

# Concentrations of dissolved organic carbon along an altitudinal gradient from Norway spruce forest to the mountain birch/alpine ecotone in Norway

Nicholas Clarke, Ingvald Røsberg and Dan Aamlid

*Norwegian Forest Research Institute, Høgskoleveien 8, N-1432 Ås, Norway*

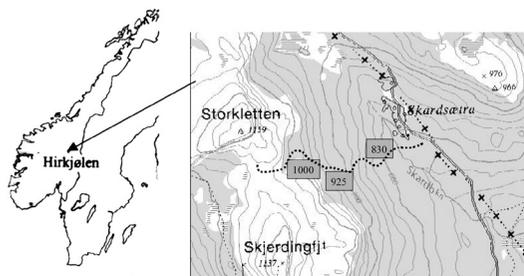
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Concentrations of dissolved organic carbon (DOC) in soil water from the base of the soil organic layer were determined at three forest plots along an altitudinal gradient in eastern Norway. The lowest plot, at 830 m above sea level (a.s.l.), was in Norway spruce forest and there were additional plots at the ecotone between Norway spruce and mountain birch at 925 m a.s.l. and at the forest line (1000 m a.s.l.). DOC concentrations in soil water did not decrease uniformly with altitude although tree biomass, above-ground litterfall and the soil C pool all did so. Significant correlations between DOC and  $\{H^+\}$  or electrical conductivity may reflect the contribution of DOC to solution acidity and the anionic charge, respectively. If mean temperature during the growing season increases, tree growth at any given altitude will tend to increase and the spruce-birch ecotone may move to a higher altitude than at present. Increased C inputs as litter to the soil might then lead to increasing DOC concentrations and fluxes in surface waters.

## Introduction

An increase in concentrations of dissolved organic carbon (DOC) in runoff water from terrestrial ecosystems has been observed, for example in Norway (State Pollution Control Authority 1999), northern England (Naden and McDonald 1989) and Wales (Neal *et al.* 1997). These increases, which have been linked to climatic factors such as increased temperatures and dry periods, have raised concerns about drinking water quality due to higher loads of organic matter in surface water together with increased colouring. It is thus important to understand the factors responsible for increasing DOC concentrations.

DOC in soil water is produced by decomposition of both new and old organic matter and by leakage of metabolites from plant and microbial cells (Christ and David 1996a, Kalbitz *et al.* 2000, Yano *et al.* 2004), and is removed largely by adsorption in the mineral soil (Qualls and Haines 1992). Variables that have been linked to DOC concentrations include solid phase properties (e.g. litter amount, soil carbon store or soil acidity), liquid phase properties (e.g. pH and ionic strength), meteorological conditions (e.g. temperature and precipitation) and land use factors (e.g. tree species) (Kalbitz *et al.* 2000). For example, Gundersen *et al.* (1998) observed a correlation between DOC in the forest floor and litterfall amount. Currie and



**Fig. 1.** The location of Hirkjølen and the locations of the plots. The forested area is marked in grey.

Aber (1997) and Tipping *et al.* (1999) suggested a positive relationship between DOC leaching or fluxes and the amount of soil organic matter. Some researchers found that DOC mobilisation increased in soils with a high C/N ratio (Gödde *et al.* 1996), although other researchers have not found this (Michel and Matzner 1999). The pH in the forest floor has been found to be positively correlated to DOC concentrations in forest floor leachates (Michalzik *et al.* 2001). Laboratory studies have generally shown a positive correlation between solution pH and DOC (Tipping and Hurley 1988, Andersson *et al.* 1999, 2000). However, negative correlations of DOC with soil water pH have sometimes been observed in the field (Cronan and Aiken 1985, Lindroos *et al.* 1995). A significant positive correlation between DOC and electrical conductivity was found for the organic layer at the Waldstein site in Germany (Michalzik and Matzner 1999). Soil temperature clearly affects microbial production of DOC (Christ and David 1996b, Gödde *et al.* 1996, Andersson *et al.* 2000). Land-use factors such as tree species may also affect DOC concentrations. Although Michalzik *et al.* (2001) found similar concentrations and fluxes of DOC in hardwood and coniferous forests in temperate forests on a regional level, a number of researchers have found higher concentrations of DOC in soil solutions from coniferous stands than in those from hardwood stands (David and Driscoll 1984, Cronan and Aiken 1985, Currie *et al.* 1996, Strobel *et al.* 2001). Vegetation cover also affects DOC production (Judd and Kling 2002).

Ecosystem changes, for example as a result of climate change, might result in changes in many of these factors, and thus also in DOC concentrations. Although DOC export depends largely

on the size and timing of water fluxes (Judd and Kling 2002), changes in mean concentrations will also have importance. Possible effects of ecosystem change as a result of temperature change might be assessed by observations along an altitudinal gradient, where temperature change due to altitude acts as a surrogate for climate change. In moorland peat soil waters, concentrations of total organic carbon have been observed to increase by as much as 26 mg l<sup>-1</sup> for every 100 m increase in altitude (Grieve and Marsden 2001). The objective of this paper is to quantify variations in DOC concentrations in soil water along an altitudinal gradient from Norway spruce (*Picea abies* (L.) Karst.) forest to the Norway spruce–mountain birch (*Betula pubescens* Ehrh. ssp. *czerepanovii*) ecotone and, further, to the mountain birch–alpine ecotone, to compare these variations with variations in climatic, soil, soil water and tree biomass variables and to suggest the implications if ecotone positions change.

## Material and methods

Hirkjølen Experimental Area lies about 280 km north of Oslo (Fig. 1), at 61°44'N, 10°36'E and between 740 and 1160 m above sea level (a.s.l.). The bedrock consists largely of Cambro-Silurian sparagmite and slate. At about 1050 m, there is a layer of dolomite-rich limestone, from which a stream arises. This layer supplies the area downslope with calcium and magnesium. The lower slopes up to about 950 m a.s.l. are covered by basal moraine. Hirkjølen has an inland climate with cold winters. Summer air temperature 2.0 m above ground level was recorded from June to September at 800 m a.s.l. in the period 1932–1966 (Mork 1968): the mean maximum and mean summer temperatures were 14.3 and 9.5 °C, respectively. The growing season is about 3.5 months (Mork 1968). No long-term measurements of winter air temperature exist for Hirkjølen. Mean annual precipitation during the period 1935–1965 was 597 mm, of which an average of 348 mm fell in June–September (Mork 1968).

Norway spruce is the dominant tree species in most of the area up to about 925–950 m

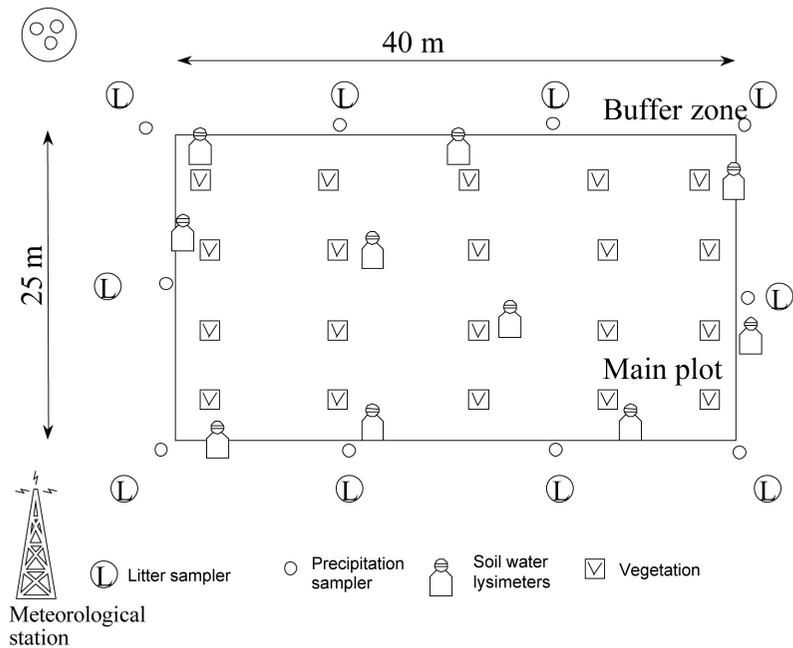


Fig. 2. Plot layout.

a.s.l. From about 925 m to about 1000–1050 m a.s.l., mountain birch is the dominant tree species. Above about 1000 m a.s.l., there is alpine vegetation. The positions of the Norway spruce–mountain birch ecotone and the forest line in the research area are not determined by grazing or felling but by climatic factors such as temperature and wind speed (Mork 1968). The forest is semi-natural: selection felling was practised until 1931, when the Hirkjølen Experimental Area was established. The area has also been used for hunting and small-scale summer pasture of sheep and cattle. Some iron mining occurred in the area previously, although not where our plots were located.

In the summer of 1998, three experimental plots were established on Skarseterlia, on the eastern side of the mountain (Fig. 1), in Norway spruce forest at 830 m a.s.l., at the spruce–birch ecotone (925 m a.s.l.) and at the forest line (1000 m a.s.l.). Each plot consisted of a rectangular inner plot (about 25 × 40 m), a buffer zone about 5 m wide and an outer area for later use (Fig. 2). The soil on the upper plot consists largely of a thin organic layer on weathered bedrock, with some podzolisation in places. On the plot at 925 m a.s.l., the soil is mostly gleysol with some podzolisation, while at 830 m a.s.l. the

soil consists of cambisol, gleysol and podzol. The organic horizon of the soil (the O horizon) is largely of mor type. At 830 and 925 m a.s.l., it is generally differentiated into distinct fermented (Of) and humified (Oh/Ah) layers, while at 1000 m a.s.l. it is undifferentiated. Soil was sampled at 25 systematically placed points on each plot, horizon depths measured and the samples pooled by horizon.

We measured air temperature at 2 m above ground level (HMP45A sensors, Campbell Scientific, Utah, U.S.A.) and soil temperature (type 107 probes, Campbell Scientific) in the O horizon on all plots. All sensors were attached to a CR10X datalogger (Campbell Scientific).

Stand precipitation (throughfall) and above-ground litterfall on all plots, and bulk precipitation on the plot at 925 m a.s.l., were sampled using methodology similar to that of the Norwegian Monitoring Programme for Forest Damage (Horntvedt *et al.* 1992). Throughfall and litterfall were collected at ten equidistant points on the perimeter of each plot. The collection bottles for throughfall were placed in the ground in holes lined with dark tubing to keep the samples cool and dark. The collection bottles for bulk precipitation, which were at 2 m above ground level, were covered with aluminium foil to avoid

the effects of sunlight and high temperatures. Sampling of bulk precipitation and throughfall was continuous and sample collection took place once a month from June until October, i.e. during the snow- and frost-free part of the year. Volumes of the water samples were measured and the samples from each plot were pooled before analysis in proportion to their volumes, so that one bulk precipitation sample was obtained, together with one throughfall sample from each plot. Above-ground litterfall was collected twice a year, in the autumn and the spring.

Soil water samples were collected from the buffer zones of ten out of twenty subplots (established for ground vegetation monitoring, Fig. 2) on each plot. In each of these ten subplots, three tension lysimeters (PRENART, Denmark) were placed directly under the O horizon. Samples were collected using a battery pump with a 600–700 hPa vacuum. Samples from the three lysimeters on each subplot were pooled, making a total of maximum ten samples per plot. However, in practice the number of samples obtained was generally smaller, as water was not always obtained from the lysimeters. Soil water samples were collected monthly from June until October. Water sampling was discontinued in 2000.

At our accredited laboratory, water samples were stored at 4 °C in the dark until analysis. DOC was determined using a Dohrman Carbon Analyser DC-190, with oxidation using a Pt catalyst at 680 °C followed by NDIR detection, in samples that had been filtered through a 0.45 µm membrane filter according to Ogner *et al.* (1999). All DOC concentrations were above the detection limit of 0.4 mg l<sup>-1</sup>. pH was determined potentiometrically using a glass membrane combination electrode at 25 °C and electrical conductivity (EC) was determined using a platinum electrode cell at 25 °C, according to Ogner *et al.* (1999). Ionic strength (I) was estimated from the electrical conductivity using the formula  $I = EC \times 0.013$  (Lindsay 1979). DOC charge was estimated using the Oliver equation (Oliver *et al.* 1983). The soil samples were dried, sieved (2 mm) and ground. Soil pH in an aqueous extract (25 ml water: 10 ml soil) was determined potentiometrically using a glass membrane combination electrode, and total C and total N were determined after combustion at 950 °C using an

Elementar Vario EL with TCD detection, according to Ogner *et al.* (1999).

Fluxes of DOC could only be estimated for the sampling periods, due to the lack of data from outside these periods. Estimates were made using measured water fluxes for throughfall and bulk precipitation, and water fluxes calculated using the programme WATBAL (Starr 1999) for soil water.

Pearson correlation coefficients were calculated for the correlation of DOC with sample volume, {H<sup>+</sup>} and EC (which is related to the ionic strength) in the same samples, for each plot and sample type. Sample volume was included as a measure of throughfall/precipitation amount or soil water content. Even though water volumes obtained using tension lysimeters have no precise physical meaning and cannot be used for flux calculations (Derome *et al.* 2001), they will still give some indication of the water content of the soil, so long as the lysimeters are functioning correctly. The programme used for the statistical analysis was Statistica (StatSoft, Oklahoma, U.S.A.) Casewise deletion of missing data was used, which reduced the number of samples included in the analysis but ensured that results obtained were all from the same samples.

## Results

Mean DOC concentrations were lower in bulk precipitation than in throughfall, and lower in throughfall than in soil water (Fig. 3). In throughfall, mean DOC concentrations clearly decreased with altitude. Mean DOC concentrations in soil water also tended to decrease with altitude, although not uniformly: mean DOC at 925 m a.s.l. was higher than at 830 m a.s.l., although within the standard errors of the means. DOC in soil water at 1000 m a.s.l. was, however, considerably lower.

A decrease with altitude was found for air temperature, total soil C, C in biomass, C in above-ground tree litter and stand age (Table 1). Summer throughfall amount showed an increase with altitude, while there was no clear trend for thickness, pH, C, C/N and soil temperature in the organic layer (Table 1).

Estimated DOC fluxes in throughfall and soil water for the sampling periods decreased with increasing altitude (Table 2). This was most clearly apparent in throughfall.

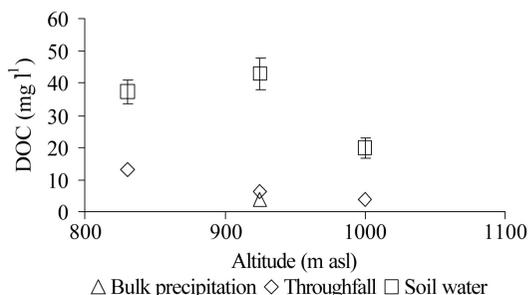
For soil water samples, highly significant ( $p < 0.01$ ) positive correlations were obtained with EC and  $\{H^+\}$  at all altitudes (Table 3), while sample volume was not significantly correlated with DOC at any altitude. For bulk precipitation and throughfall, there were fewer significant correlations than for soil water, although this probably reflects the small number of samples. Significant positive correlations ( $p < 0.05$ ) were obtained between DOC concentration and EC in throughfall at 925 and 1000 m, and a significant ( $p < 0.05$ ) negative correlation between DOC concentration and sample volume in bulk precipitation at 925 m (Table 3).

## Discussion

As expected, mean DOC concentrations were lower in bulk precipitation than in throughfall,

**Table 1.** Mean values for climatic, soil and tree variables.

	Altitude (m a.s.l.)		
	830	925	1000
Throughfall			
June–October (mm)	298	437	494
Air temperature (°C)	0.99	0.85	0.67
Soil temperature (organic layer, °C)	2.81	2.20	2.81
Mean soil organic layer thickness (cm)	2.0	1.6	2.0
Soil C (organic layer, kg C m <sup>-2</sup> )	1.13	1.48	1.03
Soil C (mineral soil, kg C m <sup>-2</sup> )	1.25	0.34	–
Soil C/N (organic layer, g g <sup>-1</sup> )	26	27	25
Soil pH (organic layer)	4.0	3.7	3.9
C in spruce biomass (g C m <sup>-2</sup> )	5332	731	–
C in birch biomass (g C m <sup>-2</sup> )	–	397	275
Above-ground litter (g C m <sup>-2</sup> yr <sup>-1</sup> )	24	8.3	3.7
Stand age in 2004 (yr)	121	111	70



**Fig. 3.** Mean DOC concentrations in bulk precipitation, throughfall and soil water at the base of the organic horizon. Error bars represent standard errors of the means: these are too small to be shown for bulk precipitation and throughfall.

and lower in throughfall than in soil water. This reflects the production of DOC both in the canopy and in the soil organic layer.

Mean annual soil temperatures were higher than mean annual air temperatures, presumably because of the insulating effect of the winter snow cover. Although mean air temperature declined with altitude, mean soil temperature did not. Soil temperature has been clearly shown to affect microbial production of DOC (Christ and David 1996b, Gødde *et al.* 1996, Andersson *et al.* 2000), but cannot explain differences in DOC concentrations at Hirkjølen. If direct temperature effects on microbial production of DOC did exist, they would have been obscured by other effects.

Two different tree species were dominant on our plots, Norway spruce on the lowest plot, mountain birch on the highest and a mixture on the middle plot. It remains uncertain to what

**Table 2.** Estimates of DOC fluxes (g m<sup>-2</sup> yr<sup>-1</sup>) for the sampling periods.

	Year	Altitude (m a.s.l.)		
		830	925	1000
Bulk precipitation	1998	–	2.0	–
	1999	–	3.0	–
	2000	–	4.0	–
Throughfall	1998	5.3	3.8	1.9
	1999	11.0	4.8	3.7
	2000	6.8	4.7	3.9
Soil water	1998	8.0	10.4	4.9
	1999	5.7	3.2	1.6
	2000	10.3	8.1	3.1

extent tree species affects DOC concentrations. On a regional scale, Michalzik *et al.* (2001) found similar concentrations and fluxes of DOC in hardwood and coniferous forests in temperate regions. However, on a site scale rather than a regional scale, higher concentrations of DOC have generally been found in soil solutions from coniferous stands than in those from hardwood stands (David and Driscoll 1984, Cronan and Aiken 1985, Currie *et al.* 1996). Strobel *et al.* (2001) found higher concentrations of DOC from Norway spruce stands than from stands of pedunculate oak, beech or grand fir. Part of the decrease in DOC concentrations with increasing altitude may reflect the change in dominant tree species from Norway spruce to mountain birch.

Tree biomass decreased with altitude and this was apparently not only an effect of tree species. Nor is it likely to have been only an effect of geological differences, as Norway spruce biomass decreased greatly from 830 to 925 m a.s.l., although both plots were on moraine and both plots were also supplied with calcium and magnesium from the limestone layer above the plots. Tree age may also have played a role, as may the length of the growing season. Mork (1968) found that at the Norway spruce timberline at 950 m a.s.l., the growing season was on average 114 days, while at the birch timberline at 1050 m a.s.l. the growing season was 109 days. He also found a positive relationship between summer temperature and radial growth in Norway spruce (Mork 1968). Clearly, a shorter growing season is likely to lead to a smaller biomass.

The decrease of biomass with altitude is likely to be related to the decrease of DOC in

throughfall with altitude. The decrease of DOC in throughfall may in turn be indirectly related to the decrease of DOC in soil water. Michalzik *et al.* (2001) found that DOC fluxes in the forest floor were positively related to DOC fluxes in throughfall, which is in general agreement with our findings (Table 2). Although throughfall DOC is not thought to be a major constituent of soil water DOC, throughfall probably provides easily decomposable C compounds that could act as co-substrates or promoters for decomposition processes in the forest floor (Michalzik *et al.* 2001).

Above-ground litterfall also decreased with altitude. It should be noted that above-ground litterfall in this case refers to litter from trees: litter from the ground vegetation was not included. The decrease of C in above-ground litterfall is likely to be related to the decrease in tree biomass. Soil water DOC is largely derived from litter (Hongve 1999), so a decrease in soil water DOC with altitude would thus be expected. Gundersen *et al.* (1998) found a correlation between DOC in the forest floor and litterfall amount.

The decrease in the total soil C pool with altitude might also reflect the smaller input from tree litter. Our data support the findings of Currie and Aber (1997) and Tipping *et al.* (1999) regarding a positive relationship between DOC leaching or fluxes and the amount of soil organic matter. The C/N ratio and soil pH in the O horizon showed no clear altitudinal trends. Although some researchers have found that DOC mobilisation increased in soils with a high C/N ratio (Gödde *et al.* 1996), this appears not always to be the case (Michel and Matzner 1999). Although previous

**Table 3.** Correlation of DOC with sample volume, {H<sup>+</sup>} and electrical conductivity (EC). *N* = number of samples included in the analysis.

Altitude (m a.s.l.)	Sample type	<i>N</i>	Volume		{H <sup>+</sup> }		EC	
			<i>r</i>	<i>p</i>	<i>r</i>	<i>p</i>	<i>r</i>	<i>p</i>
830	Throughfall	8	0.313	0.451	-0.317	0.444	0.542	0.165
	Soil water	61	-0.028	0.829	0.365	0.004	0.792	0.000
925	Bulk precipitation	9	-0.676	0.046	0.201	0.603	0.624	0.072
	Throughfall	8	-0.505	0.202	-0.665	0.072	0.946	0.000
1000	Soil water	29	-0.194	0.313	0.701	0.000	0.768	0.000
	Throughfall	10	0.220	0.542	-0.020	0.956	0.728	0.017
	Soil water	43	-0.186	0.232	0.545	0.000	0.778	0.000

work has shown a positive correlation of the pH in the forest floor to DOC concentrations in forest floor leachates (Michalzik *et al.* 2001), no such relationship was obvious at Hirkjølen.

The significant positive correlations with EC and  $\{H^+\}$  in soil water appear at first sight to contradict some previous findings. Laboratory studies have generally shown that organic matter release from organic horizons is positively correlated to pH, as protonation decreases its solubility (Tipping and Hurley 1988, Andersson *et al.* 1999, 2000, Kalbitz *et al.* 2000). Similarly, a high ionic strength might be expected to reduce the charge density of organic substances, leading to coagulation (Tipping and Hurley 1988). However, field observations by Cronan and Aiken (1985) found a negative relationship between DOC and pH in soil water from forested sites in the Adirondacks and Lindroos *et al.* (1995) showed a significant negative correlation between dissolved organic matter and pH at 5 cm depth in Finnish forest soils. Although a significant positive correlation between DOC and EC was found for the organic horizon at Waldstein in Germany (Michalzik and Matzner 1999), no significant correlation was found between DOC and pH.

Organic anions are weak acids and thus contribute to the acidity of the solution (Cronan and Aiken 1985). This might explain the significant positive correlation found between DOC and  $\{H^+\}$  in soil water.

The correlation between DOC and EC could reflect the dilution and concentration of all solutes due to amount of water supply. However, no significant correlation was found with sample volume, except for a negative correlation in bulk precipitation at 925 m a.s.l. (Table 3). Also, previous work has shown a lack of correlation between ionic concentrations and volume of soil water in Norwegian forest soils (Moffat *et al.* 2002).

An alternative explanation is that the correlation with EC might be explained by the contribution of organic acids to the total anions. Guggenberger and Kaiser (1998) found that organic anions represented 22%–40% of the total anions in the mineral soil input. At a site such as Hirkjølen, with only a small input from sea salts and pristine with respect to anthropogenic input, organic anions could represent a major

part of the anionic charge. Calculations showed that organic anions represented on average 39%, 33% and 25% of the anionic charge in soil water at 830, 925 and 1000 m a.s.l., respectively. These figures are clearly comparable with those of Guggenberger and Kaiser (1998). Corresponding figures for throughfall were 37%, 28% and 21% at 830, 925 and 1000 m a.s.l., respectively. The decrease with altitude of the organic fraction of the anionic charge is probably related to the decrease in DOC concentrations. In bulk precipitation at 925 m, organic anions represented a mean of 20% of the anionic charge. The influence of DOC on EC could thus be considerable, at least at a site like Hirkjølen.

A third possible explanation might be that hydrogen ions, which have a large equivalent ionic conductance, might dominate the EC. Thus, correlation of EC with DOC in soil water would only reflect the correlation between DOC and  $\{H^+\}$ . However, we found that hydrogen ions accounted for on average 4%, 11% and 10% of EC in soil water at 830, 925 and 1000 m a.s.l., respectively; these figures appear too small to account for the correlation between DOC and EC.

We suggest that, rather than pH and EC controlling the concentration of DOC, in soil waters at Hirkjølen it is DOC that to a large extent controls the pH and EC.

The decrease with altitude of DOC fluxes in the sampling period suggests that, at Hirkjølen, these are more dependent on DOC concentrations than on water fluxes, which showed a tendency to increase with altitude for the same period, at least in throughfall (Table 1). Thus, changes in DOC concentrations are likely to lead to changes in DOC export. It is, however, important to remember that our flux estimates are only for the period from June to October. It was not possible to estimate DOC fluxes outside the sampling period, but these might have been high, especially during the spring snowmelt period. The importance of this period has been shown by Boyer *et al.* (1997), who found high DOC concentrations in soil water in connection with spring snowmelt in an alpine catchment in Colorado.

In conclusion, although the climatic differences between the plots were small, these differ-

ences seem to have been within a crucial range with respect to tree species, tree growth and the length of the growing season. We suggest that if an increase in mean temperature during the growing season causes the spruce–birch ecotone to move to a higher altitude than at present while tree growth at any given altitude increases, this might lead to increasing DOC concentrations and fluxes in surface waters. This, which may also be related to changes in pH and electrical conductivity, could have implications for drinking water quality in some areas. Future research might evaluate the relative importance of some of the factors mentioned, for example the decrease in biomass and the change in tree species with increasing altitude, in explaining DOC concentrations. Also, the altitudinal range of the study might be increased to include the alpine area above the forest line.

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