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Fakulteten för skogsvetenskap
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Know the flow -
Spatial and temporal variation of DOC exports and the importance of monitoring site specific discharge

Foto: Johannes Larson

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Know the flow -

Spatial and temporal variation of DOC exports and the importance of monitoring site specific discharge

Rumslig och tidsmässig variation av DOC export och vikten av områdesspecifika flödesmätningar

Johannes Larson

Nyckelord / *Keywords:*
Dissolved organic carbon, DOC, export, boreal, specific discharge, spatiotemporal variation /
löst organiskt kol, DOC, export, boreal, specifik avrinning, spatiotemporal variabilitet

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Abstract

The export of dissolved organic carbon (DOC) is an important component in both water quality and carbon cycling within boreal catchments. DOC exports are mainly controlled by discharge. Therefore, the resolution and quality of discharge data is essential when quantifying DOC exports as well as for the understanding of its spatial and temporal variation. Although there are many studies quantifying DOC exports, many fail to consider the variability of discharge between different catchments within a landscape, instead often assuming uniform specific discharge. In this study, spatial and temporal variation in DOC concentrations and exports was studied for 13 nested subcatchments of a boreal catchment located in northern Sweden. The subcatchments were studied during a nine-year observation period (2009-2017). Discharge was monitored at each site and exports were calculated using daily DOC concentrations interpolated from frequent water sampling. Positive correlations between discharge and DOC concentrations were observed for most of the sites. Higher concentrations correlated with increased wetland coverage. Seasonal variations in DOC concentrations were found between subcatchments dominated by forest compared wetlands. The annual mean DOC export ranged between 26 and 108 kg ha^{-1} yr^{-1} and correlated positively with wetland coverage ($R^2 = 0.67$, $p < 0.001$). Spatial variation on both annual and seasonal timescales, could to a large extent be explained by the catchment characteristics using principal component analysis. Forest and wetland coverage, as well as the size and elevation of each subcatchment explained most of the spatial variation of DOC exports. The importance of these catchment characteristics varied with season, where the two-month long spring season contributed between 32 to 52% of the annual DOC export. For annual exports, the proportion exported during spring season was larger for forest-dominated catchments compared to wetland catchments. Comparing export calculated adopting variable discharge to exports adopting uniform specific discharge revealed an average absolute difference of 18% ranging between 5 to 32% for individual subcatchments. DOC exports from wetland-dominated catchments were underestimated while forest-dominated catchments were overestimated. This study clearly demonstrates that adopting uniform specific discharge provides erroneous quantifications of DOC exports by not being able to capture the spatial variability within the system. This highlights the importance of discharge data with high resolution and quality when estimating element fluxes.

Keywords: dissolved organic carbon, DOC, export, boreal, specific discharge, spatiotemporal variation

Sammanfattning

Exporten av löst organiskt kol (DOC) är en viktig komponent för både vattenkvalitet och kolcykeln i boreala avrinningsområden. Exporten av DOC är till största delen kontrollerad av flöde. Därför är flödesdata av hög kvalitet och upplösning essentiell vid kvantifiering av DOC export och dess tidsmässiga och rumsliga variation. Även om det finns många studier som kvantifierar exporten av DOC, är det få som tar hänsyn till den specifika avrinningens variation inom landskapet genom antagandet av likformig specifik avrinning. I denna studie, studeras den rumsliga och tidsmässiga variationen av koncentrationer och exporter av DOC. Studien omfattar 13 delavrinningsområden i ett borealt landskap i norra Sverige under en nioårsperiod (2009–2017). Flödesmätningar utfördes vid varje avrinningsområde. Exporter beräknades med dagliga koncentrationer framtagna genom linjär interpolering mellan frekventa vattenprovtagningar. DOC koncentrationer varierade med av flöde. Höga koncentrationer korrelerade med ökad andel våtmark. Årstidsvariation av koncentrationer skiljde sig mellan delavrinningsområden dominerade av våtmark jämfört med skog. Den genomsnittliga årliga exporten av DOC var mellan 26-108 kg ha^{-1} $år^{-1}$ och korrelerade positivt med andelen vårmark ($R^2 = 0.67$, $p < 0.001$). Rumslig variation för exporter under år och årstider kunde till stor del förklaras av avrinningsområdens karaktär. Andelen skogsmark och våtmark, samt storlek och höjd över havet korrelerade med den rumsliga variationen av DOC export. Betydelsen av landskapsvariablerna varierade med årstiderna. Den två månader långa vårsäsongen bidrog mellan 32% och 52% av den årliga DOC exporten. Andelen av den årliga exporten under våren var större för avrinningsområden med hög andel skogsmark jämfört med våtmark. Export beräknad med flödesdata från varje område jämfört med att använda samma flödesdata för samtliga områden resulterade i en absolut skillnad på 18%. För enskilda avrinningsområden varierade skillnaden mellan 5% och 32%. DOC exporten från våtmarker underskattades medan export från skogsmarker överskattades vid användandet av samma flödesdata för alla områden. Denna studie demonstrerar tydligt att användandet av samma flödesdata för samtliga avrinningsområden är problematiskt vid beräknande av DOC export. Metoden gör det inte möjligt att fullt ut fånga den rumsliga variationen i landskapet. Denna studie belyser därmed vikten av flödesdata med hög upplösning och kvalitet vid beräknande av export.

Nyckelord: löst organiskt kol, DOC, export, boreal, specifik avrinning, spatiotemporal variabilitet

Table of contents

1 Introduction

Water quality of streams and lakes are regulated by the hydrology and biogeochemistry occurring within the contributing catchment. In boreal landscapes, forests and wetlands dominate the areal coverage and play a central role for hydrology and stream water chemistry. The boreal biome contains vast amounts of carbon, with dissolved organic carbon (DOC) acting as an important component in the carbon cycling (Nilsson *et al.*, 2008; Cole *et al.*, 2007). The terrestrial export of DOC plays a central role for functioning of terrestrial and aquatic ecosystems, also affecting exports of other elements (Lidman *et al.*, 2017; Lidman *et al.*, 2014). Despite many studies quantifying terrestrial DOC exports from boreal catchments, many studies fail to account for the spatiotemporal variability of discharge, often assuming it to be uniform within and across catchments (Leech *et al.*, 2016; Wallin *et al.*, 2013; Ågren *et al.*, 2008a; Ågren *et al.*, 2007; Laudon *et al.*, 2004). Previous studies have discussed the need of discharge data of high quality and resolution when estimating exports (Karlsen *et al.*, 2016b), even so very few studies meet up to this requirement.

The export and concentration of DOC in surface waters are mainly controlled by the sources of DOC and the hydrological mobilisation of these sources (Grabs *et al.*, 2012; Ågren *et al.*, 2007; Dillon & Molot, 1997). In boreal ecosystems, the dominant sources are head-water wetlands (Laudon *et al.*, 2004) and the organic horizons of the forest riparian zone (Wallin *et al.*, 2015; Laudon *et al.*, 2011; Bishop *et al.*, 1990). Wetlands have in previous studies been shown to be the most important source of DOC (Creed *et al.*, 2008; Laudon *et al.*, 2004; Dillon & Molot, 1997; Hope *et al.*, 1997). Because of the great areal extent of forests in the boreal system, the organic rich riparian soils of the forests contribute largely to the overall DOC export. The majority of the DOC exported from forested catchments has its origin in the near-surface, organic rich soils of the riparian zone (Ledesma *et al.*, 2015; Grabs *et al.*, 2012). By contrast, the DOC from the wetlands is derived from deeper soil layers that are hydrologically connected to the outlet. The forest riparian zone has been shown to have a profound control on element transport from forests uplands to stream surface waters (Lidman *et al.*, 2017).

When estimating export rates high resolution discharge data is essential, however monitoring multiple small streams is expensive. Therefore, many studies make the assumption of uniform specific discharge, using flow measurements from one catchment alone to calculate specific discharge of nearby catchments (Ågren *et al.*, 2008a; Ågren *et al.*, 2007; Laudon *et al.*, 2004). However, the spatial variability of discharge is strong and is related to catchment characteristics. On an annual timescale this variation can be explained by the difference in evapotranspiration between wetland and forest cover (Karlsen *et al.*, 2016a; Lyon *et al.*, 2012). As a consequence, assuming similar specific discharge can lead to questionable conclusions about hydrological and biogeochemical processes such as DOC export (Karlsen *et al.*, 2016b; Lyon *et al.*, 2012; Lyon *et al.*, 2010; Temnerud *et al.*, 2007).

Apart from spatial variation of DOC export and discharge it is important to consider temporal variations. Temperature and discharge have been shown to be the main drivers of DOC in surface waters (Wallin *et al.*, 2015; Koehler *et al.*, 2009). Seasonal variation of discharge in boreal catchment include periods of snow cover with low base flow, high-flow during snowmelt and snow free periods with droughts and heavy autumn rains. In boreal catchments, the spring flood is the most important hydrological event and may contain more than half of both the total yearly runoff and export of DOC (Ågren *et al.*, 2007; Finlay *et al.*, 2006; Laudon *et al.*, 2004). Snowmelt events may however have different impacts on DOC concentrations depending on the catchment being wetland or forest dominated. Rise in water table in the riparian zone of the forested catchments results in higher concentrations of DOC draining the organic rich near stream soil layers. In contrast, for wetland dominated catchments DOC concentrations during snowmelt may decrease because of dilution from melt water of low DOC concentrations (Laudon *et al.*, 2011). The proportion of annual exports during spring can therefore be greater for forest dominated catchments compared to those dominated by wetland (Finlay *et al.*, 2006; Laudon *et al.*, 2004).

Previous studies have implied that small streams are acting as the largest contributor to DOC export per unit area with large variation within the catchment (Ågren *et al.*, 2007; Hope *et al.*, 1997). In a two year study by (Ågren *et al.*, 2007) DOC exports varied from 10 to 100 kg ha^{-1} yr^{-1} between subcatchments which mounts up to the same variation found between temperate and boreal rivers throughout the world(Hope et al. 1994). The study was conducted in the Krycklan catchment in northern Sweden with export calculations based on the assumption of uniform specific discharge. However, in Krycklan this assumption has been disproved in later studies and shown to lead to an average absolute error of 20-28% for DOC exports (Karlsen *et al.*, 2016b; Lyon *et al.*, 2012).

Aim and objectives

The aim of this study is therefore to further characterize the spatiotemporal variability of DOC exports within the Krycklan catchment using site specific discharge. Nine years of DOC exports from 13 subcatchments were calculated using site specific discharge measurements and linear interpolation of DOC concentrations. With principal component analysis, I assessed how terrestrial DOC exports were determined by catchment properties and how their importance vary with season. In addition, the implications for annual exports using uniform discharge were investigated. This helps move beyond previous studies by using long term high quality and resolution discharge data thereby decreasing previous systematic errors in DOC export calculations. To achieve the objectives of this study, a number of questions were to be answered.

(1) Are DOC concentrations and exports controlled by the extent of forest and wetland?
(2) Can the importance of different seasons for DOC exports vary between subcatchments?
(3) Does the use of site specific discharge result in a higher range and variation of DOC exports?

2 Methods

2.1 Site description

This study was conducted using data collected between 2008 and 2017 within the Krycklan Catchment Study in northern Sweden (64° 16´N, 19° 46´E). The Krycklan catchment is a forested watershed of a total of 68 km^2 divided into 13 monitored subcatchments of varied size ranging from 12 to 2383 ha (Figure 2). Stream order within the catchment ranges from first to forth order. Subcatchments vary in size and proportion of catchment covered by wetland, forests and different soil types (Table 2).

The forest in the northern parts of the catchment is dominated by Norway Spruce (*Picea abies* L.) in the low-lying areas and Scots Pine (*Pinus sylvestris* (L.) H. Karts) in upslope areas. In the lower parts of Krycklan, the same species are still dominant but deciduous trees become more common consisting mostly of (*Betula pendula* Roth). Wetlands and small lakes are mainly found in the northern parts of Krycklan. The bedrock shows little variation and is dominated by 94% gneissic metagreywacke/metasediments. The catchment has a gentle topography, with elevations ranging from 127 to 372 m.a.s.l. More than half of the catchment area is situated below the highest postglacial coastline (258 m.a.s.l.). The upper parts are dominated by glacial till. In the lower parts the soil is dominated by sorted sediments of sand and silt. Forest soils are dominated by well-developed iron podzol (Laudon *et al.*, 2013).

The climate is characterized as boreal with continual snow cover and soil frost during winters. Winters are long and followed by short summers. Snow generally starts to build up during early November and snowmelt usually begins in early April, with some minor mid-winter snowmelt events occurring some years. The spring flood that follows snowmelt generally peaks at the end of April (Laudon & Ottosson Löfvenius, 2016) and the 4-6 week long period of snowmelt can contribute between 40% and 60% of the annual runoff (Laudon *et al.*, 2011). Mean annual temperature at the Svartberget climate station located in the centre of the Krycklan catchment was 2.7 ± 0.8 °C during the study period. Mean annual precipitation was 652 ± 62 mm yr^{-1} and ranged from 572 to 731 mm yr^{-1} (Figure 1).

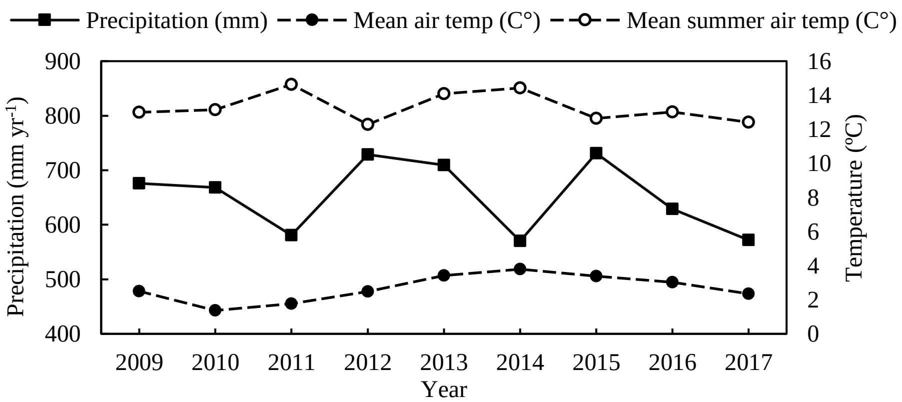

Figure 1. *Yearly precipitation (mm yr^{-1}), mean annual and summer (J-A) air temperature (°C) for water years 2009-2017.*

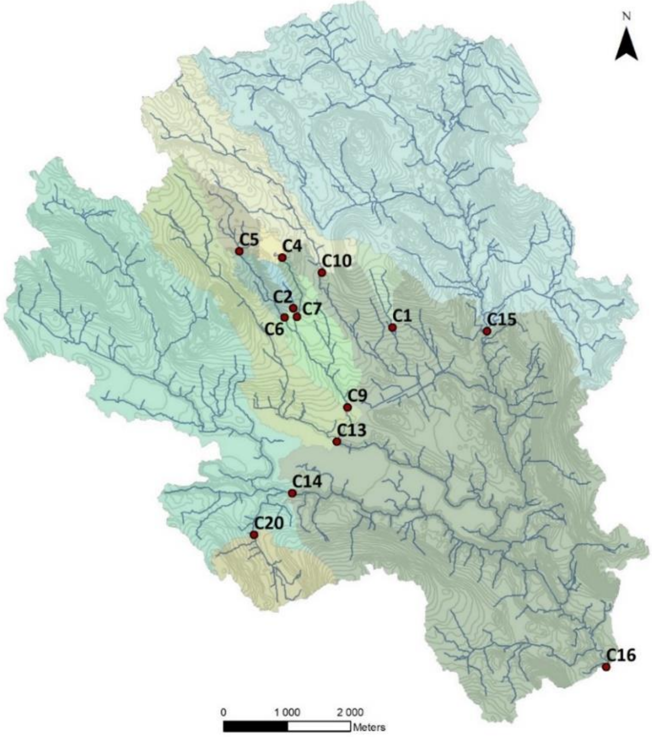

Figure 2. *Krycklan catchment study area with surface relief indicated by 10 m topographic lines and subcatchments marked in contrasting colours. Stream network is shown in blue and red circles indicate sampling and discharge monitoring locations.*

2.2 Data

2.2.1 Stream discharge data

Stream discharge was monitored 2008-2017 at 13 partly nested subcatchments including the main outlet (Table 1). The time series for catchment C13 was shorter (2009-2017) due to missing data. Monitoring discharge of smaller catchments was achieved using V-notch weirs, flumes or well defined cross sections with road culverts. Natural control sections were used to gauge the three largest subcatchments. Hourly water levels were measured continuously during the ice-free season using pressure transducers (Expert 3400, MJK A/S, Denmark) connected to dataloggers (CR100, Cambell Scientific Inc., USA), capacitance rods (WR-HT 1000, TruTrack Inc., New Zealand), radar (RLS, OTT, Germany) or floats (Recorder Model X, OTT, Germany) at the different catchments (Table 1).

Daily timeseries of discharge were gap-filled for periods with unavailable data using the HBV-model (Seibert & Vis, 2012; Bergström, 1976), following the procedure of (Karlsen *et al.*, 2016b). At six of the subcatchments year-round monitoring was made possible due to heated housings (Table 1). Discharge during winter periods for remaining subcatchments were gap filled using simulations of the HBV, modelled from nearby catchments. Frequent manual readings of water height were used as reference for correction of automatic water levels to account for logger offset. Flow values were averaged to give daily mean discharge.

Table 1. *Catchment gauging setup, (%) gap filled days and number of water samples collected.*

Site	Gauge type	Gap filled days (%)	Water level loggers	Ɛ5-year (%)	Water samples (n)
C1	90 V-notch weir	28	PT, TT	6	227
C2	90 V-notch weir[a]	14	PT, TT	8	224
C4	90 V-notch weir[a]	9	PT, TT	7	229
C5	120 V-notch weir, H-flume[b]	18	PT, TT	6	226
C6	Culvert, H-flume[c]	12	PT, TT, Float	5	228
C7	90 V-notch weir[d]	2	PT, TT	3	229
C9	Culvert	34	PT, TT	7	228
C10	Culvert	31	PT, TT	12	229
C13	Trapezoidal flume	24	PT, TT	10	201
C14	Natural section	44	TT	11	225
C15	Natural section	40	PT, TT	6	226
C16	Natural section (bridge)	33	TT, RLS	9	200
C20	Culvert	36	TT	11	223

a: heated weir since 2011; b: heated flume since 2012; c: heated flume since 2013; d: heated weir since 1981 Ɛ5-year: estimated measurement uncertainty of 5 year (2008-2013) aggregated discharge from (Karlsen et al 2016b); PT: Pressure transducer (MJK 3400, with Campbell Scientific CR1000); TT: TruTrack capacitance rods (WTHR1000); Float: OTT model X float strip chart recorder; RLS: OTT RLS Radar.

3.2.2 DOC data

A total of 2895 water samples were collected in the streams of the 13 subcatchments from October 2008 to September 2017 (Table 1). Samples were taken monthly during winter baseflow, fortnightly during high-flow snowmelt events and every second week during rest of the year. Samples were collected using acid-washed 250ml high-density polyethylene bottles after multiple rinses with stream water. Pending analyses, samples were kept cool and dark in up to a week but generally less than two days and passed through a 45µm filter before analysis. DOC analysis of water samples was conducted using a Shimadzu TOC-5000. Previous analyses in these waters have shown that particulate fractions of organic carbon (POC) contribute an insignificant proportion, suggesting that measurements of total organic carbon (TOC) and DOC essentially are the same (Laudon *et al.*, 2004; Ivarsson & Jansson, 1994). Therefore, the term DOC was used in this study.

3.2.3 Export calculation

Seasons in this study were divided into spring (A, M), summer (JJA), autumn (SO) and winter (NDJFM), following previous studies from the Krycklan catchment (Karlsen *et al.*, 2016a) based on the procedure of the Swedish Meteorological and Hydrological Institute (Verdin, 1995). Daily DOC concentrations were obtained by linear interpolation between sampling dates. The daily terrestrial DOC exports were calculated by multiplying the daily mean discharge with linear interpolated daily DOC concentrations. Many of the subcatchments are nested with upstream subcatchments. Calculations of the daily DOC exports were therefore calculated by subtracting export from upstream subcatchments according to Figure 3 and assumed to represent the DOC export of that subcatchment. Daily exports of negative values were set to zero and in-stream losses of DOC were assumed to be negligible. Annual and seasonal averages of DOC exports were calculated including annual means for the entire study period. In addition, annual exports were calculated using uniform discharge based on discharge measurements from C7. This enabled quantification of errors associated with estimating exports using the assumption of uniform specific discharge. Export calculations were performed using *R (RStudio Team, 2016).*

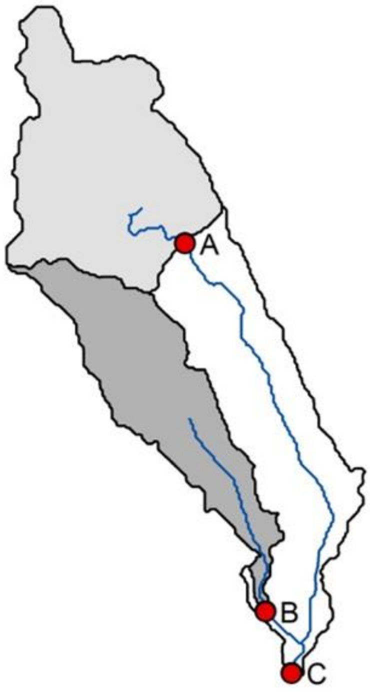

Figure 3. *Example of the export calculations for connected catchments. The DOC contribution from the downstream catchment represented by the white area was calculated by subtracting the exports from upstream catchments A and B from the export calculated at the downstream catchment C.*

3.2.4 Catchment characterization

Many landscape characteristics have the potential to influence the variance of DOC export between subcatchments. Landscape characteristics selected in this study aimed to describe aspects of the subcatchments such as soils, vegetation and location to give a representation of the variability within the whole Krycklan catchment. Catchment areas were delineated with D8 algorithm using 5m LIDAR DEM, with supporting field observations and 0.5m LIDAR DEM (Laudon *et al.*, 2013; Laudon *et al.*, 2011). Percent of catchment above highest coast line (258 m.a.s.l.) and average catchment elevation were calculated using the 2m LIDAR DEM. The Swedish property map (1:12,500, Lantmäteriet Gävle, Sweden) was used to calculate forest, lake and wetland coverage for each subcatchment (Table 2). Within Krycklan forest cover corresponds to land not covered by lakes, wetland or open land. The proportion of soil type cover was calculated for sediment soils, till and thin soils using the quaternary deposits map (1:100,000,Geological Survey of Sweden, Uppsala, Sweden). The sediment soil variable was calculated by combining cover of silt, sand and glaciofluvial sediments.

Table 2. Subcatchments used in this study and selected landscape characteristics

Site	Area (ha)	Elevation (m a.s.l.)	Forest (%)	Wetland (%)	Agr* (%)	Lake (%)	Till and Thin Soils (%)	Sediment soils (%)	Above HC (%)
C1	48	278	98	2	0	0	100	0	81
C2	12	275	100	0	0	0	100	0	85
C4	18	287	56	44	0	0	49	0	100
C5	65	293	54	40	0	6	46	0	100
C6	44	265	97	3	0	0	93	0	67
C7	17	261	97	3	0	0	100	0	54
C9	131	219	96	4	0	0	79	17	1
C10	336	297	74	26	0	0	71	0	99
C13	412	256	91	8	1	0	65	24	49
C14	1264	231	90	5	3	1	52	40	32
C15	1912	278	82	15	0	2	72	11	79
C16	2383	202	92	3	4	0	43	52	12
C20	145	211	88	10	3	0	65	21	5

* Agricultural area

2.3 Analysis

To test which catchment characteristics could explain the spatial variability of DOC concentrations, a number of regression analyses were performed. In addition, the relationships between DOC concentration and runoff were performed using Pearson's correlation.

The spatial variability of terrestrial DOC export was studied using catchment characteristics. Many of the characteristics used in this study covary and therefore a principal component analysis (PCA) was performed to obtain independent variables, so-called principal components that describe the variation of the catchment characteristics between subcatchments. The PCA attempts to explain as much variation using as few components as possible. To fulfil linear assumptions, data was transformed using Box-Cox transformation and standardized to achieve normally distributed data with equal scales. Normal distribution could not be achieved for the variables Agricultural land, Lake and Sediment soils and they were therefore excluded from the statistical analysis. The number of components explaining most of the variance was determined. Score and loading plots were then used to show the relationship between the sites and the catchment characteristics. Stepwise multiple linear regression was used to analyse linear relationships between the principal components created in the PCA and the DOC export. Diagnostic checks were carried out assure no violations of classical assumptions. Regressions were considered significant if $p < 0.05$. PCA was carried out using Minitab 17 Statistical Software (2010).

Pearson's correlation was used to investigate the impact of individual catchment characteristics on the DOC export. Partial correlation is a statistical test that describes the linear relationship between two variables while controlling for one or several additional factors. This method can be used for identifying false correlations where confounding factors create relationships where none exists and to uncover hidden relationships. Pearson's correlation and partial correlation was performed for mean annual and seasonal DOC exports. Both analyses were carried out using *R* (RStudio Team, 2016).

3 Results

3.1 DOC concentrations

Mean DOC concentrations of water samples within the studied streams ranged from 11.0 to 31.9 mg L^{-1} and absolute values varied from a minimum of 0.85 mg l^{-1} to a maximum of 58.4 mg L^{-1}. It should be noted that due to interconnection between sites DOC concentrations were dependent on upslope subcatchments. DOC concentration and runoff relationships therefore consider the actual draining area of the sampling points.

Correlation between DOC concentration and runoff varied in strength both between sampling points and with season (Figure 4). Annual DOC concentrations at site C4 were negatively correlated with daily runoff while most of the sites showed positive correlations. Seasonal DOC concentrations indicated positive correlations for most of the sites and seasons. Winter and spring was clearly different at the wetland dominated C4, showing strong negative correlations in contrast to all other sites. Comparing average DOC concentrations for winter and spring, C4 showed a decrease of 30%. In contrast, small forest catchments (C1, C2) showed a 30% increase in DOC concentrations moving from winter to summer.

Annual mean DOC concentrations were positively correlated with percent of catchment covered by wetland (R^2 = 38%, $p < 0.05$). This relationship varied with season showing the strongest relationship during winter (R^2 = 60%, $p < 0.05$) and similar during spring and autumn (R^2 = 32%, $p < 0.05$). No significant correlation was found for mean summer DOC concentrations. In addition, regression analysis showed a decrease in mean DOC concentrations for with lower elevation (R^2 = 52%, $p < 0.01$) and increased catchment area (R^2 = 55%, $p < 0.01$).

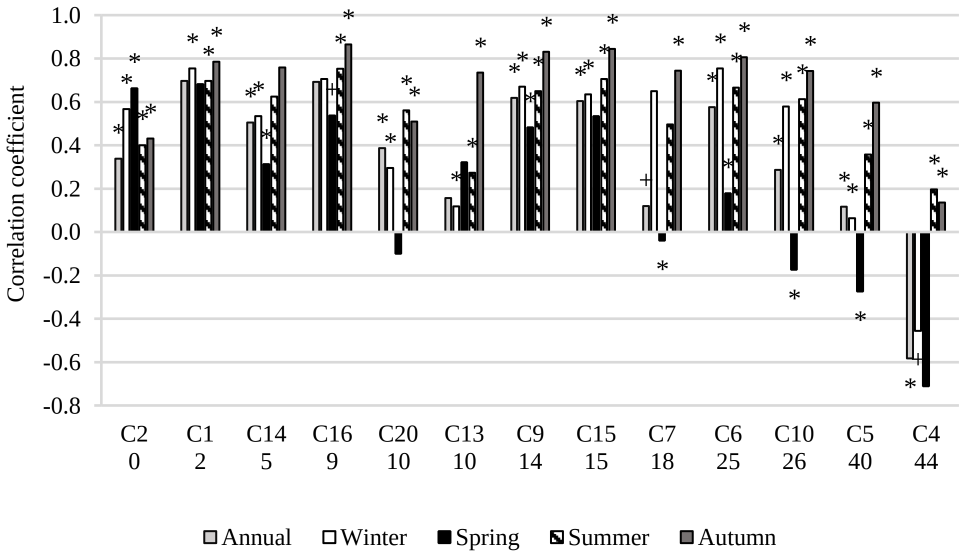

Figure 4. *Correlation coefficients for linear correlations (Pearson's correlation) between log daily runoff and log DOC concentration annually and seasonally. Significance of correlation: *p < 0.01, +p < 0.05 Analysis using data from water year 2008-2017 (2009-2017 for C13 and C16), n=34-236. Sites ordered by wetland coverage of actual drainage area for sampling point, indicated in % below site label.*

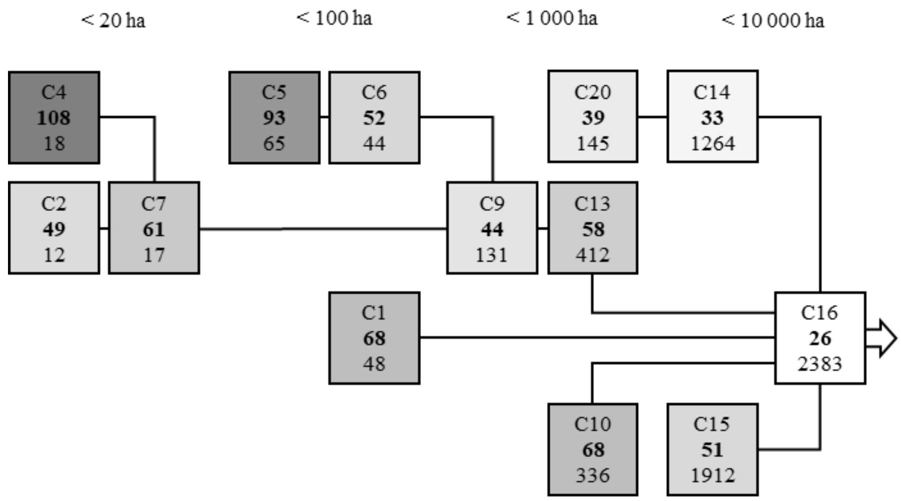

Figure 5. *DOC export per unit area (kg ha^{-1} yr^{-1}) from the 13 subcatchments (inside boxes, bold numbers) and subcatchment area in hectares (inside boxes, plain numbers). Boxes ordered in stream network (black lines) and grouped according to size with increasing area from left to right. Boxes filled in grayscale according to export per unit area, darker grey indicating higher export.*

3.2 DOC export

The annual average DOC export per unit area ranged between 26 to 108 kg ha^{-1} yr^{-1} with large variation between subcatchments with small catchments showing large export per unit area (Figure 5). Interannual variations in export were strongly regulated by variability in stream flow. Years with higher and lower annual export corresponded to years of high and low annual runoff (Figure 6).

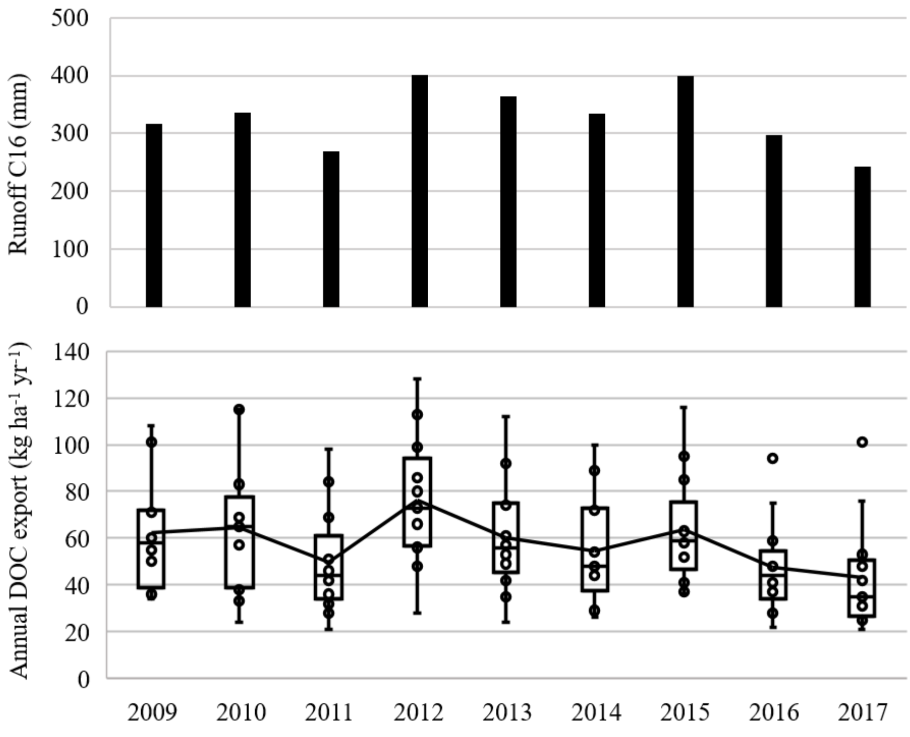

Figure 6. *(above) Annual runoff at catchment outlet and (below) annual DOC export (kg ha^{-1} yr^{-1}) for the 13 subcatchments, black line indicating mean export for all sites.*

Annual variation of DOC export for all subcatchments followed similar patterns (Figure 7). Variation between years were less pronounced at the outlet of the catchment (C16) and sites with high wetland coverage (C4, C5) had the highest export per unit area throughout the study period (Figure 7).

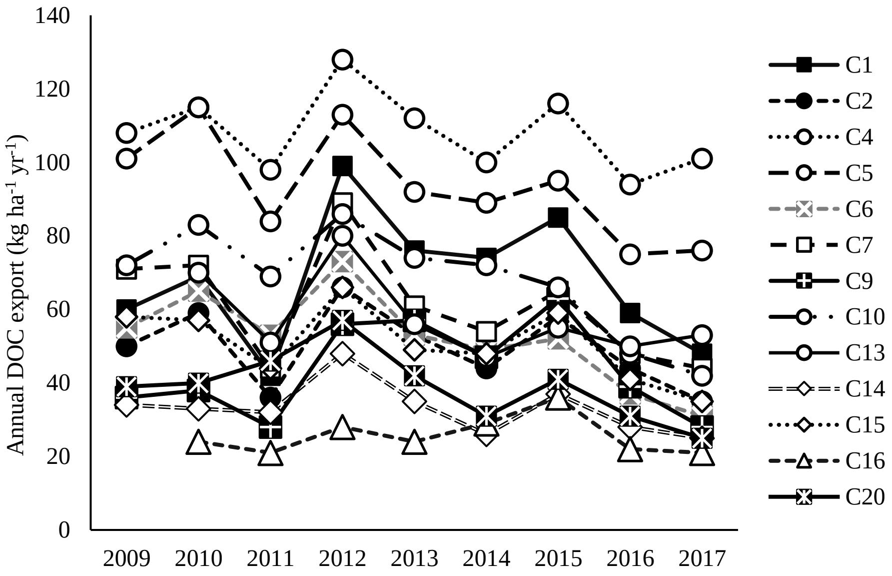

Figure 7. Annual DOC exports (kg ha^{-1} yr^{-1}) for all subcatchments

3.3 Seasonal variation

Seasonal variations of terrestrial DOC export were also strongly controlled by the variation of discharge. The two-month long spring season contributed between 30 to 60% of the annual runoff during the whole study period and the mean seasonal DOC export was highest during this season for all sites (Figure 8). The two-month long spring contributed to between 30 to 52% of the total annual export and showed clearly higher mean daily exports compared to other seasons for all catchments (Figure 8 & Table 3). Daily DOC exports were generally higher during autumn season compared to winter season (Table 3).

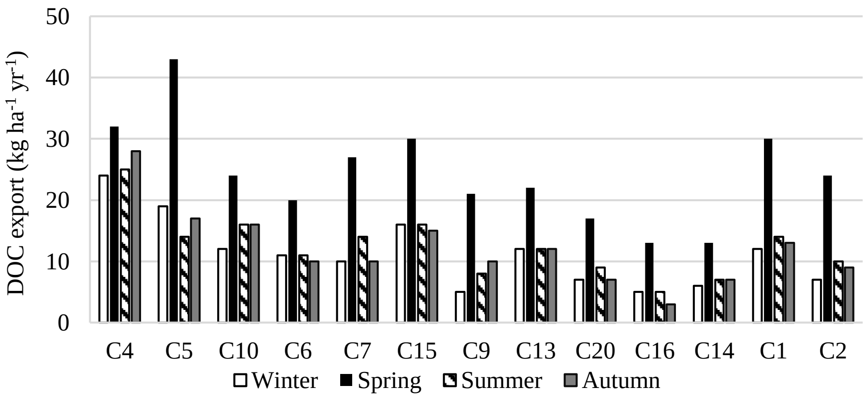

Figure 8. *Mean seasonal DOC export kg ha^{-1} yr^{-1} with sites arranged in accordance to % wetland coverage, decreasing left to right. Temporal aggregation using months with spring (AM), summer (JJA), autumn (OS) and winter (NDJFM).*

Table 3. *Average seasonal and daily mean export from all 13 subcatchments*

	Relative seasonal DOC export (%)				Daily export (kg ha^{-1} day^{-1})			
Site	Winter	Spring	Summer	Autumn	Winter	Spring	Summer	Autumn
C1	17	44	20	20	0.08	0.49	0.15	0.23
C2	14	48	19	19	0.05	0.39	0.11	0.16
C4	22	30	23	25	0.16	0.52	0.27	0.46
C5	21	46	14	19	0.13	0.71	0.15	0.30
C6	19	39	23	19	0.07	0.33	0.12	0.18
C7	15	45	22	17	0.07	0.44	0.15	0.19
C9	11	48	18	23	0.03	0.34	0.09	0.18
C10	18	36	23	24	0.08	0.39	0.17	0.27
C13	21	38	20	21	0.08	0.35	0.13	0.20
C14	18	39	22	20	0.11	0.21	0.08	0.11
C15	20	39	20	21	0.07	0.32	0.11	0.18
C16	18	52	19	12	0.03	0.21	0.05	0.05
C20	18	44	21	17	0.04	0.28	0.09	0.11

The hydrological responses of DOC export during winter and spring varied with catchment wetland coverage (Figure 9). The proportion of runoff during spring was much higher than that of DOC export for C4. The opposite was shown for the catchment outlet C16. Differences between proportions of DOC export and runoff were less during winter than during spring. Generally, the variation between sites was smaller and indicated an opposite relationship with wetland coverage compared to spring (Figure 9).

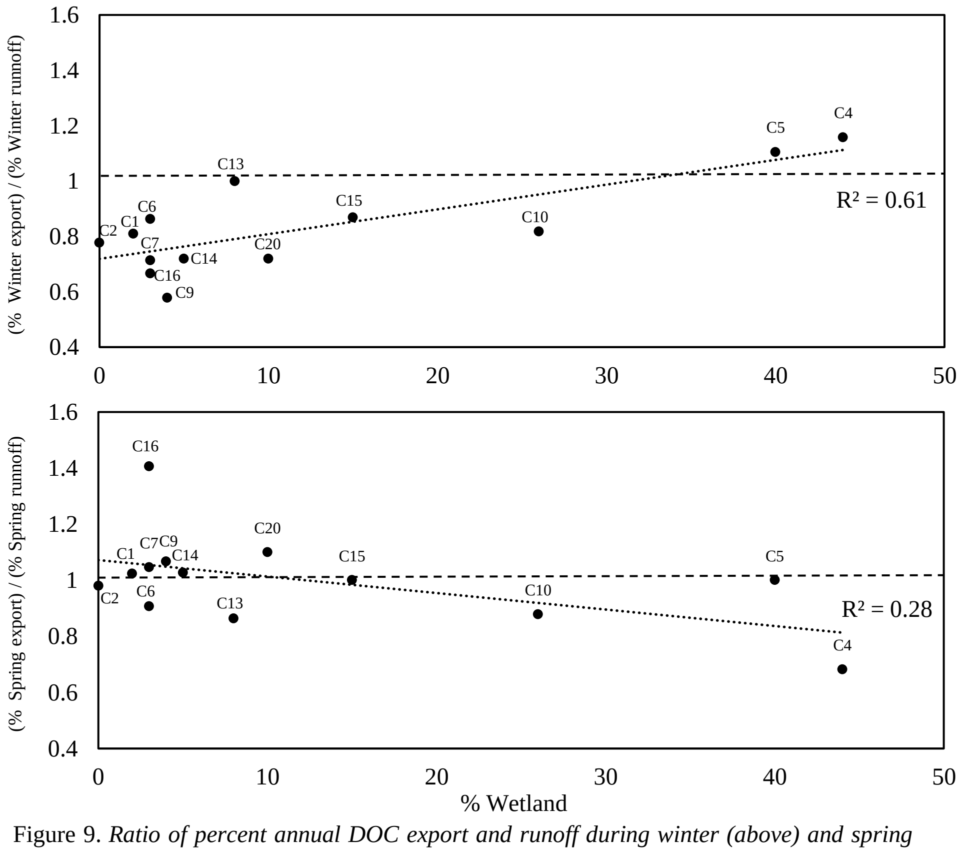

Figure 9. *Ratio of percent annual DOC export and runoff during winter (above) and spring (below) related to area of catchment covered by wetland.*

3.4 Principal component analysis

PCA including all catchment characteristics was carried out to show the variation between those variables. The three first principal components described 95% of the variation. Another PCA was then performed using only four of the catchment characteristics considered most important, simplifying the analysis. High correlation between elevation and percentage above HC resulted in double weighing in the first PCA. Only elevation was used in the second PCA to avoid double weighing. The second PCA included variables forest, wetland, elevation and area. In this PCA, the PC1 and PC2 explained 89% of the variation (Table 4). PC1 captured the variation of forest and wetland while PC2 captured the variation of area and elevation. The principal components were hence interpreted as a forest-wetland gradient (PC1) and a size-location gradient (PC2). The variation within the catchment was visualised using the score and loading plot (Figure 10). In the score plot, sites located close to each other indicate that they are more similar, while those located orthogonal indicate that they are contrasting (Figure 10). Similarly, catchment characteristics in the loading plot located close to each other indicate that they showed patterns while those located orthogonal indicated they were contrasting (Figure 10). PC1 and PC2 were non-trivial according to the broken stick stopping criteria (Jackson, 1993). The scores of the principal components were used in further stepwise linear regression analysis.

Table 4. *Eigenanalysis of the Correlation Matrix with Eigenvalues, Percentage of Explained Inertia by each component from PCA. Magnitude and direction of the coefficients for variables in the PCA.*

Eigenanalysis of the Correlation Matrix	PC1 Forest-wetland gradient	PC2 Size-location gradient
Eigenvalue	2.1951	1.3713
Proportion	0.549	0.343
Cumulative	0.549	0.892
	PCA Eigenvectors	
Variable		
Area	0.049	-0.789
Elevation	0.407	0.572
Forest	-0.654	0.109
Wetland	0.636	-0.194

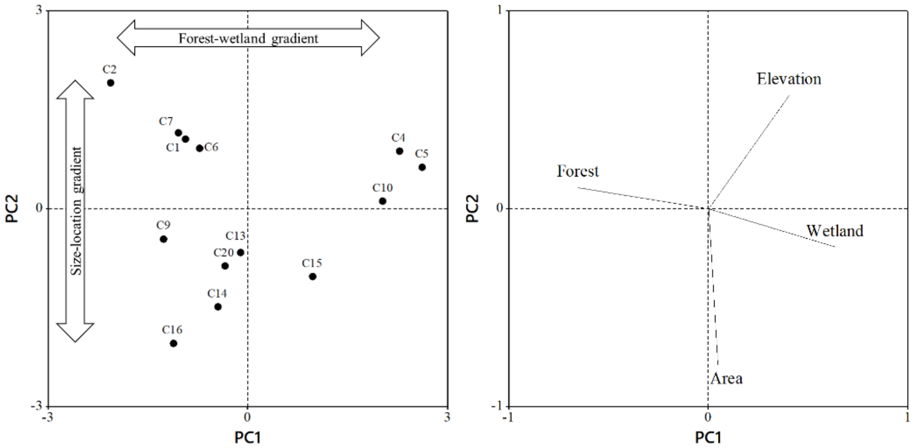

Figure 10. *(left) PCA loading plot of the two principal components and (right) PCA score plot. PC1 describes a forest-wetland gradient and PC2 a size-location gradient.*

Stepwise linear regression between DOC export and the principal components gave the following results:

(1) Mean annual DOC export = 57.7 + 11.4 PC1 + 11.6 PC2
$R^2 = 90\%$

(2) Mean DOC export during winter = 11.2 + 3.2 PC1 + 1.8 PC2
$R^2 = 82\%$

(3) Mean DOC export during spring = 24.3 + 3.5 PC1+4.0 PC2
$R^2 = 71\%$

(4) Mean DOC export during summer = 12.4 + 2.5 PC1 + 2.2 PC2
$R^2= 76\%$

(5) Mean DOC export during autumn = 12.1 + 3.3 PC1 + 2.3 PC2
$R^2= 81\%$

Importance of the different catchment characteristics on DOC exports varied with season. For mean annual DOC exports, 90% could be explained by both the forest-wetland gradient and size-location gradient. Similarly, during winter, 82% of the variation in DOC exports was explained by both principal components. However, for winter exports the forest-wetland gradient was most important by alone explaining 67% of the variation. During spring, no gradient was dominating yet together both gradients explained 71% of the variation. DOC exports both during summer and autumn could to a large extent be explained by both gradients. During summer, the forest-wetland gradient explained 52% of the variation in DOC export. Including the size-location gradient added additional 24%. For DOC exports during autumn 82% of the variation could again be explained by both principal components, but the forest-wetland gradient was the dominant factor explaining 63%. Diagnostic checks of regressions showed no sign of breakdowns of the classical assumptions.

Table 5. *Pearson Correlations between export of DOC and catchment characteristics, Partial correlation with control of wetland. Variables analysed using non-transformed catchment characteristics data. [a]For p < 0.01 [b]For p < 0.05 NS for nonsignificant.*

	C Export				
	Mean Annual	Winter	Spring	Summer	Autumn
Wetland	0.82[a]	0.84[a]	0.66[b]	0.73[a]	0.84[a]
Forest	-0.76[a]	-0.81[a]	-0.64[b]	-0.65[b]	-0.77[a]
Elevation	0.78[a]	0.75[a]	0.78[a]	0.77[a]	0.74[a]
Percent above HC	0.77[a]	0.76[a]	0.75[a]	0.75[a]	0.73[a]
Area	NS	NS	NS	NS	NS
	Partial Correlation, Control for Wetland				
Forest	0.64[b]	NS	NS	0.75[a]	0.77[a]
Elevation	0.68[b]	0.63[b]	0.66[b]	0.64[b]	0.61[b]
Percent above HC	0.63[b]	0.62[b]	0.59[b]	0.59[b]	NS
Area	-0.69[a]	NS	NS	NS	NS

3.5 DOC export correlation with catchment variables

Pearson correlation showed high correlations between several catchment characteristics and DOC export both on an annual and seasonal basis (Table 5). Till & thin soils were non-significant. Partial correlation with control for wetland showed positive correlation for forest with seasonal variations in strength (Table 5). Subcatchment area was only significant for mean annual export when controlling for wetland coverage. Using linear regression analysis, wetland coverage was found to explain 68% of the variation in mean annual DOC export ($p < 0.001$). Linear regression analysis considering actual drainage area for sampling points and mean annual DOC export (kg $ha^{-1}yr^{-1}$) showed a decrease with catchment area, indicating that the small headwaters act as the largest contributors of terrestrial DOC per unit area (Figure 11).

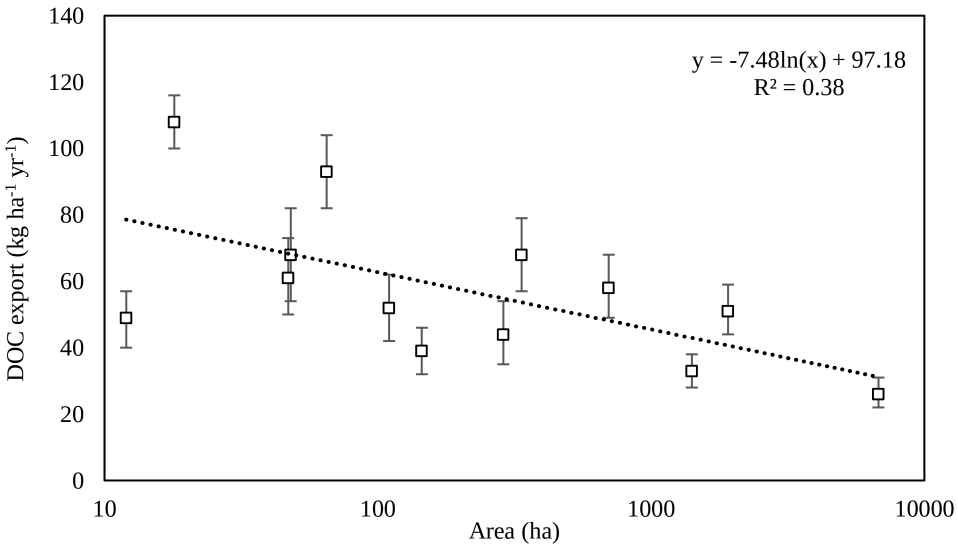

Figure 11. *Mean annual DOC export for sites plotted against subcatchment area for the actual drainage area. Error bars show the 95% confidence limits of export estimates.*

3.6 Assuming uniform specific discharge

Assuming uniform specific discharge showed clear differences in DOC exports compared to adopting site specific discharge. Calculating DOC exports using uniform discharge, resulted in both over- and underestimations with a reduction in the variability compared to the use of site specific discharge. The ratio between the inter quartile range (IQR) (defined as the difference between the 75th and 25th percentiles of the export estimates) and median showed a reduction of 7 percentage points in the overall variability using uniform discharge (IQR/median = 39%) relative to site specific discharge (IQR/median = 46%). Comparing flux estimates using uniform vs site specific discharge corresponded to an average absolute difference in DOC export of 18%. Mean differences of annual exports for individual sites ranged between 5 and 32%. Moreover, difference in DOC export estimations of the two methods was shown to correlate with wetland coverage (Figure 12). Catchments with low wetland cover were generally overestimated using uniform discharge compared to site specific. In addition, catchments with high wetland coverage tended to be underestimated. When using uniform discharge, actual drainage area could explain an additional 18% (R^2 = 55%) of the mean annual DOC exports compared to site specific discharge (Figure 11).

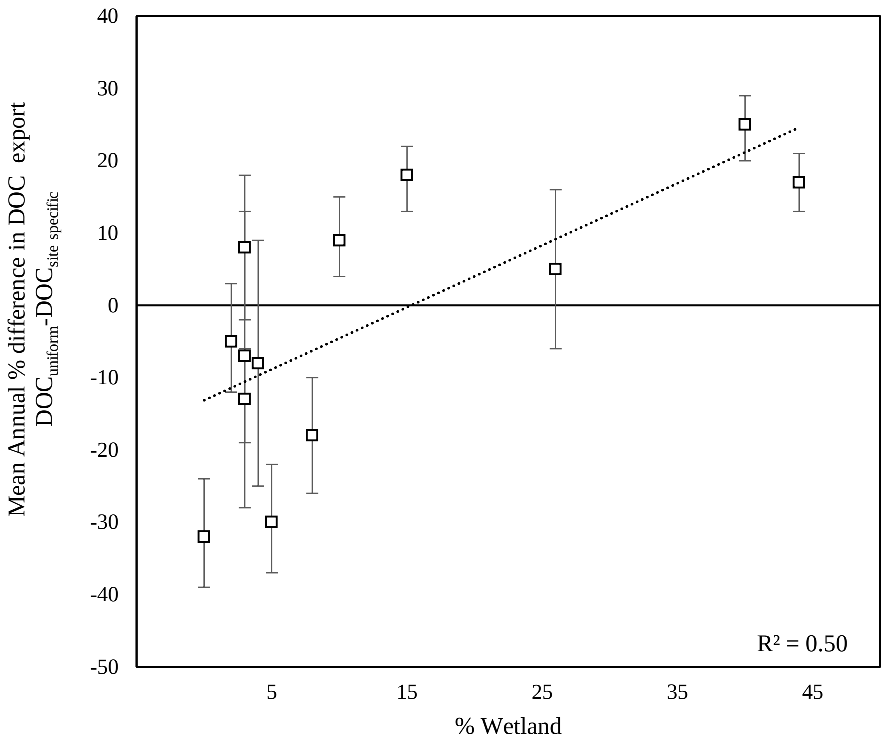

Figure 12. *Relationship between wetland coverage and the percental difference in DOC export estimation using uniform discharge compared to site specific discharge. Error bars show the 95% confidence limits of export differences.*

4 Discussion

4.1 DOC concentrations

A considerable spatial and temporal variation in DOC exports was observed between the 13 subcatchments. In accordance to many previous studies higher DOC concentrations were linked to wetland coverage (Olefeldt *et al.*, 2013; Andersson & Nyberg, 2009). In addition, the largest and lowest situated subcatchments had the lowest DOC concentrations. This relationship has previously been observed in other nearby catchments (Temnerud *et al.*, 2007). In Krycklan, this has been explained as an effect of dilution by a higher proportion of deep groundwater contribution and increased distance between the sources of DOC and stream in larger catchments (Peralta-Tapia *et al.*, 2015; Tiwari *et al.*, 2014).

Positive runoff-DOC concentration relationships has been observed in many previous catchment studies (Laudon *et al.*, 2011; Finlay *et al.*, 2006; Hope *et al.*, 1997). In line with previous studies this relationship has observed to vary with season (Dawson *et al.*, 2008; Ågren *et al.*, 2008b). The negative runoff-relationship found in the wetland dominated catchment has previously been studied in Krycklan as well as other boreal catchments (Olefeldt *et al.*, 2013; Laudon *et al.*, 2011; Jager *et al.*, 2009). The contrasting relationships found in forest and wetland catchments can be explained by the differences in DOC sources and hydrological functioning. In the forest catchments, rise in water table in the forest riparian zone results in higher concentrations of DOC caused by draining the organic rich near stream layers. During winter the water table and DOC concentrations are low. In accordance to previous studies a rise in water table during spring resulted in a large increase of DOC concentrations (Laudon *et al.*, 2011; Laudon *et al.*, 2004). In contrast to the entirely forested catchments, DOC-dynamics of wetland dominated catchments have high concentrations during winter followed by a decline during snow melt. Decline in DOC concentrations have been shown to be a result from dilution caused by overland flow over the frozen wetland surface (Laudon *et al.*, 2011).

4.2 DOC export

The annual export of DOC ranged between 26 kg ha^{-1} yr^{-1} and 108 kg ha^{-1} yr^{-1} for the 13 catchments. These DOC export estimates are consistent with previous export rates reported from other boreal catchments in Sweden (36-76 kg ha^{-1} yr^{-1}) (Laudon *et al.*, 2004) and in Finland (23-148 kg ha^{-1} yr^{-1}) (Rantakari *et al.*, 2010). Annual exports from temperate and boreal catchments around the world generally range between 10 and 100 kg ha^{-1} yr^{-1} (Hope *et al.*, 1994). This entire range could be found within the Krycklan catchment and corroborates with the large variability of DOC exports previously reported from Krycklan and other small catchments (Ågren *et al.*, 2007; Hope *et al.*, 1997). A substantial interannual and seasonal variation of DOC exports could be explained by variation in discharge. This coincides with previous studies that argue that stream discharge is the main driver for interannual and seasonal variation in DOC exports (Mattsson *et al.*, 2015; Wallin *et al.*, 2015; Köhler *et al.*, 2008).

Spatial variation of annual DOC exports could to a large extent be explained by subcatchment characteristics. Principal component regression explained 90% of the variation of DOC exports with similar importance for both the forest-wetland and size-location gradient. Explaining variation in DOC exports using similar variables have been demonstrated in previous studies (Ågren *et al.*, 2007; Temnerud & Bishop, 2005). Annual DOC exports were shown to increase with percent wetland coverage (R^2 = 67%), much in line with previous studies (Laudon *et al.*, 2004; Dillon & Molot, 1997). Wetland coverage was furthermore the single most important variable considering individual catchment characteristics on both annual and seasonal scales. However, annual and seasonal exports were also correlated with forest, elevation, percent above HC and catchment area demonstrating the complexity in spatial variation of DOC exports. Wetland coverage clearly influences the DOC export per unit area from individual subcatchments. However, it is important to note the actual contribution in the overall DOC export from the wetland dominated catchments within Krycklan. Subcatchments with high wetland coverage are among the smallest, therefore the overall contribution is low compared to exports from forests.

4.3 Seasonal variation

The seasonal variation of DOC export was substantial. Discharge during the five-month winter season was low and contributed only 22% (18-27%) of the total annual runoff. DOC export during winter added up to between 14 and 22% of the total annual export. During winter both the forest-wetland and size-location gradients explained 82% of the variation, with the forest-wetland gradient as the dominating factor explaining 67%. The importance and forest-wetland gradient can be explained by the seasonal difference in DOC concentrations between wetland and forest with low concentrations from forest riparian soils and high concentrations of DOC from wetlands. At winter base flow the majority of water is derived from deeper groundwater (Tiwari *et al.*, 2014). Tiwari et al. (2014) demonstrated that deep groundwater has a larger influence on stream chemistry than shallow groundwater, by dilution with water of low DOC concentrations compared to surface waters. The larger subcatchments of lower elevation have a larger proportion of deep groundwater input (Peralta-Tapia *et al.*, 2015), which could explain the importance of the size-location gradient in this study. High DOC exports per unit area during winter were found in subcatchments with high wetland coverage, in high elevations and high proportion above HC (Table 5).

The two-month long spring season was responsible for between 30% and 52% of the annual DOC export. The results from this study are consistent with previous studies indicating the importance of spring DOC exports (Townsend-Small *et al.*, 2011; Ågren *et al.*, 2007; Finlay *et al.*, 2006). Stepwise linear regression for showed similar importance of both principal components together describing 71% of the variation. The contrasting responses between forest and wetland for DOC concentrations during snowmelt concentration result in similar DOC concentrations between catchments. Consequently, the importance of the forest-wetland gradient was lowered compared to winter exports. Correlations with individual landscape variables showed an increase of DOC associated with increased wetland coverage, higher elevation and percent above HC (Table 5). The importance of wetland was weakest compared to other seasons, associated with the similar DOC concentrations from forest and wetland catchments.

During the winter season, the ratio between percent of annual exports and runoff changes with wetland coverage, thereby indicating different responses for forested vs wetland catchments (Figure 9). When considering spring season, this relationship is completely changed. During spring a strong opposite relationship was observed indicating that a larger proportion of the annual DOC export is derived from forests compared to wetlands. This is in line with previous studies suggesting a shift in the sources of DOC in mixed catchments when moving from winter to spring as a consequence of the contrasting discharge-concentration relationship between forest and wetland (Laudon *et al.*, 2011; Finlay *et al.*, 2006; Laudon *et al.*, 2004). The proportion of DOC exports during summer and autumn were similar with an average of 20%. Summer and autumn season are characterized by low discharge interrupted by episodes of high-flow driven by rainstorms. DOC exports during both summer and autumn could to a large extent be described using the both principal components, with the forest-wetland gradient as the dominant factor.

4.4 Assuming uniform specific discharge

This study demonstrates the implications for biogeochemical export when using uniform specific discharge. Use of uniform specific discharge resulted in significant overestimations of forest-dominated subcatchments and underestimations of wetland-dominated catchments (Figure 12). The overall variation of DOC export within the Krycklan catchment was lowered and an absolute difference of 18% was observed for annual DOC exports. This is in line with previous studies demonstrating that adopting uniform discharge is problematic and does not allow for capturing the full extent of the spatial variability of discharge and thereby DOC exports between catchments (Karlsen *et al.*, 2016b; Lyon *et al.*, 2012; Temnerud *et al.*, 2007). In Krycklan, spatial patterns of specific discharge have been shown to strongly correlate with landscape characteristics with a strong positive relationship with coverage of wetlands. On an annual timescale, higher specific discharge can be explained by differences in evapotranspiration between forested and wetland areas (Karlsen *et al.*, 2016a). As expected this corresponds well with the difference observed in this study comparing estimates of DOC export using uniform and site-specific discharge. An important factor for this difference is obviously which catchment to reference for the uniform discharge. The choice for this study was based on previous studies estimating landscape scale exports by using site C7 (Lidman *et al.*, 2014; Ågren *et al.*, 2014; Ågren *et al.*, 2007).

Ågren et al. (2007) concluded that small headwaters were acting as the largest contributor of DOC per unit area, thereby having a disproportionally large influence on DOC exports. However, as demonstrated in this study the importance of catchment area was decreased by 18% when using site specific discharge compared to uniform discharge. Similarly, in the study by Temnerud et al. (2007), the use of uniform specific discharge lead to an overestimated importance of headwaters for calculated fluxes compared to using site specific discharge. This is in line with the results from this study clearly demonstrating that the variability of specific discharge is a key factor for the spatial and temporal variation of DOC exports. Therefore, ignoring this variability by assuming uniform specific discharge may lead to misinterpretations of the spatial and temporal variation of DOC exports as well as for any other mass exports.

4.5 Uncertainties

The uncertainty of the absolute flux estimates is large, mainly due to uncertainties in discharge estimates, linear interpolation and sampling frequencies. In the study by Karlsen et al. (2016b), the five-year study period (2009-2013) average long-term discharge uncertainty was estimated to ±8%. This uncertainty was assumed to mainly be caused by errors in rating curves and gap-filling. By using linear interpolation, the variation in DOC concentration between sampling occasions is not considered. Changes in DOC concentrations between sampling occasions caused by for example rain events can therefore not be captured. At the majority of the sites discharge data during winter consists to a large extent (up to 97%) of modelled gap-filled data from sites with heated housings. Consequently, the uncertainty of winter DOC export was considerably higher. Spatial variability of exports during winter is therefore an effect of variation in DOC concentration and not variation in specific discharge. In this study no in-stream loss of DOC was assumed. While DOC removal by in-stream processes is present, studies have suggested that the loss is of no quantitative importance (Tiwari *et al.*, 2014). Due to subcatchment interconnection, export calculations for many subcatchments have a large degree of uncertainty. Exports from downstream subcatchments are to a large degree affected by upstream exports. Most studies of DOC export most likely underestimate annual exports because of inadequate sampling frequencies to completely account for the higher discharge events which lead to increased DOC concentrations and transport (Strohmeier *et al.*, 2013; Mulholland, 2003). Nevertheless, few studies use higher frequency than used in this particular study.

4.6 Conclusions

This thesis, based on a nine-year study period of 13 subcatchments, demonstrates that the variation in the main sources of DOC determine the spatial variation of annual DOC exports. Annual and seasonal variation of DOC concentration and exports between subcatchments could to a large extent be explained by the variation in catchment characteristics. Previous studies have come to similar conclusions. However, by using site specific discharge it is possible to account for the large influence of the spatiotemporal variation in discharge, revealing a more accurate and complex picture than offered previously. The importance of spring season for annual exports was shown to be greater for forested catchments compared to those with high wetland coverage. Furthermore, this study demonstrates the consequences of the assumption of specific discharge when estimating catchment exports in some cases resulting in an error above 30%. Exports from forest subcatchments were generally overestimated while wetland catchments were underestimated. This study clearly demonstrated that adopting uniform specific discharge when quantifying exports is troublesome and cannot capture the full extent of the spatial variability of DOC exports. This study confirms the importance of high quality and resolution discharge data by monitoring discharge at specific catchments.

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