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Export of DOM from boreal catchments: impacts of land use cover and climate

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Abstract. Dissolved organic matter (DOM) is an important fraction in carbon (C) and nutrient budgets for aquatic ecosystems and can have broad effects on food webs and nutrient cycling. To look at the role land use cover and climate might play in DOM transport from the boreal region, the export of total organic carbon (TOC), total organic nitrogen (TON) and dissolved organic phosphorus (DOP) was estimated for Finnish main rivers and their sub-catchments, altogether 86 catchments, situated between latitudes 60° N and 69° N and covering 297,322 km^2, 88% of the total area of Finland. On an average, 94% of the TOC, 90% of the total nitrogen (TN) and 40% of the total phosphorus (TP) in Finnish rivers was in a dissolved form. The majority of the DOM export from Finnish catchments consists of organic C. The TOC export increased with increasing peatland proportion ($r = 0.39$, $p = 0.003$), while TON export increased with the increasing percentage of agricultural land ($r = 0.60$, $p < 0.001$). Although upstream lakes covered only on average 9% of the catchment area, they were the most important predictor for TOC, TON and DOP export ($r = -0.83$, $r = -0.82$ and $r = -0.61$, respectively). The higher the upstream lake percentage, the lower the export indicating organic matter retention in lakes.

Introduction

Dissolved organic matter (DOM) is commonly a major term in carbon (C), energy, and nutrient budgets for aquatic ecosystems and can have broad effects on food webs, heterotrophy, and nutrient cycling. Organic nutrients are released by microbial metabolism and photodegradation of DOM with obvious effects on the eutrophication of downstream waters. Furthermore, the industrial and municipal nutrient input to surface waters in Finland has decreased strongly, which underlines the importance of organically bound nutrients from diffuse sources.

Sources of DOM to streams are usually dominated by inputs from soils and terrestrial leaf litter. The concentrations and fluxes of DOM are affected by soil properties, hydrological conditions, biotic factors and land use of the catchment. Many of the studies of DOM sources, transport and fate have focused on dissolved organic carbon (DOC) (e.g., Hope et al. 1994; Dillon and Molot 1997; Aitkenhead and McDowell 2000). The studies including dissolved organic nitrogen (DON) and dissolved organic phosphorus (DOP) dynamics in addition to DOC are few. However, the importance of DON in nitrogen (N) budgets have been recognised recently in several studies based on data from small catchments (e.g., Lepistö et al. 1995, Kortelainen et al. 1997; Campbell et al. 2000; Chapman et al. 2001; Perakis & Hedin 2002).

The studies of total and inorganic nutrient export in Finnish rivers have been comprehensive (e.g., Laaksonen 1970; Wartiovaara 1978; Pitkänen 1994; Räike et al. 2003), whereas considerably less information exists on the variability and sources of organic C, organic N and organic P. Kortelainen et al. (1997), Kortelainen and Saukkonen (1998), and Mattsson et al. (2003) have studied the export of TOC, TON and TOP from small forested first order catchments in Finland. However, none of the previous studies has concentrated on the export of DOM from Finnish large river basins with mixed land use.

The aim of our study was to estimate the impacts of land use cover and climate on the export of organic C and organic nutrients from boreal Finnish river catchments, covering 88% of the total area of Finland. Our study provides the largest scale geographically representative estimate on DOM export from the boreal region.

Material and methods

River basins and sub-catchments

We studied the Finnish main rivers flowing to the Baltic Sea and their sub-catchments, altogether 86 catchments, situated between latitudes 60° N and 69° N and covering 297,322 km^2, 88% of the total area of Finland (Figure 1). The area of the river basins and their sub-catchments ranged from 73 to 56,500 km^2. For each catchment, the percentage of different land use cover was derived from the satellite image-based land cover and forest classification data (25×25 m grids). The majority of the catchments is covered by coniferous forests and peatlands. The proportion of upland forests range from 29 to 64% (average 49%) and the proportion of peatlands from 3 to 60% (average 22%). The percentage of peatland is highest in northern Finland, whereas the forest proportion increases towards the south. The proportion of agricultural land is on average 12% (range 0.6–44%). The majority of the croplands in Finland is located on the southern and western coast. In contrast, in the northernmost catchments, the proportion of agricultural land is minor. The water area of the catchments range from 0.5 to 26% (average 9%). The majority of the water area consists of upstream lakes, the contribution of rivers and streams is minor. Urban areas (range 0–7%) are concentrated in southern Finland, whereas open areas (bedrock outcrops) (range 3–26%) are mostly located in northern Finland (Table 1).

Figure 1. The Finnish catchments included in the study (shaded). Finland is outlined in black.

Table 1. Mean values and range for land use cover, annual deposition, annual precipitation, annual runoff and annual mean air temperature for the 86 study catchments during the years 1995–1999.

	Mean	Standard deviation	Range
Area km^2	8700	13,000	73–56,500
Peatland %	22	15	3.0–60
Water area %	8.8	6.5	0.5–26
Agricultural land %	12	10	0.6–44
Forest %	49	7.7	29–64
Open %	7.1	3.2	2.5–26
Urban %	0.6	0.9	0.0–6.5
Precipitation mm	610	46	460–690
Runoff mm	300	58	170–480
Mean air temperature °C	3.3	1.5	−0.7–5.5
Deposit.of C kg km^{-2} a^{-1}	970	210	630–1400
Deposit.of P kg km^{-2} a^{-1}	13	2.4	8.8–20
Deposit.of N kg km^{-2} a^{-1}	500	110	350–820
Deposit.of inorg. N kg km^{-2} a^{-1}	380	100	250–670

Climate related variables

Annual atmospheric bulk deposition and annual precipitation values for the catchments were derived from the deposition stations ($n = 45$) run by the Finnish Environment Institute (Järvinen and Vänni 1990; Vuorenmaa et al. 2001). The annual mean air temperature for the catchments was estimated from the data of the weather stations run by The Finnish Meteorological Institute (2000). The deposition and weather stations are situated from the southern coast to the northernmost part of Finland. If there were several stations in a catchment, an average value was used. Moreover, if there was no deposition/weather station in the catchment, the values from the nearest station were used. Average annual values for the years 1995–1999 (Table 1) were used as an estimate for the deposition, precipitation and the mean air temperature.

The river stations in the study are included in the national discharge measuring network in Finland (Hyvärinen and Korhonen 2003) and the daily discharge measurements were available for the study period 1995–1999.

Sampling and analyses

The annual sampling frequency of the rivers was mostly between 12 and 32 during the study period 1995–1999. Some of the small rivers and sub-catchments were sampled less intensively. Total organic carbon (TOC), total nitrogen (TN), the sum of nitrite (NO_2–N) and nitrate (NO_3–N), ammonium (NH_4–N), total phosphorus (TP), total dissolved phosphorus (TDP) and phosphate phosphorus (PO_4–P) were analysed in the laboratories of the Regional Environment Centres. TOC samples were deep-frozen and analysed within 1–3 months, whereas TP samples were analysed within a week after preservation with H_2SO_4. TN, the sum of NO_2–N and NO_3–N, NH_4–N and PO_4–P were analysed on the day after sampling. TOC was oxidised to carbon dioxide by combustion and determined by infrared spectrometry. TN was analysed colorimetrically after oxidation with peroxodisulfade and reduction with Cd–Cu column. The sum of NO_2–N and NO_3–N (hereafter referred to as NO_3–N) was measured by reduction of NO_3–N to NO_2–N in Cu–Cd column followed by colorimetric determination of azo-colour. NH_4–N was determined spectrofotometrically with hypochlorite and phenol. TP was analysed by the molybdenum blue method after digestion with peroxodisulfade. TDP was analysed as TP after filtering with Nuclepore polycarbonate filters with $0.4\,\mu m$ pore size. PO_4–P was analysed from filtered samples with the molybdenum blue method.

In order to estimate the dissolved fraction of TOC and TN, a subset of N and organic C samples from 15 rivers was analysed both for particulate and dissolved components in 2001. DOC and total dissolved nitrogen (TDN) were analysed with the same methods as TOC and TN, respectively, after filtering with Nuclepore polycarbonate filters with 0.4 μm pore size.

Total organic nitrogen (TON) concentrations were calculated by the difference, TON = TN−(NO_3–N + NH_4–N). Similarly, particulate phosphorus (PP) concentrations were calculated by the difference, PP = TP−TDP and DOP concentrations were calculated by the difference, DOP = TDP−PO_4–P. Annual TOC, TON and DOP fluxes were calculated by multiplying the mean monthly flows by the mean monthly concentrations, and finally, summing the monthly fluxes over the calendar year.

Statistical analyses

The relationships between land use cover (forest, agricultural land, peatland, water, urban, open), climate related variables (annual mean air temperature, precipitation, runoff) and the concentrations or the export of TOC, TON and DOP were studied with Spearman rank correlation and multiple regression analysis. The averages of the annual export values for the years 1995–1999 were used in statistical analyses and the statistical analysis was performed using PC SAS 8.2 software. The variables were transformed to natural logarithms or square roots for the regression analysis in order to improve normality. The annual retention of TOC, TON and DOP in lakes was estimated using linear regression equations between export and the proportion of lake area in the catchment.

Results

Total and dissolved fractions

The Finnish monitoring data is mostly based on unfiltered samples. Only phosphorus (P) has been analysed in some river stations for both total and dissolved fractions. However, in 2001, a subset of N and organic C samples from 15 rivers was analysed both for particulate and dissolved components. The majority of the TOC and TN in Finnish rivers is in a dissolved form, the proportion of particulate fraction is minor. The concentration of TDN in these rivers ranged from 220 to 3 200 $\mu g\ l^{-1}$ (average 840 $\mu g\ l^{-1}$). On an average, 94% of the TOC (n = 68) and 90% of the TN (n = 85) was in a dissolved form, and nearly all of the inorganic N was in a dissolved form. Therefore, TOC and TON can be used as estimates for DOC and DON, respectively. In the same subset, only 40 and 51% of the TP and inorganic P was in a dissolved form, respectively. Therefore, the data set of DOP concentrations consists only of those 27 stations where dissolved fractions of P were analysed during 1995–1999. The annual export of DOP could be calculated for 18 catchments.

Concentrations and export of DOM and inorganic nutrients

Average concentrations of TOC were relatively high ranging from 5 to 21 mg l^{-1} (average 11 mg l^{-1}) (Table 2). TN concentrations varied between 250 and 3500 μg l^{-1} and a large part of the nitrogen, on average 66%, was in an organic form. TON concentrations ranged between 210 and 910 μg l^{-1}. Concentrations of NO_3–N and NH_4–N were on average 370 and 55 μg l^{-1}, respectively. TDP concentrations ranged from 3 to 41 μg l^{-1}. DOP accounted for on average 51% of TDP and ranged between 2.5 and 38 μg l^{-1}.

The export of DOM ranged from 1300 to 7400 kg km^{-2} a^{-1}. The majority of the DOM export from Finnish catchments consists of organic C. The export of TOC ranged from 1200 to 7100 kg km^{-2} a^{-1} (Table 2), whereas, the export of TON and DOP was significantly lower ranging from 64 to 320 kg km^{-2} a^{-1}, and from 1 to 4 kg km^{-2} a^{-1}, respectively. The total TOC and TON transport through the Finnish main rivers into the Finnish coast and Lake Ladoga was estimated to be 830,000 and 33,000 t a^{-1}, respectively. The export of NO_3–N and NH_4–N was on average 130 and 19 kg km^{-2} a^{-1}, respectively. Approximately 64% of the N export was in an organic form. The export of PO_4–P was on average 4 kg km^{-2} a^{-1}, and approximately 47% of the export of TDP was in an organic form.

There was a significant positive correlation (r = 0.81, p < 0.001) between TOC and TON concentrations in stream water samples. The molar TOC:TON

Table 2. Mean values and range for river water concentrations and exports for the 86 study catchments during the years 1995–1999.

	Mean	Standard deviation	Range
TOC mg l^{-1}	11	4.3	5.1–21
TN μg l^{-1}	900	710	250–3500
NH_4–N μg l^{-1}	55	98	2.5–670
NO_3–N μg l^{-1}	370	510	2.5–2400
TON μg l^{-1}	460	180	210–910
TP μg l^{-1}	41	37	5.0–180
TDP μg l^{-1}	17	10	3.0–41
PO_4–P μg l^{-1}	10	9.8	0.5–39
DOP μg l^{-1}	9.1	7	2.5–38
PP μg l^{-1}	38	36	2.0–150
TOC:TON	28	6.7	16–39
TOC kg km^{-2} a^{-1}	3400	1400	1200–7100
TN kg km^{-2} a^{-1}	300	240	77–1100
NH_4–N kg km^{-2} a^{-1}	19	28	1.0–180
NO_3–N kg km^{-2} a^{-1}	130	190	3.0–820
TON kg km^{-2} a^{-1}	150	61	64–320
TP kg km^{-2} a^{-1}	15	16	1.0–90
TDP kg km^{-2} a^{-1}	6.2	3.7	1.0–15
PO_4–P kg km^{-2} a^{-1}	4.1	3.6	0.0–12
DOP kg km^{-2} a^{-1}	2.4	0.92	1.0–4.0

ratio varied from 16 to 39 and was on average 28. Similarly, DOP concentrations had a significant but weaker positive correlation ($r = 0.63, p < 0.001$) with TOC concentrations.

Seasonal variability of DOM and inorganic nutrients

Concentrations of TN were higher in the winter (average 1100 μg l^{-1}) than in the summer (average 740 μg l^{-1}). Also, the concentrations of NO_3–N and NH_4–N were larger in the winter (average 640 and 110 μg l^{-1}, respectively) than in the summer (average 210 and 26 μg l^{-1}, respectively). In contrast, the concentrations of TON were slightly higher in the summer (average 500 μg l^{-1}) than in the winter (average 410 μg l^{-1}) (Figure 2). As TON and inorganic N concentrations displayed opposite seasonal patterns, the composition of TN showed seasonal variation. The proportion of TON was larger in the summer (average 78% of TN) than in the winter (average 49% of TN).

Seasonal variation in TOC concentrations was small. Thus, the molar TOC:TON ratio was larger in the winter (31) and lower in the summer (26) following the variation in TON concentrations.

The concentrations of DOP were highest in the spring and in the summer (average 10 and 9 μg l^{-1}, respectively) and lowest in the winter (average 6 μg l^{-1}) (Figure 3). PO_4–P concentrations displayed an opposite seasonal pattern, concentrations were higher in the winter (average 13 μg l^{-1}) than in the summer (average 9 μg l^{-1}). Consequently, the composition of TDP also varied between seasons. The DOP proportion was larger in the summer (averaging 55% of TDP) than in the winter (averaging 35% of the TDP). Concentrations of PP were largest in the autumn (51 μg l^{-1}) and smallest in the winter (30 μg l^{-1}).

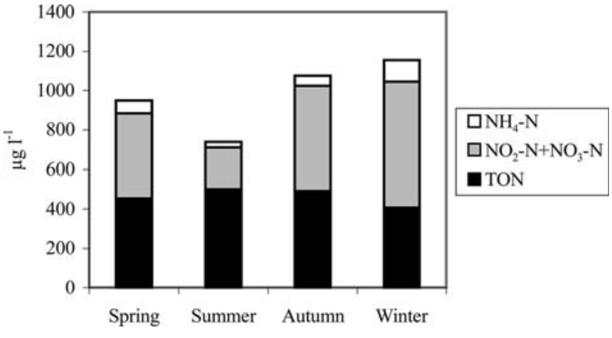

Figure 2. Seasonal variation of different nitrogen fractions.

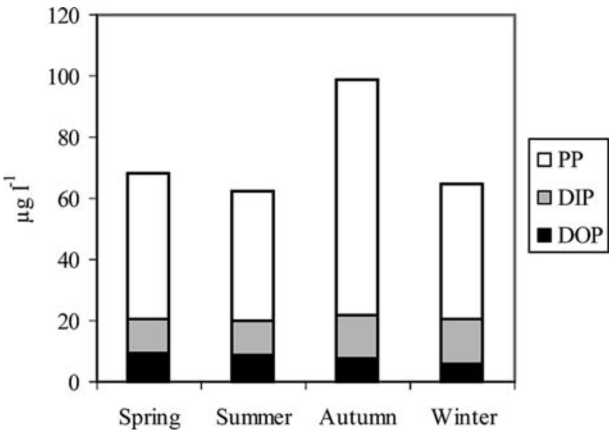

Figure 3. Seasonal variations of different phosphorus fractions.

Impact of land use cover

The TOC concentrations and export increased with increasing peatland proportion (Table 3) (Figure 4). Moreover, TOC concentrations had a positive correlation with the percentage of agricultural land cover ($r = 0.41$, $p < 0.001$). The strongest predictor for the TOC concentrations and export was the percentage of upstream lakes displaying decreasing export with increasing proportion of lakes (Figure 5a). Moreover, the area of the catchment correlated negatively with the TOC concentrations and export. The annual runoff was the only climate related variable that correlated with the TOC export.

The TON concentrations were significantly lower in the northern catchments compared to the catchments in southern Finland, and TON correlated positively with the annual mean air temperature (Table 3). The deposition of N correlated negatively with latitude ($r = -0.77$, $p < 0.001$) and the export and concentrations of TON had a positive correlation with the N deposition. Although a significant positive correlation between TON and TOC was observed, the export of TON, unlike TOC export, was not related to the percentage of peat cover in the catchment. The TON concentrations and export correlated positively with the percentage of agricultural land cover (Figure 6). TON had also a positive correlation with the percentage of urban areas and the N deposition. Moreover, the percentage of upstream lakes had a significant negative correlation with TON concentrations and export (Figure 5b). Similarly, the area of the catchment correlated negatively with the concentrations and export of TON.

The molar TOC:TON ratio correlated positively with the proportion of peatlands (Figure 7a) and negatively with the proportion of agricultural land in the catchment (Figure 7b). Consequently, in catchments with agricultural

Table 3. Spearman correlation coefficients between export, land use cover and climate related variables in 86 Finnish river catchments.

	TOC (n = 57)	TN (n = 86)	NO_3–N (n = 72)	NH_4–N (n = 78)	TON (n = 76)	TP (n = 86)	TDP (n = 38)	PO_4–N (n = 20)	DOP (n = 18)
Latitude	n.s.	−0.38***	−0.55***	n.s.	n.s.	n.s.	n.s.	−0.63**	n.s.
Annual mean air temperature	n.s.	0.48***	0.59***	0.34**	0.28*	0.29**	n.s.	n.s.	n.s.
Annual runoff	0.34**	n.s.	n.s.	n.s.	n.s.	n.s.	n.s.	0.52*	0.66**
Area of the catchment	−0.49***	−0.62***	−0.51***	−0.51***	−0.65***	−0.60***	−0.55***	−0.59**	n.s.
Peatland	0.39***	−0.25*	−0.40***	n.s.	n.s.	n.s.	n.s.	−0.62**	n.s.
Water	−0.83***	−0.73***	−0.59***	−0.73***	−0.82***	−0.85***	−0.77***	−0.80***	−0.61**
Agricultural land	n.s.	0.74***	0.82***	0.67***	0.60***	0.60***	0.50**	0.83***	n.s.
Forests	−0.58***	n.s.	n.s.	−0.24*	−0.27*	−0.28**	n.s.	n.s.	n.s.
Open areas	n.s.	n.s.	−0.30*	n.s.	n.s.	n.s.	n.s.	n.s.	n.s.
Urban areas	n.s.	0.47***	0.58***	0.40***	0.32**	0.31**	0.41*	0.59**	0.55*
N deposition	n.s.	0.51***	0.57***	0.40***	0.34**	0.35***	n.s.	0.52*	n.s.

Significant coefficients *$p \leq 0.05$, **$p \leq 0.01$ and ***$p \leq 0.001$ are shown, n.s. = not significant.

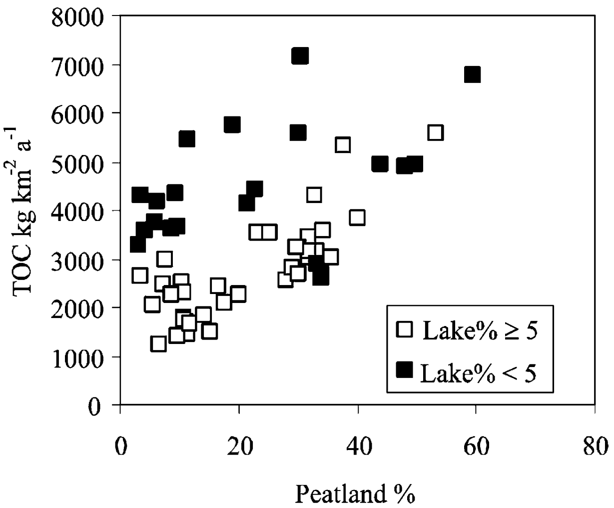

Figure 4. The relationship between the TOC export and the peatland proportion of the catchment. The catchments are shown with different symbols according to the percentage of lake coverage in the catchment.

land percentage larger than 30%, the molar TOC:TON ratio was lower than in catchments with agricultural land proportion smaller than 30% (19 vs. 30). Similarly, the TOC:TON ratio was higher (25 vs. 35) in catchments with high proportion of peatlands (> 30%) compared to catchments with a low peatland proportion (< 30%).

The concentrations and export of NO_3–N decreased towards the north, and also the concentration and export of NH_4–N was lower in the northern catchments. The TON proportion of TN was largest in the northern catchments, these rivers run to the north-eastern Gulf of Bothnia. Whereas, the inorganic fraction of TN was larger in the southern catchments. Inorganic N correlated positively with the proportion of agricultural land and urban areas in the catchment, and with N deposition. A large area of the catchment and a high percentage of upstream lakes resulted in lower concentrations and export of inorganic N.

The DOP concentrations and export decreased with increasing percentage of upstream lakes (Table 3) (Figure 5c). The DOP concentrations and export were at the same level in the northern and the southern areas, whereas PO_4–P concentrations and export decreased towards the north, and PO4–P concentrations and export were positively related to the annual mean air temperature. A large catchment area and a high percentage of upstream lakes and peatlands resulted in low export of inorganic P, whereas a high percentage of agricultural land and urban areas increased inorganic P concentrations and export.

A high percentage of lakes in the catchment resulted in lower TOC, TON and DOP concentrations and export (Figure 5). Using the linear relationship

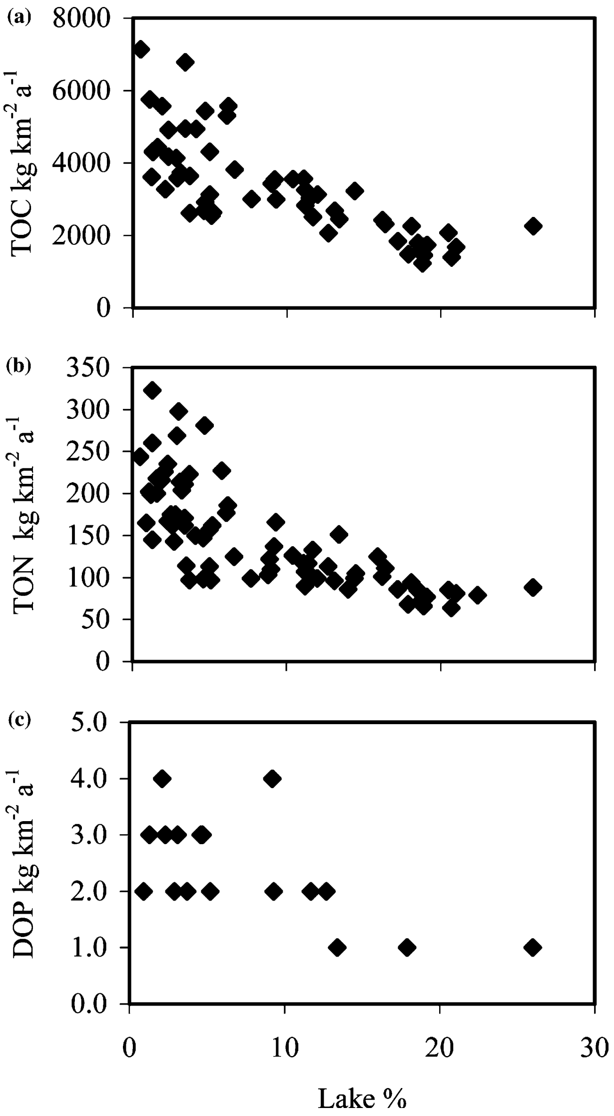

Figure 5. The relationships between the export of TOC, TON and DOP, and the proportion of upstream lakes in the catchment.

between the export and the proportion of lake area in the catchment, an average annual retention of TOC, TON and DOP in lakes were estimated to be approximately 15, 0.67 and 0.009 g m^{-2} LA (lake area), respectively.

In the multiple regression analysis, the six land use classes were used as predictors. The combination of the percentage of upstream lakes and the proportion of agricultural land in the catchment explained from 50 to 88% of

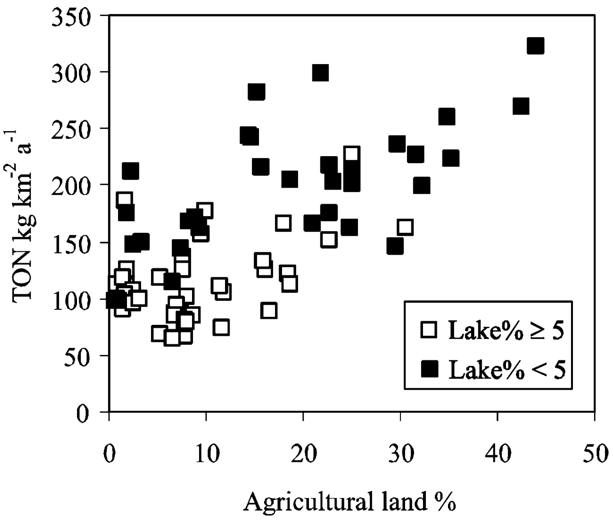

Figure 6. The relationship between the export of TON and the proportion of agricultural land in the catchment. The catchments are shown with different symbols according to the percentage of lake coverage in the catchment.

the variation in the export of N and P fractions (Table 4), whereas the proportions of peatlands, agricultural land and upstream lakes explained 85% of the variation in the export of TOC (Table 4).

Discussion

Impact of land use cover

In this study, over 90% of TOC and TN was in a dissolved form. The proportion of particulate organic carbon (POC) increases when human impact increases. Human impact and land use activity in the boreal region is, however, relatively small compared to the human impact in the temperate zone. Even in our catchments, with mixed land use (proportion of agricultural areas ranged from 0.6 to 44%) the dissolved fraction dominated. The dominance of dissolved fractions has been recognized also in previous studies based on geographically restricted areas. In the Chesapeake Bay drainage in Maryland and Pennsylvania, USA, dissolved organic N and C averaged 70–80% of the total organic N and C (Jordan et al. 1997) and in 28 streams draining from upland regions of Scotland the concentrations of TN were dominated by dissolved forms of N (Chapman et al. 2001).

Elevated TOC concentrations and export were associated with a high proportion of peatlands, as suggested in many previous studies. Peatlands and wetlands have been shown to be important contributors to organic C

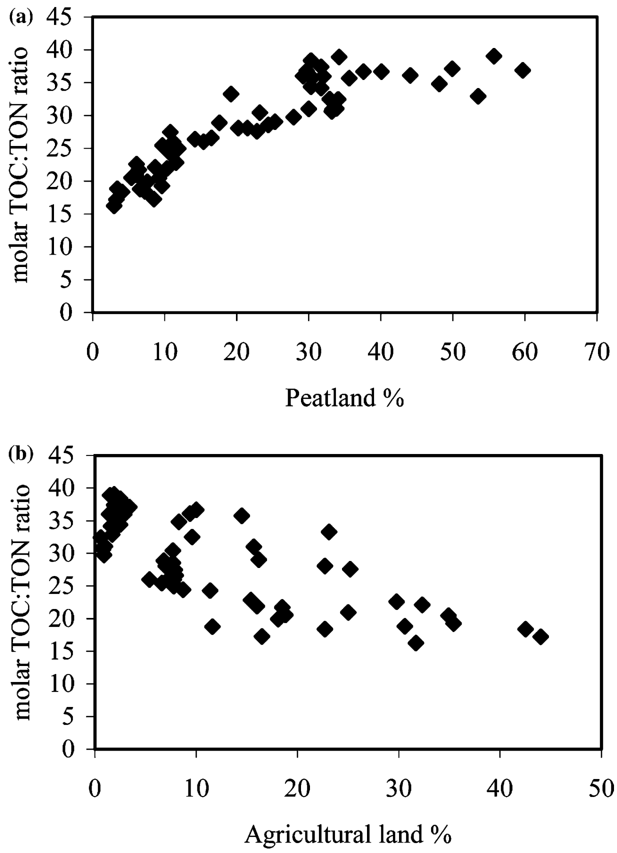

Figure 7. The relationship between molar TOC:TON ratio and the proportions of peatland and agricultural land in the catchment.

concentrations and export both in Finland (e.g., Laaksonen 1970; Pitkänen 1986; Kortelainen et al. 1997) and elsewhere (e.g., Hope et al. 1994; Dillon and Molot 1997; Aitkenhead et al. 1999; Laudon et al. 2004).

Moreover, in our study a high proportion of agricultural land in the catchment resulted in high concentrations and export of TOC. Despite the large number of studies reporting on TOC/DOC losses from forested catchments, published data on exports of organic C from agricultural land has remained limited. Recently, high organic C losses from some single agricultural catchments (Correl et al. 2001; McTiernan et al. 2001; Sharma and Rai 2004) have been reported. Our large scale boreal data was in agreement with these studies showing that agricultural land increased the TOC concentrations, although the proportion of agricultural land in the catchments was reasonably low, on average 12%. The TOC loss from fields has been suggested to be related to the inorganic and organic fertilisers. The increased dry matter

Table 4. The multiple linear regression equations for the export (kg km^{-2} a^{-1}) of TOC and different N and P fractions.

	r^2	p
$\ln TN = 5.4 - 0.33\sqrt{LAKE} + 0.30\sqrt{FIELD}$	0.88	< 0.001
$\ln NO_3\text{–}N = 3.1 - 0.40\sqrt{LAKE} + 0.63\sqrt{FIELD}$	0.82	< 0.001
$\ln NH_4\text{–}N = 2.5 - 0.60\sqrt{LAKE} + 0.40\sqrt{FIELD}$	0.71	< 0.001
$\ln TON = 5.2 - 0.24\sqrt{LAKE} + 0.096\sqrt{FIELD}$	0.78	< 0.001
$\ln TDP = 2.4 - 0.48\sqrt{LAKE} + 0.10\sqrt{FIELD}$	0.72	< 0.001
$PO_4\text{–}P = 2.6 - 1.5\sqrt{LAKE} + 1.3\sqrt{FIELD}$	0.82	< 0.001
$\ln DOP = 1.4 - 0.26\sqrt{LAKE}$	0.50	0.001
$\ln TOC = 7.0 + 0.23\sqrt{PEAT} - 0.15\sqrt{LAKE} + 0.16\sqrt{FIELD}$	0.85	< 0.001

LAKE = proportion of lakes in the catchment (%), FIELD = proportion of agricultural land in the catchment (%), PEAT = proportion of peatlands in the catchment, ln = natural logarithm.

production following the increased fertiliser inputs results in higher organic matter losses (McTiernan et al. 2001). Furthermore, Zsolnay and Görlitz (1994) have reported that the use of organic fertilisers increase the amount of water-soluble organic matter.

In areas with high N deposition, the inorganic N losses are generally high and a large part of the N export studies has therefore focused on the inorganic N. However, in areas with lower N deposition, such as Finland, the proportion of inorganic N is relatively low and a considerable proportion of N in Finnish rivers and streams (Pitkänen 1994; Lepistö et al. 1995; Kortelainen et al. 1997) is in an organic form. Recently, it has been suggested that organic N may be responsible for a large part of N losses from the forested catchments. Perakis and Hedin (2002) found that N loss from temperate forested catchments in South America was controlled by the export of organic N, with little contribution from dissolved inorganic N. Similarly, in the Rhode River watershed in Maryland, USA, most of the total N discharged from forested catchments was in an organic form (Correll et al. 1999). Campbell et al. (2000) concluded that DON made up the majority of total dissolved nitrogen (TDN) export even in areas with large anthropogenic inputs of dissolved inorganic nitrogen (DIN) in the north eastern United States. Very high proportions (75–95%) of organic N from TN have been reported also from tropical watersheds (Lewis et al. 1999), watersheds in Sierra Nevada (Coats and Goldman 2001) and watersheds in the central Cascade Mountains of Oregon (Vanderbilt et al. 2003). In our data set, about 64% of the N export was in an organic form. The percentage of TON was higher in the northern catchments running to the north-eastern Gulf of Bothnia, whereas the proportion of inorganic fraction was higher in the southern catchments with higher N deposition and larger proportion of agricultural land and urban areas in the catchment.

In our boreal rivers, both organic and inorganic N correlated strongly with the percentage of agricultural land in the catchment. Increases in TN discharge with increasing proportions of cropland have commonly been observed in

Finland (e.g., Rekolainen 1989; Pitkänen 1994) and elsewhere (e.g. Jordan et al. 1997), mostly related to applications of N fertilisers to cropland. Moreover, agricultural fields have been found to increase DON and TON export (Jordan et al. 1997; Qualls and Richardson 2002) probably related to application of organic fertilisers and higher productivity.

Although both the TOC and TON exports correlated positively with the percentage of agricultural land in the catchment, the molar TOC:TON ratio was lower in the river water running from the catchment abundant with agricultural land. In contrast, the molar TOC:TON ratio was higher in the catchments with a high peatland proportion. The organic matter exporting from agricultural land is probably more enriched in N than organic matter from peatlands. Although in some areas wetlands and peatlands have increased the export of TON (Devito et al. 1989; Dillon et al. 1991), in Finnish river catchments the TON export did not increase with increasing peatland proportion. Conversely, TOC concentrations and export showed a positive correlation with the proportion of peatlands, which results in higher molar TOC:TON ratios in areas with a high peatland percentage.

Our statistical models using the proportion of agricultural land and upstream lakes as predictors explained 50–88% of the variance in the export of different forms of N and P. The proportion of peatlands, agricultural land and upstream lakes explained 85% of the variance in the export of TOC. The relationships displayed in the present data set derived from the Finnish river basins, can be different in different climatic zones or in an area where land use cover differs considerably. However, the models formed for larger and heterogeneous areas have been shown to result in stronger explanatory power than models formed for areas with a very homogeneous land use suggested by Herlihy et al. (1998) and confirmed by the study of Rantakari et al. (2004) based on Finnish lake catchments. Moreover, Rapp et al. (1985) have suggested that the extremes tend to balance each other to produce 'average' situation when catchment size increases. Our regression models predicting the impact of land use cover on the DOM export are based on the largest river basins in Finland representing mixed land use which indicates that our models can be assumed to be applicable to similar conditions in the northern boreal zone.

Climate and seasonal variability

TON was the only fraction of organic matter that had significant correlation with the annual mean air temperature. The export of TON is linked to climate via primary production and decomposition rates, which control the overall amount of TON potentially available. However, the deposition of N is higher in the south and correlated positively with the annual mean air temperature. Consequently, the larger concentrations and export of TON in southern Finland, were probably due to higher N deposition, more active primary production and faster decomposition rate in a warmer climate. Moreover, the agricultural areas, which were found to be an important source of TON, are mostly located in southern and western Finland increasing the TON export. The composition of TN varied between the northern and the southern catchments. The proportion of TON was larger in the north, while the proportion of inorganic N was larger in the south. Higher N deposition, more fertile soils, faster mineralization and application of fertilisers on the agricultural fields increases the inorganic N export in southern Finland, while retention in peatlands and the slow rate of litter decomposition caused by the cold climate restricts N availability in the north. Similarly, the composition of TDP had a south–north variation. The inorganic P component was larger in the south, probably due to faster nutrient cycling, agricultural activity and more fertile soils in southern Finland.

Although most of the terrestrially fixed TOC in the boreal region is transported during snow melt in the spring and during rain events in the autumn (e.g., Kortelainen et al. 1997, Laudon et al. 2004), the stream water TOC concentrations did not show strong seasonal variability. Schiff et al. (1998) suggested that in upland catchments, the TOC concentrations are generally higher during high flow periods when the dominant flow paths are near the surface and through the organic-rich upper soil horizon. In wetlands, the water table remains close to the surface and additional water from rain events does not greatly increase the contact with organic rich surface horizons. Moreover, Laudon et al. (2004) suggested that the smaller relative importance of the spring runoff period for the annual TOC export from wetland dominated catchments is a result of the hydrological flow paths associated with the snow melt period. During the spring, the flow paths through wetland dominated systems include a much larger component of low-TOC snow melt water via surface flow over ice or frozen peat. Peatlands and wetlands are abundant in many Finnish river basins (average 22%, range 3–60%) and may decrease fluctuations in stream TOC concentrations.

In contrast to TOC, both TON and DOP concentrations varied seasonally being largest during the summer and lowest during the winter. As inorganic nutrients displayed an opposite seasonal pattern, the relative importance of the organic component increased in the summer. The potential availability of TON and DOP is particularly important during the summer when inorganic nutrient concentrations are low due to plant and microbial uptake. Similar seasonal variations in DON concentrations have been observed in streams in upland Scotland (Chapman et al. 2001). The largest fluxes of DON and DOP into the mineral soil under a Scots pine and a European Beech forest have been observed in the summer due to increased microbial activity in response to warmer weather conditions and thus increased organic matter decay (Kaiser et al. 2000).

In the present study, the average molar TOC:TON ratio was reasonably high (on average 28) throughout the year. Low C:N ratios, close to the Redfield OC:ON ratio of 6.6:1, are indicative of algal-derived material (Redfield et al.

1963). In contrast, terrestrially derived material has much higher OC:ON ratios ranging from 10 to 1000 (e.g., Hedges et al. 1986, 1988). All measured ratios in this study lie above the Redfield ratio emphasising the importance of terrestrially derived organic matter input to Finnish rivers. In the summer, the TOC:TON ratios were slightly narrower, but still on average over 20. It is evident that the sources of organic matter during the summer is mostly allochthonous, but due to the warmer temperatures, favourable light conditions and low flows algae growth is enhanced, and increased autochthonous sources of organic matter probably result in the narrower TOC:TON ratios.

Retention

Both TOC and TON export showed a negative correlation with the area of the catchment, probably reflecting the retention and decomposition of DOM in the catchment. In a large river basin, the flow paths are longer from the edge of the catchment and DOM can be exposed to various biogeochemical processes, including sorption to mineral soil and mineralization, before reaching the river. Large river basins in Finland have also the highest proportion of lakes in the catchments, which increases retention. Moreover, the decomposition of DOM during the river transport results in lower DOM losses per unit area from large catchments.

Both Wartiovaara (1978) and Pitkänen (1986) documented a negative relationship between upstream lake percentage and TOC/COD_{Mn} concentrations/export in Finnish rivers. Similarly, Kortelainen (1993) and Rantakari et al. (2004) have shown that TOC concentrations in lakes decrease with increasing proportion of upstream lakes in the catchment. Although in our river basins upstream lakes cover only on average 9% of the catchment area, the percentage of upstream lakes was the most important predictor for the TOC, TON and DOP concentrations and export. The higher the upstream lake proportion the lower the export indicating organic matter retention in Finnish lakes. Water residence time in a river basin can increase significantly although the percentage of lake coverage in a catchment remains reasonable low. Algesten et al. (2003) estimated that between 30% and 80% of the total organic carbon entering the swedish freshwater ecosystems was lost in lakes and closely correlated to the mean residence time of surface water in the catchment.

The average estimated annual TOC retention in lakes (15 g C m^{-2} LA, c.f. results) divided by the area of entire river basins gives the TOC retention of 1400 kg C km^{-2} WA (watershed area). Kortelainen and Saukkonen (1998) estimated the TOC export from small, first order forested catchments in Finland to be on average 5700 kg km^{-2} a^{-1}. These 22 catchments represent typical Finnish forestry land where the average peatland proportion and the mean annual runoff are comparable to the entire country and, furthermore, forestry practices have affected annually about 2.4% of the catchment area similar to the entire country. In our data set, representing at least second order catchments, the average TOC export was 3400 kg km^{-2} WA a^{-1} suggesting approximately 2 300 kg km^{-2} WA a^{-1} of TOC retention on the way from the first order catchments downstream. However, due to the differences in land use cover, the TOC loads from these two data sets are not quite comparable. The first order catchments studied by Kortelainen and Saukkonen (1998) are mostly covered by upland forests and peatlands, in contrast to the large river basins where TOC export is influenced by more heterogeneous land use cover including forests, peatlands, agricultural land and urban areas. Furthermore, the topography of the first order catchments is generally steeper compared to the flatter landscape downstream near the coast influencing the TOC load. Moreover, in large river basins, large land areas are not closely connected to the river resulting in decreasing load compared to the near stream zone. Consequently, as catchment size increases, the area specific load can decrease further increasing the retention in river basins.

The TOC retention in lakes is either due to accumulation of C in lake sediments or degradation of organic matter in aquatic ecosystems. Lake sediments have been shown to be important areal C stocks in the boreal region (Kortelainen et al. 2004). On the other hand, Kortelainen et al. (2000) have demonstrated CO_2, CH_4 and N_2O supersaturation in Finnish lakes compared to the atmospheric concentration. The majority of CO_2 gas efflux in Finnish lakes is due to degradation of terrestrially fixed C in aquatic environment (Striegl et al. 2001). Mineralization of the riverine DOM also means mineralization of organic N and organic P. Simultaneously, inorganic N and P are released with possible consequences for the aquatic productivity.

Riparian areas, wetlands, streams and lakes have been considered as key environments for N sinks. Organic N is the most important N fraction in boreal rivers and budged calculations from the northern Finnish rivers using an N export/retention coefficient-based N_EXRET model and an N process-based INCA model suggest that at the watershed scale lakes are key environments in N retention, aquatic losses were significantly higher than retention in peatlands (Lepistö et al. 2001, 2004). The retention of N in lakes is a combination of various processes such as biological uptake, sedimentation and denitrification. In our study the retention of TON by lakes was estimated to be on average 0.67 g N m^{-2} LA a^{-1}, which is within the range of 0.66–1.17 g N m^{-2} LA a^{-1} presented by Lepistö et al. (2001) for the TN retention by lakes in the Oulujoki river basin and its sub-basins located in northern Finland. Lepistö et al. (2004) estimated somewhat lower TN retention by lakes (0.2–0.4 g N m^{-2} LA a^{-1}) in the Simojoki river basin north from the river Oulujoki. They concluded that retention probably decreases towards the north with colder climate, less denitrification, and slower N cycling. The catchments studied by Lepistö et al. (2001, 2004) are also included in our study. Furthermore, Lepistö et al. (in prep.) have estimated with GIS-based assessment model that retention of N in 30 Finnish river basins ranges from 0 to 68%. The lake area specific retention rate varies due to the percentage of lake coverage in the catchment, the morphology of lake basins, the location of lakes within catchments and the trophic state of lakes. However, our estimate for average TON retention (0.67 g N m^{-2} LA a^{-1}) derived from typical boreal catchments from southern to northern Finland can be considered to indicate the average retention in the boreal region.

Conclusions

The study catchments cover almost entire Finland and are covered mostly by forests, peatlands and lakes with minor proportion of agricultural land and urban areas. Because of large areal coverage and variability in land use cover, the results can be assumed to be representative for large parts of the northern boreal region.

The major part of the organic matter consists of organic C, and most of it is in a dissolved form. The TOC concentrations did not show strong seasonal variability, while both TON and DOP concentrations varied seasonally being largest during the summer and lowest during the winter. The potential availability of TON and DOP is particularly important during the summer when inorganic nutrient concentrations are low due to intensive plant and microbial uptake.

The land use cover had stronger influence on the export of organic matter than the climate related attributes, regardless of a 6 °C gradient in annual mean air temperature. Hence, within one climatically relative homogenous biome, in this case the northern boreal zone, land use cover probably determines to a great extent the concentrations and export of organic matter. Peatlands and agricultural fields were predictors for TOC concentrations and export, while agricultural land was concluded to be an important TON source. The DOM export was significantly reduced by the upstream lakes in the catchment; lakes act as an important sink for terrestrially derived DOM in boreal river catchments.

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