution to the trend; see position of points across quadrants in Figure 7a). Of sites where overall concentration increased, all had a positive effect of watershed biogeochemical change on the trend, but 44% had a negative effect of a change in the flow regime, indicating the negative effect of the flow regime did not exceed the positive effect of changing watershed biogeochemistry. Similarly, at sites where overall concentration decreased, all had negative effects of watershed biogeochemical change. However, a larger percentage of these sites showed an opposing effect of the flow regime, with 74% of sites exhibiting a positive effect of the flow regime on the trend despite an overall decrease in concentration. Taken together, these results indicate that changing DSi concentrations were more sensitive to shifts in watershed biogeochemical and source dynamics than shifts in the hydrologic system alone. In other words, changes in hydrology were not able to overcome the influence of changing watershed biogeochemistry on long-term concentration changes.

For DSi yields, there was a more equal distribution between long-term changes that were driven by watershed biogeochemistry versus a changing flow regime (Figures 7b and 7d). Overall, changing watershed biogeochemistry drove DSi yield changes at 21 sites (43%), changing flow regime at 23 sites (47%), and a combination of watershed biogeochemistry and the flow regime resulted in DSi yield changes at 4 sites (10%; Figure 7d). Watershed biogeochemical change dominated DSi yield trends at alpine tundra, Arctic tundra, and Arctic-boreal transition sites, none of which had any influence of a changing flow regime. In contrast, flow regime change was the dominant component of DSi yield trends at most temperate coniferous and deciduous forest sites; all but five of the temperate sites in this study had either a dominant or combined effect of a changing flow regime on changes in DSi yield. In other biomes, the drivers of change were not as consistent among sites. Polar desert streams had a nearly equal mixture of sites where changes in DSi yields were dominated by watershed biogeochemistry ($n = 3$) or flow regime ($n = 4$) and tropical rainforest and savanna sites had sites in all three categories (changing yields due to biogeochemistry, flow regime, mixture). Finally, similarly to concentration, there was a nearly equal distribution of streams that had additive ($n = 23$; 53%) versus opposing ($n = 20$; 47%) effects of changing watershed biogeochemistry and flow regime on the overall DSi yield trend (note: percentages exclude streams where one component had zero contribution to the trend; see position of points across quadrants in Figure 7c). In contrast to concentration, additive or opposing effects were also nearly equally distributed among sites that had overall upward or downward trends.

3.4. Seasonal Trends in DSi by Biome

Seasonal signals were strong in both DSi concentration and yield changes over time, but the timing and magnitude varied among biomes (Figure 8). We observed three general patterns for monthly trends in DSi concentration—a shift in the direction of changes within the year (e.g., concentration increasing over time early in the year and decreasing over time late in the year), magnitude of change greatest during coldest months of the year, and magnitude of change greatest during the warmest-wettest months (see Figure S2 in Supporting Information S1 for absolute values of temperature and precipitation). First, sites where the direction of the trend in concentration changed during the year were generally in the warmest and wettest biomes, where seasonal temperature variation was smallest but wet and dry seasons were notable: the tropical rainforest, tropical savanna, and temperate coniferous forest biomes (Figure S2, Table S3 in Supporting Information S1). Tropical rainforest stream concentrations increased during the drier season (January–June) but decreased or remained stable during the wetter season (hurricane season; July–December). Tropical savanna sites showed an inverse pattern, with decreasing concentrations during the drier portions of the year (October–February/March) but increasing during the wetter months (April–September). Temperate coniferous forest sites had the strongest decreases at the end of the wet season, but then showed either upward or no trends into the dry and early wet season (June–December).

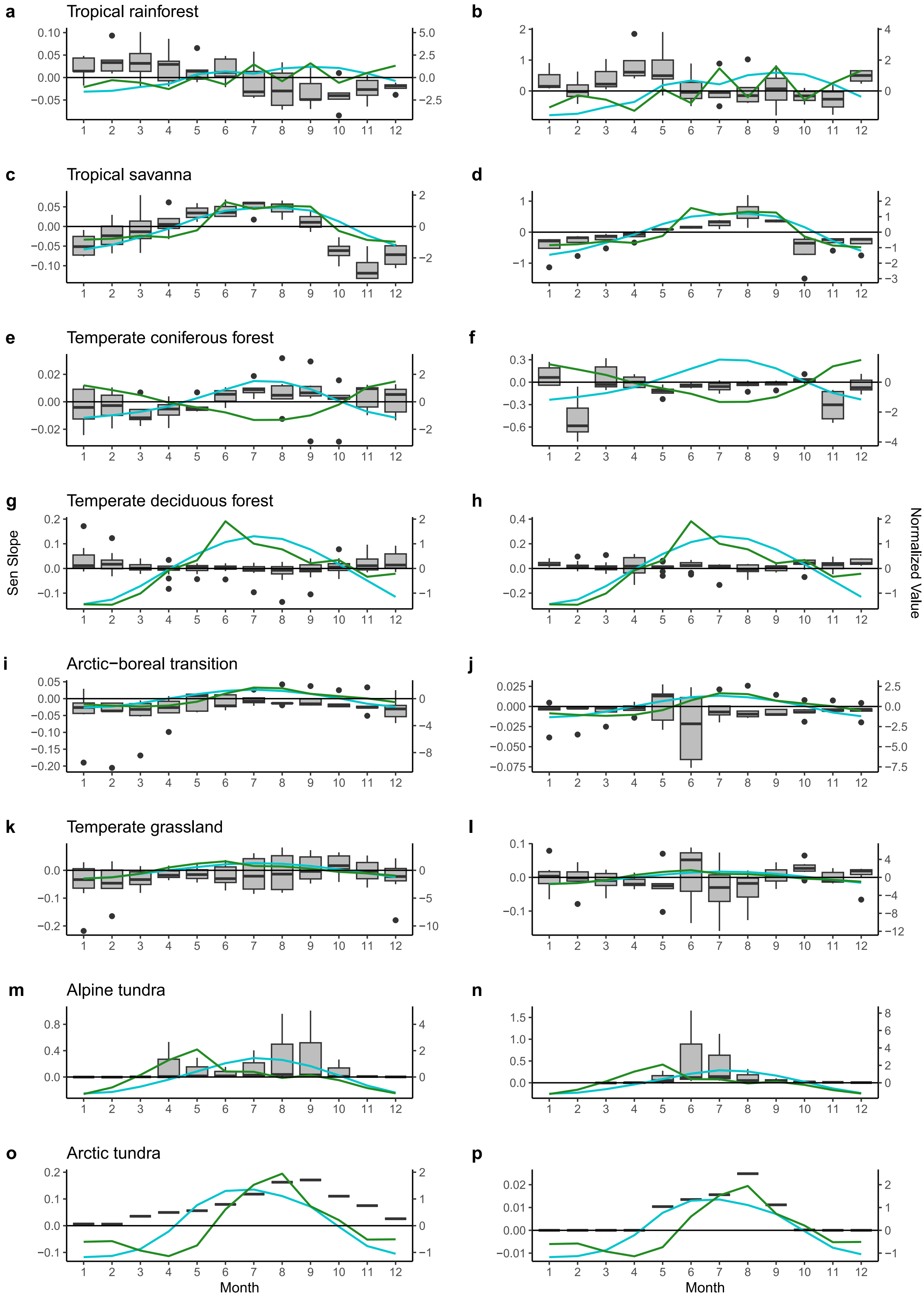

Figure 8. Monthly trends in dissolved silicon (DSi) concentration (panels a, c, e, g, i, k, m, and o) and DSi yield (panels b, d, f, h, j, l, n, and p) summarized across all rivers within each biome. Trends are reported as Sen slope values (left *y*-axis). Positive values signify increasing and negative values signify decreasing over time. Polar desert excluded because long-term record only included sampling in December and January. Temperature (blue lines) and precipitation (green lines) data are normalized to their long-term mean values (right *y*-axis) and are included to represent timing of intra-annual changes. Note differences in scales across panels.

Sites that had the greatest magnitude change in DSi concentration during the coldest months of the year were in temperate and boreal forest regions, including Arctic-boreal transition, temperate deciduous forest, and temperate grassland sites (Figure 8; Figure S3 in Supporting Information S1). Arctic-boreal transition rivers showed consistently downward trends in DSi concentration throughout the year, but concentration decreases were largest from December to April. Temperate deciduous forest sites had increasing concentrations from November to February but had little change during the rest of the year. Temperate grassland rivers had consistent decreases observed from December to May but more variable patterns from June to November.

Finally, sites with the greatest magnitude of change during the late summer months occurred in the coldest biomes where streams were frozen in the winter and seasonal temperature variation was large– the alpine and Arctic tundra (Figures 2 and 8). In both the alpine and Arctic tundra sites, the timing of the peak change in concentration occurred on average in August–September (Figure 8). The timing varied with elevation among alpine tundra streams, however, with the greatest change in concentration occurring in May–June in the lowest elevation stream, July–September in the mid-elevation stream, and August–September in the highest elevation stream (Figure S4 in Supporting Information S1).

Seasonal DSi concentration and yield trends were not always the same within a given biome, and concentration trends often had more distinct seasonal patterns than yield trends (Figure 8). Only tropical savanna sites had a consistent seasonal shift in the direction of DSi yield trends because tropical rainforest sites had high variability in DSi yield trends during the year. There were fewer sites where the change in DSi yield was greatest during colder months of the year, and temperate coniferous sites were the only group showing this pattern. In addition, some biomes had different seasonal patterns for DSi yield versus concentration. Specifically, temperate deciduous forest sites had increasing yields across all months of the year, and trends in yield in temperate grassland sites were highly variable in magnitude and direction during the year. In Arctic-boreal transition rivers, the timing of greatest changes in yield shifted later in the year than for concentration, occurring primarily in May–June.

4. Discussion

We found widespread evidence for changes in riverine DSi concentration and yield across multiple biomes over recent decades. The most substantial shifts have occurred in some of the most rapidly warming parts of the globe—the poles and the alpine zone—but also were prevalent across sites in the temperate zone, indicating that DSi fluxes are changing on human timescales, especially in response to biogeochemical and hydrologic processes (Conley et al., 2008; Sullivan et al., 2022; Vitousek et al., 1997; Zalasiewicz et al., 2019). Changes occurred across a wide diversity of biomes, but not always in the way we hypothesized. LULC explained more variation in trends than lithology, climate, and trophic status. In addition, shifts in the flow regime were not the dominant component of long-term changes in DSi concentration or yield. This indicates that shifts in watershed biogeochemical processes are important components of change in the delivery of river Si to receiving waters (Carey & Fulweiler, 2013; Conley et al., 2008; McDowell et al., 2019). Changes in DSi were not uniform through the year, with distinct seasonal patterns to changes across biomes. For example, shifts during the coldest months of the year were notable in both temperate and boreal regions, where winters are warming rapidly (USGRCP, 2017). This demonstrates the importance of considering how differences in seasonal warming trends and changes in seasonality affect the flux of Si from rivers. Taken together, our analysis indicates that long-term shifts in river DSi are driven by diverse mechanisms, vary across biomes, and tend to be specific to different seasons across biomes.

4.1. Mean Concentrations and Yield Are Highest at Low Latitudes

Our results align with global patterns showing that DSi concentrations and yields tend to be inversely related to latitude (Beusen et al., 2009; Cornelis et al., 2010; Dürr et al., 2011; Turner et al., 2003). We observed the highest mean concentrations and yields in low latitude tropical rainforest and savanna rivers and the lowest in high latitude polar regions (Arctic tundra and polar desert streams). High temperature and precipitation in tropical systems increase weathering rates and runoff, resulting in some of the highest yields globally. Although the mean concentration in streams in our study (4.72 mg L^{-1}) was in line with the global average (4.42 mg Si L^{-1}; Dürr et al., 2011; Tréguer & De La Rocha, 2013), our range of concentrations (0.47–15.3 mg L^{-1}) was wider than other global assessments (1.8–10.9 mg L^{-1}; Dürr et al., 2011). Concentrations and yields we report here from tropical rainforest streams are on the very high end of global ranges (Beusen et al., 2009). The tropical rainforest streams in this study were all located in Puerto Rico, a region that is classified as "hyper-active," having 5–10 times the global Si yield average (Dürr et al., 2011) and includes some of the fastest weathering siliceous terrain in the world (quartz-rich igneous bedrock; McDowell & Asbury, 1994; White & Blum, 1995). Some of these tropical streams drain steep mountainous catchments with volcanic lithology, both factors that are typically related to high Si yields (Beusen et al., 2009; Cornelis et al., 2010; McDowell et al., 1995). Temperate coniferous forest streams in our study had the next highest mean concentrations and yields. These rivers are underlain by volcanic bedrock (volcanic mudflow, andesite lava flow; Swanson & James, 1975) located on the Pacific Northwest coast of the United States., which has high yields due to the elevated tectonic activity and runoff observed in catchments that line the "Ring of Fire" (Dürr et al., 2011).

4.2. Widespread Changes in DSi Concentration and Yield, but Greatest in Alpine and Polar Regions

4.2.1. Evidence for Change

Most rivers in this study showed evidence of changing Si concentrations and yields over time. The largest changes occurred in alpine and polar regions, however, where sites showed both the largest relative increases and decreases over time. Specifically, the largest relative increases in concentration were observed in high elevation alpine tundra streams and a small stream in the Arctic tundra (Table 2, Figure 5). This aligns with previous work showing rapid change in permafrost and glacially impacted systems to be associated with increases in fluvial DSi. As high altitude and high elevation systems warm and permafrost thaws, new soil surfaces, especially where deeper mineral soils are exposed to weathering, soil-water interaction times increase, and flow paths lengthen and deepen, resulting in pulses of DSi to the fluvial network (Carey et al., 2020; Frey & McClelland, 2009; Shogren et al., 2019). The high elevation streams at Niwot Ridge in Colorado had increasing concentrations and fluxes that are likely connected to changing climate conditions (Crawford et al., 2019; Jones et al., 2012). These upward DSi trends also align with previous work linking warmer temperatures and mineral weathering to increasing sulfate and cation concentrations in these same streams (Caine, 2010; Crawford et al., 2019; Williams et al., 2006). The relatively lower rate of biomass growth and Si uptake by tundra vegetation compared to forests (Carey et al., 2017) could also allow most "new" DSi to be mobilized to streams in these systems rather than being taken up by plants.

We were only able to include a single Arctic tundra stream that had sufficient DSi and discharge data to estimate a trend in concentration and yield, but only reflected a short period (~8 years). Increased concentrations at that stream mirror those observed in other Arctic tundra streams over the same time period from the same northern Alaska research site (Figure S5 in Supporting Information S1). This recent increase (since ~2000) in DSi concentrations in small streams in this region of the Arctic could be related to climate warming, as permafrost thaw increases in northern Alaska (Bowden et al., 2008; Caine, 2010; Schuur et al., 2022) could increase stream DSi (Frey & McClelland, 2009). However, decadal climate oscillations (e.g., Pacific Decadal Oscillation) could be an additional driver of these observations (Jones et al., 2012), as other streams at the same research area with longer Si records had decreasing observed concentrations over the 10 year period prior to 2000 (Figure S6 in Supporting Information S1; data from these streams was not included in analysis because of a lack of corresponding discharge data). Whether our single Arctic tundra stream over this period reflects common trends in DSi across a very diverse Arctic biome is not well understood. Continuing and expanding long-term monitoring and analysis of both chemistry and hydrology in streams across the high Arctic would be beneficial for better understanding how this stream fits into broader patterns across a rapidly changing region of the globe.

Increases in DSi concentration and yield were also widespread across temperate sites, specifically sites in the temperate deciduous forest biome, where 81% and 94% of sites had increasing DSi concentration and yield, respectively. The increases in concentration and yield are meaningful when considered in absolute terms, with the period of record concentration changes ranging from −0.66 to 0.85 mg L^{-1} and yield ranging from −146 to 764 kg km^{-2} yr^{-1}. These increases were consistent across the geographic regions of the temperate forest sites in our data set (i.e., the Midwestern and Northeastern United States), despite large variation in their historical or current land use (Data Set S1; Figures S7–S9 in Supporting Information S1) and differences in time scales (Table 1). Increasing DSi concentration and yields occurred across sites with and without historical deforestation and sites with a high proportion of cropland in their watersheds (Figures S7 and S9 in Supporting Information S1). For example, several sites in the Midwestern United States had agricultural land use in their watersheds, but trend directions and magnitudes were independent of land use across rivers (Figure S9 in Supporting Information S1), which is similar to previous work showing that DSi concentration and yields in this region were not strongly related to land use (Carey et al., 2019). The consistently increasing river DSi concentrations and yields across the diverse temperate forest biome indicate that shifts in climate, weathering, forest composition, or recovery from acid deposition (Likens et al., 1996; Rodríguez-Cardona et al., 2022) may overwhelm current or historical LULC-driven differences at these sites. More work exploring the role of land use and agriculture on DSi dynamics would be useful (Sethna et al., 2022).

Although most sites had increasing DSi yields, some deviations from that pattern were notable in large rivers draining to the Arctic Ocean where we observed widespread decreases in DSi concentration and yield since the early 2000s. Several of those basins have a large percentage of permafrost cover in their watersheds (26%–100%; Holmes et al., 2012). Given previous work showing increasing DSi flux over time in permafrost-dominated systems (Frey & McClelland, 2009) and positive relationships between active layer depth and DSi loads (Carey et al., 2020), we expected DSi increases in these rivers similar to what we observed in small alpine and Arctic streams. Several factors could be driving declines in DSi that differ from drivers in small streams. This region of the globe is warming rapidly, which can increase the productivity of both the terrestrial and aquatic ecosystems (Myers-Smith et al., 2020; Song et al., 2018), thereby increasing DSi uptake on land and in the rivers. We found a negative correlation between basin forest cover and river DSi exports (Table 2), similar to previous work at lower latitudes (Carey & Fulweiler, 2013; Chen et al., 2014). Thus, given the large stocks of boreal forest biomass in their basins (Data Set S1), the terrestrial Si "sink" is potentially substantial in these watersheds and may also explain the divergence of trends between these rivers and increases in Arctic and alpine tundra streams. Furthermore, warming temperatures have the potential to increase aquatic productivity (Song et al., 2018) and reduce the duration of river ice cover in rivers around the globe (Yang et al., 2020). Thus, warmer temperature, shorter duration or thinner ice cover, and greater N and P mobilization from thawing permafrost may result in greater primary productivity (and Si uptake) in the rivers during more of the year (Jankowski et al., 2021). Finally, other work has shown multi-decadal declines in sediment export from many of these rivers because of sedimentation in upstream reservoirs (Zolkos et al., 2022). Particulate materials are often rich in Si and correlated with river DSi (Durr et al., 2011); therefore, if upstream sediment retention remains high, from historic dam construction for example, it may counteract any recent increases in Si derived from thawing permafrost or deepening active layers (Frings et al., 2014; Humborg et al., 2000; Maavara et al., 2014).

Although further work would be beneficial to understand the mechanisms driving these unexpected downward trends, such decreases have potentially substantial implications for phytoplankton productivity in the downstream coastal and marine environment of the Arctic Ocean (Baines et al., 2012; Carey et al., 2020; Pabi et al., 2008) as these large Arctic rivers account for over half of the discharge entering the Arctic basin. The declines represent a relative change in DSi yield of −17.8%–1.9% and an absolute change of −91.5–8.9 kg DSi km^{-2} yr^{-1} across the pan-Arctic region. These changes are small, but not insignificant relative to the mean annual loads of DSi of Arctic rivers (323–1,370.5 kg km^{-2} yr^{-1}; Carey et al., 2020; Dürr et al., 2011; Holmes et al., 2012) and could have implications for marine productivity in the Arctic Ocean if the trends continue.

4.2.2. Mixed Results

Despite uniform increases in concentrations and yields in small Arctic and alpine sites and the widespread decreases across large Arctic-boreal transition rivers, other biomes revealed mixed results among streams within them, including polar desert, tropical savanna, tropical rainforest, and temperate grassland streams. Rivers within the temperate grassland biome had a particularly wide range of concentration changes, from −26% to 25%. These differences could result from several watershed-specific factors, such as differences in watershed lithology, soil composition and properties, and biological processing (e.g., plant or algal uptake), which become more important in determining biogeochemical patterns at more local scales (Rodríguez-Cardona et al., 2022). Watershed lithology and soil composition affect both the amount of Si available for dissolution, as well as the water residence time and flow paths that transport Si from landscape to river.

In addition, several biomes had differences in the magnitude or direction of concentration versus yield trends. For example, polar desert streams had either decreasing or no change in DSi concentrations but nearly uniformly increasing DSi yields. Observed decreases in concentration in the polar desert may be due to several factors. There have been shifts in diatom biomass over time in some streams, although diatom communities in some streams have shifted from highly silicified to small-bodied diatoms with lower demand for Si (Stanish et al., 2011).

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Alternatively, as a major source of Si to these streams comes from hyporheic weathering (Hirst et al., 2020), decreasing concentrations in these streams could instead be from the persistent depletion of hyporheic Si reservoirs due to consistently higher discharge depleting readily dissolvable secondary clay minerals and amorphous Si from hyporheic zones (Hatton et al., 2020; Hirst et al., 2020). Thus, pulses of DSi at high flows may occur when the stream is connected to residual Si source areas, but ongoing depletion from higher median flows could result in differences in the direction of change in flow-normalized concentration and yield (Wlostowski et al., 2016).

Some sites showed small relative changes over time but large absolute magnitude of change, such as tropical rainforest and temperate coniferous rainforest sites (Figure 5), which drain watersheds with the highest terrestrial biomass. The temperate coniferous forest sites included in this study are located in the Pacific Northwest region of the United States, and despite evidence for increases in temperature (Abatzoglou et al., 2014; Jones et al., 2012), forests in both of these regions have shown little biological response to documented climate change in more recent time periods (Cowles et al., 2021; Jones et al., 2012). In tropical rainforest streams, the absolute magnitude of change ranged from 62% to 110% of the mean annual yield from tropical rivers (4,064 kg DSi km^{-2} yr^{-1}). These large absolute changes can be explained by the combination of high DSi concentrations (Figure 4) and precipitation, as well as their location in "highly active" areas of the Earth for DSi (Durr et al., 2011). If these trends are widespread, small relative changes in flux are associated with large absolute change in flux from these watersheds can have a disproportionate influence on marine processes locally and globally.

4.3. Land Cover and Watershed Biogeochemistry, Not Flow Regime, Associated With Most Long-Term Changes in River DSi

DSi flux from terrestrial to aquatic ecosystems depends on the relative contribution of different pools of Si (e.g., mineralogical and biological) as well as watershed hydrology driving subsurface and surface water flow (Beusen et al., 2009; Struyf et al., 2009), all factors that vary across the diverse biomes included in this study. Accordingly, we found that differences in LULC across sites were more strongly associated with differences in long-term trends in DSi concentration and yield than lithology, climate, drainage area, or N or P availability (Table 2). In addition, although river discharge is often considered a primary driver of DSi concentration and flux (Beusen et al., 2009; Turner et al., 2003), our results demonstrated a greater importance of changes in watershed biogeochemical cycling, compared to the flow regime alone, in fueling observed changes in DSi over time (Figure 7). Our results indicate that changes in the availability and mobility of DSi in the stream-watershed were more influential on long-term changes in concentrations than changes in the amount and timing of water moving through the hydrologic system. "Watershed biogeochemistry" captures several potential processes that span the terrestrial-aquatic continuum (Figure 1), including terrestrial Si cycling and uptake, river productivity or primary producer communities, weathering rates, or altered ground or surface water flow paths that affect the connections with Si sources and sinks. These categories of watershed biogeochemistry and flow regime are not independent of course, as biogeochemical shifts could be linked to changes in the flow regime if higher magnitude flows connect rivers with new sources of Si or changes in flood timing affect the capacity for uptake in the river (i.e., earlier floods, cooler temperatures, lower algal uptake). However, our finding highlights that factors driving changes in DSi concentration and yield go far beyond simple changes in discharge or flow regime (Murphy & Sprague, 2019).

The shifting biogeochemical signal was particularly strong at polar and alpine sites (Arctic tundra, alpine tundra, Arctic-boreal transition), where most trends were dominated by biogeochemical changes for both concentration and yield. These systems are experiencing rapid rates of change with respect to permafrost thaw, glacial melt, and increasing air temperatures, all of which may alter biogeochemical processes without changing annual mean discharge or other aspects of the flow regime. The exception to this pattern was the polar desert streams, where changing flow regimes had a greater role in explaining yield trends over time across sites. Most polar desert streams had significant or marginally significant ($p < 0.10$; Table S5 in Supporting Information S1) shifts in annual mean discharge over the period of record, consistent with other studies (Gooseff et al., 2017). Thus, even though concentrations decreased over time in most polar desert streams, the simultaneous shift in the flow regime drove increases in yield. These disparate patterns in trends and dominant mechanisms of change across alpine, Arctic, boreal and polar desert streams highlight the heterogeneity of polar and alpine regions, emphasizing that greater understanding of biogeochemical shifts occurring in these rapidly changing parts of the biosphere would be beneficial.

As expected, DSi yield was more evenly influenced by biogeochemistry and streamflow changes compared to concentration. Temperate sites had the most evidence for the role of shifting flow regime in driving changes in DSi yield, either as a mixed effect of biogeochemistry and flow (21% and 11% of temperate sites for concentration and yield, respectively) or as dominance of the flow regime alone (0% and 65% of temperate sites for concentration and yield, respectively). Shifts in flow regime encapsulate changes in timing, duration, frequency, and magnitude of flows (Poff et al., 1997), all of which likely contributed to the changes in DSi that we observed (Webster et al., 2016). For example, increases in river flow over the last several decades have occurred across multiple seasons in the Upper Mississippi River Basin (Van Appledorn, 2022) where several of the sites that had DSi trends dominated by a shift in the flow regime were located. Across all biomes, changes in annual mean discharge were significant at more than 50% of the sites where a changing flow regime dominated the yield trend. We did not explicitly quantify other aspects of a changing flow regime that could have influenced DSi yield, such as changes in minimum or maximum flows, changes in timing, or changes in flood frequency (Poff et al., 1997), but our findings indicate that some other aspects of flow regime shifts were important at sites where annual mean discharge did not change. Finally, we found a nearly equal mixture of additive and opposing effects of the flow regime and biogeochemical change on trends in DSi. This indicates that the relative role and direction of biogeochemical and hydrologic processes can vary, and better understanding of their relative contributions to Si dynamics will help us understand and forecast how Si yields might change in the future.

4.4. Seasonal Timing of Change Shows Some Common Patterns Across Biomes

Climate-driven seasonal shifts in hydrology and temperature have implications for the timing of nutrient loads (Seybold et al., 2022; Shogren et al., 2020), which can affect local and downstream productivity and food web dynamics (Myrstener et al., 2021; Woodward et al., 2010). We observed distinct seasonal patterns to long-term changes in DSi concentrations, and to a lesser degree in DSi yields.

Trend directions differed during the year in the warmest and wettest biomes (i.e., tropical rainforest, tropical savanna, and temperate coniferous forests), which had relatively stable temperatures but variable seasonality in precipitation. These sites also showed the smallest relative change in DSi over time (Figure 5), perhaps because of these intra-annual differences in the direction of change. The seasonal differences in the direction of change over time corresponded to seasonal precipitation, such as the timing of either the wet/dry season (temperate coniferous forest, tropical savanna) or the timing of the hurricane season (tropical rainforest; McDowell et al., 2013). Changes in yield were much more variable throughout the year than concentration, however. Precipitation, and therefore discharge, can be stochastic at these sites (McDowell et al., 2012) and many tropical rainforest ecosystems. Thus, it follows that seasonal changes in DSi yield would not necessarily mirror changes in DSi concentration and may be more difficult to predict into the future (Dalling et al., 2016; Zimmerman et al., 2021).

Biomes where the greatest change occurred during the coldest parts of the year included temperate deciduous forest, temperate grassland, and Arctic-boreal transition biomes, where the magnitude of monthly trends tended to be inversely related to temperature (Figure 8). Increasing concentrations during winter temperate deciduous forest systems may be a lagged signal of increases in weathering rates earlier in the year because weathering products may be stored in the groundwater and transported to the river during high flow periods. In contrast, the winter decline in Arctic-Boreal rivers a could reflect a lagged signal of greater terrestrial uptake during the summer that is detectable only in winter months (Crossman et al., 2016; Shousha et al., 2021). Cold season changes in DSi in large Arctic-boreal watersheds could also reflect earlier ice-out and spring freshets in these systems (Bintanja & Andry, 2017; Box et al., 2019; Feng et al., 2021), which may drive greater productivity in late winter or early spring periods that draw down river DSi.

The timing of change was not always consistent between concentration and yield within a given biome. Concentrations tended to have more clear seasonal patterns than yield, which may indicate that changing concentrations are more tightly linked to seasonally variable controls such as aquatic and terrestrial productivity. In contrast, yield is typically tightly coupled to changes in discharge (Carey & Fulweiler, 2013; Fulweiler & Nixon, 2005), which could be tied to a different suite of drivers or may not be changing as consistently during the year as biological processes in these regions.

These seasonal patterns indicate that considering only trends in the long-term annual average may miss important temporal shifts in the timing of peak DSi concentration and yield. The timing of change not only provides information regarding the mechanism driving the long-term shift in DSi but also has important ecological and biogeochemical implications for rivers and downstream oceans. Our finding of greater change in concentrations during the fall or winter in temperate and boreal systems has different implications for rivers and oceans than similar changes during the summer months. Increasing availability of DSi during colder times of the year could affect the development of riverine algal communities and river productivity. For example, studies in lake ecosystems have shown linkages between fall availability of DSi and the subsequent spring diatom bloom (Katz et al., 2015). Similarly, increasing higher yields to the ocean during colder months of the year may have implications for diatom uptake, annual plankton community development, and resulting carbon burial rates. Future work could focus on understanding the mechanisms driving these changes and whether the patterns observed in some months and rivers will persist or shift as watersheds respond to ongoing warming and changing hydrology.

4.5. Conclusions and Next Steps

Si is vastly understudied in rivers relative to other nutrients, despite its ecological importance for freshwater and marine ecosystems. Here, we present the first known analyses of long-term trends in DSi in rivers and streams across multiple biomes and ecosystem types. We show widespread evidence for dynamic changes in river DSi over time, with the largest shifts occurring in the streams and rivers of polar and alpine regions. In addition, we show that many changes are occurring outside of the growing season, indicating that climate-driven shifts in seasonality could affect the seasonal cycle of Si concentrations and export. Finally, using a trend attribution approach, we were able to separate the effect of changes in the flow regime from changes in watershed biogeochemistry on long-term trends in DSi, showing that changes in streamflow regimes were not the dominant driver of long-term changes in DSi. These findings emphasize the dynamic nature of river DSi and the potential for large and meaningful changes as ecosystems warm. Our work focused on quantifying the total change in Si over time using records that spanned various time scales, but further work could examine dynamics (e.g., threshold vs. linear change over time) and mechanisms driving the more recent shifts we observed, particularly in high latitude systems where changes may be rapid, abrupt, and ongoing. Future work could also investigate mechanisms driving the observed changes, potentially through examining other Si fractions in export water (e.g., BSi) and through the use of geochemical (i.e., germanium/Si ratios) or isotopic tracers. Finally, ongoing and increased monitoring of riverine Si would be useful for filling out our understanding of the Si cycle and how it may change over the long term. More long-term monitoring would be especially useful in areas outside the temperate zone and in months outside the growing season, where fewer data are available to understand the implications for concentrations and fluxes of river Si.

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Data Availability Statement

The data supporting this manuscript can be accessed at https://doi.org/10.5066/P951UKQB (Jankowski et al., 2023). Citations for original data sources are given in Table S1 of the Supporting Information S1.

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