JOURNAL OF GEOPHYSICAL RESEARCH, VOL. 112, G03003, doi:10.1029/2006JG000381, 2007

Importance of seasonality and small streams for the landscape regulation of dissolved organic carbon export

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Received 23 November 2006; revised 19 April 2007; accepted 8 May 2007; published 19 July 2007.

[1] The regulation of the spatial and seasonal variation in terrestrial dissolved organic carbon (DOC) exports was studied in a 68 km^2 boreal stream system in northern Sweden. A total of 1213 DOC samples were collected in 15 subcatchments over a 3 year period (2003–2005). The mean annual DOC exports from the 15 subcatchments (0.03–21.72 km^2) ranged from 14.8 to 99.1 kg ha^{-1} yr^{-1}. Many catchment characteristics determined the spatial variation in DOC exports. The relative importance of the different catchment characteristics varied greatly between seasons because of differing hydrological conditions. During winter base flow the spatial variation was linked to patterns in wetland coverage. During snowmelt in spring the spatial variation was connected to characteristics describing size and location, i.e., median stream size, silty sediment distribution, stream order, altitude, and proportion of catchment above highest postglacial coastline (HC). During the snow-free season the spatial variation in DOC exports was regulated by the amount of wetlands and forests, particularly forests made up of Norway spruce (*Picea abies*). Median stream size also influenced the exports during this season. A striking result in this study was the effect of size implying that small headwaters may be the largest contributor to the terrestrial DOC export, per unit area.

Citation: Ågren, A., I. Buffam, M. Jansson, and H. Laudon (2007), Importance of seasonality and small streams for the landscape regulation of dissolved organic carbon export, *J. Geophys. Res.*, *112*, G03003, doi:10.1029/2006JG000381.

1. Introduction

[2] Dissolved organic carbon (DOC) that is exported from soils to surface waters has many effects on the ecology of aquatic systems. It is a source of nutrients and energy for heterotrophic bacteria, and the mineralization of allochthonous DOC turns aquatic systems into net sources of CO_2 to the atmosphere [*Duarte and Prairie*, 2005]. In northern Sweden the episodic stream water pH decline during spring flood and autumn storm episodes is mainly driven by the organic acids associated with increasing DOC [*Laudon et al.*, 2000; *Laudon and Bishop*, 2002]. DOC also affects the export and toxicity of metals [*Bishop et al.*, 1995], but its effect on metals is complicated and double-edged. For example, the lowering of pH by the organic acids increases the aluminum levels in the aquatic system because of increased mobility and the low pH also changes the aluminum into a more toxic form. At the same time, DOC decreases the toxicity of metals by binding Al into a less toxic organic form [*Cory et al.*, 2006]. The organic carbon thereby affects the survival of fish during acid episodes by decreasing the toxicity of Al [*Laudon et al.*, 2005]. Given the large impact of DOC in the aquatic ecosystems, it is important to understand the regulation of the terrestrial carbon exports.

[3] Terrestrial DOC export is determined by interacting catchment characteristics such as soil type, vegetation, and hydrology [*Cronan et al.*, 1999; *Dillon and Molot*, 1997]. Consequently, there are large variations in the DOC export on spatial [*Clark et al.*, 2004; *Dawson et al.*, 2004; *Mulholland*, 2003] and temporal [*Hope et al.*, 1994; *Laudon et al.*, 2004a] scales. Wetland coverage is often a good predictor of stream water DOC concentrations and fluxes. Riparian wetlands, in particular, can be a major source of DOC in forested catchments, especially during high-flow situations [*Bishop et al.*, 2004; *Hinton et al.*, 1998].

[4] Although wetlands often have a high export of DOC, leaching from forest floors has also been reported to control the terrestrial carbon export and DOC concentrations in surface waters [*Clark et al.*, 2004; *Hinton et al.*, 1997; *Hongve*, 1999; *Schiff et al.*, 1998; *Thurman*, 1985]. The amount of DOC exported depends on the type of forest. Leaching is higher from Norway spruce stands compared to Scots pine stands because of the higher production of litter in the spruce forest floor [*Strobel et al.*, 2001]. Deciduous litter is most easily degraded, and the DOC yield from deciduous litter has been found to be higher than from spruce litter [*Hongve*, 1999; *Hongve et al.*, 2000].

[5] Catchment area is another important parameter linked to the spatial variation in the DOC export. Interstream variation in DOC concentrations is higher for small streams than large rivers [*Driscoll et al.*, 1988; *Sedell and Dahm*, 1990; *Temnerud and Bishop*, 2005; *Wolock et al.*, 1997]. A

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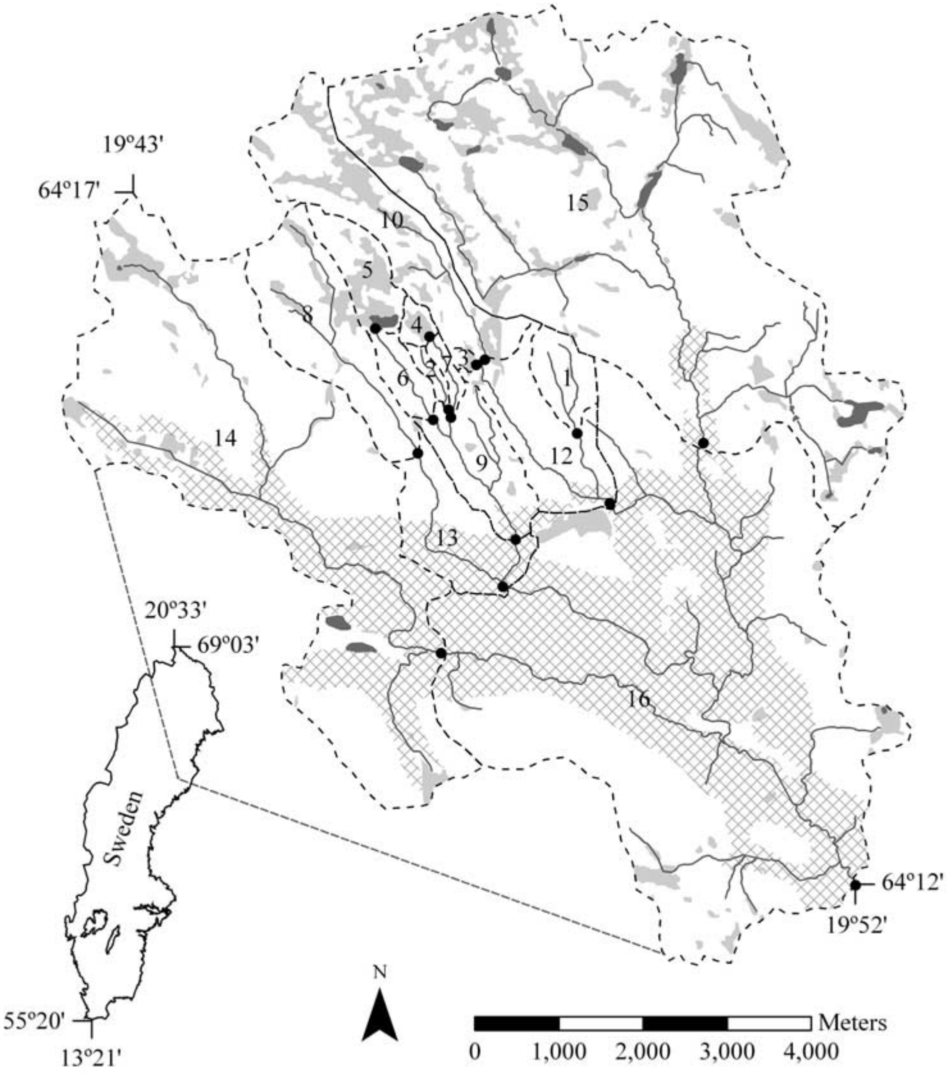

Figure 1. Krycklan catchment with the stream network (solid), the 15 subcatchments (dotted), and the sampling sites (black dots). Lakes are in dark grey, wetlands are in light grey, and silty sediments are crosshatched.

major factor in reducing the variability of DOC concentrations in rivers with distance downstream is mixing of different sources. DOC concentrations and export also often decrease with distance downstream [*Mattsson et al.*, 2003; *Temnerud and Bishop*, 2005; *Wolock et al.*, 1997]. Possible reasons for a downstream decrease in DOC include changing hydrological pathways in soils and increasing proportion of postglacial sediments deposited in the lower lying parts of a catchment that reduce the export because of DOC adsorption on the mineral surfaces [*Kalbitz et al.*, 2000].

[6] In addition to the spatial variation in DOC export caused by catchment vegetation and soil properties, there are considerable temporal variations linked to hydrological variations. The highest export is connected to high-flow episodes [*Meybeck*, 1982; *Schiff et al.*, 1998]. However, hydrological events can have a different impact on DOC depending upon soil types or other catchment characteristics. For example, in forested catchments the stream DOC levels often increase during spring flood because of rising water tables flushing out DOC-rich water previously stored in the soil [*Hornberger et al.*, 1994]. In boreal streams that drain wetlands the DOC levels sometimes decrease during spring flood because of dilution by snowmelt water that reaches the streams with minimal soil contact due to impermeable soil frost and/or saturated surfaces [*Laudon et al.*, 2004a; *Schiff et al.*, 1998].

[7] Catchment DOC export is regulated by a combination of parameters that vary in time and space. To what extent the different factors will affect the DOC export from a catchment depends on the spatial distribution of catchment characteristics and the hydrological regime. We carried out a study to assess (1) how the terrestrial DOC export was determined by different catchment properties, (2) how DOC export was dependent on, and varied with, seasonal hydrological conditions, and (3) whether small headwaters were larger contributors to catchment export than streams of

Table 1. Quaternary Deposits and Forest Characteristics for the Subcatchments[a]

Site	Name	Till, %	Silt, %	Coarse Sediments, %	Thin Soils, %	Rock, %	Total Stem Volume, $m^3\ ha^{-1}$	Spruce, $m^3\ ha^{-1}$	Pine, $m^3\ ha^{-1}$	Deciduous, $m^3\ ha^{-1}$
1	Risbäcken	94.2	0	0	5.8	0	99	53	35	11
2	Västrabäcken	86.2	0	0	13.8	0	204	99	89	16
3	Lillmyrbäcken	46.4	0	0	0	0	114	38	66	9
4	Kallkällsmyren	8.8	0	0	31.6	0	108	43	51	13
5	Stortjärnen Outlet	48.4	0	0	5.7	0	64	20	36	8
6	Stortjärnsbäcken	73.7	0	0	18.1	6.4	136	60	65	10
7	Kallkällsbäcken	97.4	0	0	2.6	0	191	82	95	14
8	Fulbäcken	62.7	0	0	20.0	1.6	85	32	43	10
9	Nyängesbäcken	80.4	13.4	3.2	0	1.7	129	43	71	16
10	Stormyrbäcken	58.3	0	1.2	11.1	0	63	19	35	9
12	Nymyrbäcken	71.4	8.4	12.9	4.2	0	121	52	55	15
13	Långbäcken	40.6	59.4	0	0	0	106	38	57	12
14	Åhedbäcken	49.9	31.4	1.9	7.5	1.7	70	23	37	9
15	Övre Krycklan	65.5	2.3	8.5	7.6	0.8	57	17	31	8
16	Krycklan	34.4	54.9	1.1	5.1	1.5	74	23	41	10

[a] Peat was excluded because it is essentially equivalent to wetland coverage in the land cover table (Table 2).

higher order. The study was carried out using data from 15 subcatchments in the 68 km^2 Krycklan experimental catchment in northern Sweden.

2. Material and Methods

2.1. Study Area

[8] The Krycklan catchment is a forested watershed situated in the central boreal zone. The whole catchment is 68 km^2 and consists of 15 subcatchments which range from 0.03 to 21.72 km^2 (Figure 1). The bedrock consists of Svecofennian rocks with 94% metasediments/metagraywacke, 4% acid and intermediate metavolcanic rocks, and 3% basic metavolcanic rocks. The quaternary deposits are dominated by till (Table 1). Wetlands are common in the upper flatter parts of the catchment and cover between 0 and 76% of the subcatchments. Approximately 56% of the Krycklan catchment area is below the highest postglacial coastline (HC). The postglacial sediments in these parts of the catchment are dominated by silt which covers up to 59% of the lower lying subcatchments. The silty sediments were deposited in the distal part of a postglacial delta. The sediment deposits form a thick layer through which the larger traversing streams have deeply incised channels forming ravines and bluffs of up to 30 m height. Agricultural land covers only 1% of the total catchment. Forest covers most of the catchment (on average 84%, ranging from 24 to 100% between subcatchments) and is composed of about 40 vol % Norway spruce (*Picea abies*), 50 vol % Scots pine (*Pinus sylvestris*), and 10 vol % deciduous forest stands, mainly birch (*Betula ssp.*). The forest soil is predominantly well-developed iron podzol. Surface waters (sum of lake and stream area) cover 0.1–4.7% of the subcatchments. Stream order ranges from first to fourth order. Mean annual air temperature is 1.3°C, and the annual precipitation is 600 mm of which about approximately 50% becomes runoff. The area has on average 5 months of snow cover, and about 35% of the precipitation falls as snow [*Löfvenius et al.*, 2003].

2.2. Sampling and Calculations

[9] Site 7 is used as an index site. In the 0.5 km^2 Nyänget catchment (composed of site 7 and up-stream sites 2 and 4, Figure 1), soil hydrologic parameters, streamflow, and chemistry have been monitored since 1980. Discharge has been monitored continuously (every 10 s) at site 7 using a 90° V notch in a heated dam house. Discrete discharge measurements using salt dilution or bucket flow ($N = 259$) at the 15 sites were used to assess the intersite uncertainty in the discharge between the 15 sites. Daily discharge was calculated using continuous registration of the stream water level and established height-discharge rating curves. A total of 1213 water samples were collected in streams in the 15 subcatchments (Figure 1) from January 2003 to December 2005. Samples were collected in acid-washed 250 mL high-density polyethylene bottles after multiple rinses with stream water. Samples were taken frequently during the high-flow snowmelt season (every 2 days) and less frequently during the rest of the year (weekly to monthly sampling). Samples were kept cool and dark up to 1 week but typically less than 2 days until processing. During 2003 and 2005, samples were frozen until analysis without filtration. During 2004, samples were filtered through a 0.45 μm mixed cellulose ester (MCE) filter and were then frozen until analyzed. A comparison between sites covering the extremes of observed flows showed that there was no measurable difference in the concentration because of filtering. This result is in agreement with other studies of Swedish surface waters [*Ingri*, 1996; *Ivarsson and Jansson*, 1995; *Laudon and Bishop*, 1999] which found particulate organic carbon concentration to be negligible relative to the dissolved fraction. Thus we use the term DOC for all samples in this study. Samples were acidified and sparged to remove inorganic carbon before DOC was measured using a Shimadzu total organic carbon-V$_{PCH}$ analyzer.

[10] Flow values were averaged to give a daily mean discharge. Higher-frequency samples (every 3 hours for 24 hours) taken at 8 of the 15 sites during spring flood and autumn low flow revealed little variation in DOC concentration on this timescale (mean coefficient of variation 4%) and no clear diurnal pattern (I. Buffam, unpublished data, 2005). We therefore assume that only a minor bias, if any, is introduced by our DOC sampling regime, which involves sampling different sites at different times of day, or in the transferring of the high-resolution flow measurement to daily mean discharge.

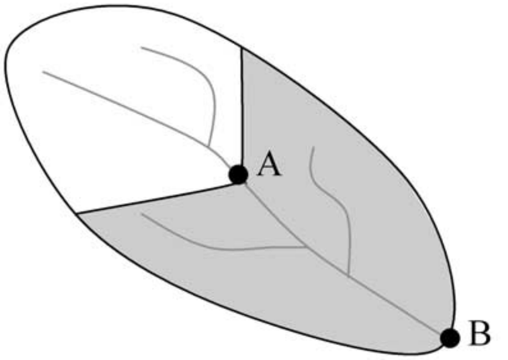

Figure 2. Example of the transport calculations for connected catchments. The transport calculated from the upstream site (A) was subtracted from the transport calculated at the downstream site (B) to obtain the DOC contribution from the downstream catchment represented by the grey area.

[11] The DOC sample was assigned to the day of the sampling. Daily values of DOC were obtained by linear interpolation. A previous comparison between linear interpolation of DOC and flow-dependent regression showed that the two methods produced comparable results (at most 10% discrepancy) [*Laudon et al.*, 2004a]. The daily terrestrial carbon exports were then calculated by multiplying the daily discharge with the linearly interpolated daily DOC. Seasonal exports were obtained by summarizing daily exports. All 15 stream sites were sampled for DOC during the same day. Specific discharge at site 7 was used to estimate the discharge in all subcatchments, assuming that specific runoff was the same in all catchments. Seasonal DOC export was analyzed for three seasons: the snowmelt season, the snow-free season, and the snow covered season. The snowmelt season, which is characterized by high flow, was defined as the period from the steep incline in the hydrograph due to the first snowmelt to the first summer base flow situation (16 March to 4 June 2003, 15 April to 10 June 2004, and 5 April to 3 June 2005). The snow-free season, which is characterized by low flow with occasional episodes due to rain, was defined as the period from the first summer base flow situation to the end of the last event of the fall, i.e., establishment of the winter base flow (5 June to 25 November 2003, 11 June to 21 November 2004, and 4 June to 24 November 2005). The snow covered season, which is characterized by a stable low flow, was subsequently defined as the period from the end of the last event of the fall to the steep incline in the hydrograph due to the first snowmelt (26 November 2002 to 15 March 2003, 22 November 2003 to 14 April 2004, and 25 November 2004 to 4 April 2005). This division was based on previous studies showing the dependence of DOC concentration on these major hydrological variations [*Heikkinen*, 1990; *Mulholland and Hill*, 1997].

[12] Because many of the sampling sites are connected with upstream catchments, we calculated the transport for the different subcatchments as shown in Figure 2. The subcatchment area is defined as the grey area.

[13] We consider that the calculated transport represents the terrestrial DOC export. We assume no in-stream loss of DOC because during high flow when the largest exports occurred, the in-stream transit time was generally less than 10 hours, which is too short for substantial degradation of the highly recalcitrant allochthonous DOC [*Hessen and Tranvik*, 1998; *Kohler et al.*, 2002].

2.3. Catchment Characteristics

[14] Maps, complemented with field observations, were used to characterize the subcatchments. A parameter "median stream size" was generated for each subcatchment using a raster stream network developed for the Krycklan catchment based on gridded elevation data (DEM) with a grid resolution of 50 m. The stream network consisted of 1654 stream cells, and for each stream cell the catchment area draining through the particular stream cell was calculated. 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 is expressed in units of area. The DEM was also used to calculate the proportion of the subcatchment above HC (areas with altitude higher than 257.5 m above sea level (asl)). The digital Swedish topography map (1:100,000) (Lantmäteriet, Gävle, Sweden) was used to define the parameters: stream order at the sampling point; the altitude of the sampling point; and the proportion of surface water, forest, wetland, and agricultural areas within each subcatchment. The soil map (1:100,000) (Geological Survey of Sweden, Uppsala, Sweden) was used to define the proportion of silt, sand, glaciofluvial sediments, till, thin soils, rock, and gravel within each subcatchment. A problem for the statistical analysis was that many of the sediment types were only found in one or a few of the subcatchments, which meant that we could not find any statistically significant relationships for those parameters. Sand, gravel, and glaciofluvial sediments (ice river alluvium, mostly gravel and sand) were therefore added into a joint parameter called coarse sediments, which increased the number of observations and the power in the statistical analysis. Forest information for the watershed was estimated from satellite data from the national forest inventory by the *k* nearest-neighbor method [*Reese et al.*, 2003]. The total stem volume and the volume of Norway spruce (*Picea abies*), Scots pine (*Pinus sylvestris*), and deciduous forest, mainly birch (*Betula ssp.*), were used. A total of 17 different landscape characteristics were used to characterize the subcatchments (Tables 1 and 2).

2.4. Statistical Analyses

2.4.1. Principal Component Analysis

[15] The catchment characteristics in Tables 1 and 2 were studied in order to explain the spatial difference in the terrestrial DOC export between subcatchments. Since many of the catchment characteristics covary, we used principal component analysis (PCA) to obtain independent variables, the principal components, which describe the variation of the catchment characteristics between the subcatchments. Before the PCA was performed, the data were preprocessed and transformed to achieve normally distributed data in order to fulfill important linear assumptions. The coverage of agricultural area could not be transformed into normal distribution and was therefore excluded from the analysis.

Table 2. Land Cover and Other Characteristics of the 15 Subcatchments[a]

Site	Name	Area, km^2	Stream Order	Median Stream Size, ha	Altitude, m asl	Above Highest Coastline, %	Forest, %	Wetland, %	Surface Water, %	Agricultural Area, %
1	Risbäcken	0.66	2	16	227	82	98.7	1.3	0.2	0
2	Västrabäcken	0.14	1	17	247	74	100	0	0.4	0
3	Lillmyrbäcken	0.03	1	3	256	82	24	76	0.3	0
4	Kallkällsmyren	0.19	1	16	282	100	59.6	40.4	0	0
5	Stortjärnen Outlet	0.95	1	76	286	100	59	36.3	4.7	0
6	Stortjärnsbäcken	0.45	1	97	236	70	99.1	0.9	0.2	0
7	Kallkällsbäcken	0.17	2	28	245	63	100	0	0.4	0
8	Fulbäcken	2.48	2	68	234	87	88.7	11.3	0.2	0
9	Nyängesbäcken	1.24	3	54	184	1	96.6	3.4	0.4	0
10	Stormyrbäcken	2.94	2	213	256	99	74.2	25.8	0.1	0
12	Nymyrbäcken	1.76	3	360	184	19	96.4	2.6	0.3	1.1
13	Långbäcken	1.60	3	318	177	0	97.9	0.1	0.3	2
14	Åhedbäcken	13.60	2	222	172	34	90.4	5.1	0.6	3.9
15	Övre Krycklan	19.91	4	87	181	78	83.2	14	1.9	1
16	Krycklan	21.72	4	644	130	9	91.5	2.8	0.5	5.7

[a] Altitude and stream order were determined at the sampling site, while all other parameters were determined for the entire subcatchment. The subcatchment area included in this table was not included in the statistical calculations because we believe median stream size to be a better measure.

The relationships between catchment characteristics and DOC export were analyzed using stepwise multiple linear regressions (stepwise criteria; probability of F to enter $p \leq 0.05$ and probability of F to remove $p \geq 0.10$). Regressions were considered significant if $p < 0.05$. Diagnostic checks were done to assure that the regression analysis did not violate classical assumptions, for example, White's test of heteroskedasticity [*Gupta*, 1999].

2.4.2. Partial Correlations

[16] Partial correlations were used to further investigate the impact of individual variables on the DOC export. The partial correlations coefficients describe the linear relationship between two variables while controlling for the effects of one or more additional variables. Using that method, we can identify false correlations, i.e., when confounding factors create a relationship where none actually exists, and uncover hidden relationships. Correlations were considered significant if $p < 0.05$ and strongly significant if $p < 0.01$. SPSS 14.0 was used for all statistical calculations.

2.5. Uncertainty Analyses

[17] On the basis of replicate injections the error in the precision of the DOC analyses was on average 2% and at worst 5%. As a conservative measure, 5% was used for the uncertainty in the DOC analysis.

[18] In extrapolation of discharge from a single stream site, there were two main potential sources of error/uncertainty arising: The first, which was incorporated into the Monte Carlo analysis, was intersite differences in annual discharge ("bias"), and the second, which was handled separately, was differences in response to snowmelt and precipitation events, named "flashiness." Bias (due to differences in subcatchment evapotranspiration, for instance) was estimated on the basis of discrete discharge measurements at the 15 sites which were compared to the continuous measurements at site 7. The mean absolute value of bias for the remaining 14 sites was calculated to 12%. This is probably a high estimate because it is based on a series of individual measurements rather than total annual discharge. Over longer time periods (e.g., seasonal or annual) the effects of having different daily discharges will tend to even out, e.g., some days with flow higher than site 7, other days with flow lower than site 7. The bias of 12% is also higher than the standard deviation of 8% in the annual discharge from seven boreal catchments in northern Sweden found by *Laudon et al.* [2004a]. In general, the longer the time period in consideration, the lower the error in mean Q. If there is a consistent overall difference in discharge between the given site and site 7, this bias will remain, however, even when we consider long time periods. The uncertainty in discharge for site 7 was estimated to be 5% based on comparing manual, instantaneous measurements to the data logger measurements and allowing for possible errors in the catchment area calculation [*Laudon et al.*, 2004b].

[19] The uncertainties in the DOC exports for the 3 year study period were estimated using Monte Carlo simulations. The combined error from both DOC analyses and uncertainty in discharge calculation was calculated using 10,000 realizations with random parameters generated from the distributions discussed above.

[20] An additional consideration for DOC export calculation is intersite differences in flow regime ("flashiness"): Even if two streams have the same total annual discharge, on any given day they are likely to have different discharge based on subcatchment hydrology characteristics. In a direct comparison of specific discharge between the reference site and any other site on the same day, we found a large difference, averaging about 30% (I. Buffam, unpublished data, 2005). In general, the wetland-dominated and very small catchments were more flashy (with higher peaks and lower base flows), while discharge in the larger catchments was more smoothed over time. To estimate how this affected our calculations of annual/seasonal DOC exports, we calculated the DOC exports using three sets of 2003–2005 discharge records from site 7: (1) measured daily discharge at site 7, (2) flashy flow regime, and (3) smoothed flow regime. All had the same total Q for the entire period of record, but the flashy and smoothed records approximate the extremes, which we measured at the other sites which were most different. The flashy and smooth data sets were

generated using the following transformation of the original discharge record (with $F = 1.26$ and $F = 0.81$, respectively):

$$\overset{n}{\underset{i=1}{Q_{Ni}}} = (1/f)e^{\mu+F(\ln Q_i-\mu)} \tag{1}$$

where

Q_{Ni}	normalized transformed discharge on day i, used, e.g., for flashy and smoothed flow regime;
Q_i	discharge on day i in original discharge record, n days in length;
F	parameter describing the "flashiness" of the transformation (for $F > 1$ the transformed Q will be flashy, whereas for $F < 1$ the transformed Q will be smoothed);
f	normalization factor applied to correct the transformed data set to give the same total discharge as the original record during the period of interest;
μ	mean of natural log transformed daily discharges in original discharge record for all days n in entire record:

$$\mu = (1/n)\sum_{i=1}^{n} \ln Q_i \tag{2}$$

[21] We found that the uncertainties in discharge during the spring flood season and especially during the snow covered season were systematic and dependent on the catchment size. That implies that some of the observed correlations between size and DOC export could be an artifact of this systematic error, i.e., that the export from small catchments was overestimated. The flashy and smoothed records approximate the extremes for the sites, which were most different. Assuming that the smallest catchment was the most "flashy" and the largest catchment was the most "smoothed," the smallest catchment was assigned the maximum overestimation, and the largest catchment was assigned the largest underestimation for the different seasons. The other sites were then ranked by size, and the overestimation and underestimation of DOC were interpolated from the maximum errors. New DOC values for the 15 sites were calculated according to the possible overestimation/underestimation, and the seasonal regressions were redone. That result was then compared to the original statistical analysis.

[22] Another factor adding uncertainty to the calculation is the sampling frequency of the DOC measurements. The terrestrial export calculations are most sensitive to gaps in DOC measurements during high-flow situations and are hence not dramatically affected by the low sampling frequency during winter. During the snowmelt season, samples were collected frequently (every 2 days), and sampling gaps were not assumed to bias the results during that season. However, during the snow-free season, there are numerous low- and high-flow situations, and because the DOC concentration is related to discharge, gaps between the measurements can cause calculation uncertainty. To assess the magnitude of this uncertainty, linear regressions were used to identify the relationship between DOC concentration and daily average discharge during the snow-free season. One small site (site 2) and one large site (site 16) were used to predict daily DOC concentrations from runoff data:

Site 2

$$\mathrm{DOC}\left(\mathrm{mg\ L^{-1}}\right) = 11.9 + 7.9\ Q\left(\mathrm{mm\ d^{-1}}\right) \qquad r^2 = 0.72 \tag{3}$$

Site 16

$$\mathrm{DOC}\left(\mathrm{mg\ L^{-1}}\right) = 6.4 + 6.0\ Q\left(\mathrm{mm\ d^{-1}}\right) \qquad r^2 = 0.71 \tag{4}$$

[23] The flow-predicted concentrations were then used to calculate DOC export for these two sites. The export obtained in this way was then compared to the export obtained using linear interpolated measurements in order to estimate errors associated with sampling gaps.

3. Results

[24] The mean annual DOC exports from the 15 subcatchments (0.03–21.72 km^2) ranged from 14.8 to 99.1 kg ha^{-1} yr^{-1}. Annual discharge varied greatly between the 3 years in this study. Total runoff was 210 mm yr^{-1} during the dry year 2003, 326 mm yr^{-1} during the wet year 2004, and 271 mm yr^{-1} during 2005. Because the interannual variations in DOC export are strongly regulated by variability in flow, the export of terrestrial DOC was hence highest during 2004 and lowest during 2003. In addition to the interannual variation, seasonal variations (average seasonal export for all 3 years) could easily be detected. Seasonal variations in DOC export were again primarily driven by variations in discharge, with low exports during the low-flow snow covered season and higher exports during snowmelt and snow-free seasons. The spatial variability was also substantial with the terrestrial DOC export per unit area from site 3 being more than 6 times that of site 16 (Figure 3). The causes of these spatial variations were further explored with PCA and partial correlations.

3.1. PCA

[25] The PCA of all catchment variables (Tables 1 and 2) resulted in five principal components that together explained 90% of the variance in the catchment parameters. Stepwise linear regression between average annual DOC export (per unit area) and the five principal components showed that 78% of the variation in DOC was explained by principal components 1 and 3 (PC1 and PC3). The rotated component matrix (varimax rotation with Kaiser normalization, converged in 8 iterations) showed that PC1 was most highly correlated with silt (0.93), altitude (−0.89), percent above HC (−0.89), median stream size (0.86), and stream order (0.72). PC3 was most highly correlated with forest (0.74) and wetland (−0.73). To further separate catchment characteristics, another PCA was performed on those seven parameters. This analysis resulted in two principal components that together explained 85% of the variance of the seven parameters. In the initial solution, all seven variables correlated highly with the first principal component. Because we were interested in how the different variables affect the DOC export, they were separated using varimax rotation. The rotated component matrix (using varimax rotation with Kaiser normalization, converged in 3 iterations) showed that the new PC1 was most highly correlated with silt (0.90), median stream size (0.88), altitude (−0.88),

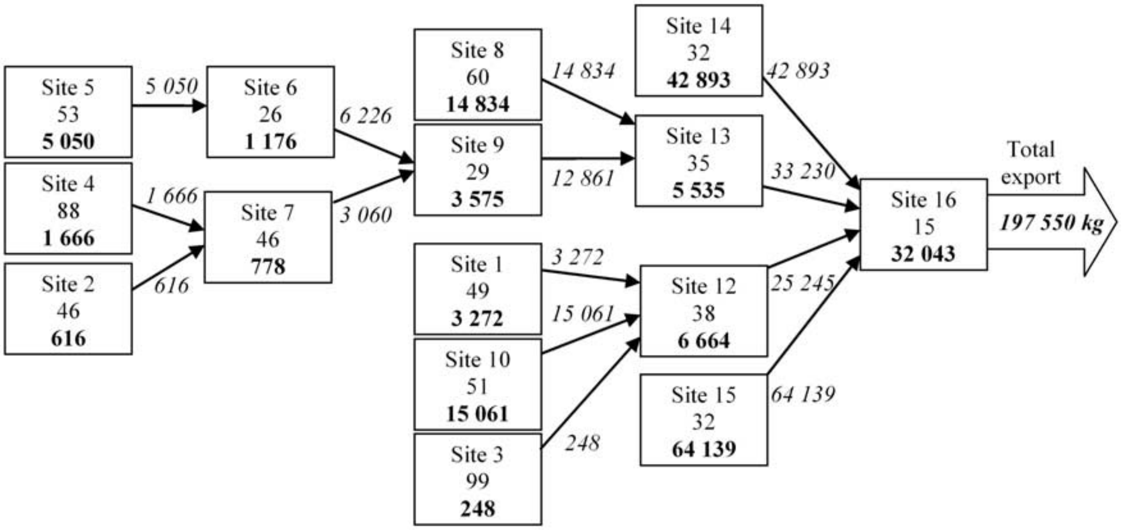

Figure 3. DOC export per unit area (kg C ha^{-1} yr^{-1}) from the 15 subcatchments (inside boxes, plain numbers), the amount of annual DOC export (kg yr^{-1}) per subcatchment area (inside boxes, bold numbers), and the cumulative amount of annual DOC export (kg yr^{-1}) per catchment area (along arrows, italic numbers).

proportion of catchment above HC (−0.81), and stream order (0.78). PC2 was most highly correlated with forest (−0.98) and wetland (0.96). The rotated component matrix (Figure 4) was easier to interpret because the variables could be separated into two gradients describing variations in the landscape. We therefore used the rotated component matrix for regression analyses. PC1 will hereafter be referred to as the size-location gradient, and PC2 will be referred to as the forest-wetland gradient.

[26] Stepwise linear regression between DOC export and PC1 and PC2 gave the following results:

$$\text{mean annual DOC export} = 34.8 + 12.1\ \text{PC2} - 8.8\ \text{PC1}$$
$$r^2 = 0.79 \tag{5}$$

$$\text{mean DOC export during snowmelt season} = 13.2 - 2.9\ \text{PC1} + 2.7\ \text{PC2}$$
$$r^2 = 0.79 \tag{6}$$

$$\text{mean DOC export during snow–free season} = 19.5 + 7.7\ \text{PC2} - 5.3\ \text{PC1}$$
$$r^2 = 0.74 \tag{7}$$

$$\text{mean DOC export during snow covered season} = 2 + 1.8\ \text{PC2}$$
$$r^2 = 0.67 \tag{8}$$

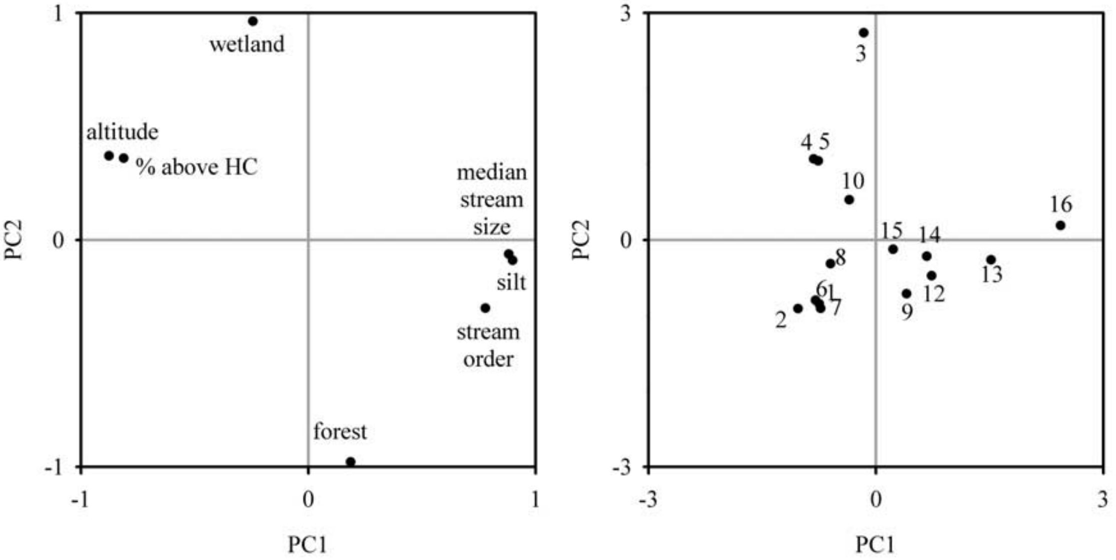

Figure 4. (left) PCA score plot of the two PCs of the second PCA, rotated solution. (right) PCA loading plot of the two principal components of the second PCA, rotated solution. PC1 describes a size-location gradient, and PC2 describes a wetland-forest gradient.

Table 3. Pearson Correlations Between Terrestrial Export of DOC and Seven Catchment Variables and Partial Correlations With Control for Wetland[a]

	C Export			
	Mean Annual	Snowmelt	Snow Free	Snow Covered
	Pearson Correlation			
Wetland	0.84[b]	0.75[b]	0.82[b]	0.86[b]
Forest	−0.80[b]	−0.71[b]	−0.78[b]	−0.83[b]
Altitude	0.73[c]	0.81[c]	0.70[c]	0.53[c]
Percent above HC	0.63[c]	0.72[c]	0.60[c]	NS
Median stream size	−0.56[c]	−0.63[c]	−0.54[c]	NS
Stream order	−0.63[c]	−0.68[b]	−0.60[c]	NS
Silt	NS	−0.65[b]	NS	NS
	Partial Correlation, Control for Wetland			
Forest	0.69[b]	0.58[c]	0.73[b]	NS
Altitude	0.60[c]	0.71[b]	NS	NS
Percent above HC	NS	0.59[c]	NS	NS
Median stream size	−0.57[c]	−0.62[c]	NS	NS
Stream order	NS	−0.58[c]	NS	NS
Silt	NS	−0.64[c]	NS	NS

[a] NS, nonsignificant.

[b] For $p < 0.01$.

[c] For $p < 0.05$.

[27] The diagnostic checks of the regressions above showed no breakdowns of the classical assumptions.

[28] The importance of the different catchment characteristics for the terrestrial DOC export varied between the different seasons. During the snow covered season, 67% of the intersite variation in DOC export was explained by the forest-wetland gradient (PC2). During snowmelt the size-location gradient (PC1) was the dominating factor and explained 43% of the variation in DOC export, while the forest-wetland gradient (PC2) added an additional 36% to the model. During the snow-free season the forest-wetland gradient explained 50%, and the size-location gradient explained an additional 24% of the DOC export variation.

3.2. Correlations With Individual Landscape Elements

[29] Wetland coverage was the single variable most highly correlated with DOC export, annually and for each season (Table 3). In order to examine effects of other variables we also analyzed partial correlations, controlling for wetland coverage. While no additional landscape variables were correlated with DOC export during the snow covered season, other important variables emerged for the other seasons and annual export (Table 3). Forest cover was positively correlated with DOC export. Because the partial correlation for forest was positive, we additionally ran partial correlations between DOC export and all forest parameters, while controlling for wetland variation. The volume of Norway spruce was found to have a partial correlation of 0.60 ($p < 0.05$) to annual DOC export. During snowmelt and snow-free seasons the partial correlation was 0.59 and 0.57 ($p < 0.05$), respectively. All other forest parameters were not significant.

[30] Annual DOC export was negatively correlated with catchment area (Figure 5). It should be noted that in Figure 5 the DOC export and areas used are not calculated for independent subcatchments but for the actual drainage area, including all subcatchments upstream of the sampling points. This relationship indicates that small headwaters may be the largest contributor to the terrestrial DOC export, per unit area.

3.3. Uncertainty Analyses

[31] The Monte Carlo analysis showed that the uncertainty in the annual terrestrial carbon export, due to uncertainty from both DOC analyses and discharge calculation, was ±13%, except for site 7 where the uncertainty was ±7%. The uncertainties given above are calculated as coefficient of variation (standard deviation divided by mean) for the distribution of values calculated by Monte Carlo analysis. The additional uncertainty due to intersite differences in flow regime (“flashiness”) showed that the maximum error is low for annual exports (±2%) and for the snow-free season (±1%) but higher during spring season (±12%) and especially during the snow covered season (±40%). The uncertainties are largest during the snow covered season because the discharge is spatially variable at low flow. Recalculation of the regressions with the potential maximum overestimation/underestimation of discharge data due to flashiness showed that the new regressions gave results similar to the original statistical analysis. We therefore conclude that the uncertainty due to “flashiness” does not affect the major conclusions of this study.

[32] The added uncertainty in the DOC concentrations during the snow-free season due to infrequent sampling was estimated to be around 12% (11 and 13% for sites 2 and 16, respectively). Sometimes the interpolated values were overestimated and sometimes they were underestimated. As a result, over the 3 year period of this study these differences averaged out, and the error was close to 0%. The absolute value of deviation between interpolated and predicted values during the snow-free season was 12% over the 3 years. However, that uncertainty is unlikely to affect the spatial analysis as it is a systematic error, which affects all

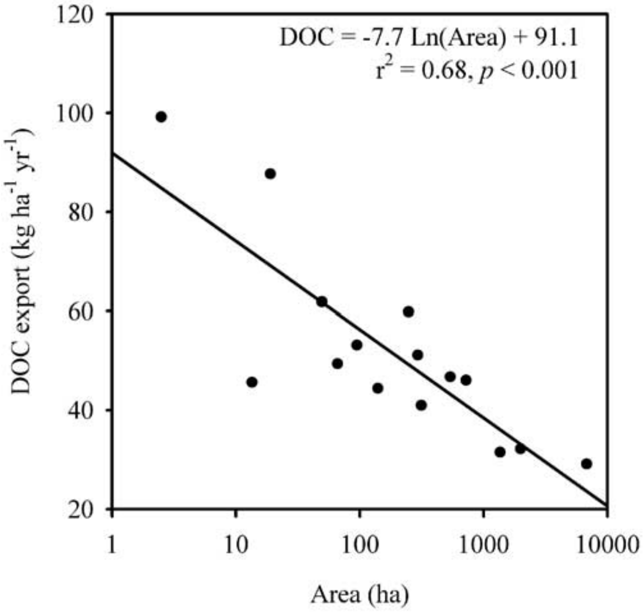

Figure 5. Relationship between area (ha) and annual DOC export (kg ha^{-1} yr^{-1}) for the actual drainage area of the sampling points.

sites similarly, because the sites were always sampled on the same dates, i.e., during the same flow situations.

4. Discussion

[33] DOC export in temperate and boreal rivers throughout the world generally varies between 10 and 100 kg ha^{-1} yr^{-1} [*Hope et al.*, 1994]. The fact that the 15 Krycklan subcatchments cover almost that entire range (Figure 3) corroborates the large variability in DOC reported for other small catchments [*Sedell and Dahm*, 1990; *Temnerud and Bishop*, 2005; *Wolock et al.*, 1997].

4.1. Snow Covered Season

[34] There were also substantial variations in DOC export between the different seasons. Krycklan has on average 5 months of snow cover [*Löfvenius et al.*, 2003], but the flow is low during winter and contributed only 9% (6–11%) to the annual discharge. Consequently, only 3–13% of the annual DOC export occurred during this season. The principal component regression indicated that the forest-wetland gradient (PC2) determined the spatial variation in DOC export during the snow covered season (equation (8)). During winter base flow the majority of the water that reaches streams is groundwater [*Stottlemyer and Toczydlowski*, 1991]. The low groundwater table during winter in the Krycklan catchment [*Nyberg et al.*, 2001] implies that the water reaching the streams has drained deeper soil in both wetlands and forests. Consequently, the amount of DOC leached from forest soils is low during this part of the year since deep soils of the forests are relatively poor in DOC and flow through the Riparian zone en route to the stream also intersects deep DOC-poor layers. In wetlands, on the other hand, the maximum pore water DOC concentration occurs significantly below the water table [*Schiff et al.*, 1998] so deep groundwater from wetlands is especially rich in DOC during winter base flow [*Laudon et al.*, 2004a]. These differences between wetlands and forests were highlighted by the partial correlations analyses in this study (Table 3), which showed that the only parameter that significantly correlated with DOC export during the snow covered season was the proportion of wetlands. Hence the coverage of wetlands regulated the spatial variation in DOC exports during the snow covered season with the highest DOC export occurring in catchments with high wetland coverage.

4.2. Snowmelt Season

[35] The snowmelt season is the major annual hydrological event in this region, and on average, 40% (36–45%) of the annual discharge and 28–65% of the DOC exports occurred during this ~2 month season in the Krycklan catchments. DOC concentrations and export from forested areas increased during the snowmelt season (Table 3). This increase has been explained by rising of near-stream water tables flushing out old DOC-rich water previously stored in the soil [*Bishop et al.*, 2004; *Laudon et al.*, 2004b]. With higher water tables, more organic-rich upper soil horizons are intersected, particularly in the Riparian zone peat layer of forested streams [*Bishop et al.*, 1995]. Riparian peat layers often cover less than 5% of the catchment areas in northern Sweden but are still a major source of DOC in forested catchments, especially during high-flow situations [*Bishop and Pettersson*, 1996].

[36] DOC export from wetlands also increased compared to the winter base flow (Table 3) because of higher discharge, but the increase was less pronounced than in the forested areas. This discrepancy was due to a decrease in DOC concentration in streams draining wetland-dominated areas [*Laudon et al.*, 2004a; *Schiff et al.*, 1997] because of dilution by DOC-poor meltwater [*Bishop et al.*, 1995; *Buffam et al.*, 2007]. The mechanisms behind this dilution could be overland flow over frozen and/or saturated wetland surfaces [*Hayashi et al.*, 2004] but also dilution of the DOC by snowmelt water in the shallow peat layers [*Schiff et al.*, 1998].

[37] The different response in concentrations between forested and wetland areas during the spring flood season resulted in similar DOC concentrations at all sites [see also *Buffam et al.*, 2007]. Thus the forest-wetland gradient was not as important for the spatial variation in DOC export during the snowmelt season as during the winter base flow when wetland explained most of the spatial variation. Instead, the principal components regressions showed that the size-location gradient (PC1) was most important during snowmelt and explained 48% of the spatial variation in DOC export, while the forest-wetland gradient (PC2) added an additional 33% to the model (equation (6)). High DOC export was associated with small stream size, low stream order, low proportion of silty sediments and a high altitude, and high proportion of the watershed situated above HC (Table 3).

[38] Processes that explain this pattern are connected to the size of the catchment but also differences in the quaternary deposits between upstream and downstream catchments. Upstream catchments, particularly those above HC, had higher DOC exports than downstream catchments dominated by silty deposits. Several characteristics potentially contribute to this spatial variation. Deep groundwater has lower DOC than water from shallow soil horizons [*Cronan and Aiken*, 1985; *Schiff et al.*, 1998; *Thurman*, 1985] and the relatively large input of deep groundwater into larger streams, suggested by increasing levels of base cations downstream in the Krycklan catchment [*Buffam et al.*, 2007], could explain the decrease in DOC export from low-order to high-order streams. Moreover, the greater distances to streams in larger catchments also increase the subsurface water transit time, increasing the potential for decomposition and oxidation of organic carbon [*Wolock et al.*, 1997].

[39] In addition, the dominating quaternary deposits change from unsorted till at the higher altitudes to silty sediments downstream in the Krycklan catchment. Silt has a higher specific surface area and is therefore rich in mineral adsorption sites for DOC, which may increase the mineralization of DOC in the soil and decrease DOC concentrations [*Kalbitz et al.*, 2000]. The Riparian soil conditions also differed between areas underlain by till, where there was a peat buildup near the stream channel, compared to the lower lying sediment areas, where there were more deeply incised stream channels and thinner soil organic surface layers. This distinction presumably results in less interaction between subsurface flow and DOC-rich pools in the sediment areas. All of these characteristics and mechanisms are likely to

affect stream DOC flux to some degree. Collectively, they contribute to a high export of DOC in upstream catchments compared to downstream catchments. Other investigations in the region have also noted the effect of stream size [*Temnerud and Bishop*, 2005] and changes in soil type with higher DOC concentrations in the "hilly terrain streams" compared to nearby "sediment plain streams" [*Ivarsson and Jansson*, 1994, 1995]. It should be pointed out, however, that the major reason why these soil characteristics strongly determined the differences in DOC export between the Krycklan subcatchments during spring was that the importance of the forest-wetland gradient was reduced.

4.3. Snow-Free Season

[40] The snow-free season is ~5 months long, and 51% (44–55%) of the annual discharge and 39–63% of the annual DOC exports occurred during this season. The hydrology is characterized by low flow interrupted by a number of high-flow episodes due to rainstorms. During this season the spatial variation was mainly driven by the forest-wetland gradient. However, the correlations in this study showed that although wetlands were more important than forests for variation in DOC export, forest coverage showed a strong positive partial correlation to the DOC export. This result suggests that leaching from forest floors or the organic-rich Riparian zone [*Bishop et al.*, 2004] contributes significantly to the DOC export during high-flow events. DOC is produced during summer within the forest soils due to degradation and solubilization of litter, stimulated by high temperature and oxygenated soils [*Kalbitz et al.*, 2000; *Lundstrom*, 1993]. Furthermore, the partial correlations analysis showed that the abundance of Norway spruce determined the spatial variation in DOC export during the snow-free season, while abundance of pine and deciduous forest did not. The importance of Norway spruce for DOC export agrees with the higher production of litter and subsequent higher leaching from the spruce forest floor compared to that of the pine stands [*Strobel et al.*, 2001]. The negligible impact of deciduous forests was probably due to the relatively small proportion and variation (7–15%) of deciduous forests between the different subcatchments.

[41] The export of DOC in the different subcatchments was dependent on different catchment characteristics, which were expressed differently during different seasons. Thus we should not expect a simple annual relationship between DOC export and the terrestrial catchment characteristics. The annual pattern is the sum of all the complex seasonal variations discussed in sections 4.1, 4.2, and 4.3. Because the amount of DOC exported is controlled by runoff [*Meybeck*, 1982; *Schiff et al.*, 1998] and over half of the annual discharge occurred during the snow-free season, it is not surprising that the annual pattern mostly resembled the snow-free season (equations (5) and (7)). The mean annual export regression showed that the forest-wetland gradient (PC2) explained 52% of the spatial variation in annual DOC exports. The partial correlations showed that it was not only wetland coverage that was of importance, forest coverage was also a significant parameter in determining the spatial variation in annual DOC exports. It is reasonable that the variation in the main sources of organic carbon determines most of the spatial variation in DOC exports, and many studies have found a relationship between the terrestrial export and these parameters [*Aitkenhead et al.*, 1999; *Clark et al.*, 2004; *Dosskey and Bertsch*, 1994; *Hope et al.*, 1994]. However, the effect of size (median stream size and stream order) and location (altitude and proportion of catchment above highest postglacial coastline (HC) and the amount of silty sediment deposits) are clearly important on an annual basis because the size-location gradient explained another 27% of the variance. The size-location gradient can be viewed upon as a gradient describing the importance of what happens between the sources and the stream. This gradient incorporates information about flow path depth and distance to streams (stream size) as well as mineral binding sites (silty soils), which together regulate the amount of DOC that reaches the streams.

[42] This study also demonstrated that small headwaters were the largest contributors to the terrestrial DOC export, per unit area, in the Krycklan catchment (Figure 5 and Table 3). A negative correlation between DOC export and catchment area as found in this study was also identified in a study of DOC export from 86 of Finland's main rivers and their subcatchments [*Mattsson et al.*, 2005]. There are many reasons for size to come out as an important factor. It is most likely not drainage area per se that is of importance but variables that covary with stream and catchment size (e.g., stream morphology, soil type, and altitude) that give rise to the trend of decreasing DOC export with increasing stream size. The importance of headwater catchments for DOC export is further underlined by the observation that most water enters stream networks via relatively small streams. In the 68 km^2 Krycklan catchment, for instance, over half of the water entering the stream network enters via streams with subcatchments 2 km^2 or smaller. Small headwater catchments might thus have a disproportionately large influence on terrestrial DOC export.

[43] **Acknowledgments.** We wish to thank Peder Blomkvist and the Krycklan crew for their help with field work. The financial support for this work was provided by Swedish Science Foundation, Formas, and Swedish EPA to H.L.

References

Aitkenhead, J. A., D. Hope, and M. F. Billett (1999), The relationship between dissolved organic carbon in stream water and soil organic carbon pools at different spatial scales, *Hydrol. Processes*, *13*(8), 1289–1302.

Bishop, K., and C. Pettersson (1996), Organic carbon in the boreal spring flood from adjacent subcatchments, *Environ. Int.*, *22*(5), 535–540.

Bishop, K., Y. H. Lee, C. Pettersson, and B. Allard (1995), Terrestrial sources of Methylmercury in surface waters: The importance of the Riparian zone on the Svartberget catchment, *Water Air Soil Pollut.*, *80*(5), 435–444.

Bishop, K., J. Seibert, S. Koher, and H. Laudon (2004), Resolving the double paradox of rapidly mobilized old water with highly variable responses in runoff chemistry, *Hydrol. Processes*, *18*(1), 185–189.

Buffam, I., H. Laudon, J. Temnerud, C.-M. Mörth, and K. Bishop (2007), Landscape-scale variability of acidity and dissolved organic carbon during spring flood in a boreal stream network, *J. Geophys. Res.*, *112*, G01022, doi:10.1029/2006JG000218.

Clark, M. J., M. S. Cresser, R. Smart, P. J. Chapman, and A. C. Edwards (2004), The influence of catchment characteristics on the seasonality of carbon and nitrogen species concentrations in upland rivers of northern Scotland, *Biogeochemistry*, *68*(1), 1–19.

Cory, N., I. Buffam, H. Laudon, S. Kohler, and K. Bishop (2006), Landscape control of stream water aluminum in a boreal catchment during spring flood, *Environ. Sci. Technol.*, *40*(11), 3494–3500.

Cronan, C. S., and G. R. Aiken (1985), Chemistry and transport of soluble humic substances in forested watersheds of the Adirondack Park, New York, *Geochim. Cosmochim. Acta*, *49*(8), 1697–1705.

Cronan, C. S., J. T. Piampiano, and H. H. Patterson (1999), Influence of land use and hydrology on exports of carbon and nitrogen in a Maine River Basin, *J. Environ. Qual.*, *28*(3), 953–961.

Dawson, J. J. C., M. F. Billett, D. Hope, S. M. Palmer, and C. M. Deacon (2004), Sources and sinks of aquatic carbon in a peatland stream continuum, *Biogeochemistry*, *70*(1), 71–92.

Dillon, P. J., and L. A. Molot (1997), Effect of landscape form on export of dissolved organic carbon, iron, and phosphorus from forested stream catchments, *Water Resour. Res.*, *33*(11), 2591–2600.

Dosskey, M. G., and P. M. Bertsch (1994), Forest sources and pathways of organic-matter transport to a blackwater stream: A hydrologic approach, *Biogeochemistry*, *24*(1), 1–19.

Driscoll, C. T., N. M. Johnson, G. E. Likens, and M. C. Feller (1988), Effects of acidic deposition on the chemistry of headwater streams: A comparison between Hubbard Brook, New Hampshire, and Jamieson Creek, British Columbia, *Water Resour. Res.*, *24*(2), 195–200.

Duarte, C. M., and Y. T. Prairie (2005), Prevalence of heterotrophy and atmospheric CO_2 emissions from aquatic ecosystems, *Ecosystems*, *8*(7), 862–870.

Gupta, V. (1999), *SPSS for Beginners*, 608 pp., Lightning Source Inc., La Vergne, Tenn.

Hayashi, M., W. L. Quinton, A. Pietroniro, and J. J. Gibson (2004), Hydrologic functions of wetlands in a discontinuous permafrost basin indicated by isotopic and chemical signatures, *J. Hydrol.*, *296*(1–4), 81–97.

Heikkinen, K. (1990), Seasonal-changes in iron transport and nature of dissolved organic-matter in a humic river in northern Finland, *Earth Surf. Processes Landforms*, *15*(7), 583–596.

Hessen, D. O., and L. J. Tranvik (1998), *Aquatic Humic Substances: Ecology and Biogeochemistry*, 346 pp., Springer, Berlin.

Hinton, M. J., S. L. Schiff, and M. C. English (1997), The significance of storms for the concentration and export of dissolved organic carbon from two Precambrian Shield catchments, *Biogeochemistry*, *36*(1), 67–88.

Hinton, M. J., S. L. Schiff, and M. C. English (1998), Sources and flowpaths of dissolved organic carbon during storms in two forested watersheds of the Precambrian Shield, *Biogeochemistry*, *41*(2), 175–197.

Hongve, D. (1999), Production of dissolved organic carbon in forested catchments, *J. Hydrol.*, *224*(3), 91–99.

Hongve, D., P. A. W. van Hees, and U. S. Lundstrom (2000), Dissolved components in precipitation water percolated through forest litter, *Eur. J. Soil Sci.*, *51*(4), 667–677.

Hope, D., M. F. Billett, and M. S. Cresser (1994), A review of the export of carbon in river water: Fluxes and processes, *Environ. Pollut.*, *84*(3), 301–324.

Hornberger, G. M., K. E. Bencala, and D. M. Mcknight (1994), Hydrological controls on dissolved organic-carbon during snowmelt in the Snake River near Montezuma, Colorado, *Biogeochemistry*, *25*(3), 147–165.

Ingri, J. (1996), Kalixälvens hydrogeokemi, *Technol. Rep. 2*, 126 pp., Luleå Univ., Luleå, Sweden.

Ivarsson, H., and M. Jansson (1994), Regional variation of dissolved organic-matter in running waters in central northern Sweden, *Hydrobiologia*, *286*(1), 37–51.

Ivarsson, H., and M. Jansson (1995), Sources of acidity in running waters in central northern Sweden, *Water Air Soil Pollut.*, *84*(3–4), 233–251.

Kalbitz, K., S. Solinger, J. H. Park, B. Michalzik, and E. Matzner (2000), Controls on the dynamics of dissolved organic matter in soils: A review, *Soil Sci.*, *165*(4), 277–304.

Kohler, S., I. Buffam, A. Jonsson, and K. Bishop (2002), Photochemical and microbial processing of stream and soilwater dissolved organic matter in a boreal forested catchment in northern Sweden, *Aquat. Sci.*, *64*(3), 269–281.

Laudon, H., and K. H. Bishop (1999), Quantifying sources of acid neutralisation capacity depression during spring flood episodes in northern Sweden, *Environ. Pollut.*, *105*(3), 427–435.

Laudon, H., and K. Bishop (2002), Episodic stream water pH decline during autumn storms following a summer drought in northern Sweden, *Hydrol. Processes*, *16*(9), 1725–1733.

Laudon, H., O. Westling, and K. Bishop (2000), Cause of pH decline in stream water during spring melt runoff in northern Sweden, *Can. J. Fish. Aquat. Sci.*, *57*(9), 1888–1900.

Laudon, H., S. Kohler, and I. Buffam (2004a), Seasonal TOC export from seven boreal catchments in northern Sweden, *Aquat. Sci.*, *66*(2), 223–230.

Laudon, H., J. Seibert, S. Köhler, and K. Bishop (2004b), Hydrological flow paths during snowmelt: Congruence between hydrometric measurements and oxygen 18 in meltwater, soil water, and runoff, *Water Resour. Res.*, *40*, W03102, doi:10.1029/2003WR002455.

Laudon, H., A. B. S. Poleo, L. A. Vollestad, and K. Bishop (2005), Survival of brown trout during spring flood in DOC-rich streams in northern Sweden: The effect of present acid deposition and modelled pre-industrial water quality, *Environ. Pollut.*, *135*(1), 121–130.

Löfvenius, M. O., M. Kluge, and T. Lundmark (2003), Snow and soil frost depth in two types of shelterwood and a clear-cut area, *Scand. J. For. Res.*, *18*(1), 54–63.

Lundstrom, U. S. (1993), The role of organic-acids in the soil solution chemistry of a podzolized soil, *J. Soil Sci.*, *44*(1), 121–133.

Mattsson, T., L. Finer, P. Kortelainen, and T. Sallantaus (2003), Brookwater quality and background leaching from unmanaged forested catchments in Finland, *Water Air Soil Pollut.*, *147*(1–4), 275–297.

Mattsson, T., P. Kortelainen, and A. Raike (2005), Export of DOM from boreal catchments: Impacts of land use cover and climate, *Biogeochemistry*, *76*(2), 373–394.

Meybeck, M. (1982), Carbon, nitrogen and phosphorus transport by world rivers, *Am. J. Sci.*, *282*, 401–450.

Mulholland, P. J. (2003), Large-scale patterns in dissolved organic carbon concentratrion, flux, and sources, in *Aquatic Ecosystems*, edited by S. Findlay and R. Sinsabaugh, pp. 139–159, Elsevier Sci., New York.

Mulholland, P. J., and W. R. Hill (1997), Seasonal patterns in streamwater nutrient and dissolved organic carbon concentrations: Separating catchment flow path and in-stream effects, *Water Resour. Res.*, *33*(6), 1297–1306.

Nyberg, L., M. Stahli, P. E. Mellander, and K. H. Bishop (2001), Soil frost effects on soil water and runoff dynamics along a boreal forest transect: 1. Field investigations, *Hydrol. Processes*, *15*(6), 909–926.

Reese, H., M. Nilsson, T. G. Pahlen, O. Hagner, S. Joyce, U. Tingelof, M. Egberth, and H. Olsson (2003), Countrywide estimates of forest variables using satellite data and field data from the national forest inventory, *Ambio*, *32*(8), 542–548.

Schiff, S. L., R. Aravena, S. E. Trumbore, M. J. Hinton, R. Elgood, and P. J. Dillon (1997), Export of DOC from forested catchments on the Precambrian Shield of central Ontario: Clues from C-13 and C-14, *Biogeochemistry*, *36*(1), 43–65.

Schiff, S., R. Aravena, E. Mewhinney, R. Elgood, B. Warner, P. Dillon, and S. Trumbore (1998), Precambrian shield wetlands: Hydrologic control of the sources and export of dissolved organic matter, *Clim. Change*, *40*(2), 167–188.

Sedell, J. R., and C. N. Dahm (1990), Spatial and temporal scales of dissolved organic carbon in streams and rivers, in *Organic Acids in Aquatic Ecosystems: Dahlem Workshop Reports on Organic Acids in Aquatic Ecosystems, Berlin 1989, May 7–12*, edited by E. M. Perdue and E. T. Gjessing, pp. 261–279, John Wiley, Chichester, U.K.

Stottlemyer, R., and D. Toczydlowski (1991), Stream chemistry and hydrologic pathways during snowmelt in a small watershed adjacent Lake Superior, *Biogeochemistry*, *13*(3), 177–197.

Strobel, B. W., H. C. B. Hansen, O. K. Borggaard, M. K. Andersen, and K. Raulund-Rasmussen (2001), Composition and reactivity of DOC in forest floor soil solutions in relation to tree species and soil type, *Biogeochemistry*, *56*(1), 1–26.

Temnerud, J., and K. Bishop (2005), Spatial variation of streamwater chemistry in two Swedish boreal catchments: Implications for environmental assessment, *Environ. Sci. Technol.*, *39*(6), 1463–1469.

Thurman, E. M. (1985), *Organic Geochemistry of Natural Waters*, 497 pp., Martinus Nijhoff, Dordrecht, Netherlands.

Wolock, D. M., J. Fan, and G. B. Lawrence (1997), Effects of basin size on low-flow stream chemistry and subsurface contact time in the Neversink River watershed, New York, *Hydrol. Processes*, *11*(9), 1273–1286.

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