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This study synthesizes the following original publications, which are referred to by their Roman numerals (I-VI) in the text.

Paper I
Mattsson T., Finér L., Kortelainen P. and Sallantaus T. 2003, Brook water quality and background leaching from unmanaged forested catchments in Finland, Water, Air and Soil Pollution 147: 275-297.

Paper II
Kortelainen P., **Mattsson T**., Finér L., Ahtiainen M., Saukkonen S. and Sallantaus T. 2006, Controls on the export of C, N, P and Fe from undisturbed boreal catchments, Finland, Aquatic Sciences 68: 453-468.

Paper III
Mattsson T., Kortelainen P. and Räike A. 2005, Export of DOM from Boreal catchments: impacts of land use cover and climate, Biogeochemistry 76: 373-394.

Paper IV
Mattsson T., Kortelainen P., Laubel A., Evans D., Pujo-Pay M., Räike A. and Conan P. 2009, Export of dissolved organic matter in relation to land use along a European climatic gradient, Science of the Total Environment 407: 1967-1976.

Paper V
Finér L., Kortelainen P., **Mattsson T**., Ahtiainen M., Kubin E. and Sallantaus T. 2004, Sulphate and base cation concentrations and export in streams from unmanaged forested catchments in Finland, Forest Ecology and Management 195: 115-128.

Paper VI
Mattsson T., Kortelainen P., Lepistö A. and Räike A. 2007, Organic and minerogenic acidity in Finnish rivers in relation to land use and deposition, Science of the Total Environment 383: 183-192.

Author's contribution to the papers:

Paper I
T. Mattsson was responsible for the processing and analysis of the data, interpretation of results and writing the paper. T. Sallantaus carried out the search and selection of the study catchments. T. Mattsson wrote the first version of the paper, which was commented by the co-authors.

Paper II
T. Mattsson participated in the processing and analysis of the data and commented the manuscript. P. Kortelainen wrote the first version of the paper, which was commented by the co-authors.

Paper III
T. Mattsson was responsible for the processing and analysis of the data, interpretation of results and writing the paper. A. Räike participated in the data processing. T. Mattsson wrote the first version of the paper, which was commented by the co-authors.

Paper IV

T. Mattsson was responsible for the processing and analysis of the data, interpretation of results and writing the paper. A. Räike participated in the data processing, and A. Laubel, D. Evans, M. Pujo-Pay and P. Conan provided data. T. Mattsson wrote the first version of the paper, which was commented by the co-authors.

Paper V

T. Mattsson participated in the data processing and commented the manuscript. L. Finér wrote the first version of the paper, which was commented by the co-authors.

Paper VI

T. Mattsson was responsible for the processing and analysis of the data, interpretation of results and writing the paper. A. Räike participated in the data processing. T. Mattsson wrote the first version of the paper, which was commented by the co-authors.

Symbols and abbreviations

A^-	Organic anion
ANC	Acid neutralizing capacity
BC	Base cations
C	Carbon
Ca	Calcium
COD	Chemical oxygen demand
DIN	Dissolved inorganic nitrogen
DOC	Dissolved organic carbon
DOM	Dissolved organic matter
DON	Dissolved organic nitrogen
DOP	Dissolved organic phosphorus
K	Potassium
Mg	Magnesium
N	Nitrogen
Na	Sodium
NH_4	Ammonium
NO_3	Nitrate
P	Phosphorus
PO_4	Phosphate
POC	Particulate organic carbon
PON	Particulate organic nitrogen
PP	Particulate phosphorus
SO_4	Sulphate
$*SO_4$	Non-marine sulphate
TDN	Total dissolved nitrogen
TDP	Total dissolved phosphorus
TN	Total nitrogen
TOC	Total organic carbon
TON	Total organic nitrogen
TOP	Total organic phosphorus
TP	Total phosphorus

Export of organic matter, sulphate and base cations from boreal headwater catchments downstream to the coast: impacts of land use and climate

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University of Helsinki, Faculty of Biological and Environmental Sciences, Department of Environmental Sciences, 2010

Mattsson, T. 2010. Export of organic matter, sulphate and base cations from boreal headwater catchments downstream to the coast: impacts of land use and climate. Monographs of the Boreal Environment Research No. 36, 2010.

The terrestrial export of dissolved organic matter (DOM) is associated with climate, vegetation and land use, and thus is under the influence of climatic variability and human interference with terrestrial ecosystems, their soils and hydrological cycles. The present study provides an assessment of spatial variation of DOM concentrations and export, and interactions between DOM, catchment characteristics, land use and climatic factors in boreal catchments. The influence of catchment characteristics, land use and climatic drivers on the concentrations and export of total organic carbon (TOC), total organic nitrogen (TON) and dissolved organic phosphorus (DOP) was estimated using stream water quality, forest inventory and climatic data from 42 Finnish pristine forested headwater catchments, and water quality monitoring, GIS land use, forest inventory and climatic data from the 36 main Finnish rivers (and their sub-catchments) flowing to the Baltic Sea. Moreover, the export of DOM in relation to land use along a European climatic gradient was studied using river water quality and land use data from four European areas. Additionally, the role of organic and minerogenic acidity in controlling pH levels in Finnish rivers and pristine streams was studied by measuring organic anion, sulphate (SO_4) and base cation (Ca, Mg, K and Na) concentrations. In all study catchments, TOC was a major fraction of DOM, with much lower proportions of TON and DOP. Moreover, most of TOC and TON was in a dissolved form. The correlation between TOC and TON concentrations was strong and TOC concentrations explained 78% of the variation in TON concentrations in pristine headwater streams. In a subgroup of 20 headwater catchments with similar climatic conditions and low N deposition in eastern Finland, the proportion of peatlands in the catchment and the proportion of Norway spruce (*Picea abies* Karsten) of the tree stand had the strongest correlation with the TOC and TON concentrations and export. In Finnish river basins, TOC export increased with the increasing proportion of peatland in the catchment, whereas TON export increased with increasing extent of agricultural land. The highest DOP concentrations and export were recorded in river basins with a high extent of agricultural land and urban areas, reflecting the influence of human impact on DOP loads. However, the most important predictor for TOC, TON and DOP export in Finnish rivers was the proportion of upstream lakes in the catchment. The higher the upstream lake percentage, the lower the export, indicating organic matter retention in lakes. Molar TOC:TON ratio decreased from headwater catchments covered by forests and peatlands to the large river basins with mixed land use, emphasising the effect of the land use gradient on the stoichiometry of rivers. This study also demonstrated that the land use of the catchments is related to both organic and minerogenic acidity in rivers and pristine headwater streams. Organic anion dominated in rivers and streams situated in northern Finland, reflecting the higher extent of peatlands in these areas, whereas SO_4 dominated in southern Finland and on western coastal areas, where the extent of fertile areas, agricultural land, urban areas, acid sulphate soils, and sulphate deposition is highest. High TOC concentrations decreased pH values in the stream and river water, whereas no correlation between SO_4 concentrations and pH was observed. This underlines the importance of organic acids in controlling pH levels in Finnish pristine headwater streams and main rivers. High SO_4 concentrations were associated with high base cation concentrations and fertile areas, which buffered the effects of SO_4 on pH.

Keywords: carbon, catchment, concentrations, export, land use, nitrogen, organic matter, phosphorus, rivers, streams, sulphate

1 Introduction

1.1 Dissolved organic matter (DOM)

In the biogeochemical cycle, inorganic nutrients are converted to organic matter by photosynthesis and are either remineralized during decomposition or remain in an organic form for a longer period. Leaching of rainwater through the vegetation canopy and soils carries these compounds as dissolved organic matter (DOM) to surface waters. DOM is a complex mixture of many different organic compounds, which can influence aquatic ecosystems via their physical and chemical properties. Dissolved organic carbon (DOC) is the major fraction of DOM transported by rivers and represents an important pathway of carbon from terrestrial to aquatic ecosystems, where it can serve as substrate for bacteria resulting in a demand for oxygen (e.g. Kortelainen et al. 2006). Furthermore, DOM also transports large quantities of nitrogen (N) and phosphorus (P) to surface waters (e.g. Kortelainen and Saukkonen 1998, Qualls and Richardson 2003). After photodegradation or microbial metabolism the nutrients are released and enter the bioavailable nutrient pool, becoming available for plant growth (e.g. Goldman et al. 1987, Wiegner and Seitzinger 2001, Qualls and Richardson 2003, Vähätalo et al. 2003). However, low molecular weight organic N and P can also be taken up directly by plants, and can significantly support primary production in nutrient-limited waters. (e.g. Antia et al. 1991, Seitzinger and Sanders 1997). The potential availability of organic N and organic P is particularly important during the summer, when inorganic nutrient concentrations are low due to plant and microbial uptake. Moreover, DOM plays an important role in the transport and availability of trace metals and contaminants (e.g. Reuter and Perdue 1977, Kukkonen and Oikari 1991, Kulovaara 1993, Muller et al. 2005). DOC in natural waters is also both a natural background source of acidity and a pH buffer in low alkalinity waters and thus affects the acid-base balance in surface waters (e.g. Oliver et al. 1983, Kortelainen et al. 1989, Perdue and Gjessing 1990, Roila et al. 1994, Mattsson et al. 1995). DOM is also an important light-absorbing agent in surface waters, both of visible and ultra-violet radiation (Kirk 1994). The transparency and heat budgets of surface waters are thus modified and partly controlled by DOM, and aquatic primary producers compete with DOM for the available light (e.g. Vähätalo et al. 2005). Hence, the optical properties of DOM have major implications for ecosystem functioning.

In many eutrophication studies the effects of inorganic nutrients have been the primary focus and the large amounts of N and P transported with DOM to surface waters have partly been overlooked. However, organic N often forms a substantial part of the total N pool in streams and rivers. This can be exemplified by the fact that about 70% of dissolved nitrogen transported by rivers worldwide is dissolved organic nitrogen (DON) (Meybeck 1982). In agricultural catchments, DON has been reported to be an important constituent of the total nitrogen load, comprising 40% of the total annual load, the proportion of DON being determined by geology and the intensity of land use (Johnes and Burt 1991, Heathwaite and Johnes 1996). The importance of DON in N budgets has also been recognised in several studies based on data from small managed and pristine forested catchments (e.g., Lepistö et al. 1995, Kortelainen et al. 1997, Chapman et al. 2001, Perakis and Hedin 2002). Moreover, very high proportions (75 – 95 %) of organic N from total N have been reported in tropical watersheds (Lewis et al. 1999), and in watersheds in Sierra Nevada (Coats and Goldman 2001) and in the central Cascade Mountains of Oregon (Vanderbilt et al. 2003). Campbell et al. (2000) concluded that DON accounted for the majority of total dissolved nitrogen (TDN) export even in areas with large atmospheric inputs of dissolved inorganic nitrogen (DIN) in the north-eastern United States. Similarly, Pellerin et al. (2006) concluded that DON is an important component of N loss in surface waters draining forested and human-dominated watersheds.

Several studies have shown increasing trends of organic carbon concentrations (Freeman et al. 2001, Worrall et al. 2004, Evans et al. 2005, Skjelkvåle et al. 2005, Vuorenmaa et al. 2006, Lepistö et al. 2008, Sarkkola et al. 2009) in lakes and streams in Europe and North America during the last 10–15 years. Several hypotheses have been suggested to explain these increases including, for example, climate warming (Freeman et al. 2001), increasing atmospheric CO_2 concentration (Freeman et al. 2004), decreased sulphate deposition (Evans et al. 2006, Monteith et al. 2007) and hydrological changes (e. g. Tranvik and Jansson 2001, Hongve et al. 2004, Worrall and Burt 2008). These increases in DOC concentrations in rivers and streams induced by one or more external drivers will also impact the interactions between DOC, nutrients and metals, and organic acidity.

1.2 Influence of land use on riverine DOM

Terrestrial inputs from soils and terrestrial leaf litter are the primary source of freshwater DOM, although decomposition products of aquatic organisms are important in eutrophic systems (Thurman 1985, Mulholland et al. 1990, Aitkenhead-Peterson et al. 2003, Mulholland 2003). Most of the DOM in pristine headwater streams is of terrestrial origin (McKnight et al. 2001). Thus the concentrations and fluxes of riverine DOM are affected by soil properties, hydrological conditions, biotic factors and land use of the catchment. The majority of the studies of DOM sources, transport and fate have focused on DOC (e.g., Hope et al. 1994, Dillon and Molot 1997, Aitkenhead and McDowell 2000). However, increasing attention has been paid to the dynamics of DON and dissolved organic phosphorus (DOP) in addition to DOC (e.g. Johnes and Burt 1991, Ron Vaz et al. 1993, Heathwaite and Johnes 1996, Harrison et al. 2005, Stedmon et al. 2006, Stanley and Maxted 2008, Stutter et al. 2008, Aitkenhead-Peterson et al. 2009).

Several catchment-scale studies have examined catchment geology, soil type, vegetation and land use effects on DOC (e.g. Hemond 1990, Mulholland et al. 1990, Dillon and Molot, 1997, Gorham et al. 1998, Cronan et al. 1999, Aitkenhead et al. 1999). Peatlands and wetlands have been shown to be important contributors to organic carbon concentrations and export (e.g. Hemond 1990, Mulholland et al. 1990, Dillon and Molot 1997, Kortelainen et al. 1997, Aitkenhead et al. 1999). Moreover, elevated organic carbon concentrations and fluxes have been reported from catchments dominated by agricultural land (Correll et al. 2001, McTiernan et al. 2001) and catchments with urban open areas (Aitkenhead-Peterson et al. 2009).

Organic N has been observed to correlate positively with the percentage of peat cover and wetlands (e.g. Ito et al. 2005), percentage cover of forestry (Chapman et al. 2001) and urban land use (Hayakawa et al. 2006). Heathwaite and Johnes (1996) showed that organic nitrogen is an important constituent of the nitrogen load from agricultural catchments and can comprise 40% of the total annual load. Moreover, agricultural fields have been found to increase DON and total organic nitrogen (TON) export (Jordan et al. 1997, Qualls and Richardson 2003) and DOP loading (Stedmon et al. 2006), probably related to application of organic fertilisers and higher productivity. Similarly, model calculations by Harrison et al. (2005) indicated that regions with high population densities and high extent of intensive agriculture tend to have highest DON and DOP yields.

Increased attention has also been paid to the role of catchment topography and hydrology as determinant factors of DOC (e.g. Dillon et al. 1991, D'Arcy and Carignan 1997, Köhler et al 2008) and DON (e.g. Correll et al. 1999, Campbell et al. 2000, Coats and Goldman 2001, Vanderbilt et al. 2003) in surface waters. Both organic C and N have shown a positive correlation with discharge (e. g. Schlesinger and Melack 1981, Correll et al. 1999, 2001, Andersson and Lepistö 2000, Dillon and Molot 2005). However, the relationship between DOC and water discharge has been reported to depend on the land cover of the catchment; organic matter can be positively correlated with discharge in forest catchments, whereas in wetland catchments the relationship can be negative (Schiff et al. 1998, Petrone et al. 2007, Erlandsson et al. 2008, Köhler et al. 2008). Moreover, Lepistö et al. (2008) observed seasonal variation in relationship between discharge and concentration. Particularly during autumn high flow rates, higher total organic carbon (TOC) and TON concentrations were detected.

The bioavailability of DOM to plankton communities can vary depending on the nature of the terrestrial source. For example, DON from anthropogenic sources (urban areas) has been shown to be more bioavailable for estuarine plankton communities than DON exported from natural areas (Seitzinger et al. 2002). Moreover, the bioavailability of riverine DOM appears to be greater under low discharge conditions and decreases with distance downstream (Sun et al. 1997).

1.3 DOM in Finnish streams and rivers

Finnish surface waters have typically high organic matter concentrations and colour values, due to high transport of terrestrially fixed carbon from catchments covered by peatlands and forests. For example, Lepistö et al. (1995), Kortelainen et al. (1997) and Kortelainen and Saukkonen (1998) studied the export of organic carbon, nitrogen and phosphorus from small managed forested first order catchments in Finland. In small streams surrounded by managed forested catchments, nitrogen flux in organic form ranged from 49% to 94% (Lepistö et al. 1995, Kortelainen et al. 1997) and TOC concentrations were relatively high, on average 17 mg l^{-1} (Kortelainen and Saukkonen 1998). Recently, increasing TOC concentrations have been detected in small streams with forested catchments in eastern Finland (Sarkkola et al. 2009).

Holmberg (1935) reported chemical oxygen demand (COD) values between 1911 and 1931 in Finnish rivers flowing into the Gulf of Bothnia. COD is an indicator of the amount of oxidizable organic material in water and has also been used to estimate TOC concentrations due to the strong correlation between COD and TOC (Kortelainen 1993a). The results of Holmberg (1935) were then compared by Alasaarela and Heinonen (1984) to the COD data collected during 1962-1972 from the same rivers, showing that annual COD flux in the non-loaded rivers had remained fairly constant.

Factors determining COD concentration variability in Finnish main rivers were studied by Laaksonen (1970). Wartiovaara (1978) also studied TOC and COD concentrations and transport in 21 rivers discharging into the Baltic Sea during the years 1974-1976, and Pitkänen (1986) the COD loads to the Gulf of Bothnia in 1968-1983. These studies documented a negative relationship between upstream lake percentage and TOC/COD concentrations and transport. Organic carbon concentrations and fluxes in some individual Finnish rivers have also been studied by, for example, Heikkinen (1989, 1990, 1994) from the river Kiiminkijoki and Lepistö et al. (2008) from the river Simojoki.

The studies of organic matter from Finnish large rivers have been focused on the variability of COD or TOC concentrations, whereas less attention has been paid to organic N and organic P. Pitkänen (1994) estimated the costal nitrogen load in organic form to be on average 53% of the total for Finland. Furthermore, Lepistö et al. (2008) detected statistically significant upward trends for TON concentration and flow of the river Simojoki during 1976–2005.

Over wide regions in Finland, lake water acidity has been shown to be dominated by organic acids, and the pH of lakes has a significant negative correlation with TOC concentrations (e.g. Kortelainen and Mannio 1988, Kortelainen et al. 1989). Moreover, stream water acidity was dominated by organic acids in the majority of the managed forested first-order streams, and 67 to 82% of the variability in stream water pH could be explained by base cation and organic carbon concentrations (Kortelainen and Saukkonen 1995). Sulphate deposition in Finland is relatively low but has a rather wide range, from 430 mg S m^{-2} a^{-1} in the south to 80 mg S m^{-2} a^{-1} in the north (Leinonen 2001). Thus in southernmost Finland, where sulphate deposition is highest, minerogenic acidity can be more important (e.g. Kortelainen and Mannio

1988, Kortelainen et al. 1989). Considerably less information exists about organic acids and SO_4 from river basins with mixed land use, although, land use-induced variations of organic carbon and SO_4 can have a significant effect on the acidity and the pH of river water. Land use has been shown to have strong relationships both with organic carbon (cf. section 1.2) and sulphate (e.g. Williams et al. 2005) export/concentrations in rivers, thus affecting the acidity and pH of the river water. For example, concentrations of SO_4, base cations and acid neutralizing capacity (ANC) in stream water have been shown to have significant positive relationships with the percentage of urban and agricultural land use (Williams et al. 2005). In Finnish rivers, however, the relationships between minerogenic and organic acidity on the one hand and land use on the other have not been studied comprehensively.

1.4 Objectives of the study

Catchment-scale studies from undisturbed forests in regions of low atmospheric deposition provide information on water quality and export of elements against which disturbed areas can be compared. Although individual unmanaged catchments have frequently been used as reference areas for managed ones in order to estimate the impacts of forestry on concentrations/export (e.g. Ahtiainen and Huttunen 1999), studies including an extensive set of catchments without human disturbance in the Fennoscandian boreal zone are rare.

In the major Finnish rivers, the studies of total and inorganic nutrient export 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. The industrial and municipal nutrient input to surface waters in Finland has decreased strongly, which underlines the importance of both organic and inorganic nutrients from diffuse sources. Moreover, detected changes in the export of organic carbon to aquatic ecosystems (e.g. Freeman et al. 2001, Worrall et al. 2004, Evans et al. 2005, Skjelkvåle et al. 2005, Vuorenmaa et al. 2006, Sarkkola et al. 2009) also influence the delivery and biogeochemical cycling of other components associated with TOC, which emphasises the importance of studying organic N and organic P dynamics in addition to TOC.

The objectives of the study were:

- to quantify the transport of organic carbon, organic nitrogen and organic phosphorus from small pristine first order catchments downstream through streams and rivers to the coast (papers I-III).
- to assess the importance of the organic nutrients with respect to the total loads (papers I-III).
- to identify the most important factors controlling the export of organic C, N and P from pristine forested catchments (papers I and II).
- to assess the impacts of land use and climate on the export of organic carbon, organic nitrogen and organic phosphorus in river catchments (paper III and IV).
- to study organic nutrient ratios in streams from pristine headwater ecosystems downstream to the coastal area (papers I-III).
- to assess organic and minerogenic acidity in Finnish pristine first order streams and main rivers (papers V and VI).

2 Materials and methods

The influence of land use and climatic drivers on the export of DOM was estimated using stream water quality, forest inventory and climatic data from 42 small pristine forested catchments, and water quality monitoring, GIS land use, forest inventory and climatic data from the main Finnish rivers (and their sub-catchments) flowing to the Baltic Sea. Moreover, the export of DOM in relation to land use along a European climatic gradient was studied using river water quality and land use data from four European areas. A data set was generated on catchment characteristics (proportion of agricultural land and urban areas, proportion of peatland, site fertility, total stem volume, and its distribution among the main tree species), climatic drivers (temperature sum, latitude, precipitation, runoff) and deposition in order to study the interactions between DOM, sulphate and base cations concentrations, and environmental drivers.

2.1 Unmanaged forested catchments

The unmanaged forested catchments consist of two sets of catchments. One set consisted of 21 catchments where stream water samples were collected during the three-year period 1997-1999 (paper I). The other set consisted of another 21 catchments where stream water quality had been monitored from 3 to 32 years (Ahtiainen 1990, Ahtiainen et al. 2003, Kubin et al. 1995, Finér et al. 1997) (paper II). These 42 unmanaged forested catchments were first order catchments with an area of 0.07 to 38 km^2 (Table 1). The two largest catchments Runkaus and Kruunuoja had areas of 38 and 14 km^2, respectively. The other catchments were significantly smaller; the third largest catchment (Murtopuro) had an area of only 4.9 km^2. The catchments were located throughout Finland (excluding the northernmost parts of the country), in nature conservation areas or areas in which the forests and soils had not been managed (Fig.1). Active silviculture has not been practised in the catchments. In the Kangaslampi and Iso-Kauhea catchments there were young (< 25 years old) plantations that covered < 30% of the area of the catchments. Otherwise the forests on upland sites were 100-300 years old, unevenly-aged and naturally regenerated. The catchments were relatively undisturbed forested catchments, and atmospheric deposition was considered to be the only significant human impact on the catchments, although the level is among the lowest in Europe.

For the Teeressuonoja, Yli-Knuuttila, Murtopuro, Liuhapuro, Koivupuro, Kivipuro, Suopuro and Välipuro catchments mean slope calculations were based on point line field surveys, using an inclinometer (Mustonen 1965). For the rest of the catchments, slope was derived from 1:20000 scale maps from the National Land Survey of Finland and converted to comparable values (Mustonen 1971).

The following variables were determined from forest inventories provided by the Finnish Forest and Park Service and the Finnish Forest Research Institute: area of peatlands, total tree stem volume, species distribution of the tree stands: proportion of Norway spruce, Scots pine and birch (*Betula pendula* Roth., *B. pubescens* Ehrh.) out of the total tree stem volume (Table 1, Papers I and II). Upland and peatland site types were classified according to fertility into five classes. For each catchment an average site type, an average upland site type and an average peatland site type were calculated by weighting with the percentage area of each site type class (Paper I and II). Data were not available for three catchments (Sidländet 1 and 2, and Rörstrand 5).

The proportion of the catchments covered by peatlands ranged from 0 to 88%. The study catchments are located in areas comparable to nature conservation areas, which are less productive than the average forest land in Finland (Sevola 1998). Consequently, although the study forests are old, the average volume of growing stock, 14995 m^3 km^{-2}, was not exceptionally high. In the entire country, the average volume of growing stock on forest land is 9200 m^3 km^{-2} and that on forests mature for final cutting 18000 m^3 km^{-2}. Norway spruce was the dominant tree species in 32 catchments and Scots pine in 7 catchments. The proportion of Norway spruce out of the total tree stand volume was on average 56%, that of Scots pine 33% and that of deciduous tree species 10% (mainly *Betula pendula* Roth., *Betula pubescens* Ehrh. and *Populus tremula* L.). The corresponding proportions in the entire country are 36% for spruce, 46% for pine and 18% for deciduous species (mainly *Betula pendula* Roth. and *Betula pubescens*) (Sevola 1998). The catchments are described in detail in papers I, II and V.

Table 1. Median and mean values, standard deviation and range for catchment characteristics and land use in the study catchments.

	Median	Mean	Standard deviation	Range
Pristine headwater catchments, n=42				
Area km^2	0.63	2.0	6.1	0.07 - 38
Deposition of N kg km^{-2} a^{-1}	560	610	190	360 - 1 000
Precipitation mm a^{-1}	560	570	70	460 - 670
Runoff mm a^{-1}	380	350	100	150 - 530
Peatland %	37	34	20	0.0 - 88
Spruce %	59	56	17	1.0 - 86
Pristine headwater catchments, North-Karelia, n=20				
Area km^2	0.85	1.2	1.1	0.17 - 4.9
Deposition of N kg km^{-2} a^{-1}	560	610	150	460 - 880
Precipitation mm a^{-1}	550	560	46	520 - 630
Runoff mm a^{-1}	380	380	43	280 - 460
Peatland %	46	41	17	8.0 - 64
Spruce %	53	54	12	30 - 74
River sub-catchments, n=50				
Area km^2	4 000	9 000	11 000	73 - 48 000
Deposition of N kg km^{-2} a^{-1}	470	480	99	350 - 820
Precipitation mm a^{-1}	590	610	45	560 - 690
Runoff mm a^{-1}	280	290	55	210 - 480
Peatland %	20	23	13	6.1 - 56
Upstream lake %	11	11	6.5	0.9 - 26
Agricultural land %	7.5	8.7	7.3	0.6 - 35
Forest %	49	50	7.4	33 - 64
Bare rock %	6.7	7.2	2.7	3.2 - 19
Urban %	0.3	0.5	0.8	0.0 - 4.6
River catchments, n=36				
Area km^2	1 600	8 300	15 000	340 - 56 000
Deposition of N kg km^{-2} a^{-1}	550	530	120	350 - 820
Precipitation mm a^{-1}	610	610	48	460 - 690
Runoff mm a^{-1}	300	300	63	170 - 430
Peatland %	18	21	16	3.0 - 60
Upstream lake %	4.4	5.8	5.2	0.5 - 21
Agricultural land %	17	18	12	0.9 - 44
Forest %	48	47	8.0	29 - 64
Bare rock %	6.5	6.9	3.7	2.5 - 26
Urban %	0.4	0.7	1.1	0.0 - 6.5
European river catchments, n=34				
Area km^2	180	3 100	9 300	1.3 - 49 400
Precipitation mm a^{-1}	750	840	240	530 - 1 300
Runoff mm a^{-1}	340	370	120	250 - 660
Wetland %	2.1	8.8	14	0.0 - 48
Upstream lake %	0.5	2.9	5.7	0.0 - 31
Agricultural land %	43	43	33	0.0 - 86
Forest %	16	24	21	0.0 - 54
Urban %	0.6	4.9	18	0.0 - 100

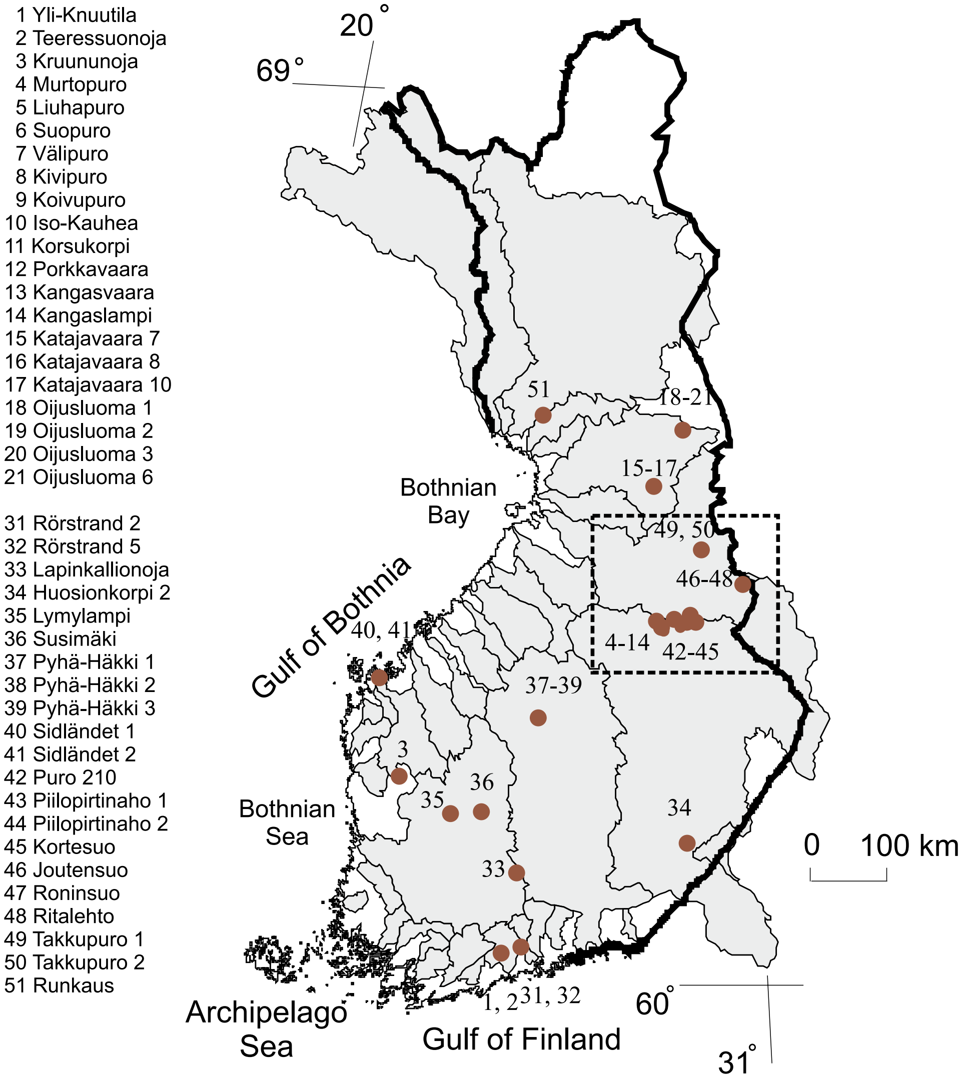

Figure 1. The Finnish river catchments included in the study (shaded) and the location of the 42 pristine first order catchments. The subgroup of 20 pristine catchments in North Karelia is outlined with a dashed line on the map.

2.2 River basins

The studied boreal river basins include 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 (Fig. 1, paper III). 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 (25x25m grids). The majority of the catchments were covered by coniferous forests and peatlands. The proportion of upland forests ranged from 29 to 64 % (average 49 %) and the proportion of peatlands from 3 to 60 % (average 22 %) (Table 1). The percentage of peatland is highest in northern basins, whereas the forest proportion increases towards the south. The proportion of agricultural land was on average 12 % (range 0.6 - 44 %). The majority of the croplands in Finland are located on the southern and western coast. By contrast, in the northernmost catchments, the proportion of agricultural land is minor. The lake area of the catchments ranged from 0.5 to 26 % (average 9 %). Urban areas (range 0 – 7 %) were concentrated in southern Finland, whereas open areas (bedrock outcrops) (range 3 – 26 %) were mostly in northern Finland (Table 1).

The European data set consists of 34 river catchments from four areas situated between latitudes 42°N and 68°N (paper IV). The four areas cover major climate and land use gradients within Europe: forested and agricultural boreal areas (Finland), a temperate agricultural area (Denmark), a wet and temperate mountain region in Wales, UK and a warm Mediterranean forested catchment in southern France (Fig. 2). The nine Finnish boreal catchments are large river basins situated in south-western Finland (Paimionjoki and Aurajoki), western Finland (Lestijoki and Siikajoki) and northern Finland (Oulujoki, Kiiminkijoki, Iijoki, Simojoki and Kemijoki). The ten Danish catchments are situated in the Horsens Fjord area on the eastern coast of Jutland, Denmark. The Welsh catchments consist of ten sub-catchments of the River Conwy watershed in North Wales, UK, and the five French catchments are sub-catchments of the Tech River watershed in southern France draining into the Gulf of Lyon.

The area of these 34 catchments varies from 1.3 to 49400 km^2 (Table 1). The largest study catchments are the Finnish catchments, on average 11200 km^2. The maximum elevation of the catchments varies from 58 to 2300 m and is highest in the French catchments. The land use in these four areas ranges widely. The Danish and Welsh catchments are dominated by agricultural land, whereas forests cover large parts of the French and Finnish catchments (Table 1 in paper IV). However, most of the agricultural land in Denmark is arable land, whereas in the Welsh catchments most is permanent grassland. Both climate and topography favour the formation and accumulation of organic matter in the soil in Finland. Consequently, wetland covers on average 27% of the Finnish catchments. In other countries, the proportion of wetlands is minor. The proportion of urban areas varies from 0 to 100% and is on average highest in Danish catchments and on average lowest in Welsh catchments. Similarly, population density is on average highest in Danish catchments and lowest in Welsh and Finnish catchments.

2.3 Temperature, precipitation, deposition and runoff measurements

For the 42 unmanaged forested first-order catchments (papers I and II) the annual precipitation and deposition were derived from the nearby local deposition stations run by the Finnish Environment Institute (Järvinen and Vänni 1990, Vuorenmaa 2004). The mean annual precipitation during the study period ranged from 460 to 670 mm (Table 1).

The temperature sum for each catchment was calculated as the sum of daily average temperatures exceeding 5 ºC by interpolating the air temperature data of climatic stations of the Finnish Meteorological Institute (Ojansuu and Henttonen 1983). The average annual temperature sum for the catchments during the period 1950-1980 ranged from 800 ºC to 1300 ºC.

Figure 2. The European study catchments; A) the rivers Oulujoki, Kiiminkijoki, Iijoki, Simojoki and Kemijoki, Finland, B) the rivers Lestijoki and Siikajoki, Finland, C) the rivers Paimionjoki and Aurajoki, Finland, D) the Horsens Fjord area, Denmark, E) the River Conwy, Wales, UK, F) the Tech River, France.

Daily runoff was recorded in 13 catchments by a V-notch weir and a water level recorder. In the other 29 catchments the discharge was derived from the daily runoff data from the nearby hydrological monitoring catchments run by the Finnish Environment Institute (Hyvärinen 1999). The mean annual runoff ranged from 150 mm in the south to 530 mm in the north (Table 1).

Annual precipitation and deposition values for the Finnish river basins (paper III) were derived from the deposition stations run by the Finnish Environment Institute (Järvinen and Vänni 1990, Vuorenmaa 2004). The annual mean air temperature for the basins 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 basin, an average value was used. If there was no deposition/weather station in a 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 precipitation and 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.

2.4 Water sampling and chemical analyses

The water quality of the streams from the unmanaged forested catchments was monitored during high flow periods from 3 to 32 years (papers I and II). The annual sampling frequency of the Finnish rivers was mostly between 12 and 32 during the study period 1995-1999 (paper III). Some of the small rivers and subcatchments were sampled less intensively. In the European data (paper IV), Danish and French rivers were sampled from October 2001 to September 2002. By contrast, the Finnish rivers were sampled from January to December in 2001 and the Welsh catchments from January to December in 2002.

Water quality parameters, total organic carbon (TOC), total nitrogen (TN), nitrate nitrogen (NO_3-N), ammonium nitrogen (NH_4-N), total phosphorus (TP), phosphate phosphorus (PO_4-P), sulphate (SO_4) and base cation concentrations were analysed in the laboratories of the Regional Environment Centres. TOC was measured by high-temperature oxidation followed by IR gas measurements. TN was measured colorimetrically after oxidation with $K_2S_2O_8$ and reduction in a Cd-Cu column**.** The sum of NO_3-N and NO_2-N was measured following reduction in a Cu-Cd column and colorimetric determination of azo-colour, hereafter referred to as NO_3-N. NH_4-N was determined spectrofotometrically with hypochlorite and phenol. TP was analysed by the molybdenum blue method after digestion with $K_2S_2O_8$. PO_4-P was measured by the molybdenum blue method. SO_4 was analyzed by ion-chromatography. Non-marine sulphate ($^*SO_4$) was estimated as the difference between total and marine concentrations, the latter being based on ratios to chloride in seawater. Base cations (Ca, Na, K, Mg) were analysed by flame-atomic adsorption spectrophotometry.

The Finnish monitoring data is mostly based on unfiltered samples. Only phosphorus (P) has been analysed from some river stations from both total and dissolved fractions. However, in 2001, a subset of samples from 15 rivers was analysed both for particulate and dissolved N and organic C components (paper III). Furthermore, in order to estimate the proportions of particulate and dissolved fractions of TOC, N and P in runoff from forested first-order catchments a subset of samples (n=120) from 11 streams in eastern Finland were analysed both for total and dissolved components in spring 2001 (paper II). DOC, total dissolved phosphorus (TDP) and total dissolved nitrogen (TDN) were analysed as TOC, TP and TN, respectively, after filtering with Nuclepore polycarbonate filters with 0.4 or 0.45 µm pore size.

In the European data, inter-calibration was used to check the adequacy of analytical methods used by the different laboratories and to ensure that all the laboratories could produce comparable results for DOM and inorganic nutrients.

Total organic nitrogen (TON) and dissolved organic nitrogen (DON) fractions were calculated by the difference: TON = TN - (NO_3-N + NH_4-N) and DON= TDN - (NO_3-N + NH_4-N). Dissolved organic phosphorus (DOP) was calculated by the difference: DOP=TDP-PO_4-P.

Organic anion (A^-) concentrations were calculated by the model of Kortelainen (1993b), which describes the dissociation of organic acids as a function of pH based on titration results of isolated hydrophobic and hydrophilic acids. The model requires only pH and DOC measurements from natural water samples.

2.5 Flux calculations

Annual export (L) of TOC, TN, NO_3-N, NH_4-N, TP and PO_4-P were calculated separately for each of the 42 first order catchments as follows:

$$L = \sum_{i=1}^{N} c(t_i) q[T_i]$$

where N is number of samples, $c(t_i)$ is the concentration value at sampling times t_i, and $q[T_i]$ is the discharge for the period $T_i = [\tau_{i-1}, \tau_i]$ with $\tau_i = \frac{1}{2} (t_i + t_{i+1})$, which is the runoff period around sampling.

Annual river fluxes were calculated by multiplying the mean monthly flows by the mean monthly concentrations, and finally summing the monthly fluxes over the calendar year.

2.6 Statistical methods

The relationships among environmental drivers (catchment characteristics and climatic variables) and concentrations/export were studied by correlation and regression analysis, stepwise multiple regression analysis and principal component analysis (PCA) performed using PC SAS (SAS Institute 2001). Average concentrations and average annual export were used as input to statistical analyses. In the data of unmanaged forested catchments, most of the concentration, export and background data were transformed into natural logarithms or square roots to improve the normality of the distributions.

Significant intercorrelation between explanatory variables made it difficult to distinguish the effect of one variable from another. The strong south-north gradient in Finland contributes to intercorrelation among the predictors. To avoid latitudinal intercorrelation in the data of unmanaged forested catchments, relationships between concentrations, export and environmental drivers were studied in a subgroup of catchments (n=20) in a climatically consistent area in eastern Finland.

3 Results and Discussion

3.1 Uncertainties associated with sampling strategies and calculations of annual loads

In the pristine forested catchments, sampling was carried out in high flow periods, when most particulates and also solutes are transported (e.g. Walling and Webb 1982, Richards and Holloway 1987, Young et al. 1988). In Finland, the high flow periods occur in spring (snowmelt) and in autumn (heavy rainfall periods). In managed headwater catchments in Finland, half of the annual runoff and leaching occurs in the spring high flow period, although this represents only 10-15% of the whole year (Kortelainen et al. 1997). If the quality of DOM differs between high flow and low flow periods, and between seasons, the used sampling strategy can affect the estimated annual fluxes. However, Rekolainen et al. (1991) compared different sampling strategies and concluded that concentrating sampling in high runoff periods gave better accuracy and precision for annual phosphorus load estimates than strategies based on regular-interval sampling throughout the year.

For the Finnish rivers, monitoring data were used in load estimates and the annual sampling frequency was mostly between 12 and 32 during the study period. Moreover, the averaging method was used for load calculation. For example, catchment characteristics, flow regime and load source have been found to be important factors in determining the impact of sampling frequency on load estimate uncertainty (Jordan et al. 2005, Johnes 2007). Johnes (2007) concluded that sampling with a monthly frequency returns highly uncertain load estimates. Moreover, Kauppila and Koskiaho (2003) found that the averaging method underestimated phosphorus and suspended solid loads in Finnish rivers, whereas in the case of nitrogen different methods produced rather similar results. Load estimates made with the traditional method are not very reliable for hydrologically different years, because it is not possible to catch temporary concentration peaks, which often coincide with the runoff peaks having a major influence on annual loading values. Thus, automatic sensors would significantly improve the accuracy and reliably of the load estimates (Linjama et al. 2009).

3.2 Total and dissolved fractions

The majority of TOC, TN and TP in Finnish pristine streams is dissolved (paper II). On average, 97% of the TOC was dissolved (< 0.45 µm; individual stream range of 93-98%) in a subset of samples from catchments in eastern Finland. Total dissolved nitrogen averaged 94% of TN (range 91-96%) and total dissolved phosphorus 79% of the TP (range 70-90%). Generally, all inorganic nitrogen was in a dissolved form and only 5% of the TON was particulate organic nitrogen (PON).

In the major Finnish rivers, the majority of TOC and TN is also in a dissolved form, and the proportion of the particulate fraction is minor (paper III). On average, 94 % of the TOC (n=68) was in a dissolved form. This is in accordance with the findings of Heikkinen (1989), who concluded that DOC represents on average 90% of the TOC transported to the Gulf of Bothnia by the river Kiiminkijoki in northern Finland. In the present study, on average 90 % of the TN (n=85) and almost all of the inorganic N was in a dissolved form. Thus, in these rivers, only about 10% of the TON was PON. In the same subset, only 40 % and 51 %, respectively, of the TP and inorganic P was in a dissolved form.

In this study, on average over 90 % of TOC and TN were in a dissolved form. The proportion of particulate organic carbon (POC) increases when human impact increases. However, human impact and land use activity in the boreal region is relatively small compared to the human impact in the temperate zone. Even in catchments with mixed land use (proportion of agricultural areas ranging from 0.6 to 44 %) the dissolved fraction dominated (paper III). The dominance of dissolved fractions has also been recognized in previous studies in geographically restricted areas. In the Chesapeake Bay drainage basin 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).

In streams and rivers, the difference between TOC and DOC was small; on average no more than 4 % of TOC was in a particulate form. Furthermore, the difference between TON and DON was small; on average no more than 8 % of TON was in a particulate form. The patterns of TOC and TON analysed in this study can hence be compared and discussed in light of literature values and patterns of DOC and DON.

3.3 TOC and TON concentrations and export from unmanaged forested catchments

The median TOC concentrations of the individual streams were relatively high, and ranged from 1.2 to 36 mg l^{-1} in the data set of 42 unmanaged forested catchments (Table 2, papers I and II). Annual export of TOC ranged from 940 to 13 700 kg km^{-2} (Table 3). The TOC concentrations in this study were higher compared with concentrations and export of organic carbon from pristine boreal (Fölster 2000), temperate (Dillon and Molot 1997) and tropical (McDowell and Asbury 1994, Newbold et al. 1995) forested areas. The TOC concentrations of Finnish surface waters are naturally high, because of the high proportion of mires in the Finnish landscape.

The median TN concentration ranged from 40 to 1400 µg l^{-1} and on average 91% was organic. TON concentrations ranged from 28 to 920 µg l^{-1} (Table 2). Annual export of TN ranged from 30 to 230 kg km^{-2} and annual export of TON from 23 to 220 kg km^{-2} (Table 3). Total nitrogen, being mostly organic, correlated strongly with TOC (papers I and II). Only the two catchments, Yli-Knuuttila and Teeressuonoja, which had their nitrogen mostly in inorganic form differed from others (Fig. 3a). The TOC concentrations explained 54% of the variation in TN concentrations. The correlation between TOC and TON concentrations was even stronger (Fig. 3b) and TOC concentrations explained 78% of the variation in TON concentrations. The strong correlation between TOC and TN or TON indicates that the losses of organic nitrogen were likely to be associated with leaching of humic substances. Similar relationships have also been observed by Hedin et al. (1995) in streams in unpolluted, old growth temperate forests and by Gorham et al. (1998) in streams in Nova Scotia. Export of TN from the studied catchments was at the same level as the values reported by Fölster (2000) (133 kg km^{-2} a^{-1}) from boreal undisturbed forested areas, but much lower than in tropical pristine streams (McDowell and Asbury 1994, Lewis et al. 1999).

Table 2. Median and mean values, standard deviation and range for stream/river water quality in the study catchments.

	Median	Mean	Standard deviation	Range
Pristine headwater catchments, n=42				
pH	5.0	5.2	0.85	4.0 - 7.1
TOC mg l^{-1}	15	17	9.0	1.2 - 36
A^- µeq l^{-1}	100	110	54	9.8 - 270
TON µg l^{-1}	350	340	170	28 - 920
TOC:TON	65	62	12	23 - 83
TP µg l^{-1}	12	14	8.1	3.0 - 37
PO_4-P µg l^{-1}	3.0	4.2	3.8	2.0 - 21
SO_4 mg l^{-1}	1.9	3.5	4.5	0.6 - 24
Base cations mg l^{-1}	3.7	4.7	3.3	1.6 - 19
Pristine headwater catchments, North-Karelia, n=20				
pH	4.9	5.0	0.7	4.2 - 6.4
TOC mg l^{-1}	16	18	7.9	5.7 - 30
A^- µeq l^{-1}	100	110	40	44 - 170
TON µg l^{-1}	290	310	110	120 - 470
TOC:TON	67	66	8.5	47 - 83
TP µg l^{-1}	12	13	7.1	4.0 - 31
PO_4-P µg l-1	3.0	4.5	3.4	2.0 - 16
SO_4 mg l^{-1}	1.3	1.6	0.7	0.7 - 3.3
Base cations mg l^{-1}	3.3	3.3	1.2	1.6 - 6.7
River sub-catchments, n=50				
pH	6.8	6.7	0.3	5.8 - 7.2
TOC mg l^{-1}	7.7	8.4	2.7	5.1 - 16
A^- µeq l^{-1}	65	73	23	43 - 140
TON µg l^{-1}	320	400	170	210 - 910
DOP µg l^{-1}	5.0	5.8	3.6	2.5 - 13
TOC:TON	28	29	6.3	17 - 39
SO_4 mg l^{-1}	6.2	8.7	11	1.7 - 61
Base cations mg l^{-1}	8.1	10	6.6	4.5 - 32
River catchments, n=36				
pH	6.8	6.6	0.6	4.8 - 7.3
TOC mg l^{-1}	12	13	4.5	5.5 - 21
A^- µeq l^{-1}	110	110	35	57 - 180
TON µg l^{-1}	570	550	160	210 - 780
DOP µg l^{-1}	8.0	10	7.5	4.5 - 38
TOC:TON	28	27	7.0	16 - 37
TOC:DOP	3 700	3 700	1 600	1 200 - 8 100
TON:DOP	155	157	68	45 - 290
SO_4 mg l^{-1}	14	21	21	2.0 - 89
Base cations mg l^{-1}	16	20	12	6.2 - 62
European river catchments, n=34				
DOC mg l^{-1}	7.1	7.6	4.9	1.0 - 21
DON µg l^{-1}	380	580	600	67 - 3 200
DOP µg l^{-1}	18	20	15	2.8 - 65
DOC:DON	18	20	11	3.2 - 41
DOC:DOP	820	1 700	1 800	220 - 5 600
DON:DOP	48	100	140	13 - 690

Table 3. Median and mean values, standard deviation and range for annual exports in the study catchments.

	Median	Mean	Standard deviation	Range
Pristine headwater catchments, n=42				
TOC kg km^{-2} a^{-1}	5 700	6 200	2 900	940 - 14 000
TON kg km^{-2} a^{-1}	110	120	48	23 - 220
TP kg km^{-2} a^{-1}	4.7	5.2	3.1	1.7 - 18
PO_4-P kg km^{-2} a^{-1}	1.1	1.7	2.0	0.3 - 12
Pristine headwater catchments, North-Karelia, n=20				
TOC kg km^{-2} a^{-1}	7 100	7 300	3 200	2 300 - 14 000
TON kg km^{-2} a^{-1}	120	130	45	49 - 210
TP kg km^{-2} a^{-1}	4.7	5.2	2.8	1.7 - 15
PO_4-P kg km^{-2} a^{-1}	1.1	1.5	1.4	0.5 - 7.0
River sub-catchments, n=50				
TOC kg km^{-2} a^{-1}	2 600	2 500	770	1 200 - 3 600
TON kg km^{-2} a^{-1}	100	120	49	64 - 300
DOP kg km^{-2} a^{-1}	2.0	2.2	1.2	1.0 - 4.0
TP kg km^{-2} a^{-1}	6.0	9.5	9.6	1.0 - 47
PO_4-P kg km^{-2} a^{-1}	1.0	3.8	5.5	0.0 - 22
River catchments, n=36				
TOC kg km^{-2} a^{-1}	4 000	4 000	1 400	1 800 - 7 100
TON kg km^{-2} a^{-1}	170	180	59	85 - 320
DOP kg km^{-2} a^{-1}	2.5	2.5	0.8	1.0 - 4.0
TP kg km^{-2} a^{-1}	19	23	19	2.0 - 90
PO_4-P kg km^{-2} a^{-1}	9	11	11	0.0 - 52
European river catchments, n=22				
DOC kg km^{-2} a^{-1}	2 700	2 900	1 400	670 - 5 700
DON kg km^{-2} a^{-1}	170	240	220	46 - 880
DOP kg km^{-2} a^{-1}	3.2	6.2	5.6	1.6 - 22

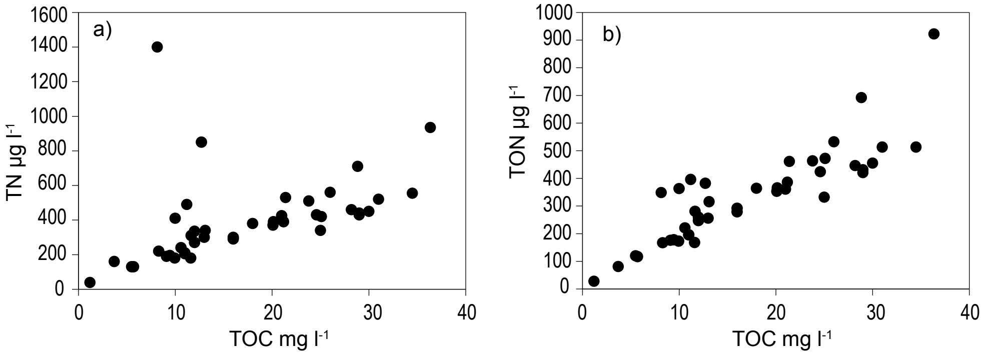

Figure 3. The relationships between stream water a) TN and TOC, and b) TON and TOC concentrations in 42 pristine forested headwater catchments (papers I and II).

Median nitrate and ammonium concentrations were generally very low. The highest NO_3-N concentrations occurred in Yli-Knuuttila, the southernmost, fertile, spruce-dominated catchment. Annual export of NO_3-N and NH_4-N was on average 11 and 3.7 kg km^{-2}, respectively (paper II).

3.4 TP and DOP concentrations and export from unmanaged forested catchments

The median concentration of TP ranged from 3 to 37 µg l^{-1}, and was on average 14 µg l^{-1} (Table 2, papers I and II). TP concentrations were much lower than in the streams studied by Lahermo (1996) in different parts of Finland, and in a temperate pristine forested watershed studied by Edmonds and Blew (1997). The concentration of PO_4-P was on average 4 µg l^{-1}. Median PO_4-P was close to the detection limit (2 µg l^{-1}) in many catchments, the highest concentrations (16 and 21 µg l^{-1}) occurring in the Murtopuro and Susimäki catchments. In 2001, when TDP was analysed from 11 streams (paper II), DOP could also be calculated. In those streams, on average 80% of TP was TDP and about 54% of the TDP was DOP (range 1-23 µg l^{-1}, mean 7 µg l^{-1}).

Annual export of TP ranged from 1.7 to 18 kg km^{-2} (Table 3, papers I and II). The highest export occurred in the Murtopuro and Susimäki catchments, 15 and 18 kg km^{-2} a^{-1}, respectively. In the other catchments, export of TP was below 10 kg km^{-2} a^{-1}. The concentration and export of phosphorus correlated with TOC, which indicates that losses of organic phosphorus were associated with leaching of humic substances.

3.5 Controls of organic C, N and P concentrations and export from unmanaged forested catchments

The majority of organic matter export from Finnish headwater catchments consists of TOC, with significantly smaller proportions of organic N and organic P. TOC concentrations were significantly lower in the north than in the south (Fig. 4a, papers I and II). However, the same pattern did not occur in the case of TOC loads. This was due to greater runoff in the north which compensated for lower TOC concentrations, leading to similar TOC loads in the south and in the north. A similar pattern was detected in managed headwater catchments (Kortelainen et al. 1997).

Export of TOC did not correlate with any of the climatic variables. However, TOC concentrations had a negative correlation with runoff and precipitation. These correlations might be linked to dilution and low contact with organic soil horizons at high flow, when a greater part of the flow can be surface runoff. This could occur especially in the northern catchments where a large part of the annual runoff takes place in the spring, when the soil is still frozen. Moreover, Schiff et al. (1998) observed decreasing DOC concentrations with increasing flows in wetlands. Similarly, temporal variations in Swedish stream TOC concentrations were primarily driven by variations in stream flow, with the mire stream generally diluting by half with increased runoff during the spring flood and TOC from forested landscape increasing during

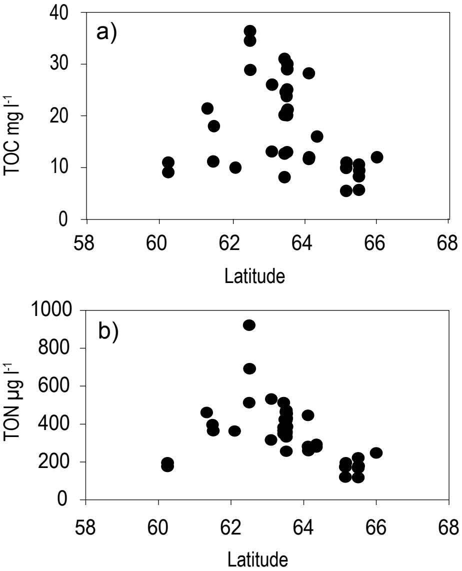

Figure 4. The relationships between river water a) TOC and b) TON concentrations and latitude in 42 pristine forested headwater catchments (papers I and II).

runoff peaks irrespectively of season (Köhler et al. 2008). In Finnish headwater catchments, runoff had a strong positive correlation with latitude; thus the negative correlation of TOC concentrations with runoff could also reflect slower production and decomposition in colder climate.

Similarly, TN and TON concentrations correlated positively with temperature sum and the deposition of N, and negatively with latitude. Thus, the concentrations of TN and TON were significantly higher in the south than in the north (Fig. 4b, papers I and II), as was the case in the study by Kortelainen et al. (1997) of managed forested headwater catchments. Export of TN and TON was also somewhat higher in the south, although the higher runoff in the north compensated for lower concentrations. Of the inorganic N fractions NH_4-N was significantly higher in the south than in the north, whereas NO_3-N did not show significant variation with latitude (paper II). Moreover, NH_4-N concentrations correlated negatively with annual runoff, whereas NO_3-N concentrations and export correlated positively with annual precipitation.

TP concentrations correlated positively with temperature sum, reflecting higher concentrations of phosphorus in the south (papers I and II). By contrast, PO_4-P concentrations did not show any significant variation between the south and the north. The PO_4-P concentrations were extremely low, which evidently contributed to the low spatial variability.

In order to eliminate the effect of climatic conditions and latitudinal intercorrelation on water quality, the relationships between concentrations, export and catchment characteristics were studied within a subgroup of 20 pristine headwater catchments located in North Karelia in eastern Finland (Fig. 1).

In a subset of 20 catchments, the peatland proportion was the best predictor for TOC and TON export (Fig. 5), as was observed in paper II. The proportion of peatlands in this subgroup of catchments from a uniform climatic regime ranged from 8 to 64%. Peatlands have been shown to be an important contributor of TOC to surface waters in Finland (e.g. Laaksonen 1970, Pitkänen 1986, Kortelainen 1993a) and elsewhere (e.g. Hope et al. 1994, Dillon and Molot 1997). Xenopoulos et al. (2003) also demonstrated that the proportion of the catchment covered by forested wetlands, in particular those with coniferous vegetation, explained the largest proportion of lake DOC from subtropical to tundra areas. Organic carbon accumulation in peatlands and metabolism and export are competing processes (Frost et al. 2006). However, most wetland types are net exporters of C. Due to a high water content throughout the year, surface runoff is dominant, which facilitates leaching of organic matter. In Harp Lake, Ontario, DOC contained relatively recent carbon, suggesting that buried peat is resistant to mobilization and that exported carbon is derived from recently fixed carbon near the peat surface (Schiff et al. 1998).

In accordance with this data, organic N has been observed to correlate positively with the percentage of peat cover and wetlands in previous studies (e.g. Ito et al. 2005). However, the relationship was not as strong as for TOC. This is probably due to anaerobic conditions in wetlands, where part of the nitrogen is denitrified instead of being converted to organic N. Similarly, Chapman et al. (2001) concluded that the relative contribution of DON to total nitrogen is generally larger in streams draining peaty catchments than in streams draining forest soils and podzols. In aerobic forest soils DON is more readily transformed to NO_3-N, whereas the high water table in peatlands promotes anaerobic conditions, which can result in increased denitrification and consequently decreased NO_3-N export.

TOC and TON concentrations and export also had strong positive correlations with the abundance of Norway spruce (Fig. 5, paper I) and strong negative correlations with the abundance of Scots pine. Norway spruce stands are known to produce more litter (including carbon and nitrogen) on the forest floor than Scots pine stands (Viro 1955). The larger amount of litter may result in higher decomposition and subsequent leaching of organic carbon and nitrogen, even though the decomposition rate is higher in Scots pine stands (Johansson 1995). Norway spruce is also a climax tree species in boreal

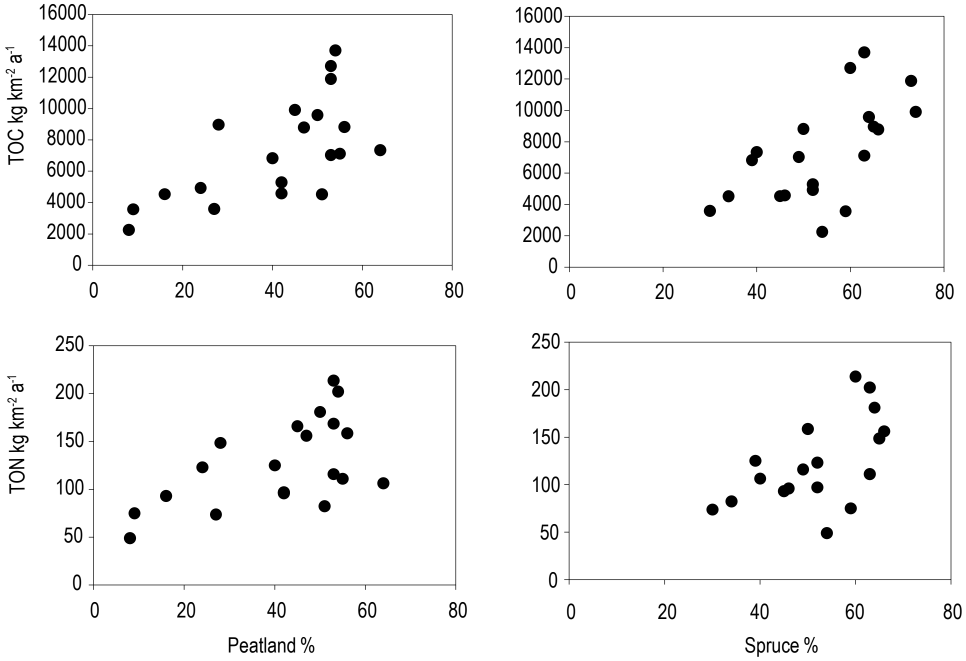

Figure 5. The relationships between stream water TOC and TON concentrations, and the proportion of peatland in the catchment and the proportion of Norway spruce of the tree stand in 20 pristine headwater catchments in North Karelia, Finland.

forests, and the stands could be older than the Scots pine stands, with more organic matter accumulation on the forest floor available for decomposition and leaching.

The proportion of peatland in the catchment and the abundance of Norway spruce explained together 70% and 77% of the variation in TOC concentrations and exports, respectively. Similarly, the proportion of peatland in the catchment and the abundance of Norway spruce explained together 72% and 62% of the variation in TON concentrations and exports, respectively (Table 4).

Inorganic N concentrations and export did not correlate with any of the catchment variables in a subset of 20 pristine first order catchments in North Karelia. However, in a subset of nine catchments with a uniform sampling period (paper I), nitrate concentrations and export were related to average site type and total stem volume of tree stands. An increase in fertility was related to larger stem volume, and higher NO_3-N concentration and export. Average site type explained 61% of the variation in NO_3-N concentrations. Nitrate leaching is also related to the soil acidity, which is lower on fertile than on poor sites (e.g. Tamminen 2000). Low acidity increases nitrification and makes leaching losses possible (e.g. Priha and Smolander 1995).

Table 4. Multiple linear regression equations for the concentrations and export of TOC and TON in 20 pristine forested headwater catchments in North Karelia, Finland. PEATL= proportion of peatlands (%), SPRUCE=proportion of Norway spruce out of the total tree stem volume (%).

	r^2	p
lnTOC (mg l^{-1}) = 1.0 + 0.017 PEATL + 0.020 SPRUCE	0.70	<0.001
lnTOC (kg km^{-2} a^{-1}) = 7.0 +0.020 PEATL + 0.019 SPRUCE	0.77	<0.001
TON (µg l^{-1}) = -123 + 5.6 SPRUCE + 3.3 PEATL	0.72	<0.001
TON (kg km^{-2} a^{-1}) = -38 + 2.0 SPRUCE + 1.4 PEATL	0.62	<0.001

TP concentrations and export did not have any strong correlations with catchment characteristics in a subset of 20 catchments in North Karelia. However, in a subset of nine catchments with a uniform sampling period (paper I), the concentrations and export of TP correlated positively with total stem volume on uplands. Total stem volume on uplands explained 69% and 56% of the variation in TP concentrations and export, respectively. On the other hand, in a subset of 18 catchments (paper II), catchment slope was an important predictor of TP: increasing slope decreased both the concentrations and the export. Similarly, in the Shield Lakes of south-eastern Quebec, a negative relationship between catchment slope and lake TP was observed and 50% of the variability in TP concentrations was explained by a slope index and one or two morphometric variables (D'Arcy and Carignan 1997). In contrast, in a majority of studies, e.g. in 32 forested catchments of Ontario by Dillon et al. (1991), TP export and catchment slope were positively correlated. In disturbed areas, P export generally increases with increasing slope due to increasing particulate P export.

Similarly to inorganic N and TP, PO_4-P concentrations and export did not correlate with any of the catchment variables**.** The median PO_4-P was lower than 5 µg L^{-1} in 31 out of the 42 headwater catchments (papers I and II), which evidently contributed to insignificant correlations with the background variables. The proportion of inorganic phosphorus was on average 32% of the TP. In forest ecosystems, the turnover of P is rapid and mineral P is quickly captured by organic matter (D'Arcy and Carignan 1997). Soil types and bedrock geology would probably have been better predictors for phosphorus concentrations. For example, Arheimer and Liden (2000) found that soil texture was the single most important factor affecting stream water concentrations of P in 35 Swedish catchments with mixed land use, where catchments with fine soil had higher P concentrations in stream water.

When the relationships between concentrations or export and catchment characteristics were studied in subgroups of catchments (papers I and II), inorganic N and TP results differed from each other (cf. previous paragraphs). Another example is TON export, which was closely associated with TOC export in two different subgroups (papers I and II) (r^2=0.95 and r^2=81, respectively) and also correlated significantly with the catchment peatland percentage in one subgroub (r^2=0.65) (paper II) but not in the other (paper I). In upland Scotland (Chapman et al. 2001), occurred significant positive correlation between DOC and DON as well as between DOC and the percentage of peatland, but stream water DON content was not associated with the percentage cover of peat in the catchment. In the Scottish streams and the study streams in paper I there was a wide scatter in the relationship between DON or TON and the percentage peat cover, suggesting that other factors are important in controlling DON or TON concentrations in stream water, e.g. transformations, decomposition and/or production within the stream channel.

The various results in different data sets are probably due to the different range and variability of the characteristics of the headwater catchments. 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, as suggested by Herlihy et al. (1998) and confirmed by the study of Rantakari et al (2004) based on Finnish lake catchments.

3.6 TOC, TON and DOP concentrations in rivers and export to the coast

Average concentrations of TOC in Finnish rivers and their sub-catchments were relatively high, ranging from 5 to 21 mg l^{-1} (Table 2, paper III). The concentrations of TOC were higher in Finnish rivers compared to European data (paper IV). The maximum values in Finnish rivers were about ten times higher than those in a French river. 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}, being on average on the same level as in the European data. In Denmark, however, DON concentrations were twofold higher than in Finnish rivers. Moreover, TDN concentrations were about sixfold higher in Danish rivers than in Finnish rivers and only on average 21 % was in an organic form. Concentrations of NO_3-N and NH_4-N in Finnish rivers were on average 370 and 55 µg l^{-1}, respectively. The concentrations and export of NO_3-N decreased towards the north, and the concentration and export of NH_4-N was lower also in the northern catchments. The inorganic fraction of TN was larger in the southern catchments compared to the northern catchments (paper III).

In areas with high N deposition, inorganic N losses are generally high and the majority of riverine N export studies have therefore focused on 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 is in an organic form (Pitkänen 1994, Lepistö et al. 1995, Kortelainen et al. 1997). Perakis and Hedin (2002) reported 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 TDN export even in areas with large anthropogenic inputs of DIN in the north eastern United States. Very high proportions (75 – 95 %) of organic N from TN have also been reported 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). Moreover, in Welsh catchments, DON was found to constitute a significant component of the TDN pool typically about 40 % but sometimes representing more than 85 % of the TDN exported in rivers (Willet et al. 2004). Even in agricultural catchments, the proportion of DON has been reported to be about 40 % of the total nitrogen load (Johnes and Burt 1991, Heathwaite and Johnes 1996).

As in the case of Finnish pristine headwater streams (papers I and II), there was a significant positive correlation ($r=0.81, p<0.001$) between TOC and TON concentrations in river water samples (paper III). The molar TOC:TON ratio in rivers varied from 16 to 39 and was on average 27 (Table 2). In the European data, a significant correlation between TOC and TON was found only in Finnish and French catchments (paper IV). In areas with a high degree of human activity, DON is not closely associated with DOC; in Danish and Welsh catchments, DON concentrations did not follow DOC concentrations. These differences probably result from human influence on DON concentrations. The proportions of agricultural land and urban areas are lower in Finnish and French catchments compared to the Danish and Welsh catchments.

In Finnish rivers, 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} (Table 2, paper III). The Finnish DOP concentrations were among the lowest in European data (paper IV). For example in Danish rivers, DOP concentrations were on average over fourfold and in the Welsh river over twofold higher compared to the Finnish rivers.

The export of DOM ranged from 1 300 to 7 400 kg km^{-2} a^{-1}. The majority of the DOM export from Finnish river catchments consists of organic C. The export of TOC ranged from 1 200 to 7 100 kg km^{-2} a^{-1}, 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 (Table 3, paper III). The total TOC and TON transport through the Finnish main rivers into the Finnish coastal waters 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.

3.7 Effect of land use and climate on river TOC, TON and DOP concentrations and export

Similarly to the case of pristine headwater streams (papers I and II), TOC concentrations and export correlated with the proportion of peatlands in the river basins (paper III). Water DOC concentrations were also positively associated with the percentage of wetlands in the catchment in the European river data (paper IV). Moreover, in Finnish rivers TOC concentrations had a positive correlation with the percentage of agricultural land cover (r=0.41, $p<0.001$). Furthermore, TOC concentrations were on average higher in river catchments (n=36) than in sub-catchments (n=50), although the average peatland percentage was almost equal in both data sets (Table 1). The higher percentage of agricultural land and the lower proportion of upstream lakes in river basins contributed to the higher TOC concentrations. The highest TOC concentrations were observed in basins which have reasonably high agricultural land and peatland percentages and a low proportion of lakes. Agricultural land and peatland percentage explained together about 60% of the variation in TOC concentrations (Fig. 6).

Despite the numerous studies reporting TOC/DOC losses from forested and peat catchments, published data on exports of organic C from agricultural land has remained limited. However, high organic C losses have been reported from some agricultural catchments (e.g. Correl et al. 2001, McTiernan et al. 2001). The large scale boreal data in the present study was in agreement with these studies, showing that agricultural land increased the TOC concentrations, although the proportion of agricultural land in the catchments was rather low, on average 12 %. The TOC loss from fields has been proposed to be related to the use of inorganic and organic fertilisers. The increased dry matter production following increased fertiliser inputs results in higher organic matter losses (McTiernan et al. 2001). In addition, some agricultural lands have organic-rich surface soil layers, which increase the riverine export of TOC. A large proportion of the agricultural fields are situated in western and south-western Finland in areas where the basins are characterized by acid sulphate soils, the sediments of the postglacial Litorina sea (7500 – 3000 BP) (Lahermo et al. 1996). These sediments have been brought into an oxidized environment by isostatic land uplift and agricultural drainage. Paasonen-Kivekäs and Yli-Halla (2005) concluded that cultivated acid sulphate soils have significantly higher concentrations of total carbon than cultivated non-acid sulphate soils in western Finland, which probably is due to organic materials sedimented in small bays of the postglacial Litorina sea. The higher carbon concentration in cultivated acid sulphate soils evidently also results in higher export of organic carbon from Finnish agricultural land to watercourses. The impact of agricultural land on TOC concentrations may be exaggerated in Finnish river data, because agricultural lands locate predominantly near river estuaries close to the water sampling stations. Moreover, point sources and urban areas in the riparian zone may result in elevated organic carbon concentrations (e.g. Aitkenhead-Peterson et al. 2009), although no significant correlation between the percentage of urban areas and TOC concentrations was observed in Finnish rivers.

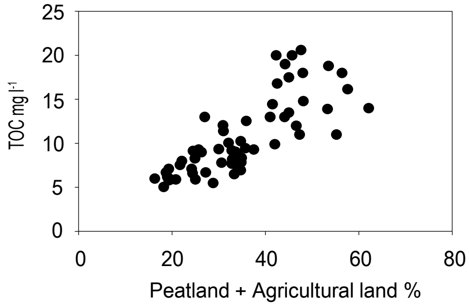

Figure 6. The relationship between river water TOC concentrations and the proportion of peatland and agricultural land in the river basins (n=86).

In Finnish rivers, the strongest predictor of TOC concentrations and export was the percentage of upstream lakes, showing decreasing concentrations with increasing proportion of lakes (Fig. 7, paper III). Both Wartiovaara (1978) and Pitkänen (1986) documented a negative relationship between upstream lake percentage and TOC/COD concentrations/export in Finnish rivers. Similarly, Kortelainen and Mannio (1988) and Rantakari et al. (2004) showed that TOC concentrations in lakes decrease with increasing proportion of upstream lakes in the catchment. Kortelainen et al. (2006) demonstrated that terrestrially fixed organic carbon is effectively degraded in Finnish lakes and released as CO_2 to the atmosphere. On the other hand, lake sediments have been shown to be important areal C stocks in the boreal zone (Kortelainen et al. 2004). In the multiple regression analysis, in which the six land use classes were used as predictors, the proportions of peatlands, agricultural land and upstream lakes explained 85 % of the variation in the export of TOC (paper III).

The TON concentrations were significantly lower in the northern river catchments compared to the catchments in southern Finland, and TON correlated positively with the annual mean air temperature. The deposition of N correlated negatively with latitude (r=-0.77, p<0.0001) 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 that of TOC, 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 (Fig. 8, paper III). Similarly, in European data, DON concentration increased signifi-

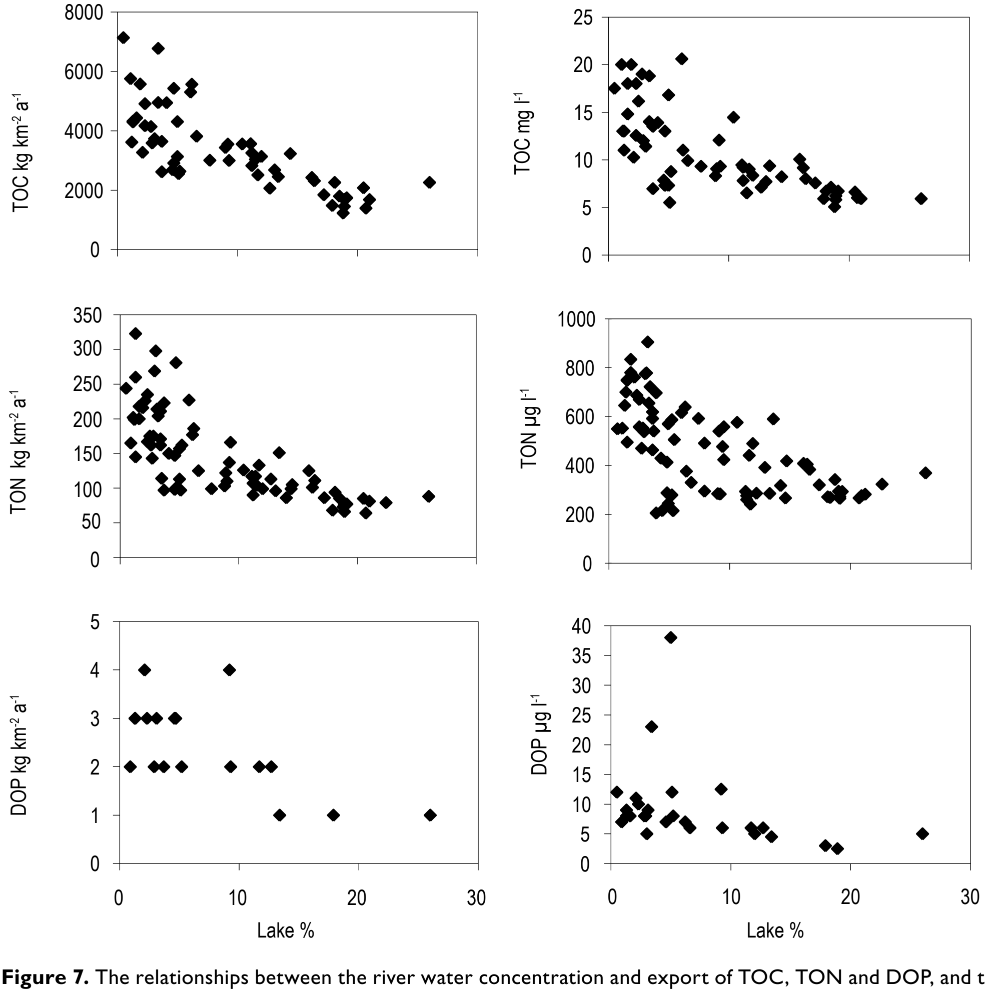

Figure 7. The relationships between the river water concentration and export of TOC, TON and DOP, and the proportion of upstream lakes in the river basin.

cantly with increasing proportion of agricultural land in the Welsh and Finnish catchments (paper IV). There was a steeper slope of the regression in Finnish data compared to Welsh data, which presumably results from the differences in the intensity of agriculture: agricultural land in Finland is mainly arable land, whereas in the Welsh catchments it is mostly permanent grassland. The baseline of DON concentrations also differs between the Finnish and Welsh catchments. Finnish non-agricultural catchments have higher concentrations compared to Welsh non-agricultural catchments. This is probably due to differences in the amount of leachable organic matter in the catchments. In Finland, both cold and humid climate and flat topography favour the formation and accumulation of organic matter in the catchments. By contrast, in Welsh catchments with steeper slopes and warmer climate, the accumulation of organic matter is lower and non-agricultural catchments are dominated by moorlands. Increases in TN discharge with increasing proportions of cropland have 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. For example, Johnes and Burt (1991), Heathwaite and Johnes (1996) and Willett et al. (2004) showed that organic nitrogen is an important constituent of the nitrogen load from agricultural catchments and can comprise about 40% of the total annual load. Moreover, agricultural fields have been found to increase DON and TON export (Jordan et al. 1997, Qualls and Richardson 2003), probably as a result of the application of organic fertilisers and higher productivity.

TON also had a positive correlation with the percentage of urban areas in Finnish river catchments (paper III), which is in accordance with the study by Hayakawa et al. (2006), who found a significant positive correlation between DON and urban land use in two Japanese watersheds with similar ranges of urban land use percentage as in Finnish river catchments. Moreover, in Finnish river basins, the percentage of upstream lakes had a significant negative correlation with TON concentrations and export. 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 71 to 88 % of the variation in the export of N fractions in Finnish rivers (paper III).

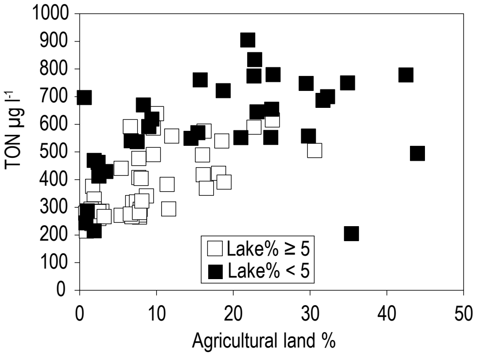

Figure 8. The relationships between river water TON concentration and the proportion of agricultural land in the catchments. The catchments are shown with different symbols according to the percentage of lake coverage in the catchment.

The DOP concentrations and export decreased with increasing percentage of upstream lakes (Fig. 7) and were at the same level in the northern and southern areas, whereas PO_4-P concentrations and export decreased towards the north, and 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. DOP export also correlated positively with the proportion of urban areas in the catchment. In the multiple regression analysis, the combination of the percentage of upstream lakes and the proportion of agricultural land in the catchment explained from 50 to 82 % of the variation in the export of P fractions in Finnish rivers (paper III). In European data, the highest DOP concentrations and loads were recorded in catchments with a high extent of agricultural land, large urban areas or a high population density. The highest DOP values occurred in Danish catchments with very intensively farmed arable land; the same percentage of pastures in the Welsh catchments resulted in significantly lower DOP concentrations (paper IV).

3.8 Effect of land use and climate on nutrient ratios

The molar TOC:TON ratio correlated positively with the proportion of peatlands and negatively with the proportion of agricultural land in the catchment. In catchments with an agricultural land percentage greater than 30%, the molar TOC:TON ratio was significantly lower than in catchments with an agricultural land proportion below 30% (19 vs. 30). Similarly, the TOC:TON ratio was higher (25 vs. 35) in catchments with a high proportion of peatlands (> 30%) compared to catchments with a low peatland proportion (< 30%). Thus, on average the highest TOC:TON ratios were found in river catchments with a peatland percentage exceeding 30%, followed by forested catchments. The lowest TOC:TON rations were found in river catchments with agricultural percentages over 30% (Fig. 9, paper III). In the European data, the molar DOC:DON ratio was on average 20, being lowest in Danish catchments and highest in Finnish catchments, and was negatively correlated with population density and the proportion of agricultural land and urban areas in the catchment, and positively correlated with the proportion of wetlands in the catchment (paper IV). The global model calculations by Harrison et al. (2005) also show that regions with a high extent of intensive agriculture or high population density exhibit elevated DON yields in comparison to DOC. Similar to the case for Finnish rivers, on average the highest DOC:DON ratios were found in catchments with a wetland percentage over 30%, followed by forested catchments. The lowest DOC:DON ratios were recorded in the catchments with a high extent of agricultural land. Thus, organic matter exported from agricultural land is 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, papers I and II), 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 (paper III). Geological parent materials and climate have also been found to impact on the stoichiometry of streams. The highest DOC:DON ratios were found in watersheds on the geological parent materials mudstone/sandstones and in watersheds classified as cool temperate rain forests (McGroddy et al. 2008). Moreover, Seitzinger et al. (2002) observed that the DOC:DON ratio in runoff was generally lowest for the agricultural sites (on average 10), intermediate for the urban/suburban storm water sites (on average 18) and highest for the forest sites (on average 53). This shows that the composition of DOM exported from catchments with different land use and human impact varies substantially.

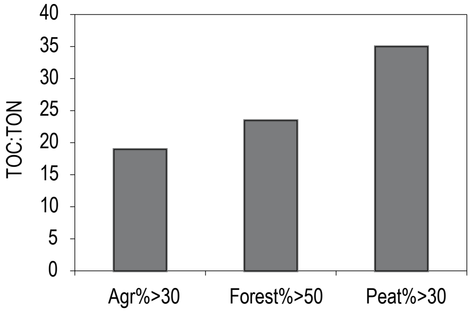

Figure 9. Mean molar TOC:TON ratio in the river catchments with agricultural land (Agr.) percentage over 30%, proportion of forests over 50% and proportion of peatland over 30%.

In Finnish rivers, TOC:DOP and TON:DOP molar ratios were on average 3700 and 157, respectively (Table 2). The TOC:DOP ratio did not correlate with any of the land use or climatic variables. However, the TON:DOP ratio correlated positively with the proportion of agricultural land in the catchment, annual mean air temperature and N deposition, and negatively with the proportion of peatland in the catchment and runoff. Thus the TON:DOP ratio was higher in southern Finland where N deposition, annual mean air temperature and agricultural land percentage are higher than in northern Finland. These variations in molar ratios result in variability in the availability of DOM for bacterial, algal and plant uptake. The

N content of natural DOM has been observed to be positively correlated with bacterial production (Vallino et al. 1996). Moreover, Sun et al. (1997) recorded positive correlation between H:C and N:C ratios of DOM and bacterial production. Consequently, the variation in molar ratios in Finnish rivers may suggest that DOM is more bioavailable in southern Finland and in agricultural and urban areas.

Variation in molar ratios between different land use patterns results in differences in the quality of DOM transported into the different sea areas around the Finnish coast. The lowest TOC:TON molar ratio (on average 19) and highest TON:DOP molar ratio (on average 240) were in river water transported into the Archipelago Sea with the highest extent of agricultural land in its catchment. DOM transported into the Gulf of Finland and the Bothnian Sea had an average TOC:TON ratio of 21 and 26, respectively. The rivers draining into the Bothnian Sea had on average the highest TOC:DOP molar ratio (4010). The highest TOC:TON ratios (on average 33) were in rivers draining into the Bothnian Bay, with the highest proportion of peatland in their catchments. Furthermore, in rivers draining into the Bothnian Bay, the DOC:DON:DOP molar ratio favours the export of DOC over DON and DOP when compared to the French river draining into the Gulf of Lyon or Danish streams draining into the Horsens estuary (paper IV), reflecting variation in land use patterns and climatic conditions in Europe.

3.9 Retention

A high percentage of lakes in the catchment resulted in lower TOC, TON and DOP concentrations and export (Fig. 7, paper III). Using the linear relationship between the export and the proportion of lake area in the catchment, the average annual retentions of TOC, TON and DOP in lakes were estimated to be about 15, 0.67 and 0.009 g m^{-2} LA (lake area), respectively**.** Although in the 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 was the export, indicating organic matter retention in Finnish lakes. Water residence time in a river basin can significantly increase although the percentage of lake coverage in a catchment remains reasonably low.

The average estimated annual TOC retention in lakes (15 g C m^{-2} LA) divided by the area of entire river basins gives the TOC retention of 1 400 kg C km^{-2} WA (watershed area) (paper III). The export of TOC from pristine headwater catchments was on average 6 200 kg km^{-2} a^{-1} (papers I and II). Moreover, Kortelainen and Saukkonen (1998) estimated the TOC export from managed, first order forested catchments in Finland to be on average 5 700 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 similarly to the entire country. In the rivers representing at least second order catchments, the average TOC export was 3 400 kg km^{-2} WA a^{-1} (paper III), suggesting approximately 2 300 kg km^{-2} WA a^{-1} of TOC retention when progressing downstream from the first order catchments. However, due to the differences in land use, 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 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, thus 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 due either to accumulation of C in lake sediments (Kortelainen et al. 2004) or to degradation of organic matter in aquatic ecosystems. Spatially representative randomly selected lake data bases demonstrate that Finnish lakes contribute significantly both to landscape C pools and fluxes and consequently to catchment C sequestration in the boreal zone. Finnish lakes are supersaturated with both CO_2 (carbon dioxide) and CH_4 (methane) throughout the year, releasing carbon gases continually to the atmosphere during the ice-free period and accumulating high amounts of CO_2 and CH_4 in the water column during the ice cover period (Kortelainen et al. 2006, Juutinen et al. 2009). The majority of CO_2 gas efflux from Finnish lakes is due to degradation of terrestrially fixed C (Striegl et al. 2001). Mineralization of the riverine DOM also means mineralization of organic N and organic P. Although organic N and P can be taken up directly by algae and plants (e.g. Antia et al. 1991, Seitzinger and Sanders 1997), the released inorganic N and P also have possible consequences for the aquatic productivity.

Riparian areas, wetlands, streams and lakes have been considered as key environments for N sinks. Budget 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 this 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 of the river Oulujoki. They concluded that retention 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 this study. Furthermore, Lepistö et al. (2006) estimated with a GIS-based N-EXRET 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.

In the pristine headwater streams, TON export was estimated to be on average 120 kg km^{-2} a^{-1} (papers I and II). Moreover, Kortelainen et al. (1997) estimated the TON export from small, managed first order forested catchments in Finland to be on average 135 kg km^{-2} a^{-1}. In the large rivers, the average TON export was 180 kg km^{-2} a^{-1} (Table 3). Thus the export of TON increased downstream, reflecting the impact of increasing extent of agricultural land and human activity. The data from 42 pristine headwater samples is based on unfiltered samples and no TDP values were available, and thus DOP exports could not be calculated, which prevents comparison between headwaters and large rivers.

3.10 Organic and minerogenic acidity in pristine streams and rivers

Average SO_4 concentration in pristine headwater streams (n=36) was 2.7 mg l^{-1} (range 0.6-12 mg l^{-1}) (paper V)). Non-marine sulphate ($^*SO_4$) was only slightly lower than total SO_4. Sulphate concentrations decreased from the south to the north, which was mainly explained by the corresponding pattern in atmospheric deposition of SO_4. Sulphate concentrations increased with increasing site fertility and catchment slope. Catchments with flat terrain were covered by peatlands, which are known to retain SO_4 more effectively than mineral soils (Kortelainen and Saukkonen 1995).

In pristine first order catchments, the concentration of A^- was on average 110 µeq l^{-1} (Table 2) and the variation was controlled by the same factors as TOC, described in section 3.5. Organic anions exceeded $^*SO_4$ in 29 catchments. $^*SO_4$ exceeded A^- only in southernmost catchments, where deposition is highest, and in three northern upland catchments, where TOC concentrations are low. According to correlation analysis A^- was a strong predictor of stream water pH ($r=-0.74$, $p<0.0001$), whereas no correlation between the $^*SO_4$ concentrations and pH was found. High sulphate concentrations were associated with high base cation (BC) concentrations, buffering the effects of $^*SO_4$ on pH. Similarly, TOC was a better predictor of pH than non-marine sulphate in managed headwater stream catchments (Kortelainen and Saukkonen 1995).

The average concentrations of A^- in the Finnish rivers were relatively high, ranging from 43 to 180 µeq l^{-1} (Table 2, paper VI). The spatial distribution of A^- was similar to that of TOC described in section 3.7. The average concentrations of SO_4 ranged from 1.7 to 86 mg l^{-1} (Table 2) and were significantly higher compared to the concentrations in headwater streams ((0.6 - 11 mg l^{-1}; Kortelainen and Saukkonen, 1995); (0.6 - 12 mg l^{-1}; paper V)). As in headwater streams, $^*SO_4$ was only slightly lower than total SO_4.

In Finnish rivers, the highest $^*SO_4$ concentrations were observed in western and south-western coastal areas, where the basins are characterized by acid sulphate soils (paper VI). The $^*SO_4$ concentrations were on average three times higher in the rivers with acid sulphate soils in their basins than in rivers with no acid sulphate soils; on average 15 and 5.3 mg l^{-1}, respectively. Moreover, the concentrations were somewhat lower in sub-basins (Table 2), demonstrating that the acid sulphate soils in the coastal areas result in high concentrations near river mouths, in contrast to the sub-basins located mostly upstream.

The $^*SO_4$ concentrations correlated strongly with the proportion of agricultural land and urban areas in the basin, indicating that sulphate derived from the application of agricultural fertilizer, and that both municipal and industrial wastewaters significantly increase the sulphate concentrations (paper VI). Similarly, Williams et al. (2005) concluded that SO_4 concentrations increase with the increasing extent of urban and agricultural area in the Ipswich River basin in north-eastern Massachusetts. Furthermore, in Finnish rivers the $^*SO_4$ concentrations decreased towards the north (Fig. 10), reflecting less fertile soils, lower sources of sulphate weathering, lower extent of agricultural land and acid sulphate soils, and lower sulphate deposition. Stronger correlation between $^*SO_4$ concentrations and latitude could be expected if the primary reason for lower concentrations in the north is lower deposition. Thus, the scatter plot (Fig. 10) reflects the influence of acid sulphate soils and land use (paper VI). This demonstrates that in large river basins the spatial variation of $^*SO_4$ concentrations is influenced by several factors including soil sources, land use and deposition.

The average A^- concentration exceeded the average $^*SO_4$ concentration in river water in 17 basins out of the 86 studied basins (paper VI). The A^- dominated areas are situated from central to northern Finland (except for one small basin located on the western coast), reflecting the high extent of peatlands in these areas. $^*SO_4$ dominated in southern Finland and in western coastal areas, where the extent of agricultural land and acid sulphate soils is highest. Hence, the $A^-/^*SO_4$ –ratio correlated positively with latitude and the proportion of peatland in the basin, and negatively with the proportion of agricultural land and urban areas in the basin. In 7 streams out of the 86, organic anion and *SO4 concentrations were almost equal. Decreasing S deposition and changing land use might change the dominance between organic and anthropogenic acidity. However, in those large basins where sampling points are situated

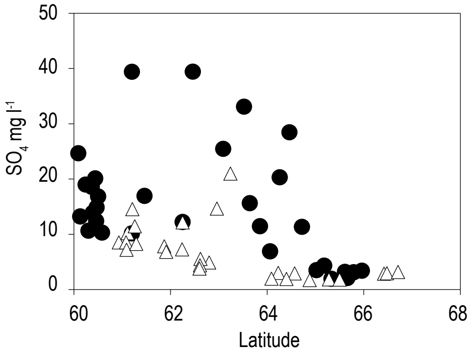

Figure 10. The relationship between river water SO_4 concentrations and latitude (basins = •, sub-basins = ∆).

only in coastal areas, the A^-/*SO_4 –ratio reflects the situation primarily in river mouths, emphasizing the influence of acid sulphate soils. Further upstream, where acid sulphate soils are less common, the A^-/*SO_4 –ratio is higher.

The high TOC concentrations were associated with low pH values in the river water, whereas no correlation between the *SO_4 concentrations and pH was found (paper VI). Similarly to pristine first order streams, high sulphate concentrations were associated with high BC concentrations, buffering the effects of *SO_4 on pH. A similar pattern was found in Finnish forested headwater streams studied by Kortelainen and Saukkonen (1995).

3.11 Changes in concentrations from headwater catchments downstream to the coast

In small pristine headwater catchments, the proportion of organic nitrogen from the total N load was very high, on average 91% (Fig. 11). In headwater catchments where forestry practices have annually affected about 2.4% of the catchment area, comparable to average values in Finland, the proportion of organic nitrogen was somewhat smaller, on average 77% (Kortelainen et al 1997). Downstream in the river basins with mixed land use, the proportion of organic nitrogen further decreased; in larger river sub-catchments the proportion of organic nitrogen was 76% and in the river mouth before entering into the estuary 53%. Pellerin et al. (2006) also concluded that DON accounted for half of the TDN concentrations from forested watersheds, but only for a smaller fraction of TDN in runoff from urban and agricultural watersheds with higher N loading.

Although the proportion of organic nitrogen decreased with increasing disturbance of the catchment from headwaters downstream, TON concentrations increased from first order streams through river sub-catchments to river mouths (Fig. 11). In headwaters, TON concentration was on average 337 μg l^{-1}, whereas in river sub-catchments and river catchments the average values were 399 and 550 μg l^{-1}, respectively. Increase in inorganic N (NO_3-N + NH_4-N) concentration was even greater: first order streams had on average the lowest inorganic N concentrations (50 μg l^{-1}), whereas in river sub-catchments the average concentration was 190 μg l^{-1}. In the river mouth before entering the estuary, inorganic N concentrations were manyfold (on average 800 μg l^{-1}) compared to the concentrations upstream. Similarly, Stanley and Maxted (2008) concluded that DON concentrations increased in a gradual, linear fashion across the human land cover gradient, in contrast to the simultaneous exponential increase in NO_3-N concentrations.

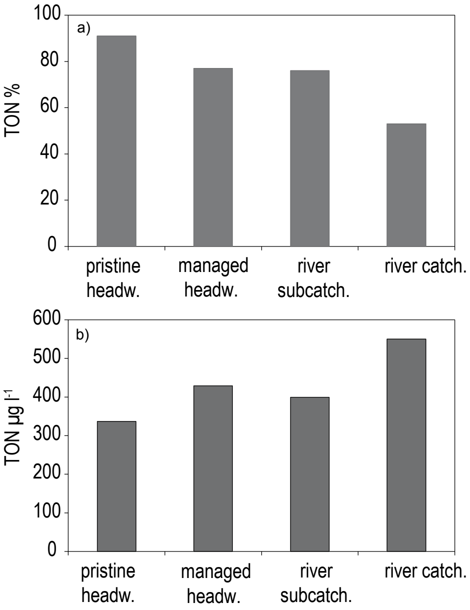

Figure 11. a) The proportion of TON of the total N and b) mean TON concentrations of pristine forested headwater catchments (n=42), managed forested headwater catchments (Kortelainen et al. 1997), river sub-catchments (n=50) and river catchments (n=36).

The concentrations of DOP in pristine headwater streams (analysed from a subset of catchments in 2001) and in river sub-catchments were lower (on average 7 and 6 μg l^{-1}) compared to large rivers (mean 10 μg l^{-1}). However, the proportion of DOP from TDP was on average highest in river sub-catchments (on average 62%). About 54% of the TDP was DOP in headwater streams (pristine 58% and managed forested 52%), whereas in larger rivers the proportion was 47% (Fig. 12). The concentrations of PO_4-P were lowest in headwater streams (on average 4 µg l^{-1}) and increased downstream, being on average 10 and 31 µg l^{-1} in river sub-catchments and larger river catchments, respectively. Both the proportion and the concentration of particulate phosphorus (PP) increased from the pristine headwaters downstream. Increasing human disturbance and mixed land use in the river catchments resulted in higher percentages and concentrations of PP.

By contrast, concentration of TOC was on average highest in pristine headwater streams (17 mg l^{-1}), whereas in river mouths the average TOC concentration was lower (13 mg l^{-1}) (Fig. 13). However, the change in TOC concentrations from headwaters to downstream was smaller compared to the changes in TON and DOP. These results indicate that the land use gradient from pristine headwaters to lowlands affects TON, DOP and TOC concentrations and has a significant effect on the stoichiometry of the study rivers. Thus, the molar TOC:TON ratio decreased from first order streams with forested catchments to the large river basins with mixed land use (Fig. 14). In pristine headwater streams, the molar TOC:TON ratio was on average 62, the lowest values being in the two southernmost catchments with highest atmospheric N deposition. The TOC:TON export ratio was lower, on average 48, in managed forested headwater catchments (Kortelainen et al. 1997), indicating the effect of human disturbance on TON yields. In large river catchments the molar TOC:TON –ratio further decreased, being 29 in river sub-catchments and 27 near the river mouth before entering the estuary.

In Finnish river catchments, the differences between headwater and downstream TOC and TON concentrations and their ratio probably depend largely on land use and the mosaic of landscape elements (e.g. mires and lakes) contributing water to the stream network. For example, an important factor affecting the differences in nitrogen concentrations between headwaters and downstream in Finnish rivers is high lake percentage in the catchment, especially in the case of one large lake with a long residence time (Lepistö et al. 2006). Downstream concentrations are the sum of headwater inputs in combination with inflowing water from sub-catchments with various land use and landscape patterns, in-stream processes having probably only a minor contribution (Temnerud et al 2009).

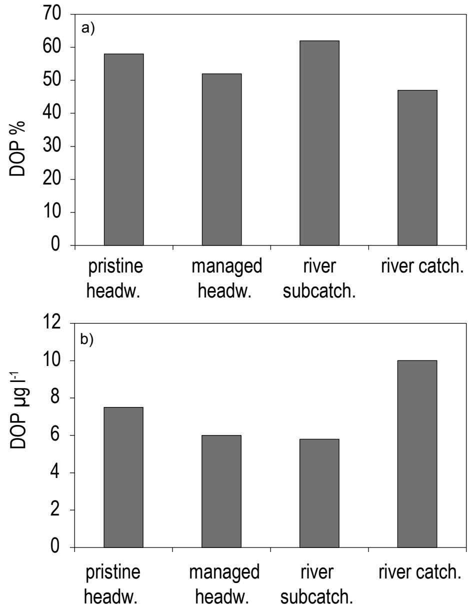

Figure 12. a) The proportion of DOP of the total dissolved P and b) mean DOP concentrations of pristine forested headwater catchments (n=42), managed forested headwater catchments (Kortelainen et al. 1997), river sub-catchments (n=50) and river catchments (n=36).

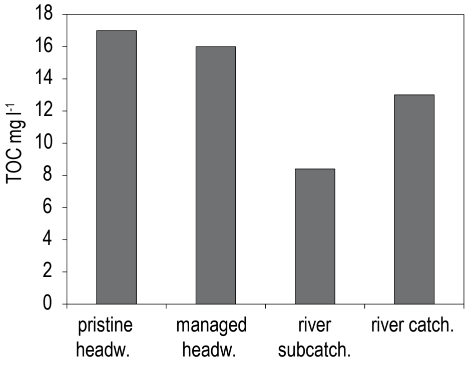

Figure 13. Mean TOC concentrations of pristine forested headwater catchments (n=42), managed forested headwater catchments (Kortelainen et al. 1997), river sub-catchments (n=50) and river catchments (n=36).

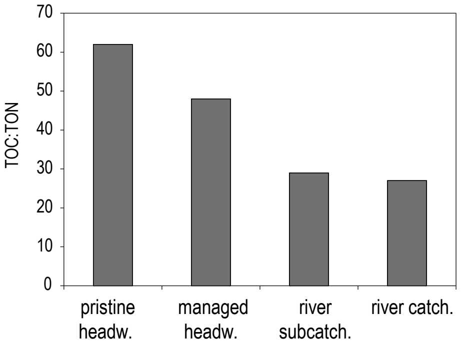

Figure 14. Mean molar TOC:TON ratios in pristine forested headwater catchments (n=42), managed forested headwater catchments (Kortelainen et al. 1997), river sub-catchments (n=50) and river catchments (n=36).

Concentrations of both BC and SO_4 were lowest in pristine forested headwater streams and increased through river sub-catchments to the downstream river, being on average highest near the river mouth (Fig. 15). In pristine headwater catchments, SO_4 and BC concentrations and the average forest site type on the catchment, which describes the productivity of the site, showed a significant positive correlation (paper V), probably reflecting higher concentrations in the soil on the fertile sites. However, in river catchments with mixed land use, sulphate and base cation concentrations were affected by the extent of agricultural land and urban areas in the catchment (paper VI).

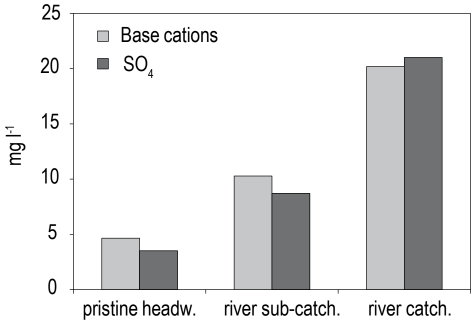

Figure 15. Mean base cation and SO_4 concentrations of pristine forested headwater catchments (n=42), river sub-catchments (n=50) and river catchments (n=36).

4 Conclusions

Several factors play a role in controlling DOM flux, including wetland and forest cover, urban and agricultural land use, precipitation and hydrology. In Finland, the cold climate and flat topography provide favourable conditions for organic matter accumulation. Water flow paths through wetlands and peatlands result in elevated TOC concentrations in streams and rivers. Organic matter transported by streams and rivers from headwater catchments to the coast is affected by processes in the river and by changing land use along the river basin. Hence, the concentrations of organic carbon, nitrogen and phosphorus show significant variability during the riverine transport from pristine first order catchments to the coast. However, no agricultural first order catchments were included in the study. The water quality in headwaters with agricultural-dominated catchments is probably different compared to forested headwater catchments, and therefore the comparison with the water quality in rivers downstream with mixed land use in their catchments might result in different conclusions.

The major part of the organic matter in Finnish river and stream water consists of organic C, most of which is in a dissolved form. In pristine headwater streams, most of the N and P were organically bound and the concentrations were relatively low. However, the concentrations and export of TOC (on average 17 mg l^{-1} and 6200 kg km^{-2} a^{-1}, respectively) were much higher in Finnish pristine streams when compared to concentrations in other undisturbed forest areas. These Finnish pristine streams also had lower concentrations of inorganic nitrogen compared to temperate and tropical streams, reflecting a higher proportion of organic nitrogen and lower N deposition. Generally, the concentrations of organic carbon, nitrogen and phosphorus were higher in southern areas, reflecting the effects of higher input of organic matter and decomposition in forest soil in southern Finland. On a national level temperature sum, precipitation and runoff were the most significant predictors for the carbon, nitrogen and phosphorus concentrations. On the catchment level, the proportion of peatlands in the catchment and the proportion of Norway spruce of the tree stand had the strongest correlation with the TOC and TON concentrations and export in pristine headwater catchments.

In the river basins, land use had stronger influence on the export of organic matter than the climate-related attributes, despite a 6 °C gradient in annual mean air temperature. Hence, within one climatically relative homogenous biome, in this case the northern boreal zone, land cover and land use probably determine to a great extent the concentrations and export of organic matter. In Finnish rivers, the TOC and organic anion concentrations are affected not only by the extent of peatlands in the basin as suggested in many previous studies, but also by the abundance of agricultural land. The riverine nitrogen flux in organic form averages 64% of the total and for phosphorus the organic load averages 47% of the total dissolved fraction. The extent of agricultural land and urban areas correlated positively with TON concentrations and exports, and DOP export also correlated positively with the proportion of urban areas in the catchment. However, 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.

The proportions of organic nitrogen and phosphorus of the total N and P concentrations decreased with increasing disturbance of the catchment from headwaters downstream, whereas the concentrations increased from first order streams through river sub-catchments to river mouths. By contrast, concentration of TOC was on average highest in pristine headwater streams, whereas in river mouths the average TOC concentration was lower. These results indicate that land use gradient from pristine headwaters to lowlands affects TON, DOP and TOC concentrations and has a significant effect on the stoichiometry of the study rivers. Thus, the molar TOC:TON ratio decreased from first order forest streams to the large river basins with mixed land use. Moreover, the variability in nutrient ratios induced by differences in land use results in distinctions in the quality of DOM transported into the different sea areas around the Finnish coast. In rivers draining into the Archipelago Sea and the Gulf of Finland with high extent of agricultural land in their catchments, the TOC:TON:DOP molar ratio favours the export of TON and DOP over TOC. Conversely, in rivers draining into the Bothnian Bay with high extent of peatland in their catchments, the molar ratio favours the export of TOC over TON and DOP. These differences in nutrient ratios might affect the decomposition and bioavailability of DOM in coastal waters.

This study also demonstrated that the land cover and/or land use of the catchments is related to both organic and minerogenic acidity in rivers and pristine headwater streams. In pristine streams, SO_4 concentrations increased with increasing site fertility and catchment slope, whereas the main source of SO_4 and minerogenic acidity in rivers with mixed land use was agricultural and urban areas. Both the catchment sources of sulphate and the anthropogenic acid deposition contribute to the variation in SO_4 concentrations. The soil sources of sulphate are most evident in areas with a high extent of acid sulphate soils and low sulphate deposition. Organic anion dominated in rivers and streams situated in northern Finland, reflecting the higher extent of peatlands in these areas, whereas SO_4 dominated in southern Finland and on western coastal areas, where the extent of fertile areas, agricultural land, urban areas and acid sulphate soils, and sulphate deposition is highest.

The high TOC concentrations decreased pH values in the stream and river water, whereas no correlation between the SO_4 concentrations and pH was observed, which underlines the importance of organic acids in controlling the pH levels in Finnish pristine headwater streams and main rivers. High SO_4 concentrations were associated with high BC concentrations and fertile areas, which buffered the effects of SO_4 on pH.

Climate change scenarios predict increasing precipitation and temperature in Northern Europe and an increasing proportion of heavy rainfalls in most land areas, resulting in major changes in seasonal runoff patterns (IPCC 2007). Changes in precipitation, runoff and temperature affect accumulation, decomposition and transport of DOM, resulting in changes in concentration and export of DOM in surface waters. For example, increase in precipitation might increase TOC fluxes, whereas increasing evaporative demand under a warmer climate might offset the effect. Significant impacts can also be expected from more intense rainfall, agricultural modifications and ecological disturbance due to climate change. Any change in TOC concentrations in rivers and streams will also impact the interactions between TOC, nutrients and organic acidity. A change in land use, for example from forests and wetlands towards intensive agriculture and urbanization, would generally change the composition of DOM load by increasing TON and DOP export.

Yhteenveto

Liuenneen orgaanisen aineen huuhtoutumiseen valuma-alueelta vesistöihin vaikuttavat useat tekijät kuten valuma-alueen ominaisuudet, maankäyttö ja hydrologia. Huuhtoutumistutkimukset ovat perinteisesti keskittyneet epäorgaanisiin ravinteisiin, vaikka erilaisilta maankäyttömuodoilta vesistöihin huuhtoutuu myös runsaasti orgaanisia ravinteita. Valuma-alueelta huuhtoutuva orgaaninen aines vaikuttaa veden laatuun, sillä se edistää rehevöitymistä sekä vaikuttaa veden lämpötilaan ja näkösyvyyteen. Tutkimuksessa selvitettiin orgaanisen hiilen, typen ja fosforin huuhtoutumista maankäytöltään erilaisilta valuma-alueilta. Valuma-alueen ominaisuuksien, maankäytön ja ilmastollisten tekijöiden vaikutusta liuenneen orgaanisen aineen (DOM) huuhtoumaan tutkittiin määrittämällä orgaanisen hiilen (TOC), orgaanisen typen (TON) ja orgaanisen fosforin (DOP) pitoisuudet ja huuhtoumat 42:lta luonnontilaiselta pieneltä latvavaluma-alueelta ja 36:lta jokivaluma-alueelta sekä 50:ltä osavaluma-alueelta. Luonnontilaiset pienet latvavaluma-alueet sijaitsivat eri puolilta Suomea. Jokiaineisto muodostui Suomen jokien valuma-alueista ja osavaluma-alueista kattaen n. 88 % Suomen pinta-alasta. Lisäksi orgaanisen ja minerogeenisen happamuuden merkitystä veden pH-tason säätelijänä tutkittiin määrittämällä orgaanisen anionin, sulfaatin ja emäskationeiden pitoisuudet luonnontilaisissa puroissa sekä suurissa joissa.

Kaikissa joissa ja puroissa orgaaninen hiili muodosti suuren osan liuenneesta orgaanisesta aineesta. TON ja DOP pitoisuudet olivat huomattavasti pienempiä. Luonnontilaisissa puroissa yli 90 % kokonaistypestä ja yli 50 % liuenneesta kokonaisfosforista oli orgaanisessa muodossa. Suurin osa orgaanisesta typestä ja hiilestä oli liuenneessa muodossa. TOC ja TON pitoisuudet korreloivat voimakkaasti keskenään. Luonnontilaisissa puroissa 78 % orgaanisen typen pitoisuuksien vaihtelusta selittyi orgaanisen hiilen pitoisuuksilla. Samankaltaisissa ilmasto-olosuhteissa pienen typpilaskeuman alueella sijaitsevassa 20 latvavaluma-alueen osajoukossa soiden osuus valuma-alueesta sekä kuusen osuus puustosta korreloivat voimakkaimmin sekä orgaanisen hiilen että orgaanisen typen pitoisuuksien ja huuhtoumien kanssa.

Orgaanista hiiltä huuhtoutui eniten alueilta, joilla topografia ja ilmasto-olosuhteet suosivat orgaanisen hiilen varastojen kertymistä valuma-alueelle, kuten Suomen runsassoisilla alueilla. Suomalaisilla puro- ja jokivaluma-alueilla TOC huuhtouma lisääntyi soiden osuuden kasvaessa. Suomalaisissa joissa TOC pitoisuuksiin lisäävästi vaikuttivat paitsi suot myös maatalousalueet. Ihmistoiminnan vaikutus näkyi myös lisääntyneinä orgaanisen typen ja orgaanisen fosforin kuormina maatalousvaltaisilta ja taajamavaltaisilta jokivaluma-alueilta. Kaikkein voimakkaimmin TOC, TON ja DOP huuhtoumiin jokivaluma-alueilla vaikutti valuma-alueen järvisyys. Mitä suurempi oli valuma-alueen järviprosentti sitä pienemmät olivat huuhtoumat, mikä indikoi orgaanisen aineen pidättymistä järviin.

Orgaanisten ravinteiden osuus kokonaisravinteiden pitoisuuksista laski luonnontilaisilta metsäisiltä latvavaluma-alueilta alavirtaan suurille maankäytöltään vaihteleville jokivaluma-alueille tultaessa. Samalla orgaanisen typen ja fosforin pitoisuudet kuitenkin nousivat alajuoksua kohden. TOC pitoisuudet sen sijaan olivat korkeimmillaan latva-valuma-alueilla ja laskivat suurille jokivaluma-alueille tultaessa. Maankäytön muutos luonnontilaisilta latva-valuma-alueilta suuriin jokiin tultaessa aiheutti

muutoksia huuhtoutuvaan orgaaniseen aineeseen, koska luonnontilaisilta, kaupunkimaisilta ja maatalousvaltaisilta alueilta huuhtoutuva orgaaninen aines on ravinnesuhteiltaan erilaista. Esimerkiksi TOC:TON suhde pieneni suo- ja metsävaltaisilta latvavaluma-alueilta jokisuille tultaessa.

Myös jokien mereen kuljettaman orgaanisen aineen ravinnesuhteet (C/N/P) vaihtelivat merkittävästi heijastaen kunkin valuma-alueen maankäyttöä. Saaristomereen ja Suomenlahteen laskevissa joissa TON ja DOP pitoisuudet olivat suurempia johtuen valuma-alueen maatalousalueiden runsaudesta. Perämereen laskevissa joissa sen sijaan TOC pitoisuudet olivat suurempia johtuen suuresta suoalasta valuma-alueilla. Nämä vaihtelut orgaanisen aineen ravinnesuhteissa vaikuttavat mahdollisesti orgaanisen aineen hajoamiseen ja biologiseen käytettävyyteen.

Valuma-alueiden maankäyttö vaikutti myös sekä orgaaniseen että minerogeeniseen happamuuteen joissa ja puroissa. Orgaaninen anioni dominoi pohjoisissa puroissa ja joissa heijastaen valuma-alueiden soiden runsautta, kun taas sulfaatti dominoi Etelä-Suomessa ja rannikkoalueilla, missä on runsaasti reheviä alueita, maatalous- ja taajama-alueita, happamia sulfaattimaita sekä korkein sulfaattilaskeuma. Korkea TOC pitoisuus laski pH arvoja puroissa ja joissa, mutta sulfaatin ja pH:n välillä ei ollut riippuvuutta, mikä korostaa orgaanisten happojen merkitystä pH tason säätelijänä suomalaisissa puroissa ja joissa. Suuret sulfaatin pitoisuudet esiintyivät yhdessä suurten emäskationipitoisuuksien kanssa rehevillä alueilla, mikä puskuroi sulfaatin vaikutusta veden pH tasoon.

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