SEASONAL VARIATION AND LANDSCAPE REGULATION OF DISSOLVED ORGANIC CARBON CONCENTRATIONS AND CHARACTER IN SWEDISH BOREAL STREAMS

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Title
Seasonal variation and landscape regulation of dissolved organic carbon concentrations and character in Swedish boreal streams.

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Abstract
The seasonal variation and landscape regulation of dissolved organic carbon (DOC) concentrations in streams have been studied in two watersheds in the boreal zone. The seasonal variation was found to be highly correlated to variations in runoff. An increase in runoff was always accompanied with an increase in DOC concentration. However, there were indications that the TOC concentration was restricted by the soil TOC pool during snowmelt.

The main factors affecting DOC exports varied between seasons. During winter baseflow the spatial variation in DOC exports was strongly influenced by wetland coverage, during snowmelt the exports were correlated to factors describing the size and location of the catchment, and during the snow-free season they were heavily affected by the proportions of wetlands and forests in the catchments. Small headwaters had the highest terrestrial DOC export, per unit area.

The properties of the DOC changed during spring flood, towards lower molecular weight and more aliphatic compounds. These changes affected the bioavailability of the DOC, which increased during spring flood. There were also differences in the DOC properties between wetlands and forest soils; the forested soils yielded DOC with lower molecular weight (measured as 254 nm/365 nm light absorbance ratios), largely from superficial layers that were activated during high flow events, while wetland soils generally provided a more constant carbon source with higher molecular weight. The majority of the DOC was exported by wetlands, but most of the short-term bioavailable DOC (BP_7) was derived from the forests, during the spring flood period, indicating that bacterial production in streams and lakes is likely to be almost entirely based on DOC exported from forested areas during, and some time after, the spring flood event.

Key words: DOC, temporal variation, spatial variation, seasonal variation, forested catchment, wetland catchment, catchment characteristics, DOC characteristics, absorbance-ratio, bioavailability.

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BY

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Contents

You cannot step twice into the same river;
for other waters are continually flowing in.

Heraclitus 500 BC

1. LIST OF PAPERS

This thesis is based on the following papers, which will be referred to in the text by the corresponding roman numerals:

I **Ågren A**., Jansson M., Ivarsson H., Bishop K. and J. Seibert. Seasonal and runoff-related changes in total organic carbon concentrations in the River Öre, Northern Sweden. *Accepted by Aquatic Sciences.*

II **Ågren A**., Buffam I., Jansson M. and H. Laudon. Importance of seasonality and small streams for the landscape regulation of dissolved organic carbon export. *Journal of Geophysical Research*. 112, G03003, doi: 10.1029/2006JG000381.

III **Ågren A**., Buffam I., Berggren M., Bishop K., Jansson M. and H. Laudon. Dissolved organic carbon characteristics in boreal streams in a forest-wetland gradient during the transition between winter and summer. *Submitted to Environmental Science and Technology.*

IV **Ågren A**., Bergren M., Laudon H. and M. Jansson. Terrestrial export of highly bioavailable carbon from small boreal catchments during spring flood. *Submitted to Freshwater Biology.*

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2. LIST OF ABBREVIATIONS

Abbreviation	Meaning
A_{254}	Absorbance measured at 254 nm
A_{365}	Absorbance measured at 365 nm
BP	Bacterial production
BP_7	A highly labile fraction of carbon
BR	Bacterial respiration
DEM	Digital elevation model
DOC	Dissolved organic carbon
DOM	Dissolved organic material
cCREW	Cold climate research in boreal watersheds
CO_2	Carbon dioxide
GIS	Geographical information system
HA	Humic acid
HC	Highest postglacial coastline
HMW	High molecular weight
HPIA	Hydrophilic acid
kNN	K nearest neighbor
LIDAR	Light detection and ranging
LMW	Low molecular weight
OA	Organic acids
OC	Organic carbon
PCA	Principal Component Analysis
POC	Particulate organic carbon
POM	Particulate organic material
$SUVA_{254}$	Specific ultraviolet absorption at 254 nm DOC^{-1}
TOC	Total organic carbon
TOM	Total organic material

3. INTRODUCTION

3.1. Why study DOC?

STUDIES OF DISSOLVED ORGANIC CARBON (DOC) and aquatic humic substances have a long tradition, not least in Sweden. Early research in this field focused on the quality of drinking water [*Berzelius*, 1806], subsequent limnological studies focused on lake classification and Naumann (1921) introduced the term dystrophic to characterize Swedish lakes that were colored brown by the dissolved organic matter originating from their peaty surroundings. Naumann regarded this as an extreme class of oligotrophy. At about the same time (1927) Birge & Juday studied brown water lakes in Wisconsin, USA and found that organic carbon of terrestrial origin dominated the carbon metabolism of such lakes [*Jones*, 1992]. A major study of allochthonous DOC (dissolved organic carbon) in Swedish rivers was conducted in 1929 by Joel Eriksson who published a report entitled "The chemical denudation of Sweden", in which (*inter alia*) he reported spatial and temporal variations in DOC [*Eriksson*, 1929]. More recent research on DOC has focused on: the role of DOC in acidic streams and lakes [*Bishop et al.*, 2000; *Hruska et al.*, 2003]; its light absorption properties [*Jones*, 1992]; the mineralization of allochthonous DOC in lakes, which contributes to net lake heterotrophy and turns lakes into net sources of CO_2 to the atmosphere [*Cole et al.*, 1994]; and the metal-binding properties of DOC [*Perdue*, 1998]. It has also been recognized that allochthonous DOC can subsidize aquatic food webs through its use as a carbon source by heterotrophic bacteria [*Jansson et al.*, 2007].

In the 1960s fish were disappearing from lakes, forests were harmed, and metal structures were being rapidly corroded in Sweden. It was suggested that these phenomena were effects of air pollutants, especially sulphur emissions from the combustion of fossil fuels, which acidified the precipitation [*Gorham*, 1957; *Odén*, 1967]. Subsequent research on acidification clearly showed that allochthonous DOC plays important roles in the regulation of acidity in surface waters; it acts as a pH-buffer, but can also make significant contributions to the acidity of surface waters [*Bishop et al.*, 2000; *Hruska et al.*, 2003; *Köhler et al.*, 2000].

Research regarding DOC in aquatic environments has also been highlighted along with the ongoing global warming debate. DOC in surface waters has been shown to be important with respect to carbon dioxide (CO_2) emissions. Surface waters were previously believed to act as sinks for emitted CO_2. However, studies in the 1990s showed that mineralization of DOC, either by photolytic decomposition [*Molot and Dillon*, 1997] or microbial consumption – in which organic C is transformed to inorganic C through bacterial respiration [*del Giorgio and Cole*, 1998] – can lead to nutrient-poor streams, lakes and some oceanic regions becoming supersaturated with (and emitting) CO_2 [*Cole et al.*, 1994; *Duarte and Prairie*, 2005]. A study of boreal lakes in Sweden has shown that the CO_2 emissions from boreal lakes is closely related to the DOC concentration [*Sobek et al.*, 2003]. Hence, most boreal lakes function as sources of CO_2, instead of sinks. To illustrate the public's interest in the greenhouse effect and climate change, a recent investigation in Sweden has shown that these subjects are receiving more attention than any others in the Swedish media at the moment. A staggering 12 605 articles were written on the subject during the first quarter of 2007 [*Lundahl*, 2007].

Organic matter in both dissolved and particulate forms is an important energy source for heterotrophs in lake and stream ecosystems [*Hessen and Tranvik*, 1998; *Hope et al.*, 1994; *Tranvik*, 1998] and allochthonous DOC may serve as the principal energy source for bacteria in humic waters [*Hessen*, 1992; *Jansson et al.*, 1999]. Jansson *et al.* [2000] suggested that lakes shift from autotrophy to net heterotrophy at DOC concentrations of a few (ca. 5) milligrams per liter in natural, non-polluted lakes. DOC can also affect the biota by altering the physical environment. Due to its light absorption properties, DOC creates a poor light climate for phytoplankton and a rapid warming of the surface waters which gives a shallow and stable epilimnion in small humic lakes [*Jones*, 1992].

Dissolved organic matter (DOM) is also a strong complexing agent for metals such as iron [*Dillon and Molot*, 1997], copper [*Sciera et al.*, 2004], aluminium [*Simonin et al.*, 1993; *Teien et al.*, 2006], nickel [*Hoang et al.*, 2004] and mercury [*Ravichandran*, 2004], which thus affects their solubility, transport and toxicity [*Bishop et al.*, 1995; *Cory et al.*, 2006; *Heikkinen*, 1994]. Organic matter also affects the transport of organic pollutants [*Knulst*, 1992; *Patterson et al.*, 1996], colloid chemistry [*McKnight et al.*, 1997], and nutrient availability [*Stepanauskas et al.*, 2000]. Since DOC affects the pH, the toxicity of metals and organic pollutants [*Hayashi et al.*, 2004] and light penetration in lakes, DOC also affects the biota in aquatic systems, including bacteria [*Boyd et al.*, 2005], invertebrates [*Doig and Liber*, 2006] and fish [*Laudon et al.*, 2005].

3.2. What is DOC?

ORGANIC MATERIAL in riverine ecosystems consists of a wide variety of compounds with diverse properties [*Buffle et al.*, 1982; *Thurman*, 1985]. Organic compounds of natural waters can be divided into six major groups: humic substances, hydrophilic acids, and the simple compounds; carbohydrates, carboxylic acids, amino acids and hydrocarbons [*Thurman*, 1985].

To investigate the properties of the organic compounds, they are generally divided into groups with similar properties. Total organic carbon (TOC) can be divided into particulate organic carbon (POC) and dissolved organic carbon (DOC). The distinction between DOC and POC is generally based on whether the organic carbon is retained by a 0.45 µm filter or not. DOC accounts for 90%, on average, of the TOC in rivers and streams worldwide [*Heikkinen*, 1989; *Meybeck*, 1982; *Thurman*, 1985]. However, the ratio of DOC:POC exported varies greatly, and the relative importance of POC tends to increase with river size [*Thurman*, 1985]. In the River Öre catchment in northern Sweden POC never exceeded 5% of TOC in a study by [*Ivarsson and Jansson*, 1994], and in the Krycklan study (Paper II) a comparison between sites covering the extremes of observed runoffs showed that filtering caused no measurable changes in carbon concentrations. Thus, TOC often provides a good estimate for DOC, at least in the boreal part of Sweden studied in the investigations underlying this thesis.

The organic material can also be divided into two categories based on its origins. The allochthonous pool is derived from terrestrial organic matter and the autochthonous pool from *in-situ* biological production [*Bourbonniere*, 1989; *Hessen and Tranvik*, 1998]. This thesis focuses on DOC in streams in the boreal zone, where most of the DOC is of allochthonous origin.

3.3. Characteristics of DOC

THE COMPOSITION of DOC depends on diverse variables, including its origin, size, turnover time and functional groups. Hence, the characteristics of dissolved organic materials vary both in space and time. Key features are their molecular size and weight [*Perdue and Gjessing*, 1990], so they are often divided into two ecologically important fractions, one with low molecular weights (LMW, < 500 Da) and one with high molecular weights (HMW, > 500 Da) [[*Thurman*, 1985]], which have significantly different properties.

High molecular weight substances consist of humic substances (i.e. humic acids and fulvic acids) and hydrophilic or hydrophobic acids, bases and neutral compounds [*Kramer et al.*, 1990; *Leenheer*, 1981; *Thurman*, 1985]. Refractory humic substances may have lifetimes of months or longer [*Thurman*, 1985] and thus tend to accumulate, especially in environments with low rates of decomposition. Humic acids (HAs) are prominent in pore waters from the deeper layers of bogs, HAs are also associated with drier, low flow conditions [*Bourbonniere*, 1989]. Hydrophilic acids (HPIAs) are more soluble, less strongly coloured than HAs, and likely to be composed of strong, labile acids that are diagenetically close to their biochemical sources, such as bog flora. Their seasonal distribution suggests that HPIA concentrations are influenced by microbial degradation [*Bourbonniere*, 1989].

Low molecular weight organic acids consist of identifiable compounds; carbohydrates (sugars), carboxylic acids (e.g. nonvolatile and volatile fatty acids and phenols), amino acids and hydrocarbons [*Kramer et al.*, 1990; *Thurman*, 1985]. These compounds represent a relatively small percentage of the DOC, (<10%) [*van Hees et al.*, 2005]. Low molecular weight acids are generally thought to decompose rapidly and may have lifetimes of just a few minutes to a few hours [*Perdue and Gjessing*, 1990; *Thurman*, 1985]. For example sugars, amino acids, and volatile fatty acids are rapidly metabolized by the ubiquitous microbiota of natural aquatic systems [*Perdue and Gjessing*, 1990].

The ultra-violet and visible light absorbance spectra of the organic material provide easily measurable indicators of several important DOC parameters, notably its bioavailability. For instance, a high A_{254}/A_{365} ratio indicates that the DOC compounds have a low average molecular weight [*Dahlén et al.*, 1996; *Strome and Miller*, 1978] and will promote higher rates of bacterial growth than DOC with a lower ratio under otherwise similar conditions [*Lindell et al.*, 1995; *Obernosterer and Herndl*, 2000].

Since aquatic humus consists of colored substances (yellow to brown or black), dissolved organic matter has a significant influence on water colour [*Grieve*, 1991; *Heikkinen*, 1990]. The humic acids in particular are responsible for much of the color seen in many river waters [*Hope et al.*, 1994]. High molecular weight compounds are more brownish to blackish than the lower molecular weight acids, which are generally less strongly colored. Thus, carbon-specific ultraviolet absorbance at 254 nm per unit DOC ($SUVA_{254}$) can be used as an indicator of both the composition of DOC of river water and the origins of the dissolved organic matter [*Rostan and Cellot*, 1995]. A higher value of $SUVA_{254}$ indicates higher contents of aromatic carbon, which generally has lower bioavailability than the aliphatic compounds [*Weishaar et al.*, 2003].

3.4. Terrestrial export of DOC

THE EXPORT of dissolved organic carbon from soils to streams has been investigated in many studies. Two main factors govern the terrestrial export of DOC, and thus its concentration in surface waters: the terrestrial sources of TOC and the hydrological mobilization of these sources. The major sources in Boreal ecosystems are wetlands [*Creed et al.*, 2003; *Hope et al.*, 1994; *Mulholland*, 2003], together with the upper organic horizons of the riparian forest zone [*Bishop et al.*, 2004; *Findlay et al.*, 2001; *Inamdar and Mitchell*, 2006] as well as the podzol profile in coniferous stands [*Kortelainen et al.*, 1989; *Mattsson et al.*, 2003]. Wetlands and forests have been shown to respond differently to hydrological changes, in terms of both DOC concentrations and exports. DOC concentrations in streams usually vary considerably between seasons [*Hope et al.*, 1994; *Laudon et al.*, 2004; *Perdue and Gjessing*, 1990] and there are large variations in DOC exports both spatially (at many scales, from plots to large catchments) and temporally (from days, to seasons to years), and our knowledge of the regulation of DOC formation in terrestrial systems and its allocation to surface waters is still incomplete.

A major problem is to bridge the gap between understanding of small-scale processes and large-scale (catchment) exports. The amounts of carbon exported by many large rivers draining into the sea have been estimated, but most research on the processes controlling the exports has been conducted at a small scale, from plots and transects to small catchments with distinct properties. However, the landscape is a mosaic of patches with differing geology, soils, vegetation and micro-climates, and the quantities (and quality) of DOC generated reflect the integrated effects of these diverse variables. Thus, scaling up the results from small-scale studies is a challenging task.

The Swedish boreal forest region can be seen as part of the large taiga belt, which covers much of the northern hemisphere. Due to the spatial variation in DOC, similar studies in different parts of the world may produce conflicting results. Between-region differences in bioavailability of DOC in high flow situations provide examples of this variability. In temperate and tropical climates, hydrological pulses usually have either no effects or negative effects on the bioavailability of DOC in recipient lakes and rivers [*Farjalla et al.*, 2006; *Hood et al.*, 2006; *Kritzberg et al.*, 2004; *Leff and Meyer*, 1991; *Volk et al.*, 1997]. However, in boreal areas discharge pulses have been found to increase the bioavailability of organic matter [*Berggren et al.*, In press; *Stepanauskas et al.*, 2000] and, thus, increases in the growth rates of bacteria and BP TOC^{-1} [*Bergström and Jansson*, 2000].

The presence of a winter snow cover in boreal regions also causes their hydrological regimes to be markedly different from those in temperate and tropical regions, with, in some cases, more than half of the annual runoff being exported during the short snowmelt period [*Laudon et al.*, 2004].

4. AIMS

THE OVERALL AIM of the work underlying this thesis was to improve our ability to predict the landscape-scale regulation of DOC in boreal regions, and to help bridge the gap between understanding small-scale processes and large (catchment) scale exports.

The four papers appended to the thesis address different issues regarding DOC variations in the boreal zone. The main objectives of the studies they are based on were to answer the following questions:

- What is the role of hydrology in regulating the concentration, terrestrial exports and character of DOC? (Papers I, II, III, and IV)
- How are terrestrial DOC exports regulated by landscape properties? (Papers I, II and III)
- What are the differences in DOC exports and characteristics between the two major sources: wetlands and forests? (Papers II, III & IV)
- How can the export of bioavailable DOC vary between wetlands and forests? (Papers III & IV)

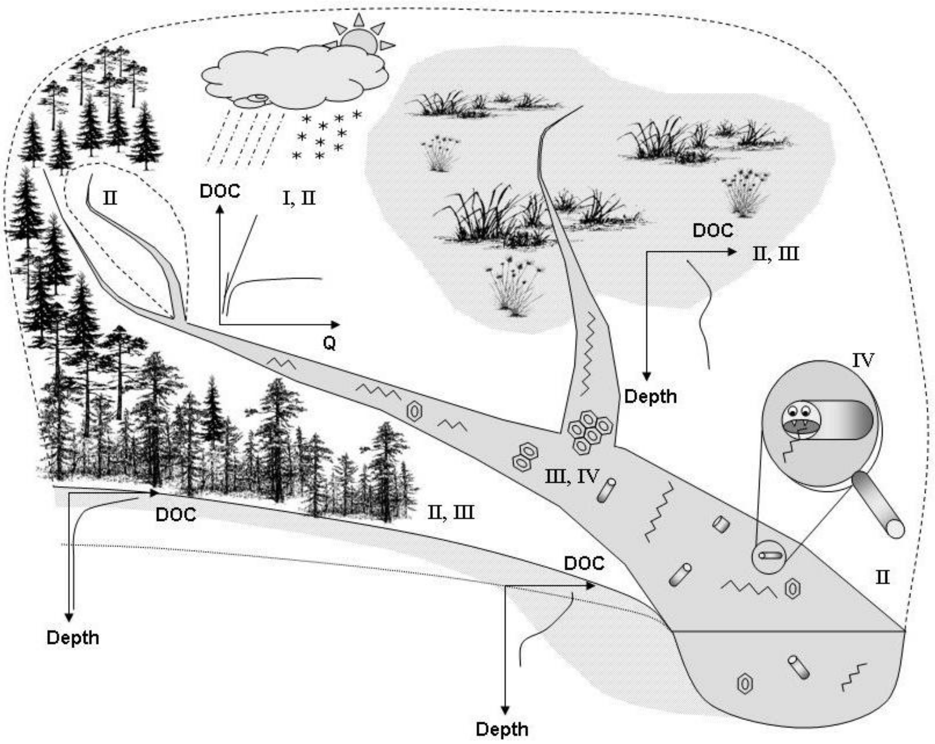

Figure 1. Schematic picture of a watershed and the issues addressed in the articles appended to this thesis, briefly: I) The seasonal variations in correlations between TOC concentration and runoff. II) Variations in DOC exports between wetlands and forests in different seasons, and with the size of the catchment. III) Changes in the properties (molecular weights and aromaticity) of the DOC during the spring flood in wetland- and forest-dominated catchments. IV) Effects of changes in DOC properties on its bioavailability.

5. STUDY AREAS

The investigations were carried out in two watersheds in the boreal zone of Sweden: the large catchment of the River Öre, covering 2940 km^2 (Paper I) and the smaller meso-scale Krycklan catchment (68 km^2), with 15 subcatchments ranging in size from 0.03 to 21.72 km^2 (Papers I-IV). The two studied catchments have both similarities and differences.

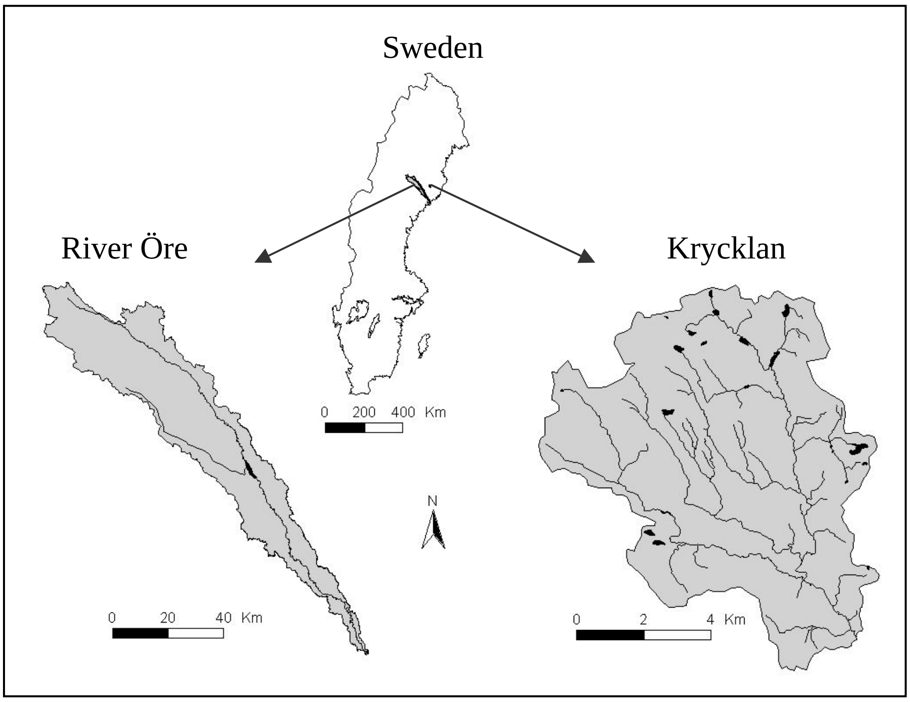

Figure 2. The catchment of the River Öre (2940 km^2) (Paper I) and the smaller meso-scale Krycklan catchment (68 km^2) (Papers II-IV). The black lines in the River Öre catchment denote the major stream channels, while those in the Krycklan catchment denote all the 1^{st} to 4^{th} order streams within it.

The geology and vegetation of the catchments show similarities. The majority of the bedrock in the two watersheds is Precambrian gneiss, further classified as Svecofennian metagreywhacke. Intrusions of acid and intermediate metavolcanic, granite and pegmatite, rocks are also common in this region [*Fredén et al.*, 1994]. The quaternary deposits are dominated by till with patches of peat, bare rock, thin soils and sediments. Both catchments are affected by isostatic uplift; 55% of the Krycklan catchment [*Buffam*, 2007], and 88 % of the River Öre catchment [*Ivarsson and Karlsson*, 1992], are situated below the highest postglacial coastline (HC). The quaternary deposits can form thick layers, with till tens of meters thick [*Ivarsson and Johnsson*, 1988]. Postglacial deltas are present in both catchments and the silty sediments in Krycklan form a thick layer through which the larger traversing streams have cut deeply incised channels forming ravines and bluffs up to 30 m high. The quaternary deposits below the HC are affected by wave washing and sorted sediments (sand, silt and clay) are common at the bottom of the valleys. Well-developed iron-podzols dominate the forest floor soils, but near the stream channels the organic content increases, forming a riparian peat zone along the streams. The wetlands mainly consist of mixed mires that are dominated by *Sphagnum* species and can be categorized as acid, oligotrophic and minerogenic, with varying proportions of ombrotrophic and minerotrophic patches [*Granberg et al.*, 1999]. Productive forests cover most of the land [*Carling*, 1998]. The dominant tree species is Scots pine *(Pinus sylvestris)* in dry upslope areas, while Norway spruce (*Picea Abies*) dominates in wetter, lower-lying areas. About 10 % is covered by deciduous forest stands: mainly birch (*Betula ssp.)*, alder (*Alnus incana*) and willow (*Salix spp*.), usually in the wetter, riparian areas. Only a small amount (1% of the catchment) is arable land.

The major difference between the catchments is in their size. The River Öre catchment extends about 180 km from its uppermost part to the river mouth. The mean annual temperature ranges from 3°C in the coastal region to 0°C in the uppermost part. Spring arrives a week earlier, and fall two weeks later near the coast than in the upstream, inland region of the catchment [*Vedin et al.*, 1995]. In altitude it ranges from sea level to 713 m a.s.l. The Krycklan catchment ranges from 126 to 369 m a.s.l, and in this catchment the mean annual temperature is 1°C.

The mean annual precipitation in the region amounts to 600-650 mm, of which approximately 50% becomes runoff. 35-40% of the precipitation falls as snow [*Eriksson*, 1991; *Ottosson Löfvenius et al.*, 2003] and the area has on average five months of snow cover. The hydrology is characterized by a strong runoff peak in May due to snowmelt, with occasional runoff peaks in summer and autumn caused by rainfall.

The properties of the River Öre catchment are further described in Paper I and the Kryckan catchment in Papers II-IV.

6. METHODS

6.1. Catchment characteristics

MAPS WERE USED in conjunction with GIS (Geographical Information Systems) overlay functions and gridded elevation data (DEM), to characterize and calculate important characteristics of the catchments. In the River Öre study the soil map (1:100 000) published by the Geological Survey of Sweden (Uppsala, Sweden) was used to define the proportions of quaternary deposits in the catchments. Paper II included a more detailed characterization of the Krycklan subcatchments. The quaternary deposits were derived from the soil map as before, and a parameter "median stream size" was calculated from gridded elevation data (DEM). The stream network consisted of 1654 stream cells (50m*50m), and for each stream cell the catchment area draining through it was calculated. The median stream size was calculated as the median value of the distribution of drainage areas for all stream grid cells within a particular subcatchment, and was expressed in units of area. The DEM was also used to calculate the proportion of the subcatchment above HC (areas with altitudes higher than 257.5 m a.s.l.). The digital Swedish topography map (1:100 000) (Lantmäteriet, Gävle, Sweden) was used to define the parameters stream order, altitude of the sampling point, and the proportions of surface water, forest, wetland, and agricultural areas within each subcatchment. Forest characteristics of the watershed were estimated from satellite data from the national forest inventory by the k nearest neighbor method (kNN) [*Reese et al.*, 2003]. The total stem volume, and the volumes of Norway spruce (*Picea Abies*), Scots pine *(Pinus sylvestris)* and deciduous species, mainly birch (*Betula ssp.)* were calculated.

6.2. Sources of data

THE DATA used in the studies, apart from the geographic and geological data described above, came from several sources. The TOC (total organic carbon) data used in Paper I were derived from (i) a study conducted between August 1990 and June 1992 [*Ivarsson and Jansson*, 1994] and (ii) the Swedish Environmental Protection Agency's national surface water quality monitoring program between January 1987 and October 2000 (http://www.ma.slu.se).

The analyses in Papers II-IV are based on data from the Krycklan Catchment Study (http://ccrew.sek.slu.se), which began in 2002 and is monitoring hydrology and water quality at many scales, from plots to transects to entire catchments. The studied catchments are situated within the Vindeln Experimental Forests. The DOC values from Krycklan used here were from the period January 2003 - December 2005 (Paper II) and from the spring flood periods (1 March to 31 July) in 2004 and 2005 (Papers III and IV). The water samples for the bioassays were collected on four dates in 2005 and six dates in 2006.

6.3. Runoff measurements

THE MEAN DAILY RUNOFF data used in Paper I were obtained from the Swedish Meteorological and Hydrological Institute. In the Krycklan catchment site 7 (C7) is used as an index site. Soil hydrologic parameters, runoff and chemistry have been monitored since 1980 in the 0.5 km^2 Nyänget Catchment (C7). Runoff has been monitored continuously (measured every 10 seconds and stored as hourly averages) at site 7 using a 90º V-notch in a heated dam shed. Discrete salt dilution or bucket flow runoff measurements have been used to assess the intersite differences between the 15 Krycklan sites. Daily runoff was calculated using continuous recordings of the stream's water level and established height-runoff rating curves. Runoff values were averaged to obtain the daily mean runoff.

6.4. Sampling and chemical measurements

A TOTAL OF about 1500 water samples were collected for these studies in acid-washed polyethylene bottles after multiple rinses with stream water. In both catchments samples were taken frequently during the high flow snowmelt-season and less frequently during the rest of the year. Samples were kept dark and cool, or were frozen until processing. Soil water samples were also collected. The forest soils were sampled at three profiles in the riparian zone of Västrabäcken (C2) with suction lysimeters. A 50 psi vacuum was applied to the lysimeters one day prior to sampling and the initial volume was discarded before collecting samples for analysis. The wetland soil profile was sampled at a mire in the Kallkälsmyren catchment (C4), using nested wetland wells with closed bottoms and perforations in their lower 10 cm [*Sirin et al.*, 1998]. The water from each well was pumped up and then filtered before analysis.

The organic carbon was analyzed with a Shimadzu TOC 5000 or a Shimadzu TOC-V_{CPH} analyzer. The organic carbon contents of both filtered and unfiltered samples were measured, but no measurable differences due to filtering were found, even during the highest flow situations. Samples were acidified and sparged to remove inorganic carbon before DOC was measured.

Absorbance spectra were measured using a Hewlett Packard 8452A diode array spectrophotometer, 1 cm quartz cuvettes and ultra pure water as blanks. Absorption coefficients (m^{-1}) were calculated from absorbance (unitless). The absorbance measurements were carried out within 24 hours of the sampling.

6.5. Bioavailability of DOC

THE EXPORTS OF BIOAVAILABILE DOC in 1st and 2nd order streams in Krycklan catchment were calculated from the A_{254}/A_{365} ratio which was found to be correlated (Figure 3) to a readily accessible (bioavailable) fraction of the bulk DOC [*Berggren et al.*, In press], denoted BP_7:

DOC specific $BP_7 = 0.74 * A_{254}/A_{365} - 2.41$ $\qquad R^2 = 0.57$

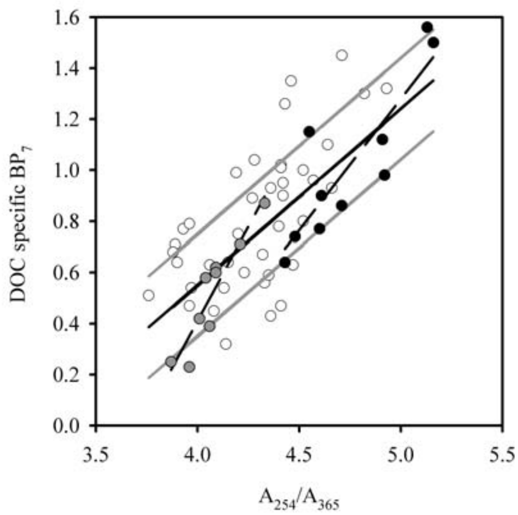

Figure 3. The regression line (solid, black) between DOC specific BP_7 (BP_7 DOC^{-1}) and the A_{254}/A_{365} ratio used to calculate BP_7. The grey lines denote the standard deviation of the residuals used in the uncertainty analysis. The grey dots are the samples from the most mire dominated catchment (C18) and the black dots represent the forest dominated catchment (C2). The dashed lines show the regression lines for C18 (R^2 = 0.87, p>0.001) and C2 (R^2 = 0.75, p>0.01). This is further described in Paper IV.

BP_7 values were obtained by measuring Bacterial Production (BP) in unfiltered stream water by the leucine incorporation method every second day during short-term bioassays (<2 weeks) in the dark at 20 °C [*Berggren et al.*, In press].

Under these conditions BP decreased rapidly during the first week of incubation, before stabilizing at a low level (Figure 4). We used the bacterial production during this first week (BP_7), as a measure of highly bioavailable DOC. BP_7 was estimated from case to case by calculating the area beneath linear BP regression lines for the first seven days of incubation (Figure 4). The method is further described in Paper IV.

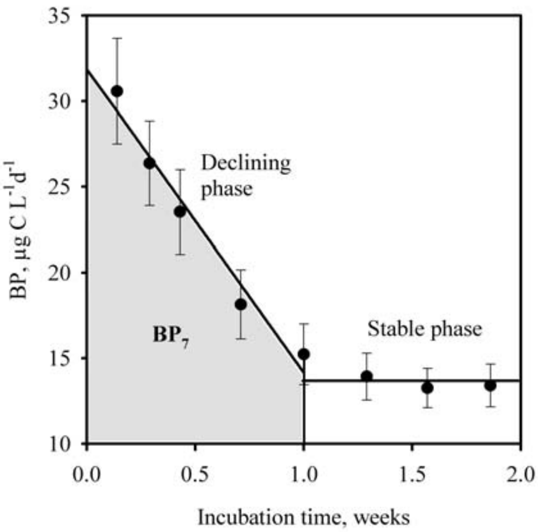

Figure 4. Illustration of BP_7 (the grey area).

7. CALCULATIONS

This chapter provides a brief description of the calculation tools used to probe the relationships between DOC and the regulating factors. The software package SPSS 14 was used for all statistical calculations.

7.1. Regressions

THE STRENGTH AND STATISTICAL SIGNIFICANCE of relationships between DOC and the measured catchment properties were assessed by linear regression analysis and curve estimation, in conjunction with tests of certain "classical assumptions" [*Gupta*, 1999].

One of the "classical assumptions" that must be taken into consideration is the form of the function. Sometimes the relationship between variables is non-linear, and in such cases use of a linear model will bias the results. SPSS's function "curvefit" was used to select the most appropriate functional form. The curvefit procedure applies 11 different models and the model that gave the highest R^2 was chosen (if it was significant). With exception of the cubic model which does not make any sense ecologically. Correlations were considered significant if $p<0.05$ and very significant if $p<0.01$.

Heteroskedasticity i.e. lack of constancy in the residuals can also pose problems. A formal test (White's test) was, therefore, applied to check that the regressions did not violate this assumption [*Gupta*, 1999].

Another "classical assumption" is that the level of collinearity between variables is sufficiently low to neglect. In cases where this assumption is violated it can be accounted for by using various methods, including Principal Component Analysis (PCA), as described below.

7.2. Principal Component Analysis

PRINCIPAL COMPONENT ANALYSIS (PCA) is a multivariate projection method used to compress information of many, often correlated variables, into a few Principal Components (PC) [*Eriksson et al.*, 2001; *Jolliffe*, 2002]. From a set of original data the PCA generates a new set of latent variables that describes the underlying variation of the original data. The method facilitates the interpretation of data by reducing the dimensionality and creating an overview of the data.

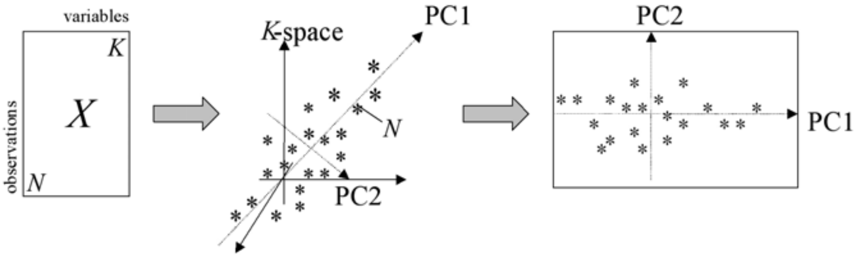

Figure 5. The principles underlying PCA, after Holm [2006].

In short, a multivariate data matrix ***X*** (Figure 5) representing *N* observations of *K* variables can be viewed graphically as *N* points in *K*-dimensional space [*Eriksson et al.*, 2001]. PCA can then be used to compress the data and extract the variation in ***X*** by generating a set of new latent variables. The *N* observations in *K*-space are thereby projected onto a straight line/vector named Principal Component 1 (PC1) by minimizing the squared residuals. Hence, the first vector, PC1 describes the largest variation in ***X***. The second Principal Component (PC2) is placed orthogonal to the first and explains the second greatest degree of variation, and so on. Together, the PCs create a hyperplane on which the observations are assigned new values, called scores (***t***) and loadings (***p***). The score can be regarded as the new variable and the loadings as the link between the score and the original variables. In a score plot, variables that have similar properties are positioned close to each other while variables of different properties are separated from each other and can normally be found on opposite sides of the plots. By superimposing the corresponding loading plot on the score plot, the observations responsible for the variation in ***X*** can be found. The new PC-based axes can, mathematically, be expressed as follows:

$$X = 1\bar{x}' + t_1 p'_1 + t_2 p'_2 + ... + t_A p'_A + E$$

The data that cannot be explained by the model are referred to as residuals (*e*), and collectively form the residual matrix (***E***). Principal Components were judged to be significant if their eigenvalues were >1. The PCA was performed using SPSS 14.

As mentioned above, the original solution of the PCA maximizes the explanation along the first vector (PC1), which describes the largest variation in ***X***. However, sometimes it is more interesting to maximize the separation of the different variables along the different vectors. This can be done by rotating the axes, for instance by Varimax rotation (as used in these studies), which keeps the axes perpendicular to each other, and thus ensures that the Principal Components are not correlated.

7.3. Monte Carlo simulations

THE UNCERTAINTIES in the measurements in the studies described in Papers II and III were assessed using Monte Carlo simulations, in which variables are generated that have normal, random distributions around an average with a certain standard deviation. The average and standard deviations used in our simulations were calculated for each variable used in the analyses. The combined uncertainty was then calculated via the propagation of error, using 10 000 iterations. These calculations were done in Excel.

7.4. Model validation

IN PAPER I TOC CONCENTRATIONS were calculated from seasonal relationships and compared to measured values. To assess the model performance two goodness-of-fit measures G were calculated: G_1 and G_2. G_1, is the model efficiency [*Nash and Sutcliffe*, 1970], which has been widely used to verify the fit of runoff series, for the evaluation of concentrations. It compares the model errors with the deviations of the observations from the observed mean concentration:

$$G_1 = 1 - \frac{\sum_t \left(C_{obs}(t) - C_{calc}(t)\right)^2}{\sum_t \left(C_{obs}(t) - \overline{C_{obs}}\right)^2}$$

where C_{obs} are measured values, and C_{calc} are calculated values from the seasonal regressions at time t.

A value of one indicates a model with a perfect fit, while negative values indicate that the model performs more poorly than the simple benchmark of the (constant) observed mean value.

However, a systematic bias leads to low values even if the dynamics are simulated acceptably. Therefore, another goodness-of-fit measure was calculated, which allows for a constant offset between observed and simulated concentrations. This measure, G_2, corresponds to the model efficiency, but with a correction for deviations in the mean values. It also equals the coefficient of determination, R^2, if the linear regression is constrained by using a fixed value of 1 for the slope (*i.e.* $y = a + x$):

$$G_2 = 1 - \frac{\sum_t \left((C_{obs}(t) - \overline{C_{obs}}) - (C_{calc}(t) - \overline{C_{calc}}) \right)^2}{\sum_t \left(C_{obs}(t) - \overline{C_{obs}} \right)^2}$$

where C_{obs} are measured values and C_{calc} are calculated values from the seasonal regressions at time t.

In other words, G_2 evaluates how well the variations are captured, but allows for a systematic difference between the absolute measured and calculated values.

8. RESULTS AND DISCUSSION

8.1. Temporal variations - the importance of runoff

THE TEMPORAL VARIATIONS in DOC concentration were most strongly correlated with runoff. A major finding was that there are seasonal relationships between runoff and TOC that could explain 60-70% of the variation in TOC, and that these relationships were similar from year to year (Paper I). Increases in runoff led to higher TOC concentrations and reductions in runoff led to lower concentrations, except during the spring flood. The spring TOC concentrations leveled out at about 10 mg L^{-1} (Figure 6) and the concentrations were independent of runoff when runoff exceeded 50 m^3 s^{-1}.

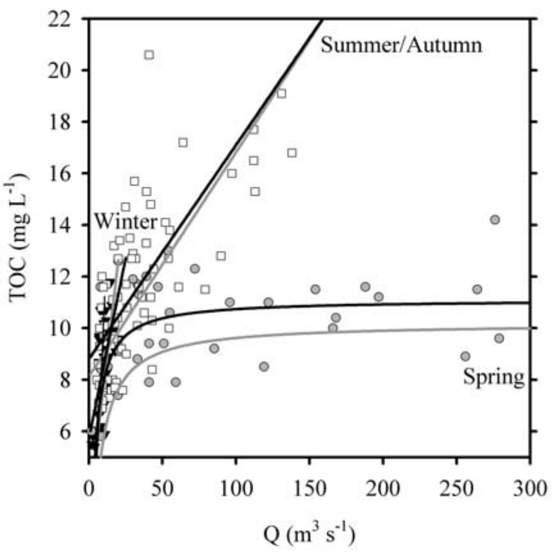

Figure 6. Seasonal regressions obtained between TOC and runoff in the detailed study (grey lines) and the long term study (black lines). The results are further described in paper I.

The results indicate that the TOC concentration in the River Öre was restricted by the size of, or access to, the soil TOC pool during snowmelt. The increase in TOC concentrations in the river when flow was high during the summer/autumn period reflected the fact that the concentration of DOC in the soil was much higher closer to the surface of the soil than at greater depths [*Bishop et al.*, 2004; *Thurman*, 1985]. During an episode the water table rises and more water reaches the stream via superficial soil layers, especially in riparian discharge areas

(Paper III) [*Bishop et al.*, 1994; *Bishop and Pettersson*, 1996; *Laudon et al.*, 2004], resulting in the increases in TOC observed during episodes.

Paper III discusses the variation in DOC characteristics during the period from winter baseflow, through spring flood and into the summer baseflow. The quality of the carbon changed with flow. The A_{254}/A_{365} absorbance ratio increased and the $SUVA_{254}$ decreased during the spring flood, suggesting that more recent and labile DOC was flushed out of the catchment soils during the high flow period (Figure 7). The absorbance ratio has been shown to reflect the bioavailability of the DOC and the high A_{254}/A_{365} ratio during spring flood indicated that the DOC compounds had a low average molecular weight [*Dahlén et al.*, 1996; *Strome and Miller*, 1978] and the bacterial growth rate was high during this time (Paper IV) [*Lindell et al.*, 1995; *Obernosterer and Herndl*, 2000].

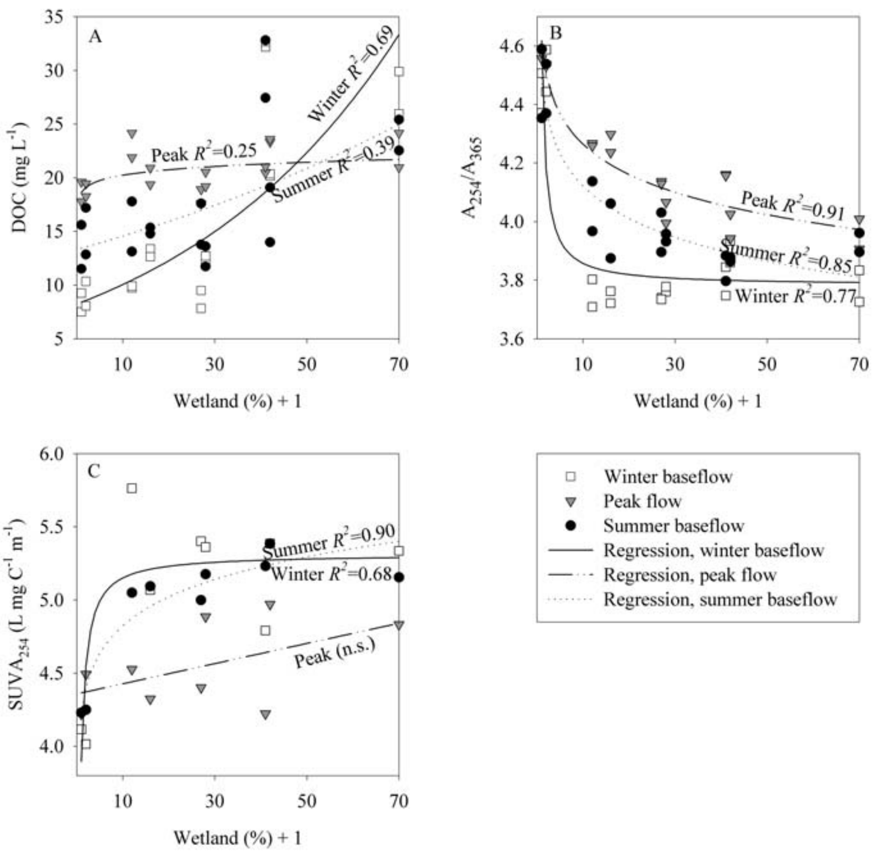

Figure 7. Variations with wetland coverage (%), in (A) stream DOC concentration, (B) absorbance ratio A_{254}/A_{365}, and (C) $SUVA_{254}$ during different flow situations. The results are further described in Paper III.

8.2. Spatial variations in DOC

IN PAPER II THE SPATIAL VARIABILITY in DOC exports from different subcatchments was related to catchment characteristics using Principal Component Analysis. Since the variations in space and time were linked, the exports were investigated during different seasons. The major finding was that the relative importance of the different catchment characteristics varied greatly between seasons due to differences in the hydrological conditions. During the winter baseflow the spatial variation of DOC was linked to patterns of wetland coverage. The amounts of DOC leached from forest soils were low during this period since the upper layers of the forest soils were above the water table, while their deeper layers, which are hydrologically connected during baseflow, are relatively poor in DOC. In wetlands, on the other hand, the porewater DOC concentration is highest below the water table [*Schiff et al.*, 1998], so deep groundwater from wetlands is especially rich in DOC during winter baseflow [*Laudon et al.*, 2004], hence the linkage to patterns of wetland coverage. During snowmelt the spatial variation in DOC export was connected to parameters describing the size and location of the catchment. The main reason for this was that the DOC levels increased in water draining forests (due to the water table rising into more organically rich soil horizons), but decreased in waters draining wetlands (due to dilution by melt water) during this period, resulting in similar DOC concentrations at all sites. Consequently, other properties became more important, i.e. the catchment size and location. The effects of these two properties will be discussed in a separate chapter below. During the snow-free season the spatial variation in DOC exports was primarily regulated by the amount of wetlands and forests, particularly forests with large proportions of Norway spruce (*Picea Abies*) trees, but median stream size also influenced the DOC exports during this season.

Paper III discusses the differences in DOC properties between the two major sources: wetlands, and the riparian zone of the forests. The A_{254}/A_{365} absorbance ratios were lower in the wetland streams (3.7-4.2) than in the forest streams (4.3-4.7), in accordance with the differences in the quality of DOC between the wetland and forest soils. $SUVA_{254}$ showed the opposite pattern, being low in the forest dominated-streams and high in the wetland-dominated streams (Figure 7). The results indicate that the materials derived from the forests have a lower molecular weight and are more aliphatic than those derived from the wetlands.

8.3. The importance of catchment size

A STRIKING FINDING of this study was the effect of catchment size on DOC exports, implying that small headwater catchments may be the largest contributors to terrestrial DOC exports, per unit area. Paper II showed that size of the catchment significantly affects DOC exports during the snowmelt and snow-free season. The highest DOC exports were found in small upstream catchments (Figure 8).

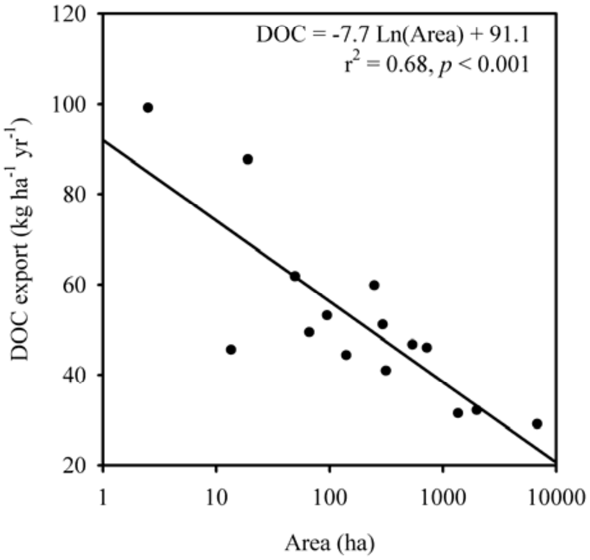

*Figure 8. The relationship between Area (ha) and annual DOC export (kg ha^{-1} yr^{-1}) for the actual drainage area of the sampling points in the Krycklan catchment***.**

In Krycklan this pattern was related not only to the size of the sub-catchments but also to differences in the quaternary deposits between upstream and downstream parts of the catchment. Catchment size may influence the DOC levels due to:

- The higher proportional input of deep groundwater, with low DOC concentrations [*Cronan and Aiken*, 1985; *Schiff et al.*, 1998; *Thurman*, 1985], in high order streams than in lower order streams.

- The greater distances between terrestrial DOC sources and streams in larger catchments increasing the subsurface water transit time, and thus the potential for decomposition and oxidation of organic carbon [*Wolock et al.*, 1997].

Since there are differences in the quaternary deposits between upstream and downstream sites in the Krycklan catchment, the location of the sub-catchments may influence the DOC in predictable ways:

- Soils change from unsorted till at higher altitudes to silty sediments downstream in the Krycklan catchment. The higher specific surface area of silt allows for more mineral adsorption sites for DOC, which may increase the mineralization of DOC in the soil and hence decrease DOC concentrations [*Kalbitz et al.*, 2000] in the downstream silty area.

- The riparian soil conditions also differ between silty soils and soils underlain by till. On till soils there were peat accumulations near the stream channel, comprising large sources of allochthonous organic carbon. In the lower-lying sediment areas there were more deeply incised stream channels, thinner soil organic layers and, consequently, less interaction between lateral water flow and organic-rich pools.

All of these characteristics and mechanisms are likely to affect stream DOC flux to some degree, collectively enhancing the export of DOC in upstream catchments compared to downstream catchments.

Another effect of stream size is that the chemical variability decreases as one moves downward in a stream system, due to mixing of water from different sources, with differing vegetation, soil, hydrology and land use characteristics [*Temnerud and Bishop*, 2005].

8.4. Bioavailability of DOC

THE BIOAVILABILITY of the exported DOC was much higher from forested catchments than wetland-dominated catchments (Paper IV). Wetlands are important for the export of DOC (Paper II) [*Hinton et al.*, 1998; *Raymond and Hopkinson*, 2003], but in Paper IV the forests were shown to be the major sources of exports of the highly labile compounds of DOC during the spring flood (Figure 9).

The mobility and biodegradability of DOC are related to the age and degree of degradation of the soil organic matter [*Bourbonniere and Creed*, 2006]. The forest DOC has higher quality than DOC from wetlands (Figure 5, Paper IV), perhaps due to exudation of low molecular weight organic acids by roots and mycorrhizal fungi in the forest soil, with contributions to some degree from other labile C sources such as dead roots and recent litter [*van Hees et al.*, 2006]. The DOC exported from the sphagnum-dominated peat wetlands has higher molecular weights and the mires have low nutrient contents, which can adversely affect the bacterial growth in water draining from wetlands. The sphagnum also contains anti-bacterial substances that can further inhibit microbial growth on DOC derived from wetlands.

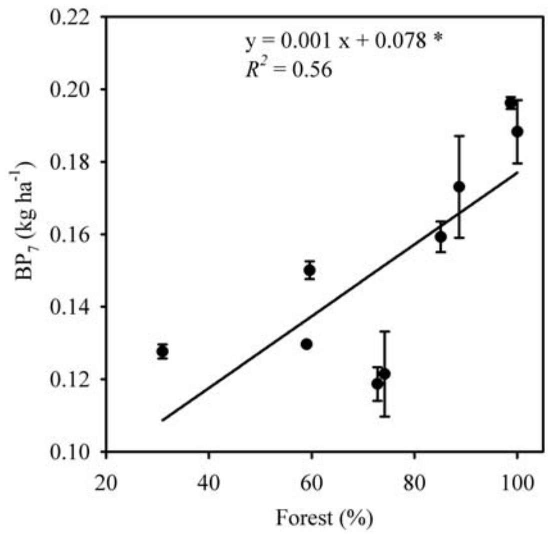

Figure 9. Average amounts of highly labile C (BP_7), calculated from A_{254}/A_{365} ratios, exported from the nine catchments examined during the spring floods in 2004 and 2005.

As mentioned earlier, most of the DOC that supported bacterial growth came from the forest. Application of the results of the bioavailability analyses to a typical catchment in boreal Sweden indicated that approximately 65 % of the DOC exported to freshwaters, and up to 90 % of the short-term bioavailable DOC (BP_7), was derived from the forests during the spring flood period. If these results are generally valid, bacterial production in boreal streams and lakes is likely to be almost entirely dependent on DOC exported from forested areas during, and some time after, the spring flood event.

9. CONCLUSIONS

THE RESULTS FROM THESE STUDIES clearly show that DOC in aquatic systems varies considerably, in time and space, quantity and character, and at different scales (Papers I-V). Runoff was found to be a major determinant of the temporal variations in DOC concentration, and TOC concentrations were positively correlated with runoff during summer/autumn and winter. However, the results also showed that during spring the TOC concentration in large rivers like the River Öre can be restricted by the size of, or access to, the soil TOC pool (I). Evidence of changes in DOC characteristics with runoff was also found. The quality of the DOC shifted during the spring flood, with increases in both aliphatic and lower molecular weight components (Papers III and IV). Changes in DOC quality observed during the spring flood were consistent with increases in DOC contributions from higher soil horizons during this period (Paper III).

The spatial variations in DOC exports and character were related to differences in the two major sources, forests and wetlands, and variations in their relative contributions to DOC between different seasons (Papers II and III). However, catchment size and location also affected the DOC exports (Paper II), especially during spring flood, and small headwater catchments exported most DOC, per unit area (Paper II). Wetlands exported more DOC (Papers II, IV), with higher molecular weight and higher aromacity (Paper III), than forested areas.

DOC from forested areas (more LMW) supported bacterial growth better than the wetland-derived DOC, in accordance with its relatively high content of LMW compounds (Paper IV). Due to the higher bioavailability of the DOC derived from forests, bacterial production in streams and lakes is likely to be almost entirely based on DOC exported from forested areas in connection with the spring flood event (Paper IV).

10. FUTURE PROSPECTS

THE OVERALL AIMS of the studies underlying this thesis were to improve the predictability of landscape regulation of DOC in boreal regions and to bridge the gap between understanding small-scale process and large-scale (catchment) exports.

For future analysis the scale resolution needs to be improved, both spatially and temporally. A way of improving the spatial scale is to use LIDAR (Light Detection and Ranging) measurements, which dramatically improve the data on the catchment topography and vegetation density, compared to the data from the maps which give a more simplified picture of the catchment. LIDAR measurements have now been conducted in the Krycklan catchments and it will be possible to view the results of the new DEM (Digital Elevation Model) in the near future.

Although the main focus of my studies was on the DOC concentration and character in streams, they have demonstrated the usefulness of soil profiles when studying the regulation of catchment exports of DOC. They also show that combining analyses of soils and streams facilitates elucidation of the links between terrestrial sources of DOC and both the quantity and quality of stream water DOC. Together with knowledge about the hydrological processes in a catchment (i.e. which soils are hydrologically connected at a certain point of time), soil profiles can provide valuable information that can help attempts to understand the regulation of terrestrial exports of DOC, and the use of soil profiles should be extended and improved in future studies.

Regarding the temporal scale, much of the research in the Krycklan catchment has been focused on the spring flood. It is, however, necessary to study rain-driven events as well. For such studies the resolution of the temporal scale must be improved. Samples for chemical analyses were collected every two days during peak flow in the studies underlying this thesis. While that may be adequate during the snowmelt flood, it is not sufficient to capture the variations during rain-driven events. More frequent registration of absorbance properties coupled with intense DOC sampling would be highly desirable for such an analysis.

In addition to the spectroscopic properties that were used to asses the quality of the DOC in these studies, future studies should evaluate the chemical variation in DOC more extensively. Since the spectroscopic properties indicate that the LMWOAs (i.e. carbohydrates, carboxylic acids, amino acids, hydrocarbons) strongly influence the bioavailability of DOC, it would also be highly desirable to monitor their abundance and composition in more detail. For example, studies on differences in the concentrations of these compounds between wetland streams and forest streams, in water from different soil horizons, and both before and after incubation for a week in the bioassays, should be given priority.

Another important aspect is the effect of catchment size on terrestrial DOC exports highlighted in this thesis. It would be of great interest to compare the results from the Krycklan catchment study in this respect with similar studies in other types of catchments to find out how well the results from this study represent boreal systems in general.

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