

# Spatial and temporal variability of organic C and N concentrations and export from 30 boreal rivers induced by land use and climate

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## ***Abstract***

Climate change scenarios for northern boreal regions indicate that there will be increasing temperature and precipitation, and the changes are expected to be larger in winter than in summer. These precipitation and discharge patterns, coupled with shorter ice cover/soil frost periods in the future would be expected to contribute significantly to changing flow paths of organic matter over a range of land use patterns. In order to study the impact of climate change on the seasonality of organic matter export we compared total organic carbon (TOC) and total organic nitrogen (TON) concentrations and export, during different seasons and climatically different years, over 12 years for 30 Finnish rivers separated into forest, agriculture and peat dominated catchments. The mean monthly TOC concentrations were highest during autumn and there was also a peak in May during the highest flow period. The mean monthly concentrations of TON were lowest during winter, increased in spring and remaining high throughout summer and autumn. The TOC/TON ratios were lowest during summer and highest during winter, and in all seasons the ratios were lowest in catchments with a high proportion of agricultural land and highest in peat-dominated catchments. The seasonality of TOC and TON export reflected geographical location, hydrology and land use patterns. Most of the TOC and TON were transported during the high flow following the spring snowmelt and during rainfall in autumn. In all catchments the relative importance of the spring snowmelt decreased in wet and warm years. However, in peat-dominated catchments the proportion of spring period was over 30% of the annual export even in these wet and warm years, while in other catchments the proportion was about 20%. This might be linked to the northern location of the peat-dominated catchments and the permanent snow cover and spring snow melt, even in warm years.

Keywords: organic carbon, organic nitrogen, rivers, seasonal variations, hydrology, land use, climate change

## **1. Introduction**

Hydrology is a key driver for seasonal and inter-annual variability of organic matter concentrations and export. Generally, the concentration of dissolved organic matter (DOM) correlates positively with discharge, and so the concentrations of dissolved organic carbon (DOC) in rivers are highest during heavy rain and high flow periods (Hope et al., 1994; Schiff et al., 1997; Ågren et al., 2007; Lepistö et al., 2008; Austnes et al., 2010). During high flow, water flow paths are closer to the soil surface, and the water is increasingly in contact with the organic-rich uppermost soil horizons (Mulholland, 2003), resulting in higher DOM concentrations. In wetlands, however, the soils are water-saturated and a rising water table will result in an increased surface water flow and reduced contact of the water flow-path with the organic-rich uppermost soil layers. This results in lower DOC export and a dilution of DOC concentrations (Schiff et al., 1998).

The concentrations of dissolved organic nitrogen (DON) have also been observed to increase with increasing discharge (Lepistö and Kortelainen, 2011). However, the relationship between DON and discharge may not be as strong as for DOC and discharge (Campbell et al., 2000), evidence that the variability of DON concentrations may be more affected by other factors such as productivity and litter returns of plants (Chapman et al., 2001a).

Most of the organic matter from boreal catchments are transported during high flow periods in spring (snowmelt) and autumn (heavy rainfall) (Kortelainen et al., 1997; Laudon et al., 2004; Köhler et al., 2008; Hulatt et al., 2014). In the River Simojoki, a forest and peat dominated catchment in northern Finland, the highest total organic carbon (TOC) and total organic nitrogen (TON) concentrations and flow were detected in April–May, whereas the TOC:TON ratio was highest during the dormant season (October–February) and decreased in summer. This was interpreted as there being a more effective TON production in catchment soils and/or more effective leaching of N-rich organic compounds compared with C-rich compounds during the summer (Lepistö et al., 2008).

Seasonal variations of organic matter in rivers and streams have mostly been studied in forest and peat dominated catchments (Chapman, 2001a; Laudon et al., 2004; Köhler et al., 2008; Lepistö et al., 2014). Less attention has been paid to catchments with more intensive land use, even though the land use of the catchment is known to contribute to the seasonal variability in organic matter (Stedmon et al., 2006). In Danish streams draining more natural areas, the seasonal patterns of organic matter concentrations were largely driven by seasonal temperature fluctuations, whereas the organic matter exported from agricultural areas was more variable and largely controlled by precipitation (Stedmon et al., 2006). Aitkenhead-Peterson et al. (2007) observed that spring DOC export was negatively correlated both with the percentage cover of arable land and the sum of improved and rough grass in stream catchments in Scotland. During the summer months, DOC export was positively correlated with percentage cover of coniferous species and also inversely correlated with both the percentage of heather and montane vegetation. During the autumn and winter seasons, DOC export was positively correlated to peat cover. On the other hand, although catchment characteristics and land use have been observed to affect the temporal variability of organic matter, seasonal and inter-annual patterns of DOC concentration could be modeled using climate-related parameters alone (Futter et al., 2008).

Climate change scenarios for Finland indicate that there will be increasing temperature and precipitation, and the changes are expected to be larger in winter than in summer (Jylhä et al., 2009). Widespread changes in seasonal patterns, in freeze-and-thaw periods, as well as in the frequency and intensity of weather episodes are expected (Jylhä et al., 2009). The length of snow

cover will also be reduced, especially in southern Finland. It is also thought that thaws causing snow-melt will occur more often during winter and the winter soil frost layer will become thinner (Jylhä et al., 2009). Climate change has already affected the seasonal distribution of stream flow in Finland. Winter and spring mean monthly discharges have increased, especially in northern Finland, and the spring peak occurs earlier in most catchments (Korhonen and Kuusisto, 2010). Such changing precipitation and discharge patterns, coupled with shorter ice cover/soil frost periods would be expected to contribute significantly to changing flow paths of total organic carbon and nitrogen (TOC/TON) over a range of land use patterns. Earlier melting periods in winter and spring, coupled with the decreasing role of spring runoff peak and the increasing role of autumn peak, can be predicted to significantly compound the consequences of climate change to dynamics of TOC and TON in aquatic environments.

Despite the numerous studies showing increases in DOC concentrations in streams and rivers in the northern hemisphere (Freeman et al., 2001; Worrall et al., 2004; Evans et al., 2005; Skjelkvåle et al., 2005; Monteith et al., 2007; Sarkkola et al., 2009), Räike et al. (2012) found evidence of increases in DOC export to the northern Baltic Sea only from few Finnish catchments since 1975. However, an increasing export of DOC during autumn/winter was observed in the five-year mean export values (Räike et al., 2012). Moreover, over the last 27 years, TOC concentrations have increased in the Finnish coastal zone of northernmost Bothnian Bay and Quark sub-basins and in parts of the eutrophic southern Gulf of Finland sub-basin (Fleming-Lehtinen et al., 2014), whereas based on the few available data from the open-sea area of the Baltic Sea no DOC increases were detected from the 1970s to 2010 (Hoikkala et al. 2015). In addition, increasing TON concentrations have been observed in Finnish rivers/streams (Lepistö et al., 2008; Sarkkola et al., 2012).

Räike et al. (2012) studied the long term trends in annual DOC export from Finnish rivers. The aim of our study built on this earlier broad synthesis to report a more detailed quantification of the seasonal and interannual variations in both TOC and TON concentrations and their export from Finnish rivers. We hypothesize that changes in hydrology and runoff regimes induced by climate change strongly affect the seasonality of TOC and TON concentrations and export from terrestrial to aquatic environments. We further postulate that variability in autumn/winter precipitation affects the hydrologic flow paths increasing surficial flow that bypasses the mineral soil and its sorption processes and that the effect of increased surficial flow paths on organic matter export is emphasized in agricultural dominated catchments lacking permanent snow cover during warm winters. In this study, we compared the TOC and TON concentrations, and export, during different seasons and climatically different years over a 12 year study period. The data base includes rivers located along a climatic gradient between the latitudes 60°N and 69°N enabling us to assess how changing climate might change the patterns of TOC and TON fluxes from Finnish river basins. Since variation and changes in TOC and TON fluxes reflect geographical location and land use patterns of the catchment, the impact of climate change on fluxes is identified separately for forest, agriculture and peat dominated catchments.

## ***2. Material and Methods***

### **2.1 River basins**

We studied 30 river basins in Finland flowing to the Baltic Sea (Fig. 1). The rivers are located between the latitudes 60°N and 69°N, and the areas of the river basins range from 357 to 61466 km<sup>2</sup>. For each basin, the different land use classes were derived from satellite image-based land

cover and forest classification data (CORINE Land Cover 2006: 25×25 m grids). The proportion of upland forests ranges from 33 to 54% (average 42%) and the percentage of peat varies from 3 to 43%, and is highest in northern Finland. The proportion of forests on mineral soils increases towards the south. The majority of the agricultural land in Finland is located in the southern and western coastal zone, and its proportion is on average 17% (range 1 - 43%). In contrast, in the northernmost basins, the proportion of agricultural land is minor (<3%). Agricultural land in Finland is mostly crops, but also includes some grassland. The surface water area of the basins ranges from 0 to 19%. Urban areas (range 1–20%) are concentrated in southern Finland and in three of the catchments the proportion of urban areas is over 10%, whereas open rock areas (bedrock outcrops) are mostly located in the north accounting for between 10 and 25% of the catchment area (Table 1).

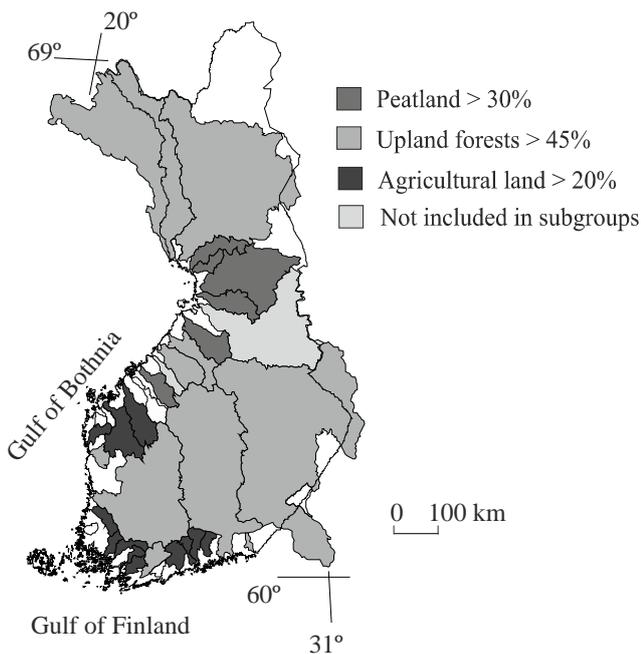


Figure 1. Finnish river catchments included in the study. Subgroups described by the dominating land use of the catchment are marked with different colors.

In order to study the seasonal variability, and the potential impact of climate change on concentrations and fluxes in catchments with different land use patterns, the study catchments were divided into three major sub-groups described by the dominating land use of the catchment (Fig. 1, Table 2):

- 1) Agricultural catchments, where the proportion of agricultural land is over 20% and the peat proportion is <30%.
- 2) Peat catchments, where the proportion of peat is over 30% and the proportion of agricultural land is <20%.
- 3) Forest catchments, where proportion of upland forests is over 45% and the proportions of agricultural land is <20% and the proportion of peat is <30%, respectively.

## 2.2 Water sampling, chemical analyses, flow measurements and flux calculations

Data on water quality and water flow for the years 2000 to 2011 were collected from national data bases maintained by the Finnish Environment Institute (SYKE). The river stations in the study are

included in the national hydrological database of Finland (Hyvärinen and Korhonen, 2003), and daily discharge measurements are available. Monthly river fluxes were calculated by multiplying the mean monthly flows by the mean monthly concentrations. Annual river fluxes were calculated by summing the monthly fluxes over the calendar year.

Water quality data was derived from the Finnish national monitoring program of riverine material inputs into the Baltic Sea. The median annual sampling frequency of the Finnish rivers was 12. The acidified TOC samples were bubbled with nitrogen to remove inorganic carbon (CO<sub>2</sub>) and TOC was measured by high-temperature oxidation followed by IR gas measurements. Total nitrogen (TN) was measured colorimetrically after oxidation with K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> and reduction in a Cd-Cu column. The sum of nitrate (NO<sub>3</sub>-N) and nitrite (NO<sub>2</sub>-N) nitrogen was measured following reduction in a Cu-Cd column and colorimetric determination of azo-color. Ammonium concentrations (NH<sub>4</sub>-N) were determined spectrophotometrically with hypochlorite and phenol. TON was calculated by the difference:  $TON = TN - (NO_2-N + NO_3-N + NH_4-N)$ . In Finnish rivers, over 90% of TOC and TON is in dissolved form and the proportion of the particulate fraction is minor (Mattsson et al., 2005). The patterns of TOC and TON analyzed in this study can hence be compared and discussed in light of literature values and patterns of DOC and DON.

Relationships between concentrations of TOC and TON and land use of the catchments were examined with Spearman rank correlation analysis. Monthly mean concentrations were used in statistical analysis performed with PC SAS 9.3 software.

### **2.3 Weather and hydrological conditions in Finland between 2000 and 2011**

The annual precipitation and annual mean temperature in Finland were provided by Finnish Meteorological Institute, Climate Service Centre. Annual precipitation was on average 616 mm and the annual mean temperature was on average 2.9 °C between 2000 and 2011. The highest annual precipitation of 724 mm was in 2008, and the lowest annual precipitation of 521 mm was in 2009 (Fig. 2). The highest annual mean temperature (3.7 °C) was recorded in both 2000 and 2011, and the lowest (2.2 and 1.3 °C) was in 2001 and 2010, respectively (Fig. 2). The highest mean annual runoff in the study rivers was measured in 2000 and 2008, at 407 and 444 mm, respectively, and the lowest rates were recorded in 2002 and 2003, at 231 and 192 mm, respectively (Fig. 2). The long-term mean runoff (1991-2010) in the study rivers was 287 mm (Korhonen and Haavanlammi, 2012). Thus, in 2000 and 2008, the annual runoff was 141 and 155% of the long-term mean, and in 2002 and 2003, 81 and 69% of the long-term mean. Accordingly, the years 2000 and 2008 were chosen as being representative of wet years, and 2002 and 2003 of dry years for this study.

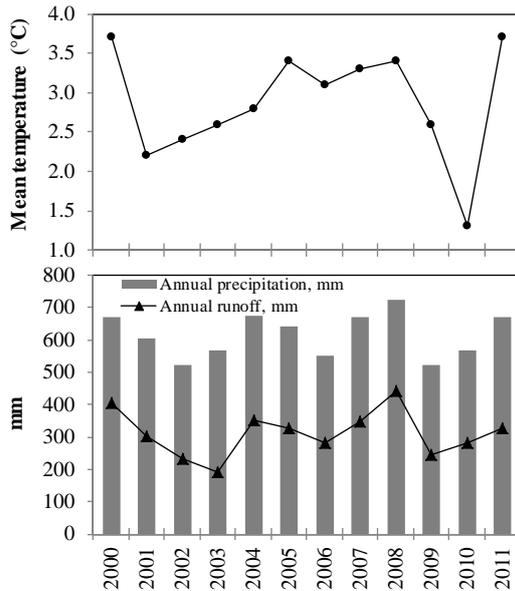


Figure 2. Annual mean air temperature and annual precipitation in Finland from 2000 to 2011 (Finnish Meteorological Institute, Climate Service Centre), and annual runoff in 30 Finnish rivers during 2000-2011.

The second highest annual runoff during the study period was measured in 2000 which was also the warmest year. Accumulation of snow was heavy, and substantial spring floods occurred in western Finland during April, and in northern Finland in May. Heavy precipitation beginning in October increased both surface and groundwater levels above the seasonal mean in many areas by the end of the year. The weather was still mild in November and December in most parts of the country. Freezing of watercourses was at least three weeks later than average, and ice cover at the end of the year was exceptionally weak, or even totally absent, in southern and central Finland (Hyvärinen and Korhonen, 2003).

The highest annual precipitation and runoff were measured in 2008. Snow cover was well below average and southern parts of the country had no permanent snow cover. Also in autumn the temperature and precipitation were above normal (Finnish Meteorological Institute, 2013). Water levels in lakes and rivers were above the mean both at the beginning and the end of the year, and annual discharges were above the mean in almost all areas (Korhonen and Haavanlammi, 2012). Thus, the weather in years 2000 and 2008 can be hypothesized to be examples of a likely future climate in Finland where higher precipitation, milder autumns and winters, and shorter snow cover periods in southern Finland are predicted.

The second lowest annual runoff in the study period was recorded in 2002, which began with a very mild weather. Spring was unusually early and warm, and water levels began to decrease from their spring maxima as much as one month ahead of the norm. The annual precipitation for 2002 was low except in northernmost Finland. The winter season began early, with exceptionally cold weather at the end of the year, ice thicknesses increased to high levels and snow depths were also greater than normal at the end of the year (Korhonen, 2007).

Another dry year, 2003, had the lowest annual runoff, although the annual precipitation was near the long-term mean in most parts of Finland. The groundwater table was unprecedentedly low at the beginning of the year and wells dried up in many areas, particularly in southern Finland. In late autumn the groundwater table was again very low in the southern and western coastal zone. At the

end of the year accumulation of snow and ice was generally below the seasonal mean (Korhonen, 2007).

### **3. Results and Discussion**

#### **3.1 Seasonal and inter-annual variation of TOC and TON concentrations**

The mean monthly concentration of TOC was  $14 \text{ mg l}^{-1}$  in the 30 rivers during 2000 - 2011 (range from  $3.0$  to  $38 \text{ mg l}^{-1}$ ). The mean monthly TON concentration was  $600 \text{ } \mu\text{g l}^{-1}$  (range 0 to  $5100 \text{ } \mu\text{g l}^{-1}$ ) and the molar TOC/TON ratio was on average 30 (Table 1). The inter-annual variation of the molar TOC/TON ratios was small and the average TOC/TON ratio of the river water stayed relatively unchanged during hydrologically different years. This is evidence that there are similar effects of changes in hydrology on both TOC and TON concentrations. The mean monthly TOC concentrations were highest during autumn and there was also a peak measured in May during the high flow period (Fig. 3). The mean monthly concentrations of TON were lowest during winter, increased in spring and stayed high throughout summer and autumn (Fig. 3). The molar TOC/TON ratio was lowest during summer and highest during winter (Fig.3). The average TOC, TON and TOC/TON patterns based on these 30 rivers are surprisingly similar compared to the patterns observed in the River Simojoki (Lepistö et al. 2008), which is located in the north and which catchment is covered mostly by forests and peatlands. Thus the land use patterns seem not to play any major role in the seasonal patterns of TOC and TON concentrations and TOC/TON ratio.

The lower TOC/TON values in summer indicate more effective TON production in catchment soils and/or more effective leaching of N-rich organic compounds compared with C-rich compounds (Lepistö et al., 2008). Further, differences in the source, mineralisation and age of organic matter also contribute to TOC/TON ratios, although these processes play a more important role in systems with longer water retention times like in lakes or sediments resulting in decreasing average TOC/TON ratios 23 and 12, respectively (Kortelainen et al., 2013). In Baltic Sea, DOC/DON ratio has been shown to vary widely from 9 to 41 (Hoikkala et al. 2015). The seasonal changes in the TOC/TON ratios indicates that the sources of both TOC and TON changes during winter and summer: During the winter with deep flow paths, organic C-rich compounds may originate from different, deeper sources compared with N-rich compounds, resulting in high TOC/TON ratios (Lepistö et al., 2008). Also Chapman et al. (2001b) observed higher concentration of DON during summer compared to winter. Thus, the organic matter leached to the rivers during the summer is more bioavailable due to higher amount of organic nitrogen (Chapman et al., 1999). They concluded that larger DON concentrations and narrower DOC:DON ratios in the summer are probably related to biological activities of both macrophytes and microflora, which are at a maximum in the summer (Chapman et al., 2001b). On the other hand, according to our results TON concentrations remained high also during autumn (Fig. 3). Similarly, high DOC concentrations during autumn have been observed by Johnes and Burt (1991) and Vanderbilt et al. (2003). High concentrations of TON during autumn may be due to inputs of litter with high concentrations of organic nitrogen. Decomposer activity may be stimulated as soils wet up in autumn, resulting in increased TON in soil solution. Flushing from the upper soil horizons results in the increased concentration of TON in stream water. Another possible source of organic nitrogen to the stream in the autumn is throughfall, which was identified as a major source of DON to streams in a watershed in Switzerland (Hagedorn et al., 2000).

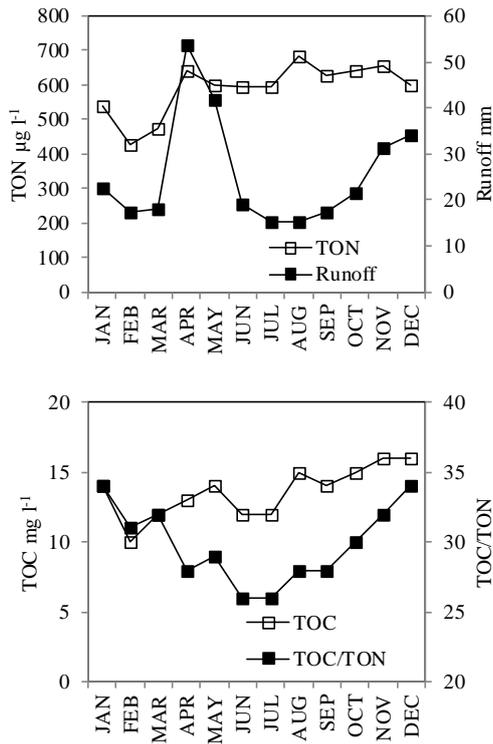


Figure 3. Mean monthly TOC and TON concentrations, molar TOC/TON ratio and runoff in 30 Finnish rivers during 2000-2011.

### 3.2 Impact of land use on TOC and TON concentrations

Similar seasonal patterns in TOC/TON ratio can be seen in the monthly averages from catchments with different land use (Fig. 4), which again implicates the minor impact of land use patterns to seasonal variation of TOC and TON concentrations. However, in all seasons the ratio was lowest in those catchments with a high proportion of agricultural land and highest in peat-dominated catchments (Fig. 4). The seasonal pattern in the TOC/TON ratio was relatively similar, also during hydrologically different years, except in peat-dominated catchments where the ratio was higher during wet years compared with the dry years (Fig. 5).

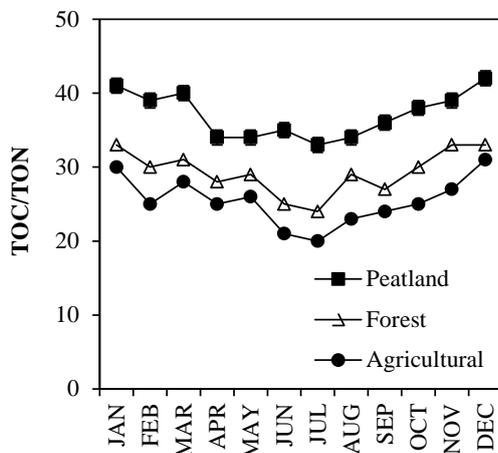


Figure 4. Mean monthly molar TOC/TON ratio in subgroups described by the dominating land use of the catchment.

The river-specific TOC/TON ratio was lowest (19) in southern Finland in the River Porvoonjoki, with 10 and 31% of urban and agricultural land use in the catchment, respectively. The highest river-specific TOC/TON ratio (39) was in northern Finland in the River Kiiminginjoki and in the River Kuivajoki, which both have peat and forest dominated catchments. Similarly, Asmala et al. (2013) observed variation in DOC:DON ratios in Finnish rivers with different land use in their catchments. Moreover, DOM originating from the catchments dominated by forests and peatlands had the lowest proportions of biodegradable DOC and DON and a greater proportion of agricultural land in the catchment increased the bioavailability of DON (Asmala et al., 2013). Seitzinger et al. (2002) observed that the DOC:DON ratio in runoff was generally lowest for agricultural sites (mean = 10), intermediate for urban/sub-urban stormwater sites (mean = 18) and highest for forest sites (mean = 53). In an extensive European dataset, DOC:DON ratios had a significant negative correlation with population density and the proportion of agricultural land and urban areas in the catchment whereas there was a positive correlation with the proportion of wetlands in the catchment (Mattsson et al., 2009). The global model calculations by Harrison et al. (2005) also show that regions with a high extent of intensive agriculture, or high population density, have elevated DON yields in comparison to DOC.

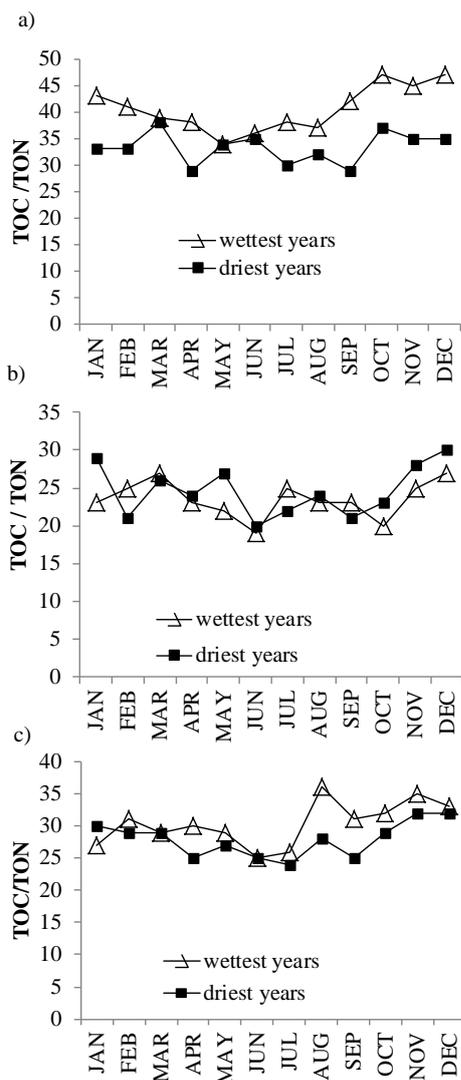


Figure 5. Mean monthly molar TOC/TON ratio during the wettest years (2000 and 2008) and the driest years (2002 and 2003) in a) subgroup of peat dominated catchments, b) subgroup of agriculture dominated catchments and c) subgroup of upland forest dominated catchments.

Both the monthly TON and TOC concentrations were negatively correlated with the monthly discharge during all seasons, except in April, when TOC concentrations had no correlation with discharge (Table 3). In all seasons, the TON concentrations correlated positively with the proportion of agricultural land and urban areas in the catchment, except in March when TON concentrations did not have a significant correlation with the proportion of urban areas in the catchment. In addition, there was a positive correlation between TOC concentrations and the proportion of agricultural land in the catchment, except during March and April. The TOC concentrations correlated with the proportion of peat in the catchment during all seasons yet in November and December, the correlation was weaker, but still significant. However, when the correlation between TOC and peat was weaker in November and December, the correlation between TOC and the proportion of agricultural land in the catchment was stronger (Table 3). The croplands in southern and central Finland can still be without snow cover in November and December and the export of organic matter can be high during heavy precipitation, whereas the peat areas in northern Finland may be frozen and covered with snow, and the export of organic matter will be low.

Both TOC and TON concentrations had year-round a strong negative correlation with the proportion of upstream lakes in the catchment. The proportion of upstream lakes in the catchment has shown to be the most important predictor for TOC and TON concentrations and export in Finnish rivers (Mattsson et al., 2005). The higher the upstream lake percentage, the lower the concentrations and export, indicating organic matter retention in lakes. Organic carbon is lost from inland waters in boreal zone mainly by mineralization to the atmosphere whereas sedimentation has a minor role depending on residence time and temperature (Algesten et al., 2004; Hanson et al., 2003; Kortelainen et al., 2006).

### 3.3 Seasonal and inter-annual variation of TOC and TON exports

The annual TOC and TON exports were on average 4900 and 190 kg km<sup>-2</sup>a<sup>-1</sup>, respectively (Table 1). The variation in export between catchments and years was high. During the 12-year study period, the highest annual TOC and TON exports and runoff were observed during the years 2000 and 2008 (Fig. 6), when the temperature and precipitation were above the long-term mean. The lowest annual TOC and TON exports and water discharge were observed during the years 2002 and 2003 (Fig. 6), when the annual precipitation was near or below the long-term mean. Thus, interannual variations in TOC and TON exports were primarily driven by variations in hydrology.

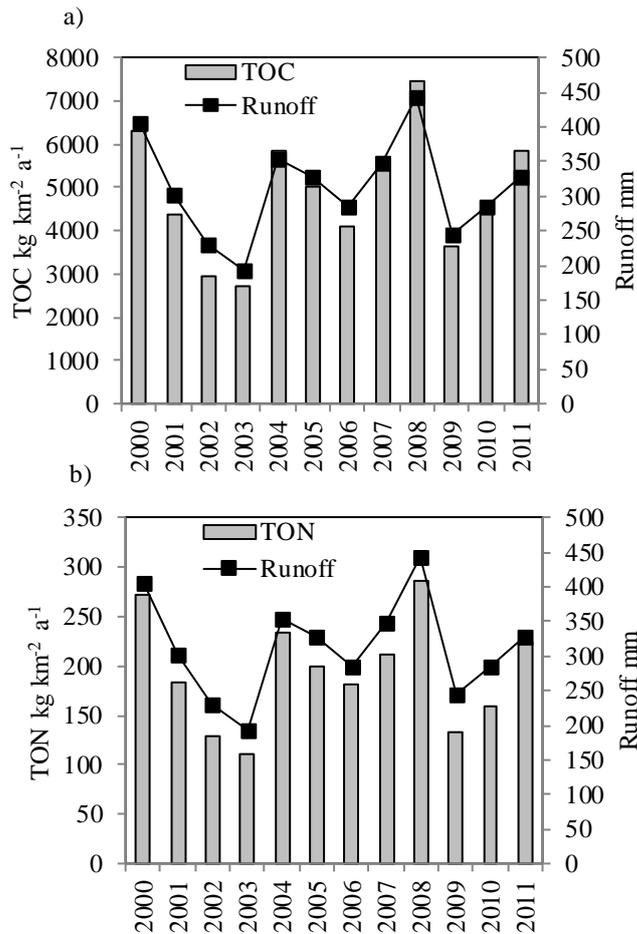


Figure 6. Annual runoff and annual export of a) TOC and b) TON in 30 Finnish rivers during 2000-2011.

### 3.4 Impact of hydrology and land use on TOC and TON exports

The results indicate that the seasonality of TOC and TON export vary between catchments, because of differences in their geographical location, hydrology and land use patterns. The catchments with high percentage of peat cover are located in northern Finland (Fig. 1), where permanent snow cover is typical every winter resulting in clear spring peak in TOC and TON exports during snowmelt even in warm years (Figs. 7 and 8). In peat catchments, the TOC and TON export during two months in spring (April-May) constituted 54 and 57% of the annual TOC and TON flux, respectively, during the two driest years (2002, 2003), and 31 and 34%, respectively, during the two wettest years (2000, 2008) (Figs. 7 and 8). Thus the relative importance of spring peak decreased during warm and wet years, because of the rainfall events in autumn. The proportion of autumn period (September-December) of annual fluxes of TOC and TON was 22 and 19%, respectively, during the two driest years, and 37 and 34%, respectively, during the two wettest years. Both TOC and TON exports were lowest during winter and summer. Thus, in peat-dominated catchments, most of the organic matter was transported during the high flow in the spring snow melt and during rainfall events in autumn.

The river basins with a high percentage of agricultural land in their catchments are located in southern and western Finland (Fig. 1). In these basins, the influence of spring peak is smaller compared to peat-dominated catchments located in northern Finland (Figs. 7 and 8). In southern Finland, the snow cover during winter is not as thick as in northern Finland and occasional melting periods can also occur during winter resulting in flow peaks in winter and a lower flow during spring snow melt. During the two driest years, the contribution of spring (April-May) and

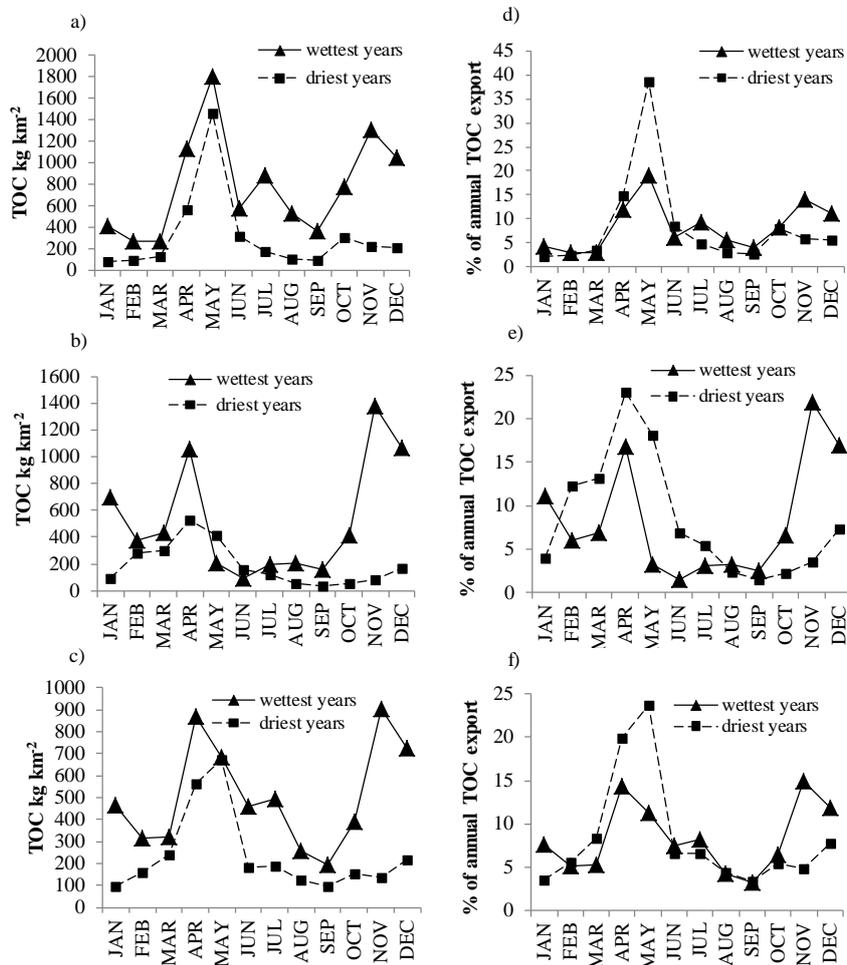


Figure 7. Monthly export of TOC and percentage of annual TOC export for the peat dominated catchments (a, d), agriculture dominated catchments (b, e) and upland forest dominated catchments (c, f) during the wettest (2000 and 2008) and driest (2002 and 2003) years.

autumn (September-December) to the annual flux of TOC was 41 and 15%, and to the annual flux of TON they were 42 and 13%, respectively (Fig. 7 and 8). Furthermore, the relative importance of the spring snowmelt decreased in wet and warm years. The proportion of spring (April-May) to the annual fluxes of TOC and TON was only 20 and 22%, respectively, during the two wettest years. However, the role of autumn got stronger during the wettest years, when the proportion of autumn (September-December) to the annual fluxes of TOC and TON was 48 and 47%, respectively (Figs. 7 and 8).

The rivers with a high proportion of upland forests in their catchments are located in both southern and northern Finland (Fig. 1), and in this subgroup the proportion of upstream lakes in the catchment is twice as high as in the other subgroups (Table 2). In these catchments, the role of spring snow melt is not as pronounced as in northern peat-dominated catchments, but more

important than in southern agricultural catchments (Figs. 7 and 8). The TOC and TON export during two months in spring (April-May) constituted 44 and 45% of the annual TOC and TON fluxes, respectively, during the two driest years (2002, 2003), and 26 and 25% during the two wettest years (2000, 2008) (Figs. 7 and 8). However, in the wettest years, autumn period was composing a significant part of the annual export of TOC and TON, on average 36 and 34%, respectively (Figs. 7 and 8). Similar climate induced changes in seasonal TOC export were shown in forested boreal headwater catchments, where the importance of snow melt period decreased whereas other seasons played a more important role, and total TOC export increased during a wet year (Rantakari et al., 2010).

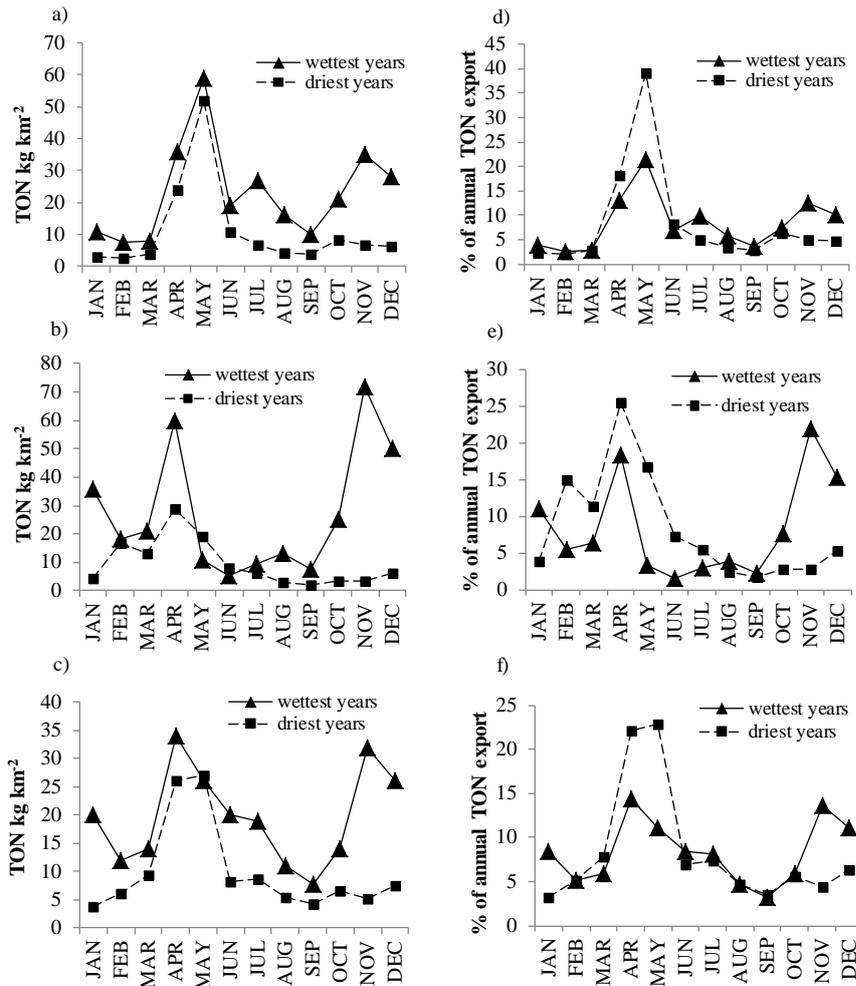


Figure 8. Monthly export of TON and percentage of annual TON export for the peat dominated catchments (a, d), agriculture dominated catchments (b, e) and upland forest dominated catchments (c, f) during the wettest (2000 and 2008) and driest (2002 and 2003) years.

The similarity of the seasonal variation in both TOC and TON exports indicate that hydrology is the main driver in seasonal variation and changes in concentrations play only a minor role. In all subgroups with different dominating land use, the relative importance of the spring snowmelt decreased in wet and warm years. However, in peat dominated catchments the proportion of spring period was over 30% of the annual export even in the wettest years, while in other catchments the proportion was about 20%. This is probably due to the northern location of the peat dominated catchments and the permanent snow cover and spring snowmelt, even in warm years. Similarly, in a

small peat catchment in eastern Finland, snowmelt dominated DOC export in the dry year (61%) but contributed less (29%) in the wet year (Jager et al., 2009).

When analyzing the long time series of DOC export from Finnish rivers (Räike et al., 2012), the increasing export during autumn was observed. In 1980 to 1984 DOC export was higher than the long-term mean monthly export in almost every month. The highest proportional increase (50%) was in October. In 2005 to 2010, DOC export was higher than the long-term mean monthly export in autumn and winter. The highest proportional (55%) and absolute increase happened in winter (especially in December). In contrast, spring export during that period did not differ remarkably from the long-term mean export and the export in summer was at a lower level (Räike et al., 2012).

In small Swedish catchments, the relative importance of the spring snowmelt period for the annual TOC export, however, correlated negatively with the percentage of wetlands (Laudon et al., 2004; Ågren et al., 2007). It is suggested that the smaller relative importance of the spring runoff period, for the annual TOC export from wetland dominated catchments, is a result of a much larger component of low-TOC snowmelt water via surface flow over ice and frozen peat (Laudon et al., 2004; Ågren et al., 2007).

#### ***4. Conclusions***

Regardless of different land use patterns, the seasonal variability of TOC and TON concentrations in the catchments is similar. Moreover, seasonal variation in TOC/TON ratio is similar in different land use patterns although the absolute value of the TOC/TON ratio is highest in peat catchments, followed by forests and agricultural catchments. Fast flowing rivers, where water retention time is low, just transport terrestrially fixed C and N and river processes seem not to play any major role in element ratios.

Between 2000 and 2011 most of the TOC and TON in the 30 rivers were transported during the high flow during the spring snowmelt, and during rainfall events in autumn. However, the seasonal pattern of TOC and TON exports during warm and wet years was significantly different to these average seasonal trends, and export in autumn significantly exceeded the export during spring snowmelt. The results provide evidence that climate change and changing runoff regime are likely to significantly alter the timing of the TOC and TON exports from the catchments. The climate change induced effects on TOC and TON exports varied between catchments, because of differences in their geographical location and land use patterns. This will further increase the variability in TOC and TON transported through rivers into different parts of the northern Baltic Sea. Earlier melting periods in winter and spring, reduced the role of the spring runoff peak, and higher temperature and precipitation in autumn increased the autumn export peak. These effects, if extrapolated to the predicted climate change scenarios will further add to the altered seasonal dynamics of TOC and TON along the hydrological pathways. This is especially true for the river catchments, with a high extent of agricultural land, situated in southern and western Finland.

#### ***Acknowledgments***

We thank the Academy of Finland (projects: “Biogeochemistry of the Baltic Sea in a Changing Climate: From Catchment to Open Sea (FiDiPro)” and “Fluxes of Terminal Electron Acceptors: Linking Human Disturbance to the Health of Aquatic Systems (TEAQUILA)” (decision no. 263476)), and the Research Council of Norway (project: “Effects of climate change on boreal lake

ecosystems: Productivity and community responses (ECCO)” (grant no. 224779)) for financial support.

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Table 1. Mean, minimum and maximum monthly mean concentrations and export, annual runoff and land use from the 30 Finnish rivers.

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	<u>mean</u>	<u>min</u>	<u>max</u>
TOC mg l <sup>-1</sup>	14	3.0	38
TON µg l <sup>-1</sup>	600	0	5100
TOC/TON	30	3.2	290
TOC kg km <sup>-2</sup> a <sup>-1</sup>	4900	610	13300
TON kg km <sup>-2</sup> a <sup>-1</sup>	190	33	490
Annual runoff mm	310	72	770
Area km <sup>2</sup>	9807	357	61466
Peatland %	17	3	43
Upland forest %	42	33	54
Agricultural land %	17	1	43
Lake %	5	0	19
Urban area %	5	1	20
Open area %	14	10	25

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Table 2. Mean values and ranges of land use from the three sub-groups (agricultural, peat and forest catchments) of the study rivers.

	<u>mean</u>	<u>min</u>	<u>max</u>
<u>Agricultural catchments, n=12</u>			
Peatland %	8	3	19
Upland forest %	39	33	48
Agricultural land %	29	21	43
Lake %	3	1	13
Urban area %	8	4	20
Open area %	13	10	17
<u>Peat catchments, n=6</u>			
Peatland %	36	30	43
Upland forest %	40	36	45
Agricultural land %	5	2	10
Lake %	4	2	6
Urban area %	2	1	3
Open area %	15	10	18
<u>Forest catchments, n=10</u>			
Peatland %	14	3	24
Upland forest %	49	45	54
Agricultural land %	10	1	18
Lake %	8	0	19
Urban area %	4	1	9
<u>Open area %</u>	<u>15</u>	<u>11</u>	<u>2</u>

Table 3. Spearman correlation coefficients between mean monthly concentrations and land use in 30 Finnish river catchments. Nominally significant coefficients \* $p < 0.05$ , \*\* $p < 0.01$  and \*\*\* $p < 0.001$  are shown, ns.=not significant.

Month	Urban%		Agricultural%		Peat cover%		Lake%	
	TON $\mu\text{g l}^{-1}$	TOC $\text{mg l}^{-1}$						
Jan	0.33***	ns.	0.47***	0.20***	-0.15*	0.25***	-0.49***	-0.55***
Feb	0.24***	ns.	0.43***	0.15**	ns.	0.34***	-0.45***	-0.50***
Mar	ns.	-0.18***	0.25***	ns.	ns.	0.42***	-0.40***	-0.42***
Apr	0.39***	-0.14**	0.54***	ns.	-0.26***	0.36***	-0.49***	-0.46***
May	0.34***	ns.	0.45***	0.14**	-0.21***	0.29***	-0.39***	-0.52***
June	0.39***	ns.	0.51***	0.12*	-0.25***	0.31***	-0.47***	-0.48***
July	0.43***	ns.	0.58***	0.21***	-0.29***	0.26***	-0.51***	-0.55***
Aug	0.45***	ns.	0.59***	0.14**	-0.30***	0.29***	-0.49***	-0.50***
Sep	0.44***	ns.	0.59***	0.14**	-0.29***	0.28***	-0.47***	-0.44***
Oct	0.42***	ns.	0.56***	0.21***	-0.29***	0.20***	-0.46***	-0.48***
Nov	0.58***	ns.	0.58***	0.27***	-0.33***	0.12*	-0.48***	-0.50***
Dec	0.41***	ns.	0.54***	0.26***	-0.25***	0.13*	-0.45***	-0.53***