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Increased organic carbon concentrations in Estonian rivers in the period 1992–2007 as affected by deepening droughts

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Abstract There are 10,091 km^2 of peatlands in Estonia and human activities may have changed the role of northern peatlands from global sinks to global sources of carbon. The aim of this work was to explain the changes in organic carbon exports from eleven Estonian rivers in the period 1992–2007 in terms of land use change, climate change quantified by trends in stream-water discharge and hydrological droughts and reductions in atmospheric sulfate quantified by change in water chemistry. Direct TOC (total organic carbon) measurements had been initiated in 1998. We used $CODKMnO_4$ (permanganate oxygen consumed) as its surrogate for the whole time span (Spearman's determination coefficient in six small northern Estonian rivers $0.95 > \rho^2 > 0.72$; $p < 0.01$). The Mann–Kendall test revealed significant trends in the TOC proxy in five small rivers in northern Estonia (M–K stat > 2.35; $p < 0.05$). The trends in the eleven investigated streams correlated closely with the increased 28 ratios of drought days (Spearman's $\rho^2 = 0.68$; $p < 0.01$). The correlations with land use compositions, decreases in water discharges and SO_4^{2-} concentrations were insignificant ($p > 0.05$). We conclude that the main factor in the increase of organic carbon export is the deepening of droughts driven by climate change, magnified by man-made drainage.

Keywords Bog · Catchment · Climate change · Landscape · Mire · Sulphate deposition

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Introduction

Northern peatlands comprise a third of the global soil carbon pool (Gorham 1991). This accounts for an equivalent of 60% of the atmospheric carbon pool (Oechel et al. 1993), with the net annual carbon sequestration rate in Baltic mires estimated at 8–55 t C km^{-2} (Eriksson 1991). This carbon store and its annual C sequestration are in danger due to global warming, land use change and reductions in sulphur deposition (Freeman et al. 2001; Mattsson et al. 2007). For late 1980s, an annual loss of 4–13 t C km^{-2} into the Baltic waters was reported (Eriksson 1991). For the last decades, an increase in these export rates has been reported from a number of northern regions in North America and Europe (Monteith et al. 2007). There are several papers that argue reasons for increased riverine organic carbon, including climate and hydrology (Freeman et al. 2001; Lepistö et al. 2008), changes in deposition chemistry (Monteith et al. 2007), decreases in ionic strength (Hruška et al. 2009), liming (Driscoll et al.

1996), upland burns (Yallop and Clutterbuck 2009), cold winter soils (Haei et al. 2010) and finally a complex of multiple factors (Roulet and Moore 2006). The importance of this study is the threat to northern peatland carbon store as well as the driving control of this threat which results in increased riverine organic carbon and likely additional C mineralisation to CO_2.

There are 10,091 km^2 of peatlands in Estonia, constituting 22.3% of the country's total area. These are situated under various moisture regimes and management practices, ranging from bogs and swamps to artificially drained forests and agricultural fields on peatlands (Allikvee and Ilomets 1995). Of these, 60–70% are artificially drained (Ilomets and Kallas 1995). Man-made drainage creates aerobic conditions which intensify the mineralisation of peat into CO_2 and organic acids (Perelman 1975). In natural mires, biological decomposition is inhibited by phenolic compounds. These in turn can be removed by the enzyme phenol oxidase provided aerobic conditions. Freeman et al. (2001) have suggested that this oxygen limitation on the single mire enzyme may be all that prevents the release of the northern peatland carbon stock into the atmosphere. This lock-up of carbon in natural peatlands is called enzymatic latch. The same processes are prone to take place in the occurrence of droughts (Freeman et al. 2001).

A semi-empirical model based on the enzymatic latch concept captured the approximate trend in DOC fluxes (dissolved organic carbon; Worrall and Burt 2005). Other studies testing the impact of lowered water tables provide diverse results, with some proposing that aerobic conditions increase peat-dissolved organic carbon production (e.g., Tipping et al. 1999), while others suggest a decrease (e.g., Freeman et al. 2004) or no significant change (e.g., Blodau et al. 2004). The number of extreme rainy and extreme dry days increased in Estonia between 1957 and 2006 (Tammets 2007). In the similar climatic conditions of southern Sweden, a slight trend towards prolonged hydrological droughts has been observed since the 1960s (Hisdal et al. 2003). Models of the Estonian climate simulate a rising trend in drought risk and gradually drier soils in summer between now and the 2070s (Lehner and Döll 2001; Järvet 2004).

Another proposed reason for the increase in DOC in northern European catchments may be a decrease in SO_4^{2-} (sulphate ion), causing a greater dissolution of soil organic carbon. Specifically, the reduction of the SO_4^{2-} deposition resulting from smaller atmospheric pollution increases soil organic matter solubility by changing the acidity of soils and the ionic strength of soil solutions. It has been suggested that this mechanism caused an increase in DOC export from the water bodies of Great Britain from the mid-1990s to the mid-2000s (Evans et al. 2005). The reduction in the atmospheric deposition of nitrogen compounds can affect soil chemistry in a similar manner (Findlay 2005). In Estonia, the post-Soviet re-organisation of industry that took place in the 1990s led to a great decrease in the atmospheric deposition of SO_4^{2-} and nitrogen compounds (Treier et al. 2004), while nitrate fluxes from agriculture dramatically decreased as well (Mander et al. 1998; Iital et al. 2010).

The objective of this study was to examine land use, number of hydrological drought days, hydrological discharge and stream chemistry as drivers of change in organic carbon concentration in Estonian rivers for the period 1992–2007.

Materials and methods

Study area

We obtained water chemistry and river discharge data from eleven Estonian rivers with a total catchment area of 57,619 km^2 (Fig. 1). The largest investigated catchments were Narva (measured in Vasknarva; 47,815 km^2), Suur Emajõgi (in Tartu; 7,828 km^2) and Pärnu (in Oore; 5,154 km^2). The rest of the rivers can be grouped as follows: (1) small rivers in northern Estonia (Kasari, Vihterpalu, Keila, Vääna, Pudisoo, Valgejõgi) and (2) small rivers in southern Estonia (Väike Emajõgi and Võhandu).

The northern catchments lie upon Ordovician and Silurian limestones, whereas the southern ones are on sandy-silty and clayey Devonian sandstones. The rocks are overlaid by Quaternary deposits that are mostly less than 5 m thick. The thickest of the sediments (>100 m) are found in the southern Estonian uplands. The limestone plateaus of northern Estonia are characterised by karst phenomena that typically have no Quaternary sediments. The topography is fairly low and flat, with maximum elevations of mostly about 30–100 m above sea level.

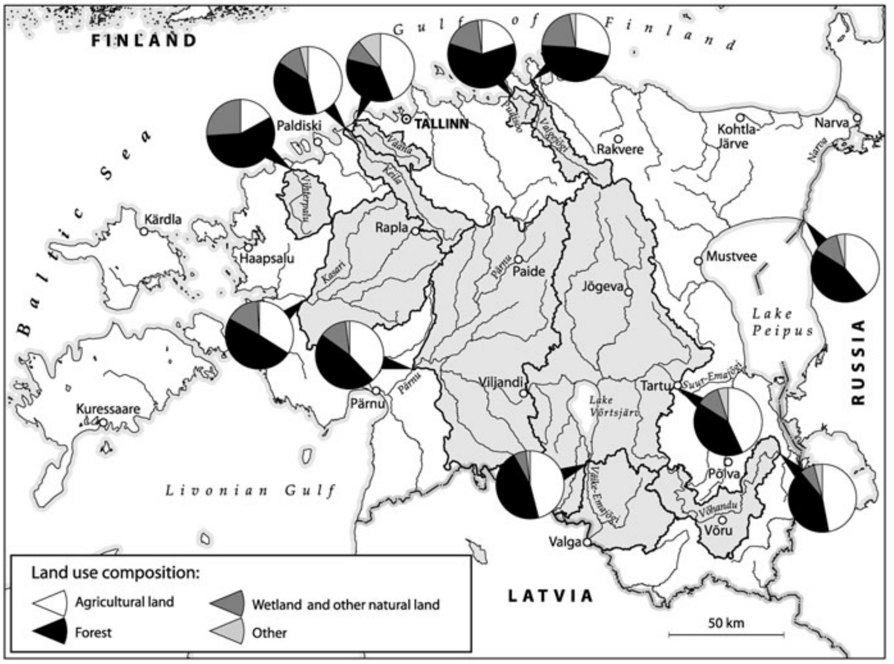

Fig. 1 Studied catchments in Estonia and their land use composition. Map designed by R. Aunap

The largest part (38–60%) of the investigated catchments are covered by coniferous and mixed types of forests, the rest being mires (6–26%) and agricultural land (17–47%; Iital et al. 2010). The main forest tree species in Estonia are pine (35%), birch (30%) and spruce (17%; Adermann 2008). The mires mainly include open fens and peat bogs, but also inland and coastal marshes. The investigated catchments are highly variable in the share of mires (Iital et al. 2010; Fig. 1). Detailed information on the land use composition of the individual catchments is presented by Iital et al. (2010; Fig. 1).

The Narva, Suur Emajõgi and Võhandu rivers mainly originate from lakes. The Väike Emajõgi is also considerably influenced by the water level of its sink Lake Võrtsjärv, while the Pärnu River and the small rivers of northern Estonia are not significantly influenced by standing freshwater bodies (Järvekülg 2001).

Water chemistry data

The Estonian national environmental monitoring programme initiated the measurements of COD-$KMnO_4$ (permanganate oxygen consumption), SO_4^{2-} and phenolics in Estonian rivers in 1992. TOC measurements (total organic carbon) began in 1998. The gauges were selected in order to determine the transport of pollutants through the main rivers of Estonia to the Baltic Sea, Lake Peipus and Lake Võrtsjärv. Water samples were subsequently collected and analysed by the Department of Environmental Engineering of Tallinn University of Technology (northern Estonia), Tartu Environmental Research Ltd (southern Estonia) and the affiliate laboratory of the Estonian Environmental Research Centre in Pärnu County (south-western Estonia). The analysis of the water samples was carried out using standardised methods (ISO 8245 for TOC, using catalytic oxidation at up to 1,200°C and subsequent CO_2-measurement, and ISO 15705 for COD$KMnO_4$, using potassium permanganate to oxidise the organic matter and subsequent CO_2-measurement). Water was sampled from 6 to 12 times a year, resulting in 40–50 TOC measurements for most of the streams in the years 1998–2007. Exceptionally, there were only eight TOC measurements from the Vihterpalu and Pudisoo gauges from February 1998 to April 1999. Little data was available on phenolics, as only three investigated gauges had more than 10 phenolics measurements (Keila, Suur Emajõgi and Narva). The investigated data can be freely downloaded from the directory http://loodus.keskkonnainfo.ee.

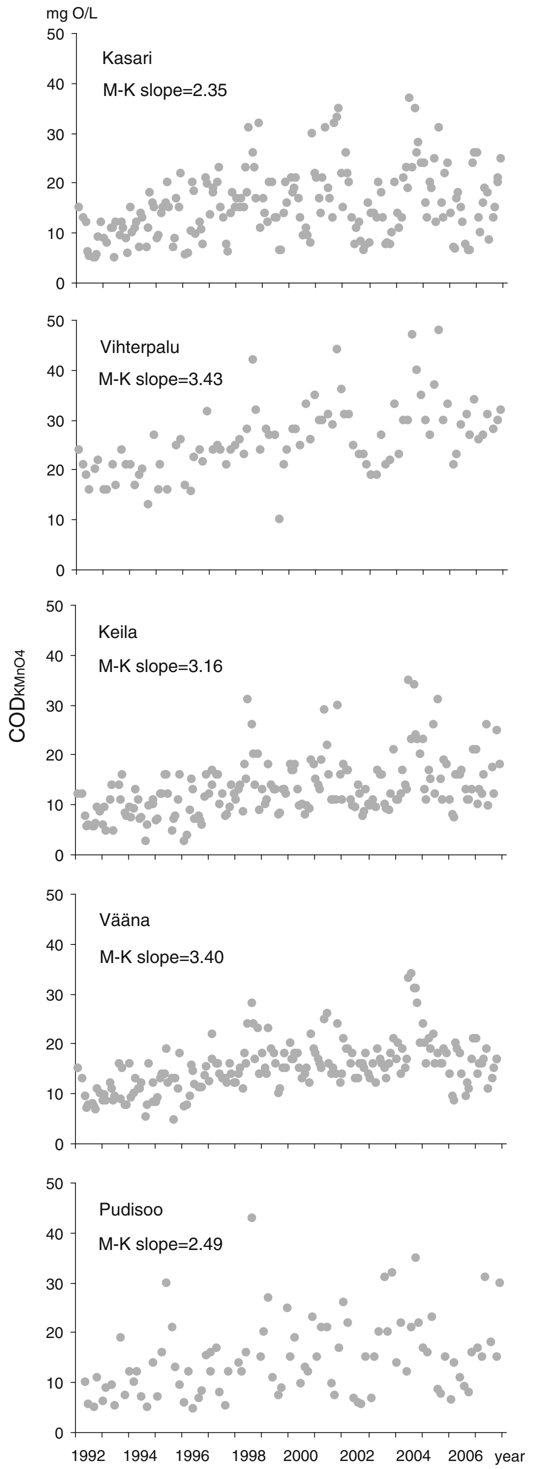

Fig. 2 Trends in TOC surrogate in five small northern Estonian streams

Discharge analysis

The daily discharge data was collected by EMHI (the Estonian Meteorological and Hydrological Institute). The discharges in $m^3 s^{-1}$ had been calculated from the water level measurements in the river gauges performed by the trained staff of EMHI. In order to obtain an annual parameter for the amount of hydrological droughts, we counted days with discharge below 10% of the summer half-year average (April–September) for each year.

Statistical analysis

The statistical properties of chemical concentrations in fresh water are usually not normally distributed (Gilliom and Helsel 1986). Therefore we used the univariate Mann–Kendall test (Libiseller and Grimvall 2002; see von Brömssen 2004 for the software package) to detect trends over time in $CODKMnO_4$, SO_4^{2-} concentrations, annual average discharges and days with discharge below 10% of the summer half-year average for each river. The univariate Mann–Kendall statistic for a time series $\{Zk, k = 1, 2, n\}$ of data is defined as

$$T = \sum_{j<i} \operatorname{sgn}(Z_i - Z_j), \qquad (1)$$

where

$$\operatorname{sgn}(x) = \begin{cases} 1, & if\ x > 0 \\ 0, & if\ x = 0 \\ -1, & if\ x < 0 \end{cases}$$

If there are no ties between the observations, and there is no trend in the time series, the test statistic is asymptotically normally distributed with

$E(T) = 0$ and $\operatorname{Var}(T) = n(n-1)(2n+5)/18.$

Correlation analyses

We ran Spearman's correlation analyses to test the relationships between the magnitudes of trends of $CODKMnO_4$ and the trend slopes in the water discharges, the numbers of hydrological drought days and SO_4^{2-} concentrations. We also correlated the trends with 2009 land use percentages as presented by Iital et al. (2010). In the analysis, each individual trend slope of a river constituted a data point ($n = 11$). In order to test the power of $CODKMnO_4$ as the proxy for organic carbon (Kopáček et al. 1995;

Table 1 Mann-Kendall slopes of TOC proxy concentration (COD_{KMnO4}), water discharge (Q), number of hydrological drought days and sulphate concentration (SO_4)

River	COD_{KMnO4}	Q	Hydrological drought days	SO_4
Kasari	2.35*	–0.18	0.61	–1.13
Vihterpalu	3.43***	–0.99	1.58	1.00
Keila	3.16**	–0.99	0.89	–2.57*
Vääna	3.40**	–0.86	1.07	–1.58
Pudisoo	2.49*	–1.53	1.19	–3.17**
Valgejõgi	1.71	–0.54	0.00	–2.89**
Narva	0.00	–1.62	0.00	0.50
Suur Emajõgi	1.48	0.09	0.00	–3.65***
Võhandu	0.50	–0.36	0.00	–2.66*
Väike Emajõgi	0.45	0.27	0.00	–1.89*
Pärnu	1.98	–0.45	1.20	–2.62*

* $p < 0.05$; ** $p < 0.01$; *** $p < 0.001$

Cheng et al. 2005), we calculated a Spearman's correlation between the concentrations of COD-$KMnO_4$ and TOC for each river.

Results

Trends related to organic carbon

The Mann–Kendall test yielded significant slopes for five of the six small streams of northern Estonia ($p < 0.05$) showing upward trends (M–K slope > 2.35; Fig. 2; Table 1). In the Pärnu River, the positive trend of 1.98 was close to significance ($0.05 < p < 0.1$). In the rivers of southern Estonia, the slopes were considerably flatter (0.45 < M–K slope < 1.48; $p > 0.1$). A zero magnitude trend was observed in the Narva, the largest of the rivers. No significant slopes were observed in either water discharges or annual numbers of drought days (Table 1). The greatest downward slopes in discharges were shown by the Narva, and four of the six small northern Estonian rivers, while in the rest of the streams, the slopes were below 0.5. The Narva, the Suur Emajõgi and the small rivers of southern Estonia did not have any drought days and therefore showed zero trends in the parameter. At the same time, five of the small northern Estonian rivers showed Mann–Kendall slopes over 1.03, and the Pärnu River also had a positive trend of drought days. None of the three gauges with data on phenolics showed a significant Mann–Kendall statistic. However, in the case of the Keila River, this was only due to the shortness of the time series, starting from 2004, as the phenolics varied from 13.8 to 74.9 $\mu g\ l^{-1}$ from June 2004 to April 2005 and then plummeted below 2 $\mu g\ l^{-1}$ for the entire period from June 2004 to December 2007. Significant downward slopes of SO_4^{2-} were ascertained in eight of the eleven investigated streams ($p < 0.05$; –3.61 < M–K slope < –1.88; Table 1). Among the exceptions were the Narva River and the small Vihterpalu River in northern Estonia, which had slightly positive trends.

Relationships between the trends

Trends in CODKMnO_4 showed a weak Spearman's correlation with trends in water discharge slopes ($\rho = –0.34$; $p > 0.05$; $n = 11$). We obtained a significant correlation of 0.82 between the magnitudes of trends in CODKMnO_4, and trends in drought days ($\rho^2 = 0.68$; $p < 0.01$; $n = 11$; Fig. 3). Only weak correlations were obtained between CODKMnO_4 and percentages of agricultural land, forest, and mires ($\rho = –0.40$, $\rho = 0.15$, and $\rho = 0.49$, respectively; $p > 0.05$ in all cases). Trends in SO_4^{2-} concentrations showed no significant relationship with the slopes of CODKMnO_4 either ($\rho = –0.20$; $p > 0.05$; Fig. 4).

CODKMnO_4 as indicative of organic carbon

We obtained significant Spearman's correlation coefficients between TOC and CODKMnO_4 for the six

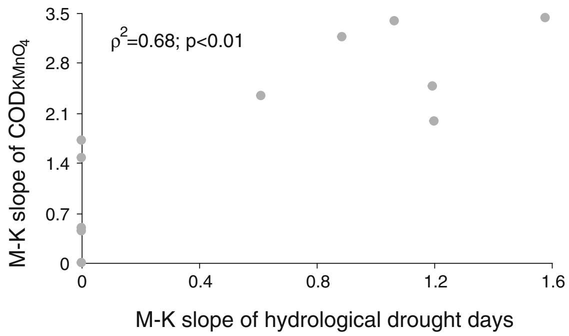

Fig. 3 Correlation between trends in hydrological drought days and trends in the TOC surrogate. Spearman's $\rho^2 = 0.68$; $p < 0.01$; $n = 11$

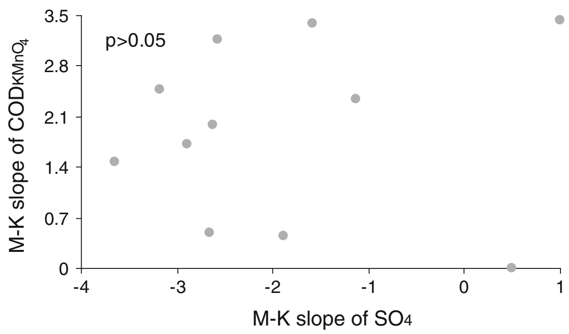

Fig. 4 No significant correlation between trends in SO_4^{2-} concentrations in TOC surrogate. $p > 0.05$

small rivers situated in northern Estonia possessing $0.95 > \rho^2 > 0.72$; $p < 0.01$. Pärnu showed a determination coefficient $\rho^2 = 0.38$; $p < 0.05$. The rest of the streams of southern Estonia had $0.25 < \rho^2 < 0.5$; $p > 0.05$.

Discussion

Increases in DOC concentration have been observed in the northern hemisphere and have been attributed to climate and hydrology (Freeman et al. 2001; Roulet and Moore 2006; Lepistö et al. 2008), changes in deposition chemistry (Monteith et al. 2007), decreases in ionic strength (Hruška et al. 2009), liming (Driscoll et al. 1996), upland burns (Yallop and Clutterbuck 2009), and cold winter soils (Haei et al. 2010). In order to give an explanation of the increase in $CODKMnO_4$ concentrations (used as a proxy for TOC) in the small rivers of northern Estonia and the Pärnu River while the exports remained the same in the Narva, the Suur Emajõgi and the two small rivers of southern Estonia, we found the trends in COD-$KMnO_4$ closely correlated with the rising trends in hydrological drought days. Because a large percentage of the variance in TOC is explained by COD-$KMnO_4$ we reasoned that increased TOC is related to the number of hydrological drought days.

The dependence of the proxy for TOC on the parameter of hydrological droughts is in agreement with what has been proposed on droughts affecting the decomposition processes that produce dissolved organic carbon through the enzymatic 'latch' mechanism (Tipping et al. 1999; Freeman et al. 2001; Worrall and Burt 2005). This is also somewhat supported by a drop in the phenolics, which was observed in 2005 in the Keila River, the gauge which showed a significant upward trend in the TOC surrogate, while in the Narva and Suur Emajõgi rivers, which had no significant trend in COD-$KMnO_4$, no noticeable change was present. The correlation with droughts, however, conflicts with the conclusions of Freeman et al. (2004) and Blodau et al. (2004) who suggested a negative or non-existent relationship with droughts.

We obtained no significant correlation of COD-$KMnO_4$ trends with trends in total runoff. The findings contradict the general pattern of organic carbon export following an increase in discharge as explained by Pastor et al. (2003). Nor do our findings correspond with the analysis of terrestrial organic carbon transport to Lake Võrtsjärv by Tamm et al. (2008), which proposes that the total load is mainly dependent on water discharge.

We were unable to reliably confirm reduced sulphate deposition as a possible cause for an increase in organic carbon as previously suggested by Monteith et al. (2007), since the recorded decreases in SO_4^{2-} concentrations in Estonian stream water did not correlate significantly with the increase slopes of $CODKMnO_4$ concentrations. As there has also been a dramatic decrease in the deposition and agricultural input of nitrogen compounds in Estonia (Mander et al. 1998; Treier et al. 2004), further investigation is needed to clarify the impact of the soil chemistry on the increase in organic carbon exports (Findlay 2005; Evans et al. 2006; Monteith et al. 2007). One possible explanation could be the great sulphur supplies accumulated in the soil during the decades of air pollution. For example, in the Lake

Saare monitoring station, the organic horizon of the pine forest floor contained an average 90 kg S ha^{-1} and the spruce forest contained 210 kg S ha^{-1} in 2008 (Frey et al. 2009). Therefore it is reasonable to assume that despite the sulphate reductions, the S levels remained high enough not to seriously affect soil organic matter solubility.

The impact of hydrological droughts observed in our study sites can be explained by the high proportion of man-made drainage systems. Between 20 and 53% of the catchments with significant trends in the TOC surrogate are covered with peatlands (Järvekülg 2001), and 60–70% of Estonian peatlands are artificially drained (Ilomets and Kallas 1995). For the studied catchments, no sufficient data yet exist to quantify the influence of ditching. We had only enough historical data to conduct a preliminary analysis in order to assess the relationship between the loss of natural mires and trends in TOC surrogates in six catchments. The first set of mire percentages in the catchments was based on expert opinion from the period 1955–1960 (collected by Dr. August Loopmann, published by Järvekülg 2001) and the second set dated from 2009 (Iital et al. 2010). The losses of natural mires expressed as the negative differences between the data sets ranged from 0 to 31% of the catchment area transferred from mire to another land use. The percentages correlated closely with the trends in $CODKMnO_4$ ($\rho^2 = 0.89$; $p < 0.001$; $n = 6$), suggesting that the impact of extremely low water tables on organic carbon concentrations is magnified by artificial drainage. Alternatively the vulnerability of the northern rivers to droughts may result from the greater vulnerability of their soils to droughts, or a larger amount of forest fires.

Additionally, potential influence of in-lake removal of TOC can be considered. Three of the six rivers without significant increases in TOC surrogate, namely the Narva, Suur Emajõgi and Võhandu rivers, originated from Lake Peipus, Lake Võrtsjärv and Tamula and Vagula lakes respectively, whereas none of the streams with increasing $CODKMnO_4$ concentrations received a significant amount of water from lakes. Schindler et al. (1997), Kothawala et al. (2006), Vuorenmaa et al. (2006), and Toming et al. (2009) have explained the removal mechanisms in standing water bodies. In any case, further analysis is necessary to clarify the relationship between organic carbon trends and catchment properties, especially the amount of artificial drainage, soil cover, and forest fires.

In conclusion, our study demonstrated that concentrations of organic carbon compounds in five northern Estonian streams increased in the period 1992–2007. As the change was closely correlated with rising trends in hydrological drought days, one can assume that the extremely low water tables, deepened by man-made drainage, are the main drivers of the increased dissolution of peat.

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