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# Increases in organic carbon and nitrogen concentrations in boreal forested catchments — Changes driven by climate and deposition

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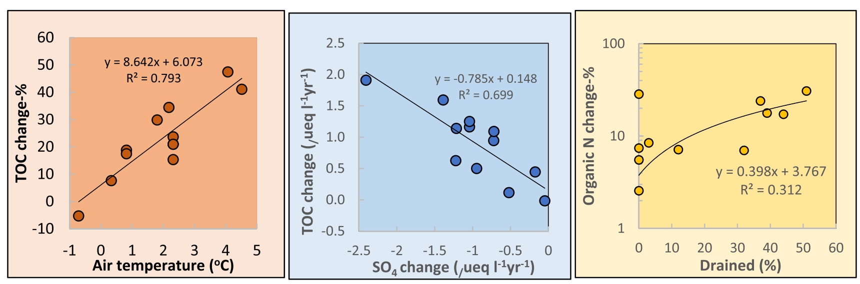
## HIGHLIGHTS

- Brownification is an increasing threat to aquatic ecosystems.
- Reasons behind changes in C and N concentrations in forested streams were studied.
- TOC and TON concentrations increased significantly in 7–10 of 12 forested catchments in 30 yrs.
- Air temperature and sulphate concentrations explained 83% of the TOC variation.
- TON trends were connected to TOC and linked to climatic factors and drainage-%.

## GRAPHICAL ABSTRACT

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## ABSTRACT

Brownification, caused by increasing dissolved organic carbon (DOC) concentrations is a threat to aquatic ecosystems over large areas in Europe. The increasing concentrations of DOC in northern boreal streams and lakes have attracted considerable attention with proposed important drivers such as climate, deposition and land-use, and complex interactions between them. Changes in total organic N (TON) concentrations have received less attention, even though carbon and nitrogen losses are highly related to each other. We used long-term (1990–2019) monitoring records of 12 small data-rich headwater forested catchments in a large gradient of climate and deposition. We found that total organic carbon (TOC) concentrations were significantly increasing in almost all study catchments. The mean air temperature and change in sulphate concentrations had a strong, significant correlation to TOC change-%. Both explained, alone, more than 65% of the change in TOC concentrations, and, together, up to 83% of the variation. Sulphur deposition has already decreased to low levels, our results indicate that its importance as a driver of TOC leaching has decreased but is still clearly detected, while the impact of climate warming as a driver of TOC leaching will be even more pronounced in the future. A positive correlation was found between drainage-% and increases in TON, suggesting also importance of land management. TON trends were tightly connected to changes in TOC, but not directly linked to decreasing S deposition.


## 1. Introduction

The Water Framework Directive (WFD) aims for a good ecological, chemical and hydro-morphological status in European waters by the end of 2027, but it seems that management and restoration actions will be insufficient in reaching that target. In particular, mitigation

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methods to decrease nutrient loads originating from diffuse sources have been inadequate (Hering et al., 2010; Tattari et al., 2017). Several factors linked to climate change have counteracted mitigation measures targeted at reducing nutrient loads (Räike et al., 2020), and studies in northern Europe imply that water bodies across the entire landscape are browning (de Wit et al., 2016; Sepp et al., 2018). Brownification is closely related to increased leaching of dissolved organic carbon (DOC) and linked to climate change. It is an increasing threat to aquatic ecosystems, with profound effects including the absorption of solar radiation, plankton and microbial communities, and ecosystem services such as recreation, fishing and drinking-water supply. Therefore, brownification requires further attention when developing the WFD.

The increasing concentrations of DOC of northern boreal streams and lakes has attracted considerable attention in scientific literature over the last decades, (e.g. Freeman et al., 2001; Evans et al., 2005; Vuorenmaa et al., 2006; Porcal et al., 2009; de Wit et al., 2016; Meyer-Jacob et al., 2019; Kritzberg et al., 2020). Changes in nitrogen (N) concentrations have received less attention, even though in boreal headwater catchments, carbon and nitrogen losses are highly related to each other, due to the dominance of organic N compounds in N cycling (Kortelainen et al., 2006). Besides inorganic nutrients, terrestrial organic matter is increasingly recognized as a strong driver of aquatic productivity (e.g. Deininger and Frigstad, 2019). Organic N (ON) is an important constituent of organic matter and may comprise a major part of N loading in boreal watercourses, but it has been largely ignored. The export of dissolved organic nitrogen (DON) is typically related to DOC export within individual catchments or across regions (e.g. Campbell et al., 2000; Willett et al., 2004). In some cases, however, there is evidence that organic N concentrations were increasing but organic C were not (Lepistö et al., 2008).

Various hypotheses have been put forward to explain brownification, e.g. factors related to climate change i.e. an increase in temperature, enhanced decomposition of organic soils, changes in hydrology and flow paths, elevated atmospheric $CO_2$ levels and decreased acid deposition, or land use changes and disturbances. Warming can affect DOC and DON export in different ways, depending on whether it is accompanied by increased or decreased precipitation. The variation in DOC and DON export is related to hydrology, as well as to biological productivity (Finstad et al., 2016), and how productivity is balanced by decomposition (Tranvik and Jansson, 2002). Changes in climate may intensify the hydrological system by more extreme flows, accelerating biogeochemical processes (Mellander et al., 2018) and increasing total organic carbon (TOC) leaching in large river basins dominated by forests and peatlands (Lepistö et al., 2014). Hydrological conditions and processes, as well as interannual variability, are undergoing major changes due to climate warming. Large areas are becoming warmer and wetter (Øygarden et al., 2014; de Wit et al., 2016) and these trends will most probably continue in the future (Arheimer et al., 2005; Huttunen et al., 2015).

Atmospheric emission control has reduced acid deposition over recent decades resulting in higher soil pH and changed ionic strength, which has increased the solubility of soil organic carbon and, hence, its delivery to aquatic systems (Evans et al., 2006). Water-monitoring data have shown strong temporal correlations between changes in water chemistry resulting from reduced acid deposition and increasing DOC concentrations (e.g. Monteith et al., 2007; Hruška et al., 2009). Atmospheric deposition can affect soil organic matter (SOM) solubility through at least two mechanisms—by changing either the acidity of soils or the ionic strength of soil solutions, or both (Monteith et al., 2007). Recently, it was argued (Meyer-Jacob et al., 2019) that acid deposition suppressed naturally high DOC concentrations during the 20th century, but that a “re-browning” of lakes is now occurring with emission reductions in formerly high deposition areas. However, in contrast, in low deposition areas climate change is forcing lakes towards new ecological states, as lake-water DOC concentrations begin to exceed pre-industrial levels.

An increased extraction of forest biomass and intensified forestry are likely to have an impact on water quality (Laudon et al., 2011). Local increases of nitrogen and phosphorus concentrations due to forestry are well-documented (Ahtiainen and Huttunen, 1999; Löfgren et al., 2009), but its impact on a wider temporal and spatial scale is less clear (Sponseller et al., 2016). According to recent studies, N export from old drained peatlands may be considerably higher than formerly estimated (e.g. Nieminen et al., 2018; Finér et al., 2021). Furthermore, an increase in N concentrations and export from the northern Finnish river basins to the Baltic Sea has been linked to the drainage of peatlands (Räike et al., 2020), and it seems to occur simultaneously with the increase in C concentrations in these river basins in the period 1995–2014 (Räike et al., 2016).

Small catchments, representing various land-use characteristics, provide a relevant framework to monitor long-term changes in diffuse loading (Vuorenmaa et al., 2002; Palviainen et al., 2013; Tattari et al., 2017; de Wit et al., 2020; Marttila et al., 2020). Drivers and their interactions affecting C and N fluxes in stream water from small forested catchments are still poorly understood, including those that are related to the climate, acid deposition and forest management. Thus, the most important mechanisms behind the increasing DOC trends still remain a subject of discussion. Our key questions were: what are the most important drivers explaining trends in TOC and N concentrations in boreal forest stream water? Based on earlier scientific findings, we hypothesized that either climatic factors, a decrease in S deposition, or forest management were most important drivers, or combination of all of them.

In order to test these hypothesis, we used unique long-term monitoring records of small data-rich headwater catchments in a large, about 1000 km north-south gradient of climate and deposition, under varied combinations of these drivers. The study was conducted in three steps: Firstly, we selected 12 forestry dominated or unmanaged catchments and analysed both annual and seasonal trends in total organic carbon (TOC), total N and organic N (TON) concentrations during the time period from 1990 to 2019. Secondly, we studied the relationships between potential drivers by quantifying trends in precipitation, runoff, air temperature and stream water sulphate concentration, and linked those trends to the trends in C and N concentrations. Thirdly, we estimated the potential impacts of forest management on changes in stream water N concentrations.

## 2. Material and methods

### 2.1. Catchment characteristics

The study was based on long-term monitoring data collected during 1990–2019 from the outlet streams of 12 forested headwater catchments in Finland (Fig. 1, Table 1). The data were derived from the national databases maintained by the Finnish Environment Institute, n.d. (SYKE) (https://www.syke.fi/en-US/Open_information/Open_web_services/Environmental_data_API).

Most of these forest catchments have been managed: 7 of the 12 catchments have been drained for forestry (Table 1). On average, 18% of the area of the catchments have been drained (variation 3–51%) (Table 1), which is comparable to the average of 23% in Finland. In most cases, other forest management operations have also been carried out, with the period-specific practices including wood harvesting, forest regeneration, soil scarification and fertilization. Peatlands covered, on average, 39% of the catchment area (Table 1), which agreed well with the average peatland percentage of 33% on forestry land in Finland (Vaahtera et al., 2018). There were very few lakes (average 0.5%) or agricultural fields (0.3%) in the catchments.

### 2.2. Chemical analyses, runoff, export estimates, and meteorological data

Water was predominantly sampled by grab sampling with an average of about 12 samples/year, and samples were taken at the

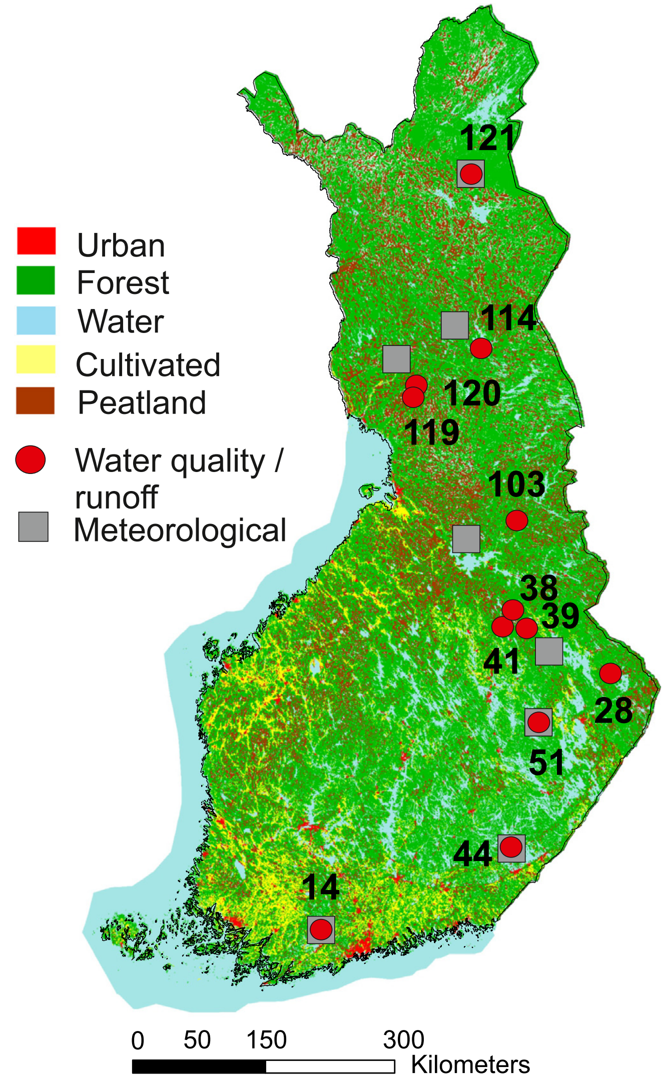


**Fig. 1.** Map of the study catchments and meteorological stations in Finland. The land cover information is based on CORINE land cover information (https://land.copernicus.eu/pan-european/corine-land-cover/clc2018) and peatland data.

outlet of catchments from overflow of the measuring weirs. The sampling frequency varied from fortnightly to monthly, with the sampling strategy concentrating on spring and autumn high flow periods plus additional regular interval sampling throughout the year (Rekolainen et al., 1991). All chemical analyses were performed from unfiltered samples with accredited methods. Nitrogen determination was initiated by digestion with peroxodisulphate, followed by a reduction of $NO_3$ with a Cd amalgam and a determination of $NO_2$ through the azo colour method. Nitrate was reduced to nitrite by a copper-cadmium reductor column. Nitrite that is originally present in the sample together with nitrite formed with the reduction of nitrate are determined by diazotizing with sulfanilamide and coupling with N-(1-naphthyl)-ethylenediamine to form a reddish-purple azo dye that is measured at 550 nm. The sum of nitrate ($NO_3$-N) and nitrite ($NO_2$-N) nitrogen was measured following the reduction in a Cu—Cd column and colorimetric determination. $NH_4$-N was analysed by the indophenol blue method. Organic N fraction (TON) was calculated by the difference: TON = total N − ($NO_3$-N + $NH_4$-N). The TOC samples were sparged after acidification in order to remove the inorganic carbon. TOC was then oxidised to carbon dioxide through combustion and determined by infrared spectrometry with Shimadzu TOC-VCPH analyzer. TOC in microequivalents (μeq $l^{-1}$) was estimated from measured TOC concentrations (mg $l^{-1}$) by multiplying them by a factor 5.0 (Kortelainen, 1993). The differences between TOC and DOC are very small in Finnish forest waters: on an average, 94% of TOC was in dissolved form (DOC) and only 6% in the particulate form (POC) (Mattsson et al., 2005), so the TOC values presented in this study can also directly be regarded to represent DOC. Site-specific S deposition estimates were not available for most of the catchments for the whole study period, so we used measured concentrations of $SO_4^{2-}$ in stream water as deposition surrogates. Sulphate was analysed through ion chromatography (Kortelainen et al., 2006; Mattsson et al., 2017).

Runoff was measured continuously from all 12 catchments by using overflow measuring weirs with a stage-height relationship (Seuna, 1983). The annual export of TOC was calculated for the monitored catchments with the periodic method, in which the temporally nearest concentration observation is multiplied by the runoff of each day (e.g. Rekolainen et al., 1991; Kauppila and Koskiaho, 2003) and daily exports were summed up annually. Meteorological data, daily precipitation and air temperature, were obtained from the nearby weather stations run by the Finnish Meteorological Institute, n.d (https://ilmasto-opas.fi/en/datat).

**Table 1**
Major characteristics of the 12 study catchments.

| Number | Catchment | Latitude °N | Longitude °E | Area ($km^2$) | Peatland % | Drainage % |
|---|---|---|---|---|---|---|
| 14 | Teeressuonoja | 60.4 | 24.4 | 0.7 | 12 | 0 |
| 44 | Huhtisuonoja | 61.4 | 28.7 | 5.0 | 44 | 51 |
| 51 | Kesselinpuro | 62.7 | 29.0 | 21.0 | 41 | 44 |
| 28 | Kelopuro | 63.2 | 30.7 | 1.7 | 48 | 0 |
| 41 | Liuhapuro | 63.8 | 28.5 | 0.7 | 58 | 3 |
| 39 | Kivipuro | 63.9 | 28.7 | 0.5 | 34 | 0 |
| 38 | Välipuro | 63.9 | 28.7 | 0.9 | 56 | 0 |
| 103 | Myllypuro | 64.7 | 28.6 | 11.0 | 32 | 32 |
| 120 | Kotioja | 66.1 | 26.2 | 18.1 | 50 | 37 |
| 119 | Ylijoki | 66.1 | 26.2 | 56.0 | 56 | 39 |
| 114 | Vähä-Askanjoki | 66.6 | 27.7 | 16.0 | 26 | 12 |
| 121 | Laanioja | 68.4 | 27.4 | 13.6 | 6 | 0 |

14 Teeressuonoja and 39 Kivipuro had drainage-% of 0, but, otherwise, they were under normal forestry use. 28 Kelopuro, 38 Välipuro and 121 Laanioja are in pristine state.

### 2.3. Trend analysis

Trends in concentrations, runoff and meteorological variables were analysed with the seasonal Kendall tests (Hirsch et al., 1982, 1991). If the test statistics were greater or lesser than zero on the 95% significance level, we detected an 'upward trend' or a 'downward trend', respectively. The magnitude of the trend was determined by the Theil–Sen slope estimator (Hirsch et al., 1982). The total change over the entire time series (%) was calculated by multiplying the slope with the number of years minus one in the time series. In some of the study catchments, the time series of concentrations, particularly sulphate and runoff, did not totally cover the whole period of 1990–2019.

### 2.4. Correlations and multivariate regression analysis

Pearson correlations coefficients and their significance were estimated between all measured concentrations of water quality variables in 1990–2019, together with runoff, and precipitation and temperature observations in meteorological stations. Forward stepwise regression analysis was used to relate changes in TOC, total N and TON concentrations with potentially impacting variables: temperature, runoff, precipitation, catchment properties such as peatland% and drainage% and $SO_4$ concentration in stream water.

## 3. Results

### 3.1. Concentrations levels

Annual TOC concentrations averaged 19.5 mg $l^{-1}$ and varied between 1.8 and 35 mg $l^{-1}$. The highest concentrations (30–35 mg $l^{-1}$) were found in Eastern Finland (41 Liuhapuro, 39 Kivipuro and 38 Välipuro), while the lowest concentrations were found in Lapland (121 Laanioja). The average total N concentrations varied from 109 to 1152 μg $l^{-1}$ (Table 2) with the highest concentrations mostly in the southern–south-eastern catchments. Humic substances strongly dominated the water quality: TON consisted of up to 71–97% of total N, with the exception of the mineral soil dominated 14 Teeressuonoja (43%) in southern Finland.

Correlations between hydro-meteorological variables and concentrations were analysed using data for 12 catchments in 1990–2019 (n varied between 316 and 346; Appendix 1, supplementary data). TOC correlated strongly ($p < 0.0001$) with TON ($r = 0.848$) but did not have any correlation with sulphate. Instead, temperature strongly correlated with both TOC ($r = 0.284$, $p < 0.0001$) and TON ($r = 0.194$, $p=0.000$). The total N concentration correlated strongly ($p < 0.0001$) with TOC ($r = 0.510$), inorganic N ($r = 0.783$), TON ($r = 0.777$) and sulphate ($r = 0.693$) concentrations, and monthly precipitation ($r = 0.224$). Runoff had typically negative correlations with water quality variables such as TOC ($r = -0.185$), inorganic N ($r = -0.319$), TON ($r = -0.184$) and sulphate ($r = -0.380$), indicating dilution processes.

### 3.2. Annual trends for 1990–2019 of water quality and hydrometeorological variables

Statistically significant increasing TOC concentrations were found in almost all (10/12) of the catchments (Table 2). The strongest increases were found in the most southern catchments (14 Teeressuonoja, change 41%; 44 Huhtisuonoja change 47%). In the 10 catchments with TOC increase, also TON concentrations were increasing (in 7 out of 12 catchments), and total N in 4 catchments. The increase in TOC concentration varied from 15 to 47% during the observation period and the annual increase from 0.09 to 0.38 mg $l^{-1}$ $yr^{-1}$. At the same time, TON concentrations increased from 7.4 to 31% and the annual increase was from 1.4 to 5.9 μg $l^{-1}$ $yr^{-1}$, respectively (Table 2).

Statistically significant decreasing sulphate concentrations were found in almost all (10/12) of the catchments (Table 2). The strongest decreases were found in 44 Huhtisuonoja (−75%) and 38 Välipuro catchments (−95%). In Huhtisuonoja, the TOC increase was also the strongest.

Air temperature increased statistically significantly in almost all 12 catchments, represented by 8 climate stations (Fig. 1). Considerable increases of 1.2–1.6° were detected during the 30-year study period. There were no statistically significant trends for precipitation, and only few changes for runoff: increases in 2/12 and decreases in 2/12 catchments (Table 3).

Mostly due to the increase in TOC concentrations, TOC export also increased: an increase from an average of 6110 kg $km^{-2}$ $yr^{-1}$ (1990–1999) to 7010 kg $km^{-2}$ $yr^{-1}$ during the 2010s (2010–2019), i.e. about 15%, was detected (Fig. 2). Total N export increased by 13% during the same periods, respectively. These increases were not statistically significant. There was a strong variability between very dry and wet years.

### 3.3. Monthly trends of concentrations and hydrometeorological variables

Monthly trend analyses revealed that increases of TOC concentrations concentrated more to spring (April–May increases in 6–7 out of 12 catchments), but increases were also found in November in half of the catchments (Table 4). Increasing concentrations of total N were more common in the autumn (in September and November increase

**Table 2**
Statistically significant ($p < 0.05$) increasing (brownish) and decreasing (grey) trends of TOC, total N, organic N (TON) and $SO_4$ concentrations in 1990–2019, in the 12 study catchments. Higher intensity of colour describes higher change-%. p values, slopes, average concentrations and non-significant trends (no colour) are given.

| | TOC | | | | total N | | | | Organic N | | | | $SO_4$ | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | p | Change % | Conc. mg $l^{-1}$ | Slope mg $l^{-1}$ $yr^{-1}$ | p | Change % | Conc. µg $l^{-1}$ | Slope µg $l^{-1}$ $yr^{-1}$ | p | Change % | Conc. µg $l^{-1}$ | Slope µg $l^{-1}$ $yr^{-1}$ | p | Change % | Conc. mg $l^{-1}$ | Slope mg $l^{-1}$ $yr^{-1}$ |
| 14 Teeressuonoja | 0.013 | 41.1 | 17.0 | 0.25 | 0.000 | 56.7 | 1152 | 22.5 | 0.032 | 28.5 | 492 | 5.0 | 0.127 | -13.4 | 10.5 | -0.05 |
| 44 Huhtisuonoja | 0.000 | 47.4 | 23.3 | 0.38 | 0.050 | 16.3 | 787 | 4.4 | 0.012 | 30.8 | 561 | 5.9 | 0.000 | -75.4 | 4.4 | -0.12 |
| 51 Kesselinpuro | 0.004 | 34.4 | 26.8 | 0.32 | 0.073 | 14.2 | 764 | 3.8 | 0.020 | 17.2 | 655 | 3.9 | 0.017 | -23.1 | 8.4 | -0.07 |
| 41 Liuhapuro | 0.007 | 21.0 | 30.1 | 0.22 | 0.023 | 8.3 | 558 | 1.6 | 0.028 | 8.5 | 536 | 1.6 | 0.001 | -55.9 | 1.7 | -0.03 |
| 28 Kelopuro | 0.004 | 23.7 | 10.9 | 0.09 | 0.900 | 0.0 | 266 | 0.0 | 0.357 | 5.5 | 232 | 0.4 | 0.001 | -34.5 | 0.7 | -0.01 |
| 39 Kivipuro[2] | 0.006 | 20.9 | 31.6 | 0.23 | 0.017 | 8.6 | 560 | 1.7 | 0.041 | 7.4 | 544 | 1.4 | 0.009 | -43.0 | 3.1 | -0.06 |
| 38 Välipuro[12] | 0.003 | 15.4 | 34.9 | 0.23 | 0.507 | 2.5 | 577 | 0.6 | 0.497 | 2.6 | 556 | 0.6 | 0.000 | -94.7 | 1.2 | -0.05 |
| 103 Myllypuro[2] | 0.002 | 29.8 | 18.4 | 0.19 | 0.284 | 8.6 | 462 | 1.4 | 0.481 | 7.0 | 428 | 1.0 | 0.000 | -52.7 | 1.6 | -0.03 |
| 120 Kotioja[2] | 0.005 | 18.8 | 16.6 | 0.13 | 0.001 | 17.1 | 587 | 4.0 | 0.001 | 24.0 | 491 | 4.7 | 0.000 | -49.6 | 2.1 | -0.06 |
| 119 Ylijoki | 0.007 | 17.5 | 14.3 | 0.10 | 0.492 | -2.3 | 611 | -0.6 | 0.001 | 17.7 | 495 | 3.5 | 0.000 | -62.4 | 1.4 | -0.05 |
| 114 Vähä-Askanjoki | 0.310 | 7.7 | 8.7 | 0.02 | 0.501 | 2.6 | 248 | 0.2 | 0.183 | 7.1 | 229 | 0.6 | 0.000 | -55.2 | 1.3 | -0.03 |
| 121 Laanioja | 0.544 | -5.3 | 1.8 | 0.00 | 0.024 | -17.7 | 109 | -0.7 | 0.015 | -24.4 | 78 | -0.7 | 0.206 | -2.4 | 2.8 | 0.00 |

[1] 1990-2013 Välipuro

[2] sulfate from 1990 until 2010-2015

| Change-% |
|---|
| 0–20 |
| 20–40 |
| 40–60 |
| >60 |
| 0 – -20 |
| -20 – -40 |
| -40 – -60 |
| < -60 |

**Table 3**
Statistically significant ($p < 0.05$) increases (brownish) and decreases (grey) of hydrometeorological variables in 1990–2019. The higher intensity of colour describes a higher change-%. For temperature, the slope equals the change in a year (°C $yr^{-1}$). $p$ values, slopes, averages and non-significant trends (no colour) are given.

| | Temperature | | | | Precipitation | | | | Runoff | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | Change | Average | Slope | | Change | Average | Slope | | Change | Average | Slope |
| | p | °C | °C | °C $yr^{-1}$ | p | % | mm | mm $yr^{-1}$ | p | % | mm | mm $yr^{-1}$ |
| **14 Teeressuonoja** | 0.004 | 1.5 | 4.5 | 0.052 | 0.747 | 0.3 | 641 | 0.073 | 0.008 | -1.2 | 263 | -0.105 |
| **44 Huhtisuonoja** | 0.013 | 1.2 | 4.1 | 0.040 | 0.221 | 0.0 | 620 | -0.261 | 0.850 | 0.0 | 217 | 0.003 |
| **51 Kesselinpuro** | 0.005 | 1.3 | 2.2 | 0.044 | 0.104 | 1.1 | 612 | 0.222 | 0.295 | 0.5 | 235 | 0.036 |
| **41 Liuhapuro**[1] | 0.003 | 1.6 | 2.3 | 0.053 | 0.830 | -0.3 | 573 | -0.050 | 0.727 | 0.1 | 358 | 0.018 |
| **28 Kelopuro** | 0.003 | 1.6 | 2.3 | 0.053 | 0.830 | -0.3 | 573 | -0.050 | 0.076 | 0.6 | 320 | 0.067 |
| **39 Kivipuro**[1] | 0.003 | 1.6 | 2.3 | 0.053 | 0.830 | -0.3 | 573 | -0.050 | 0.840 | 0.0 | 329 | -0.006 |
| **38 Välipuro**[1] | 0.003 | 1.6 | 2.3 | 0.053 | 0.830 | -0.3 | 573 | -0.050 | 0.530 | 0.1 | 342 | 0.020 |
| **103 Myllypuro** | 0.007 | 1.3 | 1.8 | 0.045 | 0.064 | -2.1 | 585 | -0.411 | 0.087 | 0.5 | 371 | 0.061 |
| **120 Kotioja** | 0.006 | 1.5 | 0.8 | 0.050 | 0.722 | -0.5 | 574 | -0.100 | 0.392 | 0.2 | 387 | 0.023 |
| **119 Ylijoki** | 0.006 | 1.5 | 0.8 | 0.050 | 0.722 | -0.5 | 574 | -0.100 | 0.025 | 0.6 | 440 | 0.081 |
| **114 Vähä-Askanjoki** | 0.005 | 1.6 | 0.3 | 0.058 | 0.423 | -1.8 | 505 | -0.300 | 0.044 | 0.4 | 402 | 0.051 |
| **121 Laanioja** | 0.097 | 0.9 | -0.7 | 0.029 | 0.218 | -0.9 | 589 | -0.167 | 0.006 | -0.6 | 427 | -0.083 |

[1] Runoff time-series cover 21-22 yrs, during 1990-2011

**Precipitation and runoff change-%**

0–20
20–40
40–60
>60
0 – -20
-20 – -40
-40 – -60
< -60

**Temperature change**

<0.04 °C $yr^{-1}$
0.04-0.05 °C $yr^{-1}$
>0.05 °C $yr^{-1}$

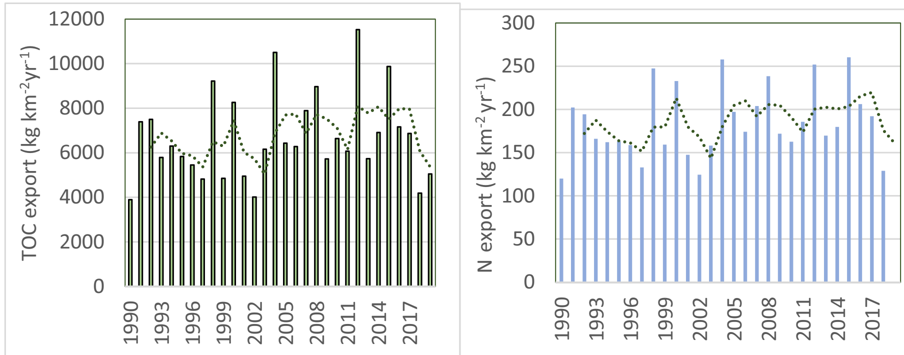


**Fig. 2.** Annual TOC and total N export (kg km$^{-2}$ yr$^{-1}$) in 1990–2019 as an average of 12 study catchments, together with 3-year moving averages.

in 6 out of 12 catchments). In addition, 1–3 increases were found in the winter-spring period. Upward TON trends occurred in the same months as total N trends, but there were more of them, particularly in January and November. For sulphate, downward trends occurred during almost the entire year, at the highest during the spring season (9–10 of 12 in April–May) and in October (7 of 12).

For air temperature, upward trends occurred in May and September (8 out of 12), with some also in August and November. Runoff increased during late autumn-winter-early spring (November–March), in 1–3 catchments out of 12. These trends indicate milder winters and a shift of the earlier pronounced spring high flow period towards lower peaks in winter or early spring. Runoff decreased mostly in early summer (June), in 3 catchments.

### *3.4. Factors explaining changes in concentrations*

Air temperature had a strong, significant correlation with TOC concentration change-% ($R^2$ = 0.79, $p$ = 0.0001) (Fig. 3a). The highest TOC increases occurred in the two southernmost, warmest catchments. The lowest TOC increases occurred in the northernmost sites. Between TOC change and sulphate change (μeq l$^{-1}$ yr$^{-1}$), a high statistically significant negative correlation was also found ($R^2$ = 0.70, $p$ = 0.001) (Fig. 3b). These two explaining variables, which were not considerably correlated with each other ($R^2$ = 0.34), were studied further in the multivariate regression analysis.

The leaching of organic matter can be seen in both TON and TOC: TOC change-% and TON change-% had a strong positive correlation ($R^2$ = 0.67, $p$ = 0.001) (Fig. 3c). Higher drainage-% affects higher TON concentration change-% ($R^2$ = 0.31, $p$ = 0.05) (Fig. 3d).

In the regression analysis with one or two explaining variables, most of the change in TOC concentrations (μeq l$^{-1}$ yr$^{-1}$) was explained by only one factor: $SO_4$ change (μeq l$^{-1}$ yr$^{-1}$) explained alone 70% ($R^2$ = 0.70, $p$ = 0.0007), or the mean air temperature alone 68% (p = 0.001) of the change. Together these variables explained up to 83% of the change in TOC concentration ($p$ = 0.0001) (Table 5). TOC change-% was logically the most important explaining variable for total N change-% ($R^2$ = 0.54, $p$ = 0.006) since TON strongly dominates N fractions. Change-% in runoff was the second most explanatory variable ($R^2$ = 0.28, $p$ = 0.079). Even though the change in runoff was not statistically significant, it acted as a supporting variable: together with TOC change-%, it explained 72% of the variation in N change-% ($p$ = 0.0014). The only factor which significantly explained TON change-% was the TOC change-% ($R^2$ = 0.66, $p$ = 0.0012). Drainage-% together with average temperature explained equally much of the TON change-% as the TOC change-% alone ($R^2$ = 0.66, $p$ = 0.003). Somewhat surprisingly $SO_4$, tightly linked to the TOC change, did not improve the explanatory power of the TON change.

## 4. Discussion

### *4.1. TOC concentrations were increasing — combined impacts of climate and deposition*

Long-term water quality and runoff records from forested catchments, spanning over relatively large environmental and climate

**Table 4**
Monthly number of significant ($p$ < 0.05) brownish upward (↑) and grey downward (↓) monthly trends of TOC, total N, organic N (TON), sulphate and hydrometeorological variables in the 12 study catchments in 1990–2019. The higher intensity of colour describes a higher number of detected trends. At the minimum, data from 10 years during a certain month was needed for analysis. n is the number of catchments with enough data for a trend test, and empty cells mean a lack of significant trends.

| | TOC | | | Total N | | | Organic N | | | Sulphate | | | Air Temperature | | | Precipitation | | | Runoff | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | ↑ | ↓ | n | ↑ | ↓ | n | ↑ | ↓ | n | ↑ | ↓ | n | ↑ | ↓ | n | ↑ | ↓ | n | ↑ | ↓ | n |
| JAN | 1 | | 5 | 2 | 1 | 5 | 4 | | 5 | | | 1 | | | 8 | | | 8 | 3 | 1 | 12 |
| FEB | | | 3 | 1 | 1 | 3 | 2 | | 3 | | | 1 | | | 8 | | 2 | 8 | 1 | 2 | 12 |
| MAR | 2 | | 8 | 3 | 1 | 8 | 3 | | 8 | | 2 | 6 | | | 8 | | 1 | 8 | 1 | 1 | 12 |
| APR | 6 | | 12 | 1 | 1 | 12 | 1 | | 12 | | 9 | 12 | | | 8 | | | 8 | | 1 | 12 |
| MAY | 7 | 1 | 12 | 1 | | 12 | 1 | 1 | 12 | | 10 | 12 | 8 | | 8 | | | 8 | | 1 | 12 |
| JUN | 1 | | 10 | 2 | 1 | 10 | 3 | 1 | 10 | | 6 | 10 | | | 8 | | | 8 | | 3 | 12 |
| JUL | | | 4 | | | 6 | | | 6 | | 1 | 1 | | | 8 | | | 8 | | 1 | 12 |
| AUG | 1 | | 10 | | | 10 | | | 10 | | 2 | 8 | 1 | | 8 | | | 8 | | 1 | 12 |
| SEP | 2 | | 12 | 6 | | 12 | 5 | | 12 | | 5 | 12 | 8 | | 8 | | | 8 | 1 | 1 | 12 |
| OCT | 2 | | 12 | 2 | | 12 | 2 | | 12 | | 7 | 12 | | | 8 | | | 8 | | | 12 |
| NOV | 6 | | 12 | 6 | 1 | 12 | 7 | 1 | 12 | 1 | 5 | 12 | 4 | | 8 | | | 8 | 2 | | 12 |
| DEC | 1 | | 5 | | | 6 | | | 5 | | 1 | 2 | | | 8 | | | 8 | 1 | 1 | 12 |

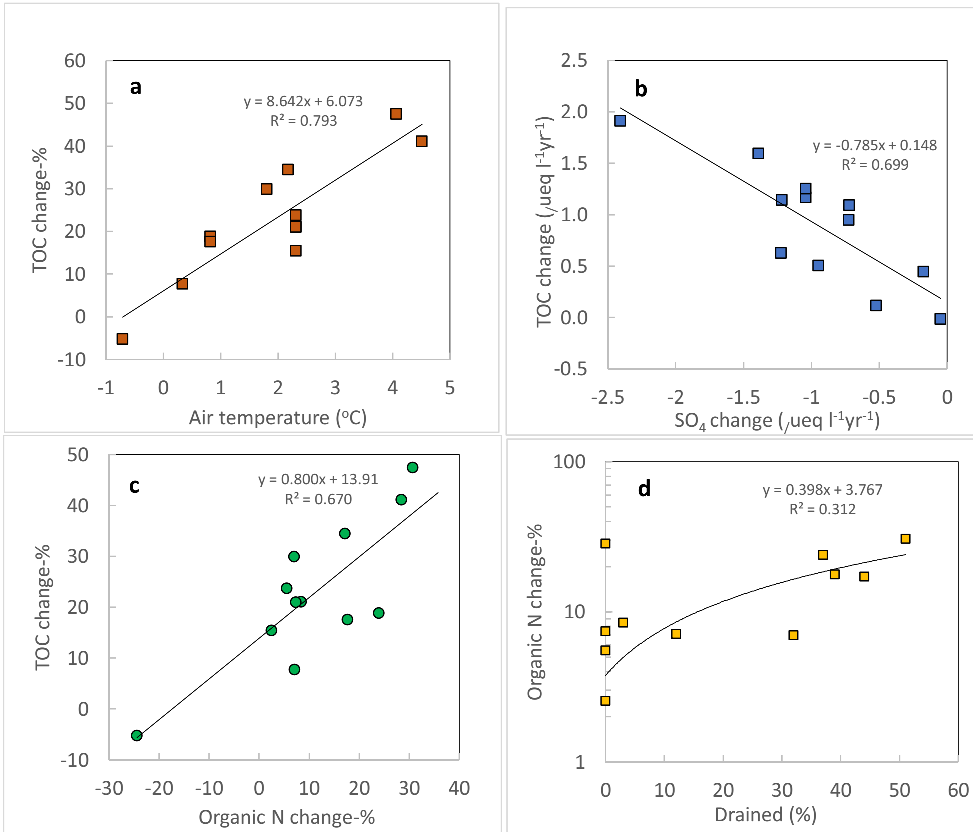


**Fig. 3.** a) TOC concentration change-% as function of annual mean air temperature, b) TOC concentration change vs. sulphate change (µeq $l^{-1}$ $yr^{-1}$), c) correlation between TOC and TON (organic N) change (%), and d) organic N change-% as a function of drainage (%) (one negative value out of scale).

gradients, offered us a unique possibility to evaluate the effects of the climate, deposition and land use on surface water quality. We used a 30-year time-series from well documented, data-rich forested catchments. Our key question was, which are the most important driving factors explaining changes in TOC concentrations: i) climate, particularly temperature and precipitation, ii) declining S deposition with sulphate in stream water used as a surrogate, or iii) drainage indicating forest management, or all of them?

TOC concentrations were increasing significantly in almost all catchments (Table 2), which was also reflected in TOC export: during the 2010s, a 15% higher average TOC export was measured compared with the 1990s (Fig. 2). The most significant increasing TOC concentrations were found in the catchments with the warmest climate conditions. Either air temperature or a change in sulphate concentrations alone explained more than 65% of the change in TOC concentrations, and together up to 83% of the variation (Table 5), being the most important drivers of TOC leaching. However, the increase in TOC concentrations was not directly related to upward trends in air temperature, but, instead, related strongly to the average air temperature which typically correlates to soil temperatures. Thus, it remains unclear which processes have the most important contribution to increasing TOC trends: organic matter decomposition and mineralization are both sensitive to variations in moisture and temperature (e.g. Christ and David, 1996).

An important driver to the upward TOC trends in our catchments was a decrease in sulphate deposition reflected in stream water concentrations. It has been more pronounced in southern Finland than in the northern parts of the country (Vuorenmaa et al., 2018). The decrease in sulphate deposition has levelled off in integrated (ICP IM) sites throughout Europe, up to 70–90% (Vuorenmaa et al., 2018), therefore its importance as a driver of TOC leaching has decreased, and in the future the impact of climate warming as a driver of TOC leaching will most

**Table 5**
Combined results of linear and multiple linear regression analysis with TOC change (µeq l−1yr−1), total N, and organic N change-% as dependent variables. The first two equations 1–2 are based on one explaining variable, and the third equation 3 gives combined impacts of both variables.

| Mode | Model diagnostics | | | | | Parameter estimates | | | |
|---|---|---|---|---|---|---|---|---|---|
| | n | Intercept | p | VIF | Adj. $R^2$ | Slope $SO_4$ (µeq $l^{-1}$ $yr^{-1}$) | Air temp °C | TOC (% change) | Runoff (% change) |
| TOC 1 (slope µeq $l^{-1}yr^{-1}$) | 11 | 0.15 | 0.0007 | 1.00 | 0.70 | −0.79 | | | |
| TOC 2 (slope µeq $l^{-1}$ $yr^{-1}$) | 11 | 0.27 | 0.0010 | 1.00 | 0.68 | | 0.32 | | |
| TOC 3 (slope µeq $l^{-1}$ $yr^{-1}$) | 11 | 0.04 | 0.0001 | 1.56 | 0.83 | −0.50 | 0.20 | | |
| Total N 1 (% change) | 11 | −11.9 | 0.0062 | 1.00 | 0.54 | | | 0.92 | |
| Total N 2 (% change) | 11 | 11.6 | 0.0791 | 1.00 | 0.28 | | | | −17.8 |
| Total N 3 (% change) | 11 | −9.34 | 0.0014 | 1.01 | 0.72 | | | 0.88 | −16.0 |
| Organic N (% change) | 11 | −8.57 | 0.0012 | 1.00 | 0.66 | | | 0.86 | |

probably increase further. Many authors have reported either a decline in acid deposition or climate related factors dominating an increase in TOC. Decreasing mineral acid deposition may increase organic acidity, resulting in increased DOC concentrations (e.g. Evans et al., 2005; Vuorenmaa et al., 2006; Oni et al., 2013). Sarkkola et al. (2009) found that hydro-meteorological factors were more important than declining acid deposition in predicting TOC concentration trends in boreal headwater streams located in eastern Finland in a low sulphate deposition area.

Hydrological conditions and processes are undergoing major changes due to climate warming. Changes in temperature may directly impact DOC exports from wetlands by altering DOC production via increased organic matter decomposition and mineralization, which are both sensitive to variations in moisture and temperature (e.g. Dalva and Moore, 1991; Christ and David, 1996). Increased air temperature may result in increased depth to the water table in organic soils as a result of higher evaporation rates. If the water table is lowered below the surface, the carbon sink–source relationship is likely to be disturbed because a greater percentage of the peat is available for oxidation in biochemical reactions (Freeman et al., 2001).

In laboratory experiments, Clark et al. (2009) found a significant interaction ($p < 0.001$) between temperature, water table draw-down and net DOC production across the whole soil core. The implications of their results are that increased water table draw-down due to decreased summer rainfall and increased evapotranspiration not only increases the net production of DOC but also the temperature sensitivity of production, thereby enhancing the release of C from the peatland C store that would be caused by a temperature increase alone (Clark et al., 2009).

In the catchment scale, Worrall et al. (2004) estimated a 12% increase in the production rate of DOC in peat catchments in the UK, where the temperature increased by 0.78 °C during the observation period of 1970–2000. Evans et al. (2006) suggested that in catchments in Scotland, a 0.66 °C temperature increase could have generated a DOC increase of around 10–20%, depending on the degree of soil aeration. This contribution could be higher if there has been a net shift towards increased soil aeration, particularly in peat soils. These results suggest that temperature is a significant driver of long-term DOC trends but is unlikely to explain the full magnitude of observed DOC increases (Evans et al., 2006). In our catchments, however, the temperature has increased in 1990–2019 by over double of that, at an average of 1.4 °C, and might potentially contribute correspondingly to the increase of TOC by several tens of percent. We detected an average TOC increase of 25% (range 8–47%). Further, due to drainage works in most catchments, there has also been a shift towards increased soil aeration.

Wen et al. (2020) emphasized the role of temperature controlling DOC production, and hydrology controlling export or DOC at the catchment scale, in an organic-rich catchment in the US. The DOC production rate depended more on temperature than on water storage or soil moisture. This finding was expected, as DOC production is biologically mediated and, thus, influenced by temperature and the metabolic dependence on temperature (Gillooly et al., 2001). Future warming and increasing hydrological extremes could accentuate temporal asynchrony, with DOC production occurring primarily during dry periods and the export of DOC dominating in major storm events (Wen et al., 2020).

### 4.2. TON increase together with TOC

In our study catchments, TOC and TON trends were strongly related (Fig. 3c) as significant trends for both TOC and TON were found in 7 out of 12 catchments. The total N mainly consisted of TON, but upward trends were found in only 4 catchments. This indicated that inorganic fractions, mostly $NO_3$-N, disturb the relationship between N and TOC. The export of DON has often been reported to be related to that of DOC within individual watersheds or across regions (e.g. Campbell et al., 2000; Willett et al., 2004). In boreal headwater catchments, TOC and N losses are highly related ($R^2 = 0.95$) to each other, due to the dominance of organic compounds in N cycling (Kortelainen et al., 2006), and most of the organic N and C occurs as dissolved organic fractions (Mattsson et al., 2005).

Since TON concentrations increased simultaneously with TOC concentrations, a proportional (%) increase in TOC concentrations was the best explanatory variable of the increase in organic N ($r^2 = 0.66$). The addition of other explanatory variables (e.g. sulphate) did not improve the coefficient of determination, demonstrating that changes in the TOC concentration, temperature and drainage-% were controlling changes in the TON concentration. An increase in TON has also been observed in large scales, in response to multi-stressors. The concentrations of TON have been observed to increase in the northern Simojoki river catchment (Lepistö et al., 2008), mostly related to climate factors. Moreover, Deininger et al. (2020) reported recently of large N load increases over the past decades in Norwegian rivers, with, in particular, an increase in the organic nitrogen fraction.

### 4.3. Role of forest drainage

Land-use changes and disturbances may be expected to result in an increased decomposition of soil organic matter and release of DOC (e.g. Neal et al., 1998; Pärn and Mander, 2012). We studied the relationship between the change in TOC and TON concentrations and forest drainage, and found a positive correlation between drainage-% and an increase in organic N concentrations (Fig. 3d). However, forest management may significantly contribute to organic matter and associated C and N fluxes. Forest drainage, which was one of the dominant forest management practices in 1950–1990 in Finland, increases the decomposition of surface peat and mineralization of elements, as well as soil erosion, and, therefore, also the export of elements both in dissolved and particulate forms (Ahtiainen and Huttunen, 1999). Due to relatively high groundwater levels in peatlands throughout the year, surface runoff is dominant, which may facilitate erosion and C leaching processes, while lower water levels in drained peatlands may facilitate decomposition and $CO_2$ emissions (e.g. Ojanen and Minkkinen, 2019). Mitchell and McDonald (1995) found that areas with the greatest peat drainage density were the most important sources of DOC.

It has been recently suggested that forestry drainage contributes to the increasing C and N fluxes in large river basins (Asmala et al., 2019; Räike et al., 2020). The same phenomenon was also evident in small headwater catchments in Finland: Both N and TOC concentrations and exports increased with the proportion of drainage area within a catchment area (Finér et al., 2021).The discrepancy between those results and our results may be explained by the high number of catchments (n = 89) in the study of Finér et al. (2021), allowing for a more accurate examination of the impacts of drainage than the 12 highly varying catchments of our study. The impacts of drainage on the total N concentrations have been suggested to last or even increase over several decades after drainage (Nieminen et al., 2018).

### 4.4. Seasonal changes in organic matter leaching

Most upward trends for TOC were found in April–May and in November. Most decreases in $SO_4$ and increases in temperature also occurred during the spring and autumn periods, suggesting that these parameters are linked to each other. TON behaved differently, however, practically no trends were detected during the spring high flow. Instead, increasing trends were detected in the autumn and all through the winter season, particularly in January when most of the upward trends also concerned runoffs (Table 4). During the winter, cold-season processes are known to contribute substantially to annual organic budgets and cycling (e.g. Kielland et al., 2006).

Mattsson et al. (2015) found that, annually, the concentrations of TON increased during the spring high flow, peaked in April and remained high throughout the summer and autumn, while the TOC pattern was different with the highest concentrations in November–December. Most of the TOC and TON were transported during the high flow periods following the spring snowmelt and rainfalls in the autumn.

The concentrations of TON have been observed to increase with increasing runoff (Lepistö and Kortelainen, 2011). However, the relationship between DON and runoff may not be as strong as for DOC and runoff (Campbell et al., 2000), and there is evidence that the variability of DON concentrations may be more affected by other factors, such as productivity and the litter returns of plants (Chapman et al., 2001). The delivery of terrestrial TON and TOC to aquatic systems depends on the production/decomposition rates and on hydrological transport. Results from a northern, peatland dominated Simojoki river basin have suggested that the production of both TON and TOC had increased over the long term, making higher leaching losses possible in flow situations of the same volume. However, a difference was detected between the leaching of TON and TOC. While TOC concentrations remained quite stable, TON concentrations had statistically significant upward trends, which may indicate more effective leaching of N-rich organic compounds compared to C-rich compounds (Lepistö et al., 2008).

### *4.5. Seasonal changes in hydrology*

Most increases in runoff were detected in the middle of the winter in January. On the contrary, downward trends were detected in 1–3 catchments, almost entirely through the year, but mostly in June. These detected changes indicate that wetter winters and summers with more frequent periods of droughts are becoming more common. Wen et al. (2020) also emphasized the role of temperature controlling the DOC production, and hydrology controlling export or DOC at the catchment scale. This temporal asynchrony suggests the sensitivity of these forest ecosystems to climate change impacts with increasing extremes. Piao et al. (2008) discussed the need to acquire a greater understanding of responses of terrestrial ecosystems to climate trends at the edges of the growing season (i.e. autumn and spring). Possible drivers include changes in hydrological regimes, including increasing flow volumes and consequent changes in flow paths (Tranvik and Jansson, 2002; Hejzlar et al., 2003; Erlandsson et al., 2008) and the frequency of severe droughts (Worrall et al., 2004).

It has been found that DOC concentrations may be highest in surface soil layers and decline sharply in lower soil horizons, because of adsorption/co-precipitation in mineral soils with iron and aluminium (e.g. McDowell and Wood, 1984) and microbial decay. DOC concentrations in streams draining organo-mineral soils typically increase following rainfall or snowmelt, as the dominant flow path shifts from the lower mineral horizons which adsorb DOC, to the closer-to-the-surface organic horizons that produce DOC (McDowell and Likens, 1988). These flow path shifts support increased concentrations during periods of high flow (e.g. Tranvik and Jansson, 2002).

There is numerous indirect evidence to support the conclusion that droughts may be drivers of TOC release (Worrall and Burt, 2007). In the Simojoki river basin with a high number of drained peatlands, there is some indication of stepwise changes in the TOC flux after droughts have been detected, particularly when comparing periods of several wet and dry years (Lepistö et al., 2014). Droughts could augment DOC production. Changes in the relationship between runoff and DOC were observed after a severe drought that persisted even through more minor droughts (Worrall and Burt, 2004). It may not be changes in the amount of runoff, but rather its source, i.e. as flow paths shift and richer sources of DOC are accessed (Worrall and Burt, 2007). In Poland, a drought in autumn 2000 was one of the most severe in many years, resulting in a decrease of about 30% in TOC concentrations. The average TOC and water colour were two times higher in the wet autumn than in the dry period (Zielinski et al., 2009). In a Swedish catchment, stepwise increases in DOC concentration did follow some, but not all, summer droughts; the most notable changes occurred following a sequence of dry summers (Jennings et al., 2010).

## 5. Conclusions

Long-term monitoring records of small headwaters under varied combinations of land use, climate and land cover are valuable and necessary for assessing combined effects of stressors on water quality and nutrient cycling and retention at the landscape level. From these small research catchments, which are not disturbed by multiple land uses which exist in large river basins, we will get more detailed estimates of interactions between water quality, forestry and climate.

TOC concentrations were significantly increasing in almost all study catchments. The mean air temperature and change in sulphate concentrations both had a strong, significant correlation to TOC change. S deposition has already decreased to low levels, our results indicate that its importance as a driver of TOC leaching has decreased but is still clearly detected, while the impact of climate warming as a driver of TOC leaching will be even more pronounced in the future. A positive correlation was also found between drainage-% and increases in TON, suggesting importance of land management. The existence of long-term impacts detected in 12 catchments was in line with the detected observations in the large scale, which show upward trends of nitrogen and carbon concentrations and export from the northern Finnish river basins to the Baltic Sea. Most of the increasing trends occur in the hot spot area of the rivers discharging into the Bothnian Bay, where major drainage works have been conducted. This implies that the loads originating from diffuse sources remain a huge and possibly increasing challenge, both accelerating eutrophication and contributing to the brownification of surface waters. Better knowledge of the climate-driven impacts in drained peatland forest ecosystems affecting the surface water quality is needed, together with innovations in developing water protection measures.

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## CRediT authorship contribution statement

**Ahti Lepistö:** Conceptualization, Investigation, Data curation, Funding acquisition, Methodology, Project administration, Writing – original draft, Writing – review & editing. **Antti Räike:** Conceptualization, Data curation, Methodology, Formal analysis, Writing – review & editing. **Tapani Sallantaus:** Conceptualization, Data curation, Writing – review & editing. **Leena Finér:** Conceptualization, Funding acquisition, Project administration, Investigation, Writing – review & editing.

## Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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