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Several Mechanisms Drive the Heterogeneity in Browning Across a Boreal Stream Network

Xudan Zhu[1], Frank Berninger[1], Liang Chen[1], Johannes Larson[2], Ryan A. Sponseller[3], and Hjalmar Laudon[2]

[1]Department of Environmental and Biological Sciences, Joensuu Campus, University of Eastern Finland, Joensuu, Finland, [2]Department of Forest Ecology and Management, Swedish University of Agricultural Science, Umeå, Sweden, [3]Department of Ecology and Environmental Sciences, Umeå University, Umeå, Sweden

Key Points:

- This study evaluated the multiple drivers behind browning using a 19-year time series across 13 nested boreal catchments
- We revealed that, despite a history of low deposition, the decline in ionic strength driven by sulfate recovery is the main driver of browning, rather than recovery from acidification per se
- Our results provided an explanation for the spatiotemporal heterogeneity of browning trends within a boreal catchment network

Supporting Information:

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

Correspondence to:

X. Zhu,
xudanzhu@uef.fi

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Abstract Over the past few decades, many catchments in Northern hemisphere have experienced increases in dissolved organic carbon (DOC) concentrations, resulting in a brownish color of the water, known as aquatic browning. Several mechanisms have been proposed to explain browning, but consensus regarding the relative importance of recovery from acid deposition, climate change, and land management remains elusive. To advance our understanding of browning mechanisms, we explored DOC trends across 13 nested boreal catchments, leveraging concurrent hydrological, chemical, and terrestrial ecosystem data to quantify the contributions of different drivers on observed trends. We first identified the related environmental factors, then attributed the individual trends of DOC to potential drivers across space and time. Our results showed that all catchments exhibited increased DOC trends from 2003 to 2021, but the DOC response rates differed by five-fold. No single mechanism could fully explain the browning; instead, sulfate deposition, climate-related factors, and site properties jointly controlled the variation in DOC trends. Specifically, the long-term increases in DOC were primarily driven by recovery from sulfate deposition, followed by increases in terrestrial productivity, temperature, and discharge. However, catchment area and landcover type also regulated the response rate of DOC to these drivers, creating spatial heterogeneity in browning among sub-catchments despite similar deposition and climate forcing. Interestingly, browning has weakened in the last decade as sulfate deposition has fully recovered and other current drivers are insufficient to sustain the long-term increases. Our results highlight that multifaceted, spatially structured, and nonstationary drivers must be accounted for to predict future DOC changes.

Plain Language Summary In recent decades, many streams, rivers and lakes in Europe and North America have seen a rise in dissolved organic carbon (DOC), giving the water a brownish color. Several explanations for this phenomenon have been suggested, including recovery from acid rain, climate change, and land use change. Yet it is still unclear which of these drivers is most important. To better understand this, we evaluated DOC changes in 13 nested catchments in northern Sweden, considering all plausible causes. We found that all catchments had an increase in DOC from 2003 to 2021, but the magnitude of increase varied among sites. The main drivers of long-term increases in DOC were recovery from sulfate deposition, followed by increased plant productivity, stream water temperature, and discharge. Catchment area and land cover properties also affected how DOC levels changed over time. Strikingly, browning has slowed during the last 10 years as these systems have recovered from sulfate deposition, and other factors appear too weak to maintain rates of DOC increase at the same level. Our study shows that we need to consider multiple environmental factors that vary over space and time to predict DOC trends in the future.

1. Introduction

The flux of dissolved organic carbon (DOC) from terrestrial to aquatic ecosystems is an important aspect of the global carbon (C) cycle (Aitkenhead & McDowell, 2000), with far-reaching consequences for the chemistry, biology, and ecology of streams, rivers, and lakes (Gao et al., 2022; Gómez-Gener et al., 2021; Karlsson et al., 2009). Globally, riverine DOC fluxes account for approximately 25%–50% of the total C exports to oceans (Drake et al., 2018; Li et al., 2017). Yet, over the last few decades, many catchments in Europe and North America have witnessed rising DOC concentrations in surface waters, often termed "browning" (Clark et al., 2010; Lawrence & Roy, 2021; Monteith et al., 2007). Increases in water color caused by elevated DOC supply affect light penetration and thermal regimes that can further alter the biodiversity and food webs of aquatic ecosystems

(Conley et al., 2011; Kritzberg et al., 2020; Leach et al., 2019). Further, increasing DOC reduces the value of aquatic landscapes from the recreational and esthetic aspects and boosts the cost of treating drinking water (Blanchet et al., 2022).

Several mechanisms have been proposed to explain the rising DOC concentration, including recovery from atmospheric acid deposition, climate change, land use alteration, and increases in terrestrial productivity (Kritzberg et al., 2020). Indeed, recovery from acid deposition after its peak in the 1970s is a well-established driver of browning, with reductions in acidity and ionic strength of soil water increasing the solubility of DOC and thus its potential for lateral export (Lawrence & Roy, 2021; Monteith et al., 2007; Pagano et al., 2014). There is also mounting evidence that land-use changes drive increases in aquatic DOC, either by enhancing terrestrial organic C accumulation or by altering DOC routing from soils to streams (Härkönen et al., 2023; Kritzberg, 2017). Finally, a range of climate change-related factors, including increased temperature (Keller et al., 2008), altered hydrology (Tiwari et al., 2022), and elevated atmospheric CO_2 (Schlesinger & Andrews, 2000), along with a longer growing season and higher productivity (Finstad et al., 2016), have also been suggested as drivers of browning. Collectively, these factors can be linked to enhanced organic matter pools on land but also to elevated rates of soil C decomposition, shifts in hydrological pathways, and reduced travel time of DOC in aquatic networks (Hongve et al., 2004; Tranvik & Jansson, 2002). Of these, connections between ongoing increases in terrestrial productivity (Myers-Smith et al., 2020) and elevated DOC export have gained some of the most recent interest (Finstad et al., 2016; Larsen et al., 2011; Mzobe et al., 2018), and could be particularly important in regions not exposed to high rates of acid deposition or major land use changes. Yet, while recent research supports the role of terrestrial productivity in controlling DOC concentrations in boreal catchments (Zhu et al., 2022), the relationship between terrestrial greening and aquatic browning is not well established. Ultimately, a major challenge to understanding the mechanisms behind browning is that several of these drivers can co-occur, may be interactive, and shift in importance over time. Thus, resolving amongst them requires time series data that simultaneously capture chemical, hydrological, and terrestrial ecosystem parameters, but also new analytical tools that can isolate potentially non-stationary causal connections.

Some differences in the suggested drivers of browning across studies may be caused by spatial variation in historical acid deposition (Clark et al., 2010). For example, at regional scales, variable deposition history may determine the potential for other factors, including climate warming and changes in hydrology, to drive DOC increases (Räike et al., 2016). However, even closely co-located streams with similar deposition history, can exhibit different DOC trends (Fork et al., 2020), suggesting that local catchment properties can mediate responses to broader-scale drivers. In boreal landscapes, small-scale differences in mire (wetlands) versus forest cover appear to play this role, with DOC trends being far stronger in forest-dominated compared to mire-dominated streams (Fork et al., 2020). The mechanistic basis for these patterns remains unresolved but such distinct DOC trends suggest fundamental differences in how different land covers mediate the response to historical acid inputs. In addition, Zhu et al. (2022) found that terrestrial productivity promotes DOC production in small forested catchments via priming, a process that may underpin some of the differences in DOC trends between forest- mire-dominated catchments. Finally, moving beyond headwater systems, increases in catchment size can lead to greater supplies of deep, DOC-poor groundwater (Tiwari et al., 2018), and these inputs may regulate and/or dampen DOC trends for larger streams and rivers (Zhu et al., 2022). Overall, while broad-scale environmental changes are clearly influencing DOC production and supply from catchment soils, predicting the browning trend in catchment networks also requires considering the role of catchment size and landscape modulating factors.

In addition to recognizing spatial drivers, differences in the temporal scales considered may also give rise to a change in responsible drivers of browning, particularly in reference to the pace of acid deposition recovery. Based on the long-term monitoring programs in the northern hemisphere, most regions have shown continued browning trends (Lapierre et al., 2021; Lepistö et al., 2021; Redden et al., 2021). For example, de Wit et al. (2016) observed positive trends of DOC in 474 boreal and subarctic catchments across Europe from 1990 to 2013, suggesting that future changes in precipitation are likely to promote continued browning. Conversely, Eklöf et al. (2021) proposed that the widespread increases in DOC concentration across Sweden ceased 10 years ago due to full recovery from acidification in the recent decades. These contrasting findings cast doubt on the hypothesis that ongoing pressures, such as climate change, are driving widespread browning. Therefore, understanding the relative contributions of all the proposed mechanisms on different spatiotemporal scales remains critical for generating accurate predictions about future browning trends.

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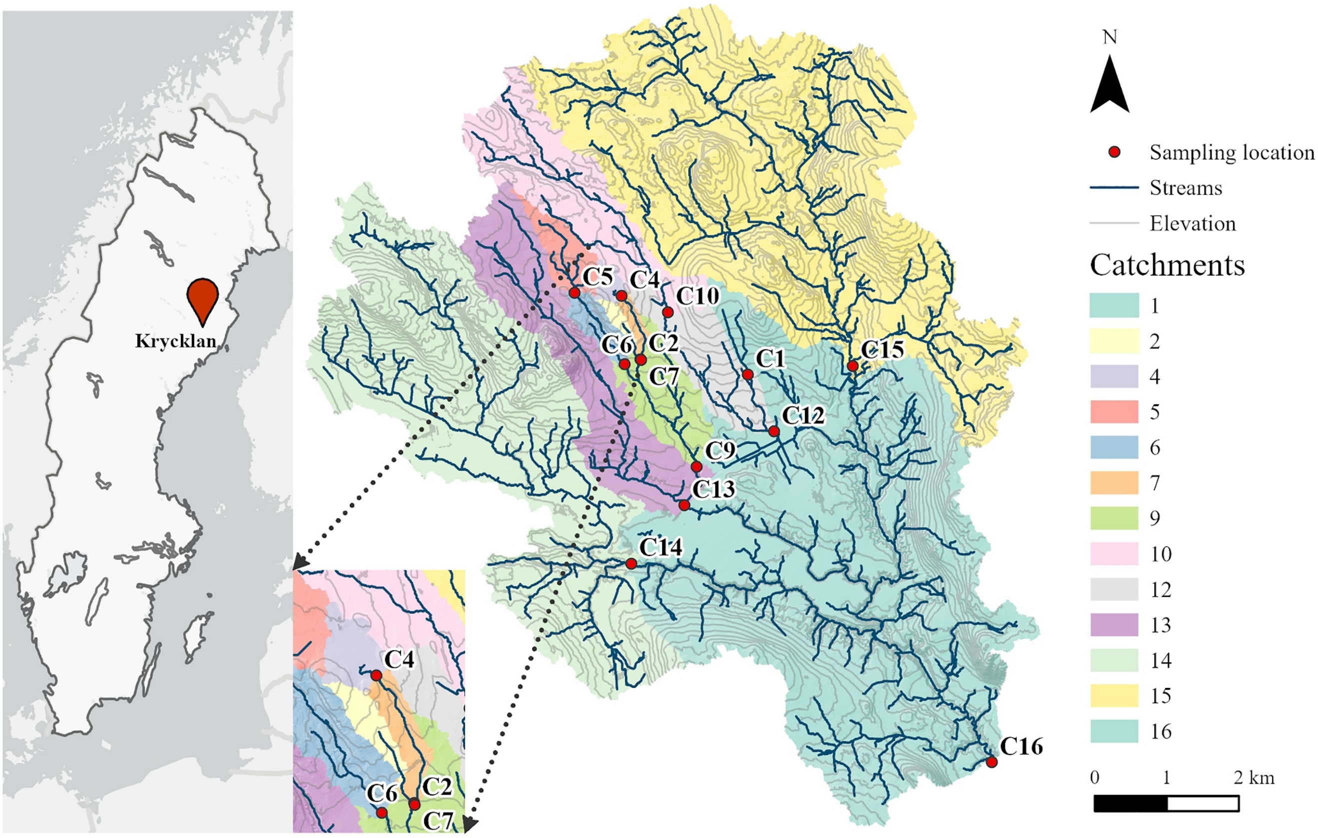

Figure 1. Nested catchments, sampling locations and study sites in Krycklan, Sweden.

To better understand the heterogeneity of browning in a catchment network, we ask how DOC trends in a northern boreal stream network relate to concurrent changes in sulfur (S) deposition recovery and climate-related factors and how these relationships are mediated by variability in catchment size and land cover. We answered these questions using two decades of monitoring data from the Krycklan Catchment Study, located in northern Sweden. Krycklan is comprised of multiple, nested sub-catchments that encompass the natural variability in land cover features (e.g., forest and mire cover) typical of the region, as well as a wide range of catchment sizes. Additionally, it is an area with comparatively low S deposition historically, while the streams are naturally acidic, anthropogenic acidity has been restricted to hydrological episodes during snowmelt (Laudon, Sponseller, & Bishop, 2021). To investigate the trends in DOC concentrations and identify potential drivers across the 13 nested boreal catchments experiencing similar climate and S deposition history, we pursued the following objectives:

1. To develop empirical models based on different mechanisms, including climate change and recovery from S deposition, as well as site characteristics including catchment size and land cover type. These models aim to reveal the underlying drivers of DOC trends.
2. To quantify the contributions of the identified drivers to the long-term trends of DOC from both spatial and temporal perspectives. This step aims to provide a comprehensive understanding of the factors controlling the spatiotemporal heterogeneity in long-term DOC trends across boreal catchments.

2. Materials and Methods

2.1. Study Area

Krycklan is located in the boreal landscape, approximately 50 km northwest of the city of Umeå in northern Sweden (64°14′N, 19°46′E) (Figure 1). This study investigated 13 long-term monitoring catchments in Krycklan with varied sizes from 0.1 to 67.9 km^2, and landscape types dominated by both forest and mires (Table 1). For 10

Table 1
Catchment Properties of All Catchments in This Study

Properties	Unit	C1	C2	C4	C5	C6	C7	C9	C10	C12	C13	C14	C15	C16
Elevation above sea	(m)	279	275	287	293	282	275	252	297	277	251	229	278	239
Elevation above stream[a]	(m)	11	10	9	2	4	8	4	8	7	6	10	10	10
Size	(km^2)	0.5	0.1	0.2	0.7	1.1	0.5	2.9	3.4	5.4	7.0	14.1	19.1	67.9
Lake	(%)	0	0	0	6	4	0	2	0	0	1	1	2	1
Forest	(%)	98	100	56	54	72	82	84	74	83	88	90	83	87
Mire	(%)	2	0	44	40	24	18	14	26	17	10	5	14	9
Open land	(%)	0	0	0	0	0	0	0	0	0	0	1	1	1
Arable land	(%)	0	0	0	0	0	0	0	0	0	1	3	0	2
Tree volume[b]	($m^3\ ha^{-1}$)	187	212	83	64	117	167	150	93	129	145	106	85	106
Land cover type[c]		Forest	Forest	Mire	Mire	Mixed	Mixed	Mixed	Mixed	Mixed	Mixed	Mixed	Mixed	Mixed

[a]Mean elevation of catchment relative to the lowest level of stream from 5 m LiDAR DEM, calculated similar to McGuire et al. (2005). [b]Calculated for the entire catchment using correlations between a forest inventory (from 110 plots) and LiDAR measurements (Laudon et al., 2013). [c]Landcover type was defined by percent mire coverage, with <2% mire as "forest," 2%–30% mire as ''mixed,'' and >30% mire as ''mire.'' C5 is the outlet to a headwater humic lake.

of the 13 catchments, the measurement period was from 2003 to 2021, but from 2003 to 2018 for C12, C14, and C15.

Underlying bedrock in the catchment consists of 94% metasediments/metagraywacke, 4% acid and intermediate metavolcanic rocks, and 3% basic metavolcanic rocks. Above the highest postglacial coastline across Krycklan (257 m a.s.l), glacial till dominates quaternary deposits, while post-glacial sedimentary deposits dominate soils below it (Laudon et al., 2013). Forests cover 87% of the area and are predominantly Scots pine (*Pinus sylvestris*, 63%), and Norway spruce (*Picea abies*, 26%) with 9% deciduous forest. Peatlands cover 9% of the catchment and are dominated by *Sphagnum* species. The climate is a cold temperate humid type with persistent snow cover during winter. The 30-year mean annual average precipitation (1981–2010) is 614 mm, of which 35% was classified as snow during winter (December to April), annual runoff is 311 mm, giving an annual average evapotranspiration of 303 mm. The mean annual temperature is 1.8°C, January −9.5°C and July +14.7°C. The average annual snow water equivalent during the snow cover period for the last 40 years of record is 180 mm, ranging from 64 (1996) to 321 (1988) mm. The 40-year average duration of winter snow cover is 167 days (Laudon, Hasselquist, et al., 2021).

2.2. Environmental Trends

2.2.1. Sulfate Deposition

The highest S deposition in the past century was recorded in the late 1970s (~4 kg S ha^{-1} yr^{-1}) at Krycklan, followed by a fall to nearly pre-industrial levels (<1 kg S ha^{-1} yr^{-1}) 20 years later (Laudon, Sponseller, & Bishop, 2021).

2.2.2. Temperature

The long-term air temperature record at Svartberget station in the central part of Krycklan from 1980 to 2020 reveals a clear pattern of overall warming. Since 1891, the annual air temperature has risen by approximately 3.0°C. However, the most notable increase of 2.5°C has occurred within the last four decades, with 2020 standing out as the warmest year on record (Laudon, Hasselquist, et al., 2021).

2.2.3. Precipitation

Over the last 40 years, no statistical trend has been observed in the total annual average precipitation. However, a significant decrease has been observed in the average duration of winter snow cover including a delay (~0.5 day $year^{-1}$) of initial snow cover in the autumn (Laudon & Ottosson Löfvenius, 2016).

2.2.4. Land Use

In Krycklan, forestry is the dominant land use in the region, and most forests are managed by conventional rotation forestry, including regeneration, thinning, and clear-cut harvesting, resulting in widespread coverage of even-aged stands. On average, less than 1% of the Krycklan catchment is clear-cut each year, but the most central catchments (C1, C2, C4, C6, C7, C9) have been unmanaged for nearly a century (Figure S1 in Supporting Information S1).

2.3. Data Collection and Interpolation

2.3.1. Site Characteristics

Catchment areas were delineated from a LiDAR derived digital elevation model (DEM) and validated in the field using a professional mapper (Laudon et al., 2013). The DEM with 2 m resolution was created from a point cloud with a point density of 15–25 points/m^2 and hydrologically corrected by burning streams and culverts across roads (Lidberg et al., 2017). The landscape type (forest, lake, and mire coverage) for each catchment was calculated according to the Swedish property map (1:12,500, Lantmäteriet Gävle, Sweden) (Table 1).

2.3.2. Climate Data

Soil temperature at 20 cm below the surface was measured in the central part of Krycklan at the Svartberget research station (Laudon, Hasselquist, et al., 2021). Climate data from the station are assumed to be representative across the broader catchment area.

2.3.3. Chemistry Data

Surface water samples were collected typically on the same day from each site in acid-washed, high-density polyethylene bottles. The sampling frequency was every third day during spring flood, biweekly during summer and fall, monthly in winter. All samples were filtered immediately after collection (0.45 μm MCE membrane, Millipore). DOC samples were analyzed promptly after filtering to minimize any potential degradation or alteration of the organic carbon compounds. DOC samples were run typically within a week. DOC concentrations were measured as total organic carbon (TOC) using a Shimadzu TOC-VCPH analyzer after acidification to remove inorganic compounds (Laudon et al., 2011). DOC and TOC are equivalent in Krycklan streams, so the term DOC is used in this study. Samples for sulfate were frozen prior to analysis. Sulfate (SO_4) was measured by Dionex DX-300 or DX-320 ion chromatography system (Fork et al., 2020). More information about field sampling can be found in Laudon et al. (2013) and Winterdahl et al. (2014). Daily DOC and SO4 concentrations from 2003 to 2021 were interpolated using "*Random Forest*" by package "*missForest*" (Stekhoven & Buhlmann, 2012) in R (R Core Team, 2019) (Figure S2 in Supporting Information S1).

2.3.4. Discharge Data

Daily stream discharge of the 13 catchments from 2003 to 2021 were measured using calibrated V-notch weirs, flumes and road culverts (Karlsen et al., 2016). Missing values were predicted using an ensemble version of a bucket-type, semi-distributed hydrological (HBV) model (Karimi et al., 2022).

2.3.5. MODIS Gross Primary Productivity (MGPP) Data

The GPP derived from the Moderate Resolution Imaging Spectroradiometer (MODIS)—hereafter MGPP—is one of the most widely used GPP products (Huang et al., 2021). Due to the absence of eddy covariance towers at each sub-catchment, MGPP rather than eddy covariance GPP was used as a proxy for terrestrial productivity in this study. Three methods were developed to extract MGPP (500 m and 8-day resolution) from the Google Earth Engine (Gorelick et al., 2017) according to the GIS data from the Krycklan database: (a) MGPP_coordinate: from the coordinate of each site; (b) MGPP_riparian: from 50-m buffer zone along both sides of each stream or river; (c) MGPP_watershed: from the watershed of each site (Figure S2 in Supporting Information S1). Daily MGPP was linearly interpolated based on 8-day MGPP (Figure S3d in Supporting Information S1). To determine the most representative MGPP, we compared MGPP and GPP derived from eddy-covariance at sites where both estimates were available (Zhu et al., 2022). These results revealed that MGPP from three different approaches accounted for 56%–67% of the variability in eddy-covariance GPP (Table S1 in Supporting Information S1).

Moreover, we evaluated the performance of Distributed-lag linear model (DLM2) when utilizing MGPP from three different methods. Our findings revealed that DLM2 performed the best when applying MGPP_riparian as it yielded the lowest AIC (The Akaike information criterion) and highest R^2 values (Table S2 in Supporting Information S1). Thereafter, MGPP_riparian was used for further analysis and referred to as MGPP.

2.4. Statistical Analysis

2.4.1. Calculation of Long-Term Trends

For each site, the long-term trends of DOC concentrations (and environmental drivers) during 2003–2021 were calculated as the slope of the simple linear regression of yearly data (aggregate from daily data). The mean slope of all catchments was used to compute the long-term trend of each variable in the Krycklan catchment.

2.4.2. Distributed-Lag Linear Model

The impact of each environmental factor on DOC concentrations was quantified using distributed-lag linear models (DLMs), where the lag effect was applied to discharge and MGPP. The delay is caused by the transport of fresh photosynthates to roots, changes in decomposition and microbial biomass after a change in root exudates and hydraulic delays required to transport DOC from soil to water bodies (Wen et al., 2020). The delayed times were determined based on the temporal synchrony among discharge, GPP and DOC across Krycklan catchment (C2, C4&C6) by wavelet coherence analysis in our previous study (Zhu et al., 2022). The cross-basis of MGPP and discharge were built by polynomial transformations of the lags of MGPP and discharge, respectively. In DLMs, fourth-degree polynomial cross-basis functions with 4–30 days lag time were built for MGPP and second-degree with 0–7 days for discharge (Zhu et al., 2022). Then, linear combinations of SO_4, soil temperature, catchment size, mire coverage and the cross-basis of discharge and MGPP were used to predict DOC concentrations. The analysis was performed using the "DLNM" package (Gasparrini, 2011) in R (R Core Team, 2019). AIC and R^2 were used to select the best model in predicting the DOC concentrations. Finally, DLM 1–7 were defined as follows:

$$\text{DLM1}: \text{DOC} = \beta_1 \text{Dis}_{\text{lag}} \tag{1}$$

$$\text{DLM2}: \text{DOC} = \beta_1 \text{MGPP}_{\text{lag}} \tag{2}$$

$$\text{DLM3}: \text{DOC} = \beta_1 \text{Dis}_{\text{lag}} + \beta_2 \text{MGPP}_{\text{lag}} \tag{3}$$

$$\text{DLM4}: \text{DOC} = \beta_1 \text{Dis}_{\text{lag}} + \beta_2 \text{MGPP}_{\text{lag}} + \alpha_1 \text{SO}_4 \tag{4}$$

$$\text{DLM5}: \text{DOC} = \beta_1 \text{Dis}_{\text{lag}} + \beta_2 \text{MGPP}_{\text{lag}} + \alpha_1 \text{SO}_4 + \alpha_2\, T_{\text{soil}} \tag{5}$$

$$\text{DLM6}: \text{DOC} = \beta_1 \text{Dis}_{\text{lag}} + \beta_2 \text{MGPP}_{\text{lag}} + \alpha_1 \text{SO}_4 + \alpha_2\, T_{\text{soil}} + \alpha_3 \text{ Area} \tag{6}$$

$$\text{DLM7}: \text{DOC} = \beta_1 \text{Dis}_{\text{lag}} + \beta_2 \text{MGPP}_{\text{lag}} + \alpha_1 \text{SO}_4 + \alpha_2 T_{\text{soil}} + \alpha_3 \text{Area} + \alpha_4 \text{Mire\%} \tag{7}$$

where β was the lag effect of discharge (Dis) and MGPP on DOC concentrations, α was the impact of sulfate (SO_4), soil temperature (T_{soil}), catchment size (Area) and mire coverage (Mire%). Dis_{lag} and MGPP_{lag} were the mean cross basis of discharge and MGPP during their lag times, respectively.

2.4.3. Total Differential Equation

To evaluate spatial patterns, we quantified the contributions of environmental drivers (sulfate, discharge, MGPP, soil temperature) to observed DOC trend during 2003–2021 for each site. This quantification was achieved by decomposing the 19-year linear trend of DOC at each site into the additive contributions of four components. To focus more on temporal patterns, we quantified the contributions of environmental drivers to 10-year DOC trend across each period. A 10-year moving window was used to cut the 19-year data set at 1-year interval to obtain 10 data sets (2003–2012, 2004–2013…and 2012–2021). Thereafter, we decomposed the 10-year linear trend of DOC across each period into the additive contributions of four components.

$$\frac{d\,\mathrm{DOC}}{dt} = \frac{\partial\mathrm{DOC}}{\partial\mathrm{Dis}} * \frac{d\,\mathrm{Dis}}{dt} + \frac{\partial\mathrm{DOC}}{\partial\mathrm{SO_4}} * \frac{d\,\mathrm{SO_4}}{dt} + \frac{\partial\mathrm{DOC}}{\partial\mathrm{MGPP}} * \frac{d\,\mathrm{MGPP}}{dt} + \frac{\partial\mathrm{DOC}}{\partial T_{\mathrm{soil}}} * \frac{d\ T_{\mathrm{soil}}}{dt}$$
$$= \Delta\mathrm{DOC}^{\mathrm{Dis}} + \Delta\mathrm{DOC}^{\mathrm{SO_4}} + \Delta\mathrm{DOC}^{\mathrm{MGPP}} + \Delta\mathrm{DOC}^{T_{\mathrm{soil}}} \quad (8)$$

where $\frac{\partial\mathrm{DOC}}{\partial X}$ represented the sensitivity of DOC to an explanatory variable X—sulfate (SO_4), discharge (Dis), soil temperature (T_{soil}) and MGPP. These sensitivities were estimated as the regression coefficients of a multiple linear regression performed with DOC against all listed explanatory variables at a certain period. The linear trend of DOC (or X) at a certain period was showed as $\frac{d\,\mathrm{DOC}}{dt}$ (or $\frac{dX}{dt}$). For each site at a certain period, this trend was calculated as the slope of the simple linear regression of mean DOC (or X) values against the year. Here, The DOC trend at a certain period ($\frac{d\,\mathrm{DOC}}{dt}$) was decomposed into the contribution of each variable X ($\Delta\mathrm{DOC}^X$), which was represented as the product of the partial derivative against that variable X as $\frac{\partial\mathrm{DOC}}{\partial X}$ and the concurrent trend of X itself as $\frac{dX}{dt}$. The approach given by Equation 8 was conducted for each site, and the total areal-averaged contribution of each factor to the trend of DOC over each period was calculated by averaging the decomposed contribution of factors ($\Delta\mathrm{DOC}^X$) across all catchments.

3. Results

3.1. Long-Term Trends of DOC and Environmental Variables

The long-term trend analysis showed that DOC concentration did increase at each site over the measured period. The mean DOC concentration trend (±s.d.) across the Krycklan catchments was 0.22 ± 0.11 mg l^{-1} year^{-1} ($p < 0.001$) (Figure 2a). The changes were significant across all sites ($p < 0.05$) except for C4 and C5 ($p > 0.05$). Among all sites, C2 had the steepest slope (0.38) while C5 had lowest (0.08) (Table 2). Overall, the small forest-dominated sites showed the highest rate of response (0.38 ± 0.05 mg l^{-1} year^{-1}, $n = 2$), followed by the larger-size mixed catchments (0.22 ± 0.09 mg l^{-1} year^{-1}, $n = 9$), whereas small-size mire catchments had the lowest rates (0.08 ± 0.001 mg l^{-1} year^{-1}, $n = 2$) (Table 2).

From 2003 to 2021, there were decreasing trends in SO_4 concentrations throughout all catchments, with a mean trend of -0.13 ± 0.06 mg l^{-1} year $^{-1}$ ($p < 0.001$) (Figure 2b). Among all sites, C1 showed the steepest decline (−0.23) and C4 the lowest (−0.001). The declines in all sites were significant ($p < 0.01$) except for C4 ($p > 0.05$) (Table 2). Forest sites had the largest declining trends (-0.22 ± 0.01, $n = 2$), followed by mixed catchments (-0.13 ± 0.03, $n = 9$), while mire outlet streams had the weakest trends (-0.02 ± 0.02, $n = 2$) (Table 2). Despite the declining trends in SO_4 concentrations, stream pH at each site decreased from 2003 to 2021 with a mean slope of -0.02 ± 0.01 year^{-1} (Figure 2f). At 10 of the 13 catchments, this decline was statistically significant ($p < 0.05$), whereas this was not significant ($p > 0.05$) at the other three sites (Table 2).

Other climatic and ecosystem variables showed increasing trends over the study period. For example, MGPP at each catchment demonstrated an increasing trend from 2003 to 2021 with a mean slope of 0.006 ± 0.001 kg C m^{-2} year $^{-1}$ (Figure 2c). The increase was significant ($p < 0.05$) at 5 of the 13 catchments (Table 2). Discharge at each site also displayed an increasing trend with a mean slope of 0.02 ± 0.003 mm day^{-1} year^{-1} in Krycklan (Figure 2d). It is important to note that these trends in discharge were strongly affected by the last 2 years of the record (Figure 2d). Nonetheless, at 10 of the 13 catchments, the increase in discharge was statistically significant ($p < 0.05$), while this trend was positive but not significant ($p > 0.05$) at the other three sites (Table 2). Finally, soil temperature also showed a rising trend in the Krycklan with a slope of 0.016°C year^{-1}, but this was not statistically significant ($p > 0.05$) between 2003 and 2021 (Figure 2e).

3.2. Environmental Drivers of DOC Variations

Including more environmental factors (discharge, MGPP, sulfate, soil temperature, catchment size and mire coverage) in the analysis resulted in an improvement in the performance of DLMs, indicated by the increase in R^2 and decrease in AIC. DLM7 ($\mathrm{DOC} = \beta_1\mathrm{Dis}_{\mathrm{lag}} + \beta_2\mathrm{MGPP}_{\mathrm{lag}} + \alpha_1\mathrm{SO_4} + \alpha_2 T_{\mathrm{soil}} + \alpha_3\mathrm{Area} + \alpha_4\mathrm{Mire\%}$) was the best-performing model among all the DLMs, which explained 53% of DOC concentrations across 13 catchments in Krycklan (Table 3). From the DLM7, we could quantify the contributions of all environmental drivers and associated mechanisms to the observed variation in DOC concentrations. Here, recovery from SO_4 deposition was the dominant mechanism, accounting for 31% of the variation in DOC concentrations, with the

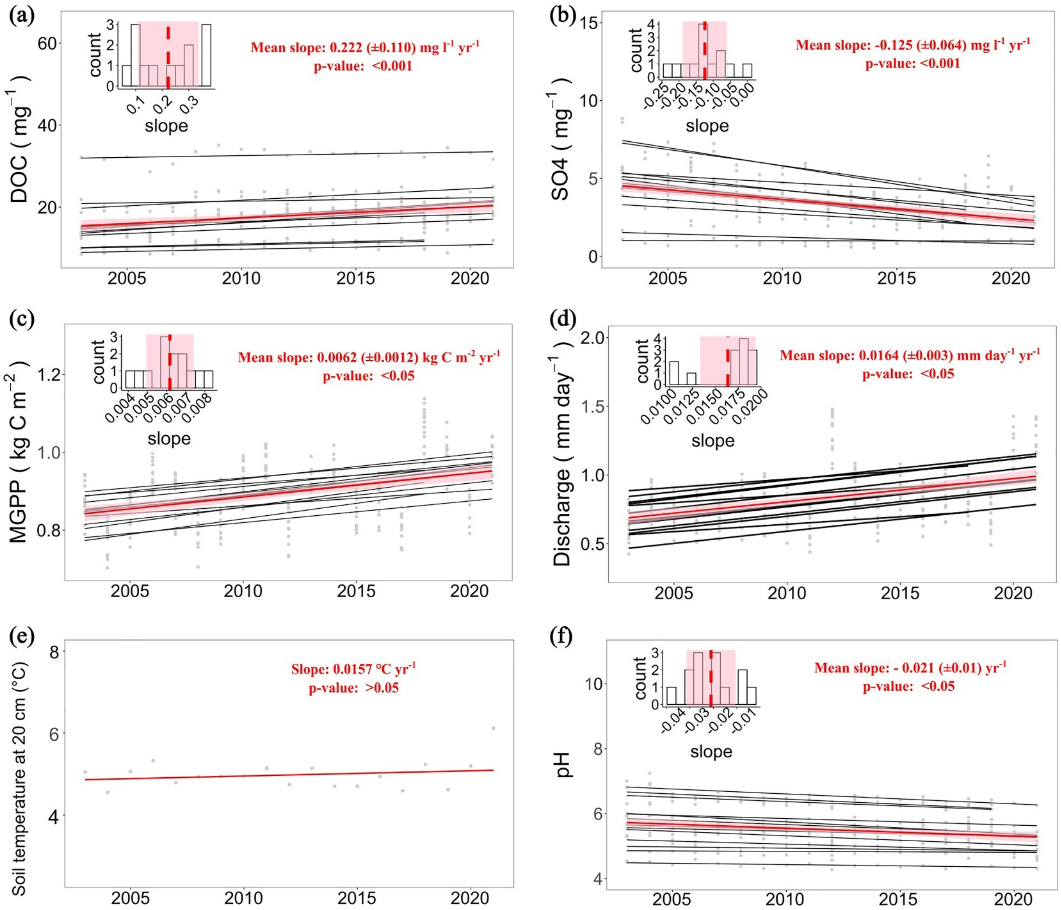

Figure 2. (a) The long-term trends of dissolved organic carbon concentration, (b) SO_4, (c) MGPP, (d) discharge, (e) soil temperature at 20 cm, and (f) stream pH in Krycklan from 2003 to 2021. MGPP means the gross primary productivity extracted from riparian zone using the Moderate Resolution Imaging Spectroradiometer. The annual changes of all variables were calculated using yearly data aggregated from daily data across all sites. The red line represents the mean trend across all sites over 19 years. The pink area highlights trends within one standard deviation of the mean trend. Individual site observations and trends are given as gray points and black lines, respectively. The inset shows the distribution of the rate of change for each variable across the Krycklan catchment. The dashed red line represents the mean slope. The red shaded area represents the mean slope ± standard deviation.

climate change mechanism contributing 7%. There was also important spatial heterogeneity, with site characteristics also playing a crucial role in regulating DOC concentrations, explaining 15% (Figure 3). Specifically, sulfate and catchment size were the most important drivers and inversely correlated with DOC concentrations (Table S3 in Supporting Information S1), explaining 31% and 13% of the variance respectively (Figure 3). Thereafter, discharge, MGPP, mire coverage and soil temperature accounted for 4%, 3%, 2%, and 0.2% of the DOC variation, respectively (Figure 3). Among these, mire coverage and soil temperature contributed positively to DOC concentrations. However, the contributions of MGPP and discharge to DOC were more complex, could be either positive or negative (Table S3 in Supporting Information S1).

3.3. Attributions of Long-Term DOC Trends in Spatial Scale

By the total differential equation, we attributed the long-term increased DOC trends of all Krycklan catchments from 2003 to 2021 to four environmental drivers. However, the contributions of the drivers varied across catchments (Figure 4a). For 12 of the 13 sites, SO_4 was the dominant driver of the long-term (19 years) trends of increasing DOC. In fact, only for C4 (mire site), soil temperature was the most crucial factor (Figure 4a). In 9 of the 13 catchments, the second most important contributor was MGPP, whereas discharge played the secondary

Table 2

The Long-Term Trends of Dissolved Organic Carbon (DOC) Concentrations, MODIS Gross Primary Productivity (MGPP), Discharge, Sulfate, Soil Temperature, and Stream pH From 2003 to 2021 Across Sites

			DOC		MGPP		Discharge		Sulfate		Soil temperature		Stream pH	
Site	Size (ha)	Land cover	Slope	*p*-values	Slope	*p*-values	Slope	*p*-values	Slope	*p*-values	Slope[a]	*p*-values	Slope	*p*-values
C1	48	Forest	0.372	<0.01	0.006	NS	0.018	<0.05	−0.234	<0.01	0.016	NS	−0.015	<0.05
C2	12	Forest	0.382	<0.01	0.006	NS	0.018	<0.05	−0.206	<0.01	0.016	NS	−0.019	<0.01
C4	18	Mire	0.085	NS	0.006	NS	0.019	<0.05	−0.001	NS	0.016	NS	−0.008	NS
C5	65	Mire	0.082	NS	0.004	NS	0.019	<0.05	−0.042	<0.01	0.015	NS	−0.003	NS
C6	110	Mixed	0.175	<0.05	0.006	<0.05	0.019	<0.05	−0.082	<0.01	0.016	NS	−0.019	<0.05
C7	47	Mixed	0.279	<0.01	0.006	<0.05	0.018	<0.05	−0.132	<0.01	0.016	NS	−0.008	NS
C9	288	Mixed	0.218	<0.01	0.005	NS	0.018	<0.05	−0.126	<0.01	0.016	NS	−0.020	<0.01
C10	336	Mixed	0.284	<0.01	0.007	<0.05	0.017	<0.05	−0.115	<0.01	0.016	NS	−0.028	<0.01
C12	544	Mixed	0.309	<0.01	0.004	NS	0.011	NS	−0.184	<0.01	−0.006	NS	−0.026	<0.05
C13	700	Mixed	0.365	<0.01	0.007	<0.05	0.017	<0.05	−0.134	<0.01	0.016	NS	−0.037	<0.01
C14	1,410	Mixed	0.110	<0.05	0.008	NS	0.011	NS	−0.157	<0.01	−0.006	NS	−0.027	<0.01
C15	1,913	Mixed	0.121	<0.05	0.008	NS	0.012	NS	−0.123	<0.01	−0.006	NS	−0.032	<0.01
C16	6,790	Mixed	0.116	<0.05	0.007	<0.05	0.017	<0.05	−0.083	<0.01	0.016	NS	−0.031	<0.01

Note. The measured period is from 2003 to 2018 in C12, C14, and C15. [a]Soil temperature trends in C12, C14, and C15 were from 2003 to 2018 to match DOC data, as records from 2018 to 2021 were missing at these three sites.

role at the other four sites (Figure 4a). In summary, SO_4 was the main factor controlling the long-term trend of DOC in Krycklan, followed by MGPP, temperature, and discharge during the study period (Figure 4b).

3.4. Attributions of Long-Term DOC Trends in Temporal Scale

A 10-year moving window from 2003 to 2021 created 10 sets of 10-year long sequences to evaluate the trend variations in DOC and all environmental variables temporally (Figure 5). The slopes of DOC decreased from the first decade at early 2000s to the last decade, indicating that the upward trend in concentrations has slowed or even ceased in recent years (Figure 5a). From the first decade to the last, the decreasing trend of SO_4 became smaller and then leveled off entirely (Figure 5b). The rising trends of discharge also moderated with time (Figure 5d). The slopes of MGPP and soil temperature were relatively stable during the first 9 periods but increased in the last decade (Figures 5c and 5e). The trends of DOC over different periods were also attributed to the trends exhibited by environmental drivers using differential equations (Figure 5). Here, the influence of SO_4 declined (Figure 5f),

Table 3

Performances of Distributed-Lag Linear Models (DLMs) Show the Relationship Between Dissolved Organic Carbon (DOC) Variations and Potential Environmental Drivers Across 13 Boreal Catchments in Krycklan

	Discharge		MGPP		Performance	
Distributed-lag linear models (DLMs)	Lag (day)	Degree	Lag (day)	Degree	AIC	R^2
1. $DOC = DIS_{lag}$	0–7	2	–	–	241,681	0.04
2. $DOC = MGPP_{lag}$	–	–	4–30	4	243,021	0.02
3. $DOC = DIS_{lag} + MGPP_{lag}$	0–7	2	4–30	4	239,037	0.07
4. $DOC = DIS_{lag} + MGPP_{lag} + SO_4$	0–7	2	4–30	4	203,458	0.38
5. $DOC = DIS_{lag} + MGPP_{lag} + SO_4 + T_{soil}$	0–7	2	4–30	4	202,970	0.38
6. $DOC = DIS_{lag} + MGPP_{lag} + SO_4 + T_{soil} + Area$	0–7	2	4–30	4	183,503	0.51
7. $DOC = DIS_{lag} + MGPP_{lag} + SO_4 + T_{soil} + Area + Mire\%$	0–7	2	4–30	4	179,979	0.53

Note. $MGPP_{lag}$ means the cross basis of MODIS GPP from riparian zone; DIS_{lag} represents the cross basis of discharge; T_{soil} is soil temperature at 20 cm; Area means catchment size. Mire% is the proportion of mire in the landscape of catchment.

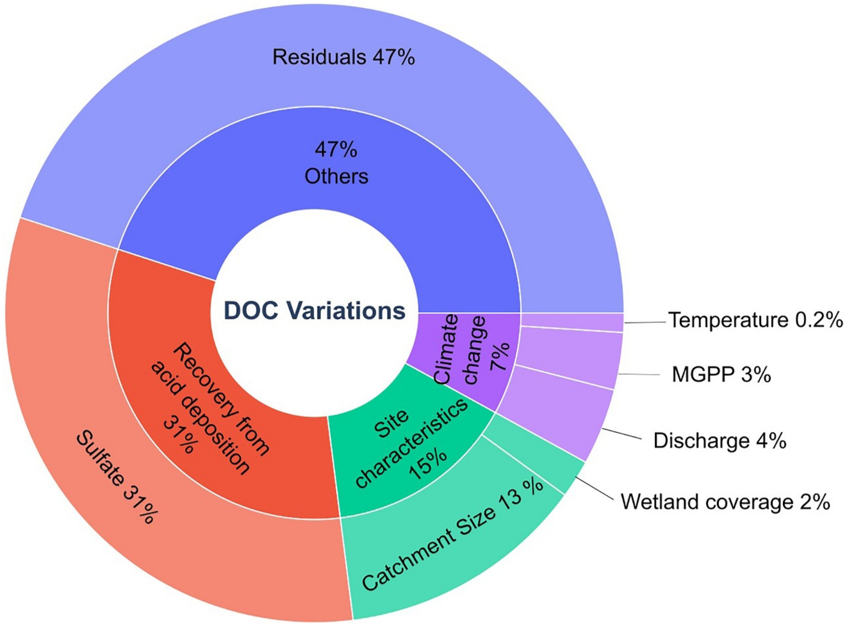

Figure 3. The contribution of proposed mechanisms and site characteristics to the variation in dissolved organic carbon concentrations in Krycklan catchments during 2003–2021 according to the best distributed-lag linear model (DLM7).

while the contributions of MGPP (Figure 5g) and soil temperature (Figure 5i) to long-term DOC trends increased during the study period. Meanwhile, the contributions of discharge to long-term DOC trends were stable during all the periods (Figure 5h).

4. Discussion

Over the period from 2003 to 2021, all catchments in Krycklan experienced increasing trends in DOC concentrations, although the strength of the upward trends varied among sites. Our study indicates that no single mechanism can account for the entire variation in DOC trends over space and time. Instead, we showed that a combination of factors, including sulfate deposition, terrestrial productivity (with delay), discharge (with delay), soil temperature, and properties of the catchment such as size and land cover type explained the overall DOC concentrations across the network. When considering all sites together, the primary drivers of the long-term DOC

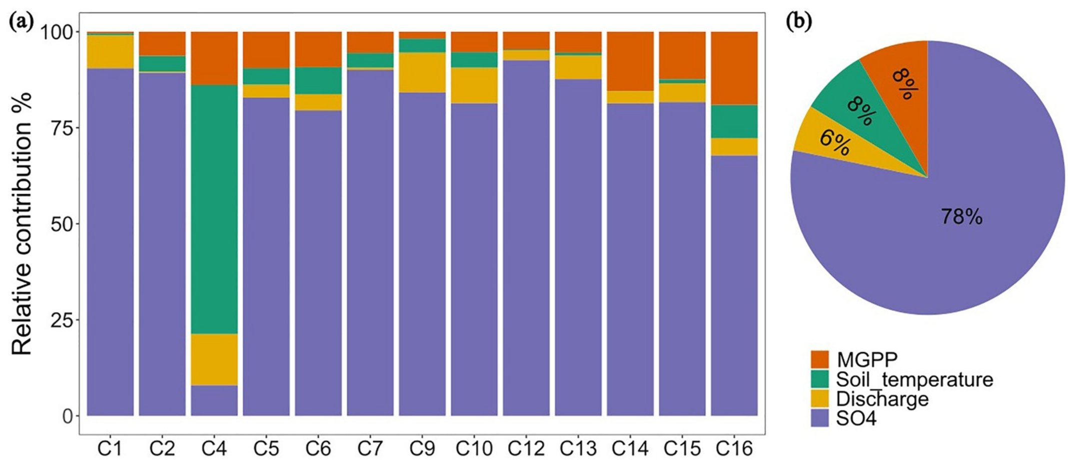

Figure 4. The relative contribution (%) of each driver to long-term dissolved organic carbon (DOC) trends across 13 catchments in Krycklan during 2003–2021 (a). The mean relative contribution of each driver to long-term DOC trend in Krycklan during 2003–2021 (b).

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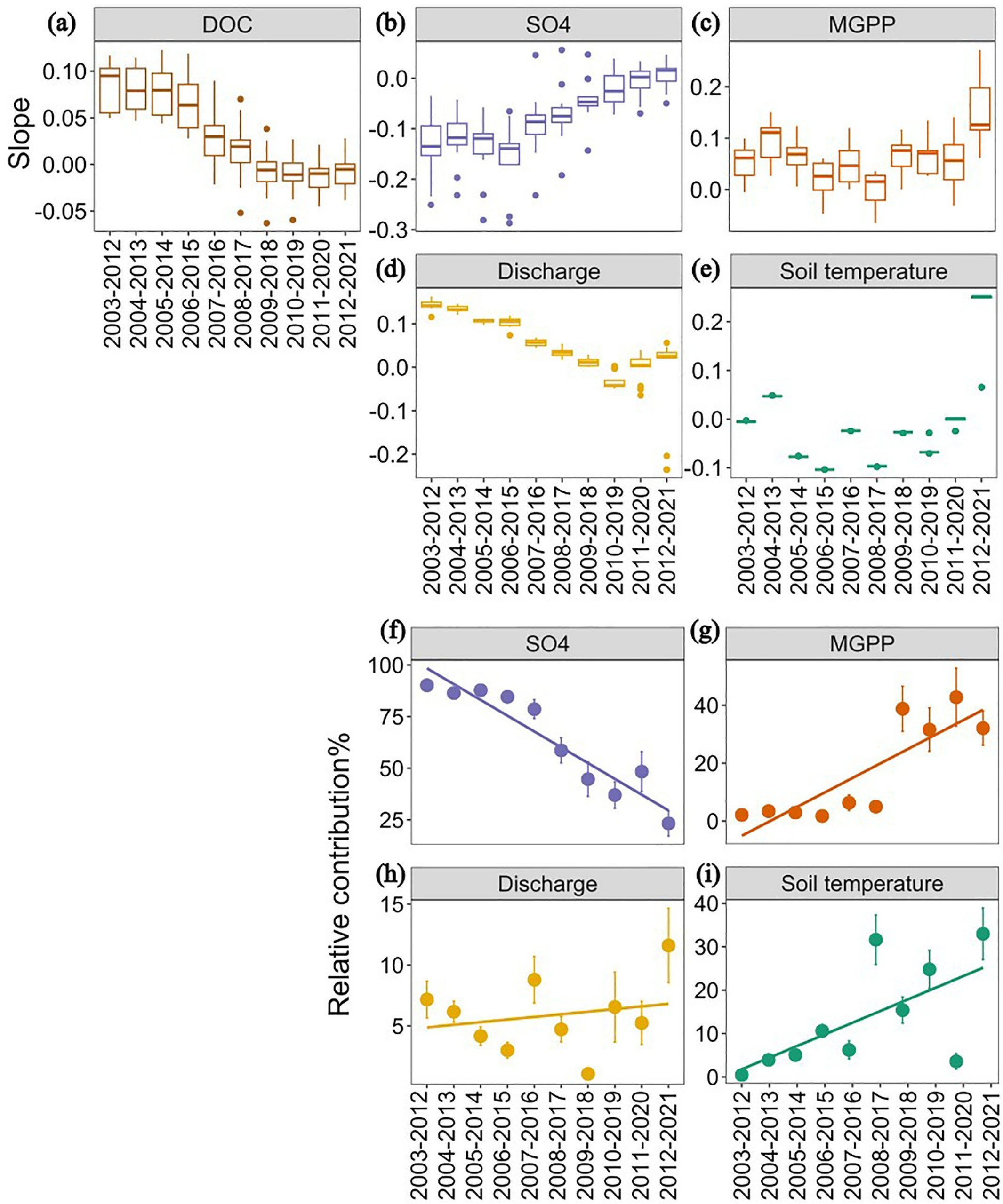

Figure 5. (a) The slope of dissolved organic carbon (DOC), (b) sulfate (SO_4), (c) MODIS GPP (MGPP), (d) discharge, and (e) soil temperature across all periods (10-year moving window from 2003 to 2021) in Krycklan catchments. (f) The relative contribution (%) of SO_4, (g) MGPP, (h) discharge, and (i) soil temperature to long-term DOC trends across all periods. Each bar (point) depicts an average slope (contribution) of all the sites at each period.

trend (spanning 19 years) were the concurrent decline in stream sulfate concentrations, followed by an increase in terrestrial productivity, soil temperature, and discharge. All these drivers can alter DOC concentrations by changing the production, solubility, and/or mobilization (Figure 6). Additionally, DOC trends varied in magnitude by five-fold across sub-catchments within the Krycklan network, highlighting the important role of catchment properties (land cover and size) as modulators of stream response to environmental changes (Figure 6). Briefly, as shown by Fork et al. (2020), the increase in long-term DOC concentration was far more pronounced in catchments with higher forest and lower mire cover (i.e., forest > mixed > mire sites), and the rate of DOC increase also tended to decline from smaller to larger catchments.

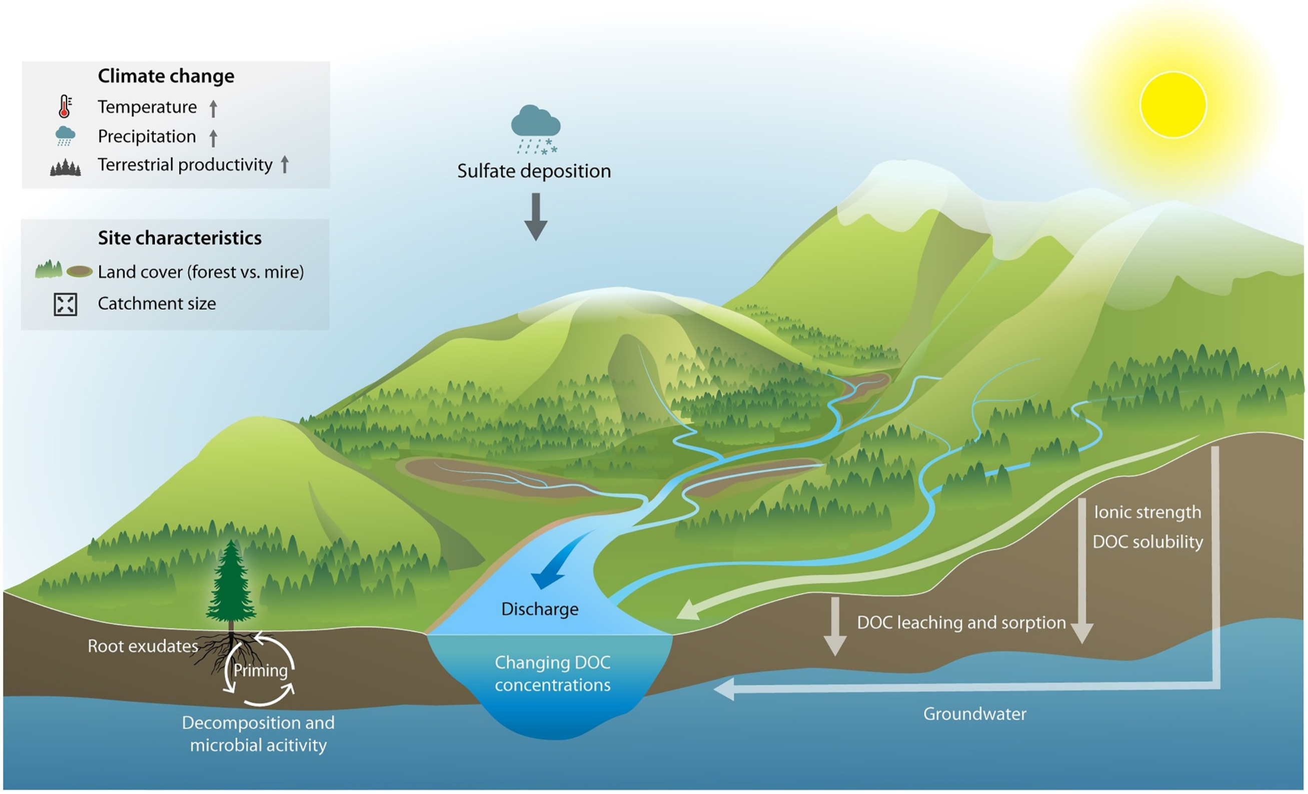

Figure 6. Conceptual diagram illustrating the mechanisms (sulfate deposition, climate change and site characteristics) of browning across 13 boreal nested catchments. DOC means dissolved organic carbon.

Whereas our modeling approach identified multiple drivers of DOC variation, changes in stream SO_4 concentrations emerged as by far the most important (Figure 3). This mechanism is supported by the first-order control that declining stream SO_4 concentrations exerted over the long-term DOC trends (Figure 4b). Further, such observations are consistent with past studies in Krycklan that have assessed DOC-SO_4 relationships in soil water (Ledesma et al., 2016). Atmospheric S deposition can alter DOC solubility by changing the acidity and/or the ionic strength of soil solution (Monteith et al., 2007). Despite significant declines in S deposition at Krycklan since the 1980s, stream pH has not increased over time; instead, it has slightly declined at all sites (Figure 2f). The most likely explanation here is that the rise in DOC and associated organic acidity has overwhelmed the influence of acid deposition recovery on stream pH (Laudon, Sponseller, & Bishop, 2021). However, the reduction in S deposition can decrease the mass of mobile anions, which co-transport base cations (BC) through the soil into the stream (Reuss & Johnson, 1986). In fact, Krycklan streams have witnessed a large decline in the sum of BC, primarily Ca and Mg, which from a charge perspective have changed in parallel with the decline in SO_4 concentration (Laudon, Sponseller, & Bishop, 2021). This concurrent decrease in SO_4 and BC represents a loss in ionic strength, which can consequently enhance the colloidal dispersion and organic matter disaggregation in soil solution (Cincotta et al., 2019), increasing the solubility of DOC in soil water and promoting its lateral export to streams (Lawrence & Roy, 2021). Therefore, the decline in ionic strength rather than recovery from acidification seems to be the main driver of the increasing DOC trends across the Krycklan catchments. It is noteworthy that the large DOC trends occurred despite the relatively low sulfate deposition in Krycklan, peaking at 4 kg S ha^{-1} yr^{-1} around 1980 (Laudon, Sponseller, & Bishop, 2021), which is more than 5 times lower than the most affected parts of Sweden (Ferm et al., 2019).

Our results also revealed important impacts of climate-related factors, including increases in forest productivity and changes in discharge. Studies elsewhere at high latitudes have also linked increasing production and mobilization of terrestrial organic C to browning of surface waters (Finstad et al., 2016). There have been apparent increases in forest growth in and around the Krycklan Catchment throughout the last 60 years (Laudon, Hasselquist, et al., 2021), and this trend has likely increased the size of soil organic matter pools that can be mobilized to streams (Jansson et al., 2008). Further, previous work in Krycklan revealed the lag-effect of terrestrial productivity on soil DOC production through priming (Zhu et al., 2022), and the current study supports these findings across a larger number of catchments and over an extended period. Finally, while the relationship between increasing discharge and elevated DOC concentrations aligns with theory (de Wit et al., 2016), this pattern should be interpreted with caution as the discharge time series was strongly weighted by the final 2 years in the record. Indeed, there is increasing evidence that hydrological patterns in northern landscapes are becoming more variable with climate change (Teutschbein & Seibert, 2012) and that more severe summer droughts in the Krycklan can have large influences on DOC, with lower concentrations during low flow, followed by elevated concentrations during rewetting phases (Tiwari et al., 2022). Regardless, our analysis illustrates how multiple, climate-related features can operate concurrently with deposition recovery to shape stream DOC trends.

One major result from our analysis is that landcover ultimately modulates how trends of S deposition, terrestrial productivity, and discharge may be translated into changes in DOC concentrations for any one stream in the network. First, there can be substantial heterogeneity in the hydrological pathways that connect soils and streams for different landscapes (Schiff et al., 2002). In Krycklan, catchments with large mire coverage support a greater amount of overland flow, due to frozen surfaces and preferential flow through deeper peat layers—both of which can support solute dilution during high discharge events (Peralta-Tapia, Sponseller, Tetzlaff, et al., 2015). By comparison, runoff from forest hillslopes, entering streams through lateral subsurface flow paths, transports newly-activated soil organic C to streams (Bishop et al., 2004; Laudon et al., 2004). Therefore, a greater amount of DOC is flushed into streams draining forest catchments, whereas dilution is more common for mire catchments, resulting in decreasing concentrations during snowmelt (Laudon et al., 2013). This may account for the fact that, despite similar discharge patterns across catchments (Figure 2d), the response rates of DOC were higher in sites with greater forest cover. SO_4 delivered to mires via precipitation may also be more readily flushed and diluted because of the greater hydrological connectivity and contribution of overland flow (Peralta-Tapia, Sponseller, Tetzlaff, et al., 2015). Additionally, mires are known to promote sulfate reduction (Pester et al., 2012), as persistent anaerobic conditions allow sulfate-reducing bacteria to convert SO_4 to sulfide, removing SO_4 from the system (Porowski et al., 2019; Taketani et al., 2010). Such hydrological and biogeochemical mechanisms may explain the observed lower mean concentrations (Figure S4 in Supporting Information S1) and weaker trends for SO_4 (Table 2) at sites with higher mire coverage. Overall, our results are consistent with the dilution and buffering function of mires, as greater peat coverage dampened the response rate of DOC to sulfate deposition. Finally, terrestrial productivity and stand biomass increased across catchments with greater forest and lower mire cover. Elevated GPP likely contributes a greater load of fresh organic matter that can be mobilized from terrestrial to aquatic ecosystems, consequently resulting in higher response rates for stream DOC concentrations in forest-dominated catchments (Crapart et al., 2023).

In addition to the influence of land cover, differences in catchment size, by regulating the relative contribution of deep groundwater sources, can also be an important mechanism regulating DOC response rates. The supply of DOC to groundwater is typically limited because the mineral soil layers and the vadose zone capture most of the DOC released from the humic soil layer (Cannavo et al., 2004; Goldscheider et al., 2006). The contribution of deeper, DOC-poor groundwater to stream is often greater in larger downstream catchments, reducing the significance of DOC inputs from near-surface soils that are more dominant sources in the headwaters (Shanley et al., 2002; Strohmenger et al., 2021). This hydrological pattern appears to be widespread across northern Sweden, with chemical signals from deeper groundwater scaling closely with the catchment area (Tiwari et al., 2018). The greater supply of deeper groundwater to larger streams likely buffers against changes in DOC production and mobilization that are generated in shallower soils. In Krycklan, this pattern is especially evident during low flow conditions, when the DOC-rich headwaters become less hydrologically connected to downstream reaches (Peralta-Tapia, Sponseller, Ågren, et al., 2015). In this way, broad-scale transitions in surficial versus deep groundwater contributions along river continua may regulate the extent to which biogeochemical responses to environmental change in the headwaters are actually manifested as "browning" trends decline in downstream sections.

Among the more novel results from our analysis is the resolution of non-stationary drivers of DOC export over time. The observed decline in browning across Krycklan catchments is consistent with the findings of Eklöf et al. (2021), who showed that increases in DOC that were prevalent throughout Sweden during 1991–2010 slowed down considerably a decade ago. The fact that browning trends have weakened during the last 10 years in Krycklan suggests that recovery from sulfate deposition was strong in the early 2000s, but not throughout the second decade (Figure 5a). As the significance of changes in SO_4 concentration have diminished over time, the relative importance of terrestrial productivity and soil temperature have increased (Figure 5). Yet, the absolute contributions of these factors to DOC trends should remain roughly consistent, suggesting that these emergent drivers are considerably weaker in their capacity to elevate stream DOC when compared to the deposition recovery response. Indeed, the contribution of terrestrial productivity to variations in DOC concentrations can be either positive or negative, according to the direction of priming effect under different landscapes and C inputs (Zhu et al., 2022). Meanwhile, the contributions of discharge across time were relatively stable despite the shift in importance of the other drivers. Although soil temperature made a relatively greater contribution during the last decade, it is unlikely to generate a substantial upward trend of DOC alone (Freeman et al., 2001; Pastor et al., 2003). Therefore, in the recent decade since the weakened driving force of sulfate, other factors seem insufficient to maintain the long-term DOC trends.

While DOC trends in the Krycklan appear to be leveling off, ongoing browning observed at other sites in Sweden can be attributed to either the influence of land use changes (Kritzberg, 2017; Lindbladh et al., 2014; Škerlep et al., 2020) or to deposition recovery at locations that received far higher inputs, particularly in the south, from which catchments may take a longer time to recover (Eklöf et al., 2021). Yet the patterns we observed in this more northern landscape largely concur with Evans et al. (2006) in that rising DOC in freshwaters to a large extent reflect recovery from sulfate deposition, and thus future predictions of dramatic intensification of C export from terrestrial ecosystems may perhaps be overly pessimistic, at least in the short term. Indeed, we acknowledge that the different variables we evaluated likely trigger stream DOC responses at hugely different time scales. For example, the effects of changing SO_4 and temperature on DOC mobilization seems almost instantaneous, whereas the effects of building up a larger humus layer from elevated terrestrial productivity could result in DOC increases many decades later. These long-term cumulative responses are much more difficult to capture with available time series.

5. Conclusion

Our study provides evidence that large (five-fold) variation in browning trends among northern streams can reflect the outcome of interactions among multiple factors, including recovery from sulfate deposition, climate-related factors, and catchment properties. Our results indicate that despite historically low deposition in this region, the decline in ionic strength, driven by recovery from sulfate, has been the main driver of DOC change, rather than recovery from acidification *per se*. Furthermore, our modeling approach reveals the important lag-effects of terrestrial production and discharge on stream DOC, albeit with weaker influences on overall DOC trends when compared to SO_4 declines. Notably, browning has weakened over the past decade, as stream sulfate levels have stabilized while other factors have not been sufficient to maintain the long-term DOC trend.

Data Availability Statement

The water chemistry, hydrological data, climate data and GIS data used in this study are available from Krycklan Data Portal via www.slu.se/Krycklan.

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