AGU PUBLICATIONS

Several mechanisms drive the heterogeneity in browning across a boreal stream network

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Key Points:

- This study evaluated the multiple mechanisms behind browning using a 19-year time series data across 13 nested boreal catchments.
- We revealed recovery from sulfate, rather than from acidification per se, as the primary driver of browning despite low deposition history.
- Our results provided an explanation for spatiotemporal heterogeneity of browning trends within a boreal catchment network.

Abstract

Increases in dissolved organic carbon (DOC) have occurred in many freshwaters across Europe and North America over the last decades. Several mechanisms have been proposed to explain these trends, 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 environmental factors related to DOC concentrations, then attributed the individual trends of DOC to potential drivers across space and time. The results showed that all catchments exhibited increased DOC trends from 2003 to 2021, but the DOC response rates differed five-fold. No single mechanism can fully explain the ongoing browning, instead the interaction of 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 terrestrial productivity, temperature, and discharge. However, catchment size and landcover type regulated the response rate of DOC trends to these drivers, creating the spatial heterogeneity in browning among the sub-catchments under 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 trends. Our results highlight that multifaceted, spatially structured, and nonstationary drivers must be accounted for to predict future browning.

Plain Language Summary

In recent decades, many lakes and rivers in Europe and North America have seen a rise in dissolved organic carbon (DOC), giving the water brownish color. Researchers have suggested different reasons for this, like recovery from acid rain, climate change, and landuse change, yet we're not sure which is the most important. To better understand, we looked at DOC changes in 13 nested rivers, considering all possible causes. We found that all rivers had an increase in DOC from 2003 to 2021, but the increase varied among the rivers. The main drivers of long-term increases in DOC were recovery from sulfate deposition, followed by increased plant biomass, temperature, and water flow. The size of river and land cover type of surroundings also affected how quickly DOC levels changed. Strikingly, browning has slowed down in the last 10 years with total recovery from sulfate deposition, while other factors are too weak to keep browning going. 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 (Driscoll et al., 1988; Karlsson et al., 2009; Martell et al., 1988). Globally, riverine DOC fluxes account for approximately 25-50% of the total C exports to oceans (Cole et al., 2007; Ciais et al., 2008; Drake et al., 2018). Yet, over the last few decades, many catchments in Europe and North America have witnessed rising DOC concentrations in surface waters, often termed “browning” (Monteith et al., 2007; Clark et al., 2010; Lawrence & Roy, 2021). Increases in water color caused by elevated DOC supply affects light penetration and thermal regimes that can further alter the biodiversity and food webs of aquatic ecosystems (Conley et al., 2011; Leach et al., 2019; Kritzberg et al., 2020). Further, increasing DOC reduces the value of aquatic landscapes from the recreational and aesthetic aspects and boosts the cost of purifying 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 (Monteith et al., 2007; Pagano et al., 2014; Lawrence & Roy, 2021). 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 (Kritzberg, 2017; Härkönen et al., 2023). 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 must 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 (Tranvik & Jansson, 2002; Hongve et al., 2004). 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 (Larsen et al., 2011; Finstad et al., 2016; 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 river networks also requires that we consider 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 (Redden et al., 2021; Lapierre et al., 2021; Lepistö et al., 2021). Wit et al., (2016) observed positive trends of DOC in 474 boreal and subarctic catchments across Europe from 1990 to 2013, even suggesting that the 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 a decade ago due to full recovery from acidification. 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 the future browning trends.

To address the open questions on the heterogeneity of browning in a river 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, et al., 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 12 to 6790 ha, and landscape types dominated by both forest and mires (Table 1). For 10 of the 13 catchments, the measurement period was from 2003 to 2021, but from 2003 to 2018 for C12, C14, and C15.

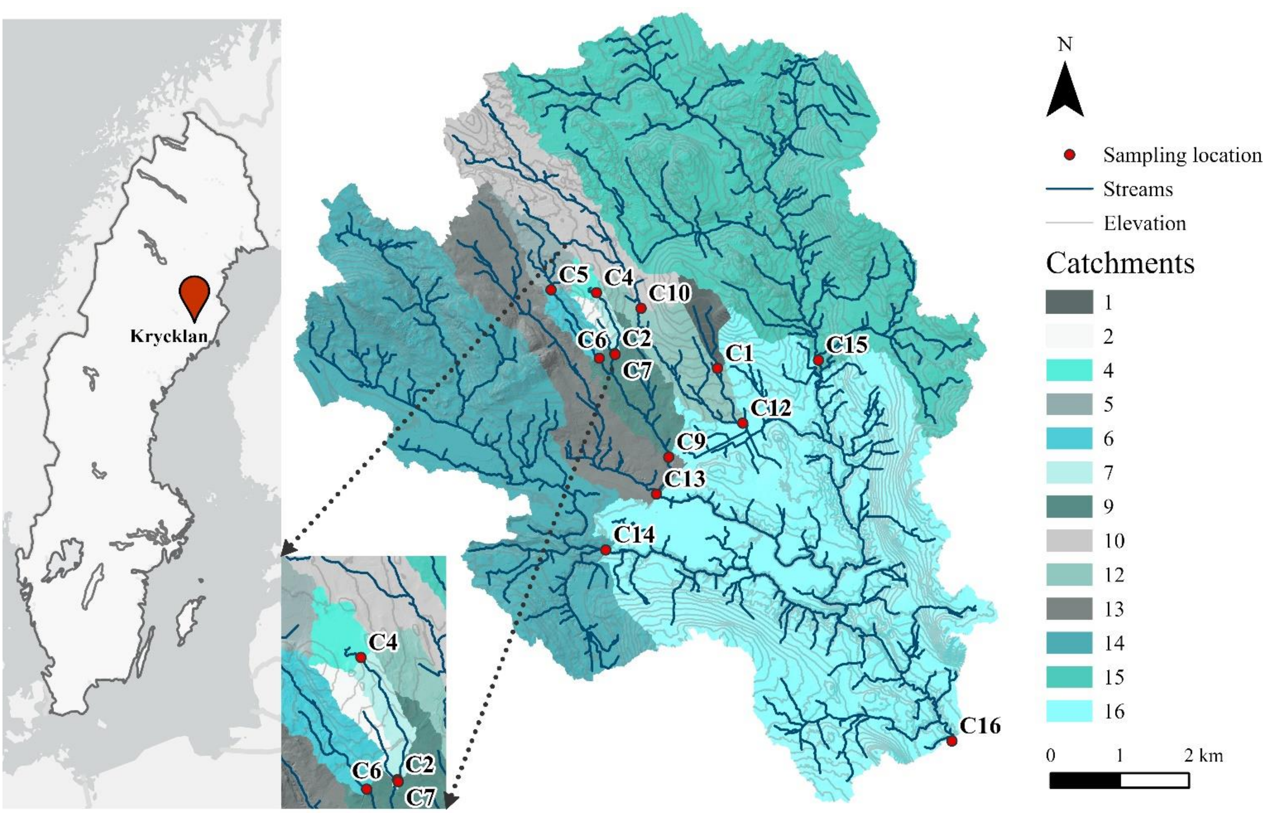

Figure 1. Nested catchments, sampling locations and study sites in Krycklan, Sweden

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 characterized as 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 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 snow water equivalent 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).

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	[m]	11	10	9	2	4	8	4	8	7	6	10	10	10
Size	[ha]	48	12	18	65	110	47	288	336	544	700	1410	1913	6790
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 [a]	$[m^3ha^{-1}]$	187	212	83	64	117	167	150	93	129	145	106	85	106
Land cover type [b]		forest	forest	mire	mire	mixed	mixed	mixed	mixed	mixed	mixed	mixed	mixed	mixed

[a] Calculated for the entire catchment using correlations between a forest inventory (from 110 plots) and LiDAR measurements (Laudon et al., 2013).

[b] 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.

2.2 Environmental trends

Sulfate deposition. In late 1970s, S deposition reached its peak (~4 kg S ha^{-1} yr^{-1}) in Krycklan. Since 20 years ago, S deposition has consistently declined by snowfall and rainfall to less than 1 kg S ha^{-1} yr^{-1}, and hence comparable to those observed during pre-industrial times (Laudon, Sponseller, et al., 2021).

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

Precipitation. Over the last 40 years, there has been no statistical trend observed in the total annual average precipitation, whereas a noticeable decrease has been observed in the average duration of winter snow cover (Laudon, Hasselquist, et al., 2021).

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

2.3 Data collection & interpolation

Site characteristic. 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).

Climate data. Air temperature and soil temperature at 20 cm were 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.

Chemistry data. Surface water samples were collected typically on the same day from each site in acid-wash, high-density polyethylene bottles. The sampling frequency is every third day during spring flood, biweekly during summer and fall, monthly in winter. All samples were filtered immediately after collection (0.45μm 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 as soon as possible. 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 practically equivalent, 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). For more information about field sampling can be found (Köhler et al., 2008; Laudon et al., 2013; Winterdahl et al., 2014). Daily DOC and SO_4

concentrations during 2003 to 2021 were interpolated using '*Random Forest*' by package '*missForest*' (Stekhoven & Buhlmann, 2012) in R (R Core Team, 2019) (FigureS2).

Discharge data. Daily stream discharge of the 13 catchments during 2003 to 2021 were predicted by an ensemble version of a bucket-type, semi-distributed hydrological (HBV) model (Karimi et al., 2022). A more detailed description about the modeling part can be found in Karimi et al., (2022).

MODIS GPP data. The gross primary productivity (GPP) derived from the Moderate Resolution Imaging Spectroradiometer (MODIS) – hereafter MGPPP – is one of the most widely used GPP products (X. Huang et al., 2021). Due to the absence of eddy covariance towers at each sub-catchment, MGPP rather than eddy covariance GPP was applied as the agent of terrestrial productivity in this study. Three methods were developed to extract MGPP (500 m and 8-day resolution) from Google Earth Engine (Gorelick et al., 2017) according to the GIS data from Krycklan database: 1) from the coordinate of each site (point); 2) from the riparian zone (50 meters on both side) of each catchment (line); 3) from the watershed of each site (area) (Figure S2). Daily MGPP was linearly interpolated based on 8-day MGPP (Figure S3). 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). The results revealed that MGPP from three different approaches accounted for 56% to 67% of the variability in eddy-covariance GPP (Table S1). Among the three approaches, MGPP derived from the riparian zone exhibited the highest explanatory power (R^2) (Table S2).

2.4 Statistical analysis

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 mean values against the year. The mean slope of all catchments was used to compute the long-term trend of each variable in the Krycklan catchment.

Distributed-lag linear model. The impact of each environmental factor to DOC concentrations was quantified using distributed-lag linear models (DLMs), where the lag effect was applied to discharge and MGPP according to the wavelet analysis described in 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). The Akaike information criterion (AIC) and R^2 were used to select the best model in predicting the DOC concentrations. Finally, DLM 1-7 were defined as follows:

$$DLM1: DOC = \beta_1 Dis_{lag} \quad (1)$$

$$DLM2: DOC = \beta_1 MGPP_{lag} \quad (2)$$

$$DLM3: DOC = \beta_1 Dis_{lag} + \beta_2 MGPP_{lag} \quad (3)$$

$$DLM4: DOC = \beta_1 Dis_{lag} + \beta_2 MGPP_{lag} + \alpha_1 SO_4 \quad (4)$$

$$DLM5: DOC = \beta_1 Dis_{lag} + \beta_2 MGPP_{lag} + \alpha_1 SO_4 + \alpha_2\ T_{soil} \quad (5)$$

$$DLM6: DOC = \beta_1 Dis_{lag} + \beta_2 MGPP_{lag} + \alpha_1 SO_4 + \alpha_2\ T_{soil} + \alpha_3\ Area \quad (6)$$

$$DLM7: DOC = \beta_1 Dis_{lag} + \beta_2 MGPP_{lag} + \alpha_1 SO_4 + \alpha_2 T_{soil} + \alpha_3 Area + \alpha_4 Mire\% \quad (7)$$

Where β is the lag effect of discharge (*Dis*) and MGPP on DOC concentrations, α is the impact of sulfate (SO_4), soil temperature (T_{soil}), catchment size (*Area*) and mire coverage (*Mire%*). Dis_{lag} and $MGPP_{lag}$ are the mean cross basis of discharge and MGPP during their lag times, respectively. In this study, we evaluated the performance of DLM2 when utilizing MGPP from three different methods. Our findings revealed that DLM2 performed the best when applying MGPP from the riparian zone, as it yielded the lowest AIC and highest R^2 values (Table S2). Thereafter, MGPP from the riparian zone was used for further analysis.

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 across each site. This quantification was achieved by decomposing the 19-year linear trend of DOC in 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 dataset at 1-year interval to obtain 10 datasets (2003-2012, 2004-2013…& 2012-2021). Thereafter, we decomposed the 10-year linear trend of DOC across each period into the additive contributions of four components.

$$\frac{d\,DOC}{dt} = \frac{\partial\,DOC}{\partial\,Dis} * \frac{d\,Dis}{dt} + \frac{\partial\,DOC}{\partial\,SO_4} * \frac{d\,SO_4}{dt} + \frac{\partial\,DOC}{\partial\,MGPP} * \frac{d\,MGPP}{dt} + \frac{\partial\,DOC}{\partial\,T_{soil}} * \frac{d\;T_{soil}}{dt}$$

$$= \Delta DOC^{Dis} + \Delta DOC^{SO_4} + \Delta DOC^{MGPP} + \Delta DOC^{T_{soil}} \quad (8)$$

where $\frac{\partial\,DOC}{\partial\,X}$ represents 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. $\frac{d\,DOC}{dt}$ (Or $\frac{dX}{dt}$) represents the linear trend of DOC (or X) at a certain period. 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 certain period ($\frac{d\,DOC}{dt}$) was decomposed into the contribution of each variable X (ΔDOC^X), which was represented as the product of the partial derivative against that variable X as $\frac{\partial\,DOC}{\partial\,X}$ and the concurrent trend of X itself as $\frac{dX}{dt}$. The approach given by Eq. (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 (ΔDOC^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). Across all the catchments, the change was significant ($p < 0.001$), whereas C2 had the steepest slope (0.38) and C5 had lowest (0.08) (Table 2). Overall, the small forest- dominated sites showed the highest rate of response (0.38 ± 0.04 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 (0.09±0.004 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 =0.95) (Table 2). As with DOC changes, forest sites had the largest declining trends (-0.22 ± 0.01, n=2), followed by mixed (-0.13 ± 0.03, n=9), while mire outlet streams had the weakest trends (-0.02 ± 0.02, n=2) (Table 2). Despite these trends of declining SO_4, stream pH at each site showed a declining trend from 2003 to 2021 with the mean slope of -0.02 ± 0.01 year $^{-1}$ (Figure 2f). At 10 of the 13 catchments, the decline was statistically significant ($p < 0.05$), while this not so ($p > 0.05$) at the other 3 sites (Table 2).

Other climatic and ecosystem variable show trends over the study period. For example, MGPP at each catchment demonstrated an increasing trend from 2003 to 2021 with the 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 mean slope of 0.02 ± 0.003 mm day^{-1} year^{-1} in Krycklan (Figure 2d). It is important to note, these trends were strongly affected by the last two 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 3 sites (Table 2). Finally, soil temperature also showed a rising trend in the Krycklan with a slope of 0.016 ℃ year^{-1}, but this was not statistically significant (p > 0.05)) during 2003 to 2021 (Figure 2e). However, In C12, C14 and C15 (2003 to 2018) the soil temperature decreased (Table 2).

Table 2. The long-term trends of DOC concentrations, MODIS GPP (MGPP), discharge, sulfate, soil temperature and stream pH from 2003 to 2021 across sites. The measured period is 2003 to 2018 in C12, C14 and C15.

Site			DOC		MGPP		Discharge		Sulfate		Soil temperature		Stream pH	
	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	0.371	<0.001	0.006	NS	0.018	<0.05	-0.234	<0.001	0.016	NS	-0.015	<0.05
C2	12	forest	0.378	<0.001	0.006	NS	0.018	<0.05	-0.206	<0.001	0.016	NS	-0.019	<0.01
C4	18	mire	0.090	<0.001	0.006	NS	0.019	<0.05	-0.001	NS	0.016	NS	-0.008	NS
C5	65	mire	0.082	<0.001	0.004	NS	0.019	<0.05	-0.042	<0.01	0.015	NS	-0.003	NS
C6	110	mixed	0.174	<0.001	0.006	<0.05	0.019	<0.05	-0.082	<0.01	0.016	NS	-0.019	<0.05
C7	47	mixed	0.278	<0.001	0.006	<0.05	0.018	<0.05	-0.132	<0.001	0.016	NS	-0.008	NS
C9	288	mixed	0.215	<0.001	0.005	NS	0.018	<0.05	-0.126	<0.001	0.016	NS	-0.020	<0.01
C10	336	mixed	0.282	<0.001	0.007	<0.05	0.017	<0.05	-0.115	<0.001	0.016	NS	-0.028	<0.01
C12	544	mixed	0.309	<0.001	0.004	NS	0.011	NS	-0.184	<0.001	-0.006	NS	-0.026	<0.05
C13	700	mixed	0.366	<0.001	0.007	<0.05	0.017	<0.05	-0.134	<0.001	0.016	NS	-0.037	<0.001
C14	1410	mixed	0.110	<0.001	0.008	NS	0.011	NS	-0.157	<0.001	-0.006	NS	-0.027	<0.01
C15	1913	mixed	0.121	<0.001	0.008	NS	0.012	NS	-0.123	<0.001	-0.006	NS	-0.032	<0.001
C16	6790	mixed	0.113	<0.001	0.007	<0.05	0.017	<0.05	-0.083	<0.01	0.016	NS	-0.031	<0.001

[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.

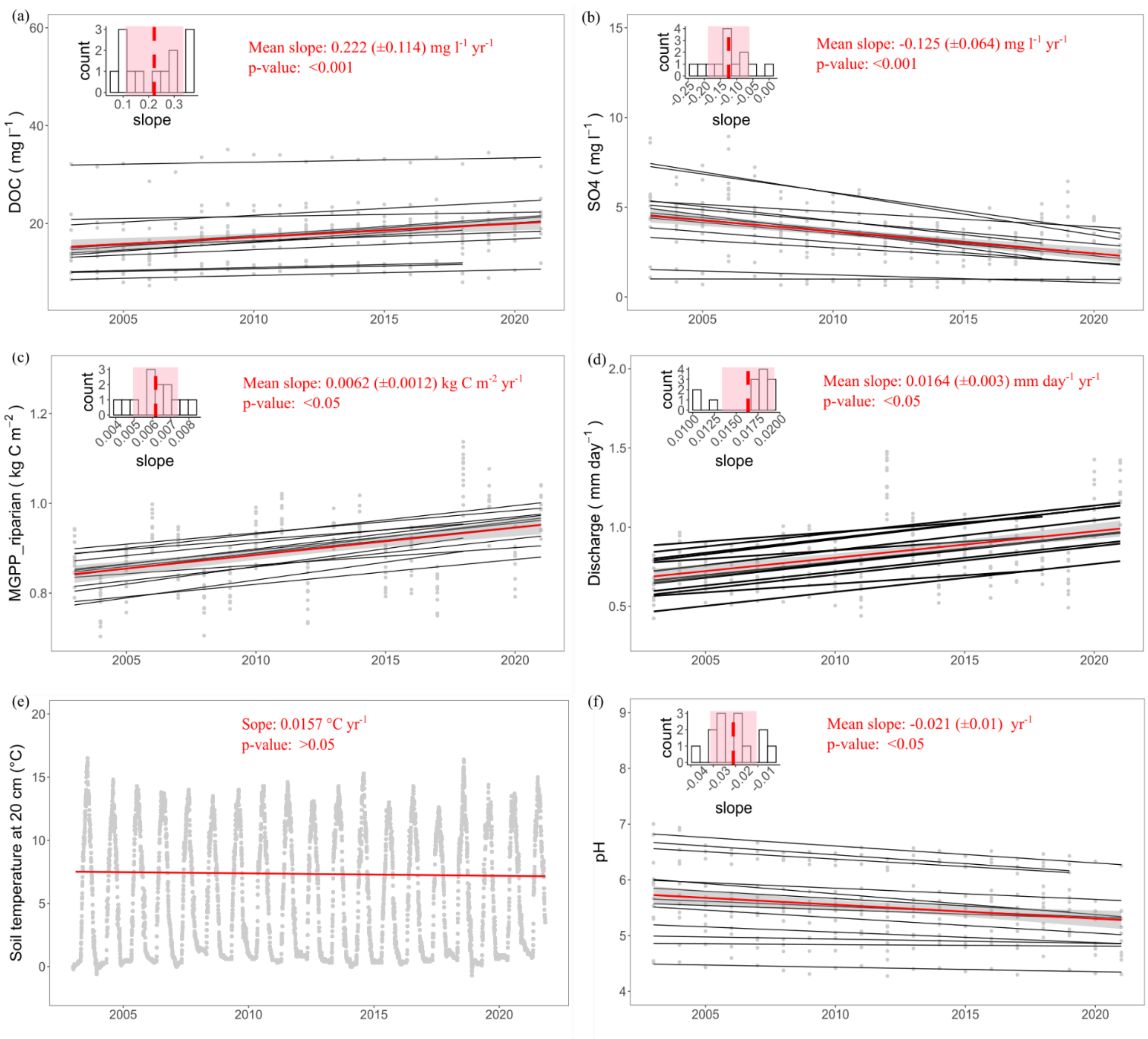

Figure 2. The long-term trends of DOC concentration (a), SO_4 (b), MGPP(c), discharge (d), soil temperature at 20cm (e) and stream pH (f) in Krycklan from 2003 to 2021. The annual changes of all variables were calculated using daily data across all sites. The red line represents the mean trend across all sites over 19 years. The grey area highlights trends within one standard deviation of the mean trend. Individual site observations and trends are given as grey points and black lines, respectively. The inset shows the distribution of the rate of change in DOC across the Krycklan catchment. Dashed red line represents the mean slope. The red shaded area represents the mean slope ± standard deviation.

3.2 Environmental drivers of DOC variations

The inclusion of more environmental factors in the analysis resulted in an improvement of the performance of DLMs, indicated by the increase in R^2 and decrease in AIC. DLM7 ($DOC = \beta_1 Dis_{lag} + \beta_2 MGPP_{lag} + \alpha_1 SO_4 + \alpha_2 T_{soil} + \alpha_3 Area + \alpha_4 Mire\%$) was the best-performing model among all the DLMs, which explained 53 % of DOC concentrations across 13 catchments in Krycklan (Table 3).

According to DLM7, the contributions of all environmental drivers under different proposed mechanisms controlling DOC concentrations were quantified. During 2003-2021, recovery of SO_4 deposition was the dominant mechanism accounting for 31% of DOC concentrations, with the climate change mechanism contributing 6.9%. 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), explaining 31% and 13% 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).

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

Distributed-lag linear Models (DLMs)	**Discharge**		**MGPP**		**Performance**	
	Lag\day	**Degree**	**Lag\day**	**Degree**	**AIC**	**R^2**
1. DOC= DIS_{lag}	0–7	2	-	-	241681.3	0.04
2. DOC= $MGPP_{lag}$	-	-	4–30	4	243021.7	0.02
3. DOC= DIS_{lag}+ $MGPP_{lag}$	0–7	2	4–30	4	239037.2	0.07
4. DOC= DIS_{lag}+ $MGPP_{lag}$+SO_4	0–7	2	4–30	4	203457.9	0.38
5. DOC= DIS_{lag}+ $MGPP_{lag}$+ SO_4+ T_{soil}	0–7	2	4–30	4	202970.3	0.38
6. DOC= DIS_{lag}+ $MGPP_{lag}$+ SO_4+ T_{soil} + Area	0–7	2	4–30	4	183503.3	0.51
7. DOC= DIS_{lag}+ $MGPP_{lag}$+ SO_4+ T_{soil} + Area+ Mire%	0–7	2	4–30	4	179979.3	0.53

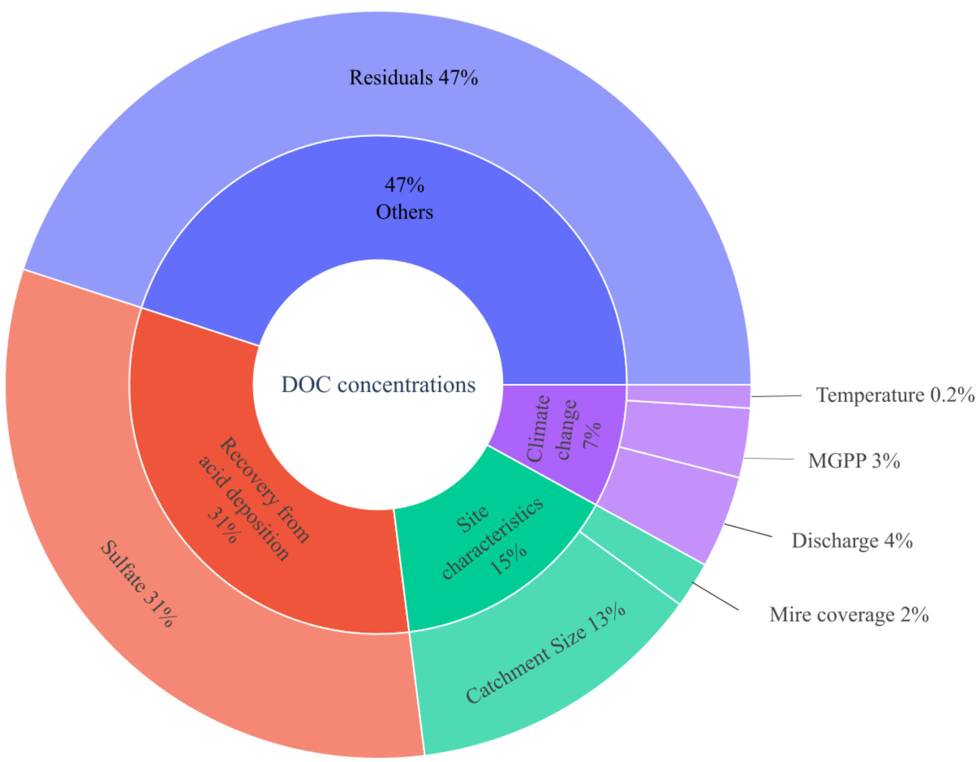

Figure 3. The contribution of proposed mechanisms and site characteristics to the variation of DOC concentrations in Krycklan catchments during 2003-2021 according to the best distributed-lag linear model (DLM7).

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 subsequent important contributor was MGPP, whereas at the other 4 sites discharge played this secondary role (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).

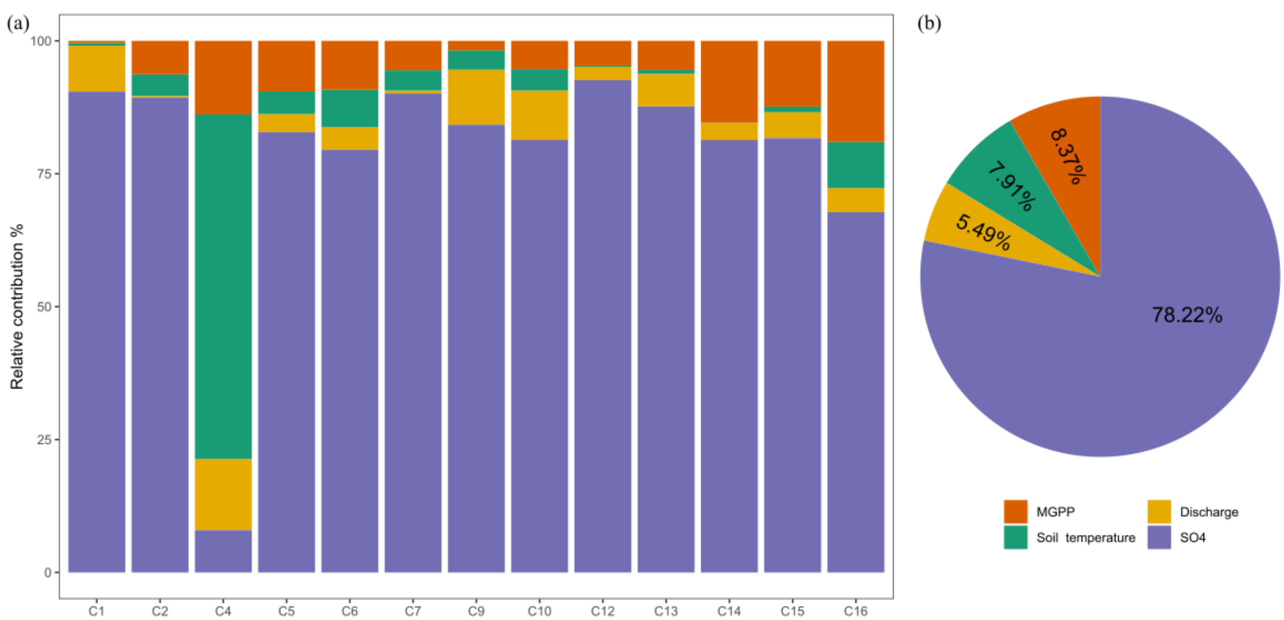

Figure 4. The relative contribution (%) of each driver to long-term DOC trends across 13 catchments in Krycklan during 2003-2021 (a). The mean relative contribution of each driver to long-term DOC trend in Krycklan during 2003-2021 (b).

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 test the trend variations in DOC and all environmental variables temporally (Figure 5). The slopes of DOC decreased from the decade in early 2000s to the last decade which indicated the upward trend of DOC slowed down or even ceased in the most recent years (Figure 5e). From the first decade to the last, the decreasing trend of SO_4 became smaller and then leveled off entirely (Figure 5a). The rising trends of discharge also moderated with time (Figure 5c). The slopes of MGPP and soil temperature were relatively stable during the first 9 periods but increased in the last decade (Figure 5b & d). The trends of DOC over different periods were also attributed to the trends exhibited by environmental drivers using differential equations (Figure 5). The influence of SO_4 reduced (Figure 5A) while the contributions of MGPP (Figure 5B) and soil temperature (Figure 5D) in controlling long-term DOC trends increased. Whereas the contributions of discharge to long-term DOC trends were stable during all the periods (Figure 5C).

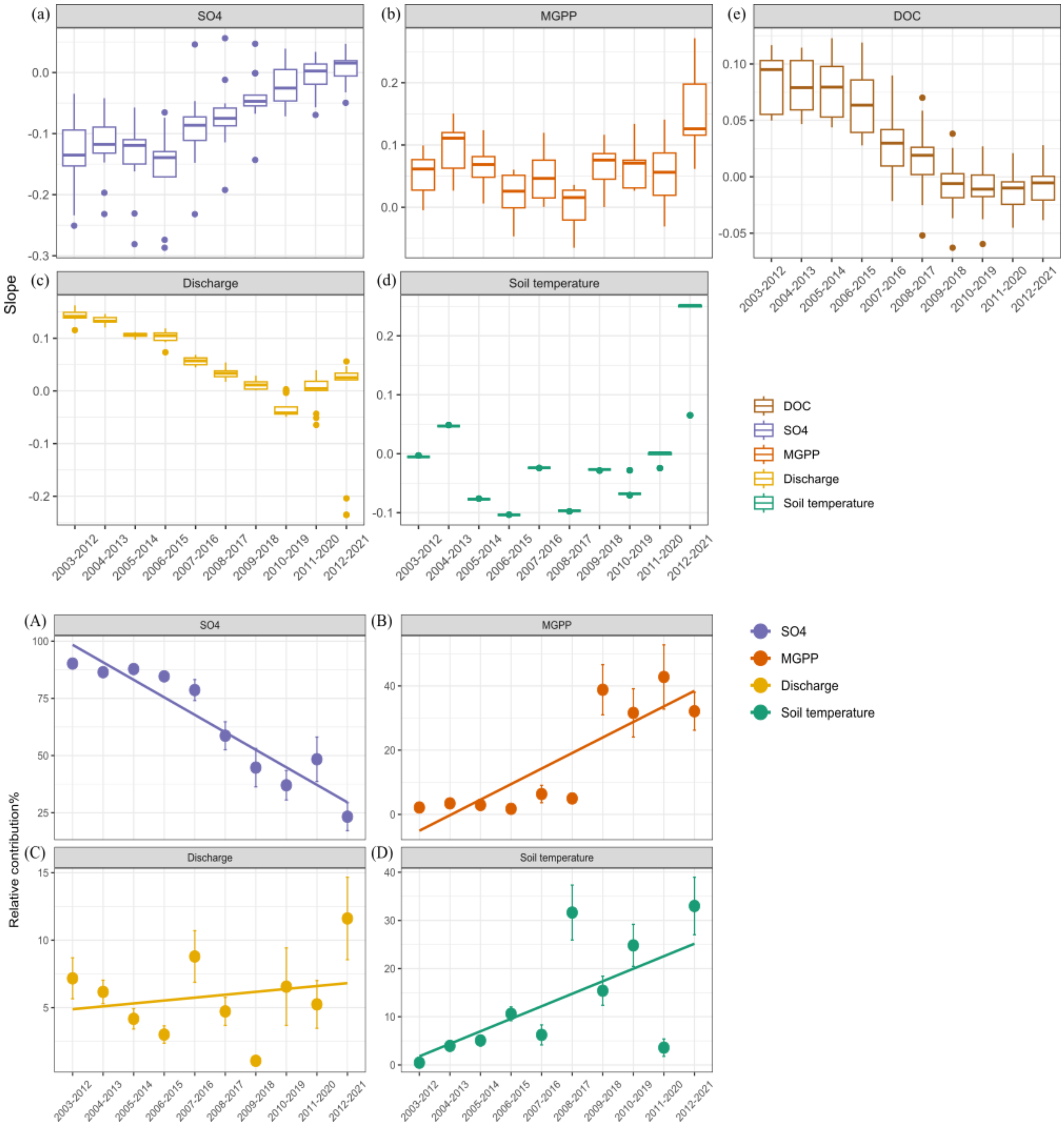

Figure 5. The slope of sulfate (SO_4) (a), MODIS GPP (MGPP) (b), discharge (c), soil temperature (d) and DOC trend (e) across all the periods (10-year moving window from 2003 to 2021) in Krycklan catchments. Meanwhile, the relative contribution (%) of SO_4 (A), MGPP (B), discharge (C) and soil temperature (D) to long-term DOC trends across all the periods.

4. Discussion

Over the period from 2003 to 2021, all catchments in Krycklan experienced an increasing trend in DOC concentrations, although these upward trends varied among sites. Our study indicated that no single mechanism could 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 govern the dynamic of DOC trends. When considering all sites together, the primary drivers of the long-term DOC trend (spanning 19 years) were the concurrent declines in stream sulfate concentrations, followed by increases in terrestrial productivity, soil temperature, and discharge (Figure 6). Additionally, DOC trends varied in magnitude by five-fold across sub-catchments within the Krycklan network, highlighting a major role for catchment properties (landcover and sizes) as modulators of stream response to environmental change (Figure 6). Briefly, the increase in long-term DOC concentrations was more pronounced in catchments with higher forest and lower mire cover (open peatland) (i.e., forest > mixed > mire sites), but the rate of increase tended to slow down from smaller to larger catchments.

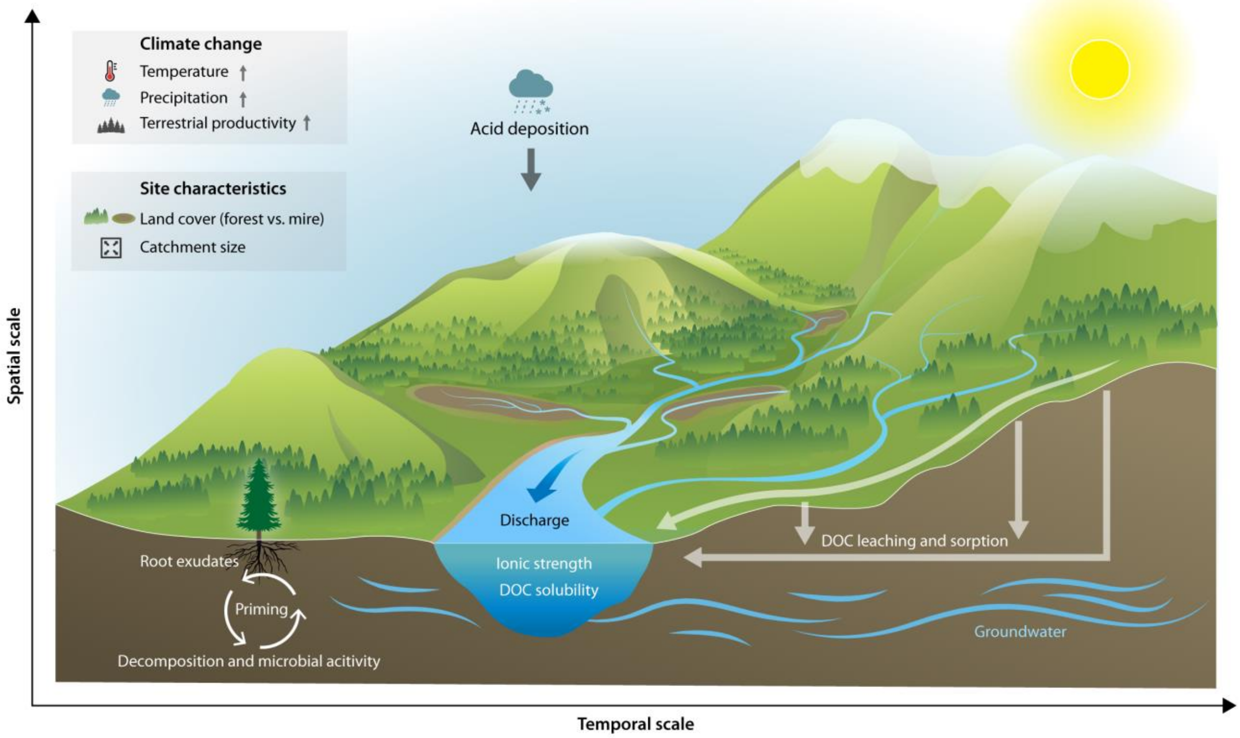

Figure 6. Conceptual diagram illustrating the mechanisms (Acid deposition, climate change and site characteristics) of browning across a boreal catchment network, spanning two-decades. DOC means dissolved organic carbon.

Whereas our modeling approach identified multiple drivers of DOC variations, 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). Furthermore, such observations are consistent with past studies in Krycklan that have assessed DOC-SO_4 relationships in soil water (Ledesma et al., 2016). S-deposition can alter DOC solubility by changing either the acidity of soils or (and) the ionic strength of soil solutions (Monteith et al., 2007). In contrast to expectation, annual pH has not recovered during the study period, but instead has declined slightly at all sites (Figure 2f). Thus, we suggest that the rise in DOC and associated organic acidity, overwhelm the trends in S-deposition from the standpoint of stream pH (Laudon et al., 2021b). Strikingly, the Krycklan streams have witnessed a large decline also in the sum of base cations (BC), primarily Ca and Mg, that in a charge perspective are comparable to the decline in SO_4 concentration (Laudon et al., 2021b). This concurrent decrease in SO_4 and BC decreased ionic strength, which consequently enhanced the colloidal dispersion and organic matter disaggregation in soil solution by expanding the diffuse double layer. Such changes, in turn, can increase the solubility of DOC in soil water and promote 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 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 et al., 2021b), more than 5 times lower compared to 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. Previous studies have also linked increasing production and mobilization of terrestrial organic C from soils to browning (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-effects of terrestrial productivity on soil DOC production through priming (Zhu et al., 2022), while the current study confirmed these findings across a larger number of catchments and over an extended period. Finally, while the relationship between increasing discharge and elevated DOC concentrations is in line with theory (Wit et al., 2016), this pattern should be interpreted with caution as the discharge time series is weighted by the final two 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.

Landcover type can further regulate the patterns between discharge, SO_4, terrestrial productivity and DOC concentrations. Firstly, there is substantial heterogeneity in the hydrological pathways that connect soils and streams for different landscapes (Laudon & Sponseller, 2018). For sites with high mire cover, a larger proportion of water travels overland due to frozen surfaces or within deeper preferential flow paths that can be diluted during high flows (Peralta-Tapia et al., 2015a). By comparison, runoff from forest hillslopes enters streams through subsurface flow pathways could carry newly activated soil organic C to the catchment (Laudon et al., 2004). Therefore, more DOC is flushed into streams draining forest catchments, while dilution is more commons for mire catchments, resulting in decreasing concentrations during rain events (Bishop et al., 2004). This may account for the fact that, despite similar discharge patterns across catchments during the study period (Figure 2d), the response rates of DOC were higher in sites with greater forest cover. Simultaneously, imported SO_4 to the mire sites has also been washed out and diluted because of much higher hydrological connectivity and greater contribution of overland flow (Peralta-Tapia et al., 2015a). Additionally, mires are known to promote sulphate reduction processes (Pester et al., 2012) as persistent anaerobic conditions allow sulphate-reducing bacteria to convert SO_4 to sulfide, removing SO_4 from the system (Porowski et al., 2019; Taketani et al., 2010). Thus, we observed lower mean concentrations (Figure S4) and weaker trends for SO_4 (Table 2) in sites with higher mire coverage. Our results highlighted the dilution and buffer function of mires, such that greater peat coverage dampen the response rate of DOC to sulfate deposition. Moreover, the terrestrial productivity and stand biomass increased with higher forest and lower mire cover, which led to higher load of fresh organic matter from terrestrial to aquatic ecosystem, consequently higher response rate of DOC concentrations (Crapart et al., 2023).

Meanwhile, catchment size can also regulate DOC response rates through changes in the dominant water pathways supporting stream flow. Accordingly, for larger catchments, the contribution of deeper, DOC-poor groundwater to streams is usually greater, reducing the significance of DOC inputs from near-surface soils that are dominant sources in the headwaters (Shanley et al., 2002; Strohmenger et al., 2021; Peralta-Tapia et al., 2015b). This hydrological pattern appears widespread in the region (Tiwari et al., 2018), and the increasing supply of deeper groundwater likely buffers against changes in DOC mobilization that are generated in shallower soils. By modifying the importance of different water sources, increased catchment sizes could moderate the response of DOC to environmental drivers.

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 aligns with the findings of Eklöf et al., (2021) who showed that increases in DOC that were prevalent throughout Sweden during 1991-2010 ended a decade ago. The fact that browning trends have weakened during the last ten years in Krycklan suggested that recovery from sulfate deposition was strong in the early 2000s, but not throughout the second decade (Figure 5a). Despite this, as the significance of changes in SO_4 concentration diminished over time, the relative importance of terrestrial productivity and soil temperature 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 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, without the strong driving force of sulfate, other factors are likely insufficient to maintain the long-term trend.

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 (Lindbladh et al., 2014; Kritzberg, 2017; 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 observe in this more northern landscape largely concur with Evans et al., (2006), in that rising DOC in freshwaters can to a large extent reflect recovery from sulfate deposition, and thus future predictions of dramatic intensification of C export from terrestrial ecosystem may perhaps be overly pessimistic, at least in the short term. Indeed, we acknowledged that the different variables we evaluated likely trigger stream DOC responses at very 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 a DOC increases decades later. These long-term cumulative responses are much more difficult to capture so far.

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 further suggest that recovery from sulfate rather than from acidification *per se* has been the main driver of DOC change, despite the low deposition history in this region. Additionally, our modeling approach revealed 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. That also led to the fact that browning has weakened in the last decade, as stream sulfate levels have plummeted while other drivers were insufficient to sustain the ongoing long-term trend of DOC.

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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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