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The impact of four decades of annual nitrogen addition on dissolved organic matter in a boreal forest soil

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Abstract

Addition of mineral nitrogen (N) can alter the concentration and quality of dissolved organic matter (DOM) in forest soils. The aim of this study was to assess the effect of long-term mineral N addition on soil solution concentration of dissolved organic carbon (DOC) and dissolved organic nitrogen (DON) in the Stråsan experimental forest (Norway spruce) in Central Sweden. N was added yearly at two levels of intensity and duration: the N1 treatment represented a lower intensity, but a longer duration (43 yr) of N addition than the shorter N2 treatment (24 yr). N additions were terminated in the N2 treatment in 1991. The N treatments began in 1967 when the spruce stands were 9 yr old. Soil solution in the forest floor O, and soil mineral B, horizons were sampled during the growing seasons of 1995 and 2009. Tension and non-tension lysimeters were installed in the O horizon (n = 6) and tension lysimeters were installed in the underlying B horizon (n = 4): soil solution was sampled at two-week intervals. Although tree growth and O horizon carbon (C) and N stock increased in treatments N1 and N2, the concentration of DOC in O horizon leachates was similar in both N treatments and control. This suggests an inhibitory direct effect of N addition on O horizon DOC. Elevated DON and nitrate in O horizon leachates in the ongoing N1 treatment indicated a move towards N saturation. In B-horizon leachates, the N1 treatment approximately doubled leachate concentration of DOC and DON. DON returned to control levels but DOC remained elevated in B-horizon leachates in N2 plots 19 yr after termination of N addition. Increased aromaticity of the sampled DOM in mineral B horizon in both the ongoing and terminated N treatment indicated that old SOM in the mineral soil was a source of the increased DOC.

1 Introduction

Soil carbon (C) in boreal forests is an important carbon pool globally (Schlesinger, 1977). Mineral soil generally contains more C than the forest floor O horizon (Callesen

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et al., 2003). Zech and Guggenberger (1996) estimated the proportion of dissolved organic carbon (DOC) on the total C input into the mineral soil in an acid forest soil in the Fichtelgebirge, Germany, to be as high as 75 %. In a more recent study of C fluxes in Swedish boreal forests this estimate was lower, ranging from 26 % in the south to 10–15 % in the north (Kleja et al., 2008). Moreover, structural similarities between dissolved organic matter (DOM) and solid-phase organic matter from the Spodosol mineral B horizon suggests that DOM is a significant source of C in spodic B horizons (Guggenberger et al., 1994). Once retained in the B horizon, adsorbed/precipitated DOM slowly mineralizes, probably due to its inherent recalcitrant nature and stabilization through the binding to Al and Fe(III) (Boudot et al., 1989; Kaiser and Guggenberger, 2000). Therefore, mobilization and transport of DOM in spodic soils are important processes in the C balance of boreal forests. Dissolved organic matter is an important component in the biogeochemical cycles of elements like nitrogen (N) and phosphorous and can act as a vector for both naturally occurring and pollutant metals (Tyler, 1981).

In many areas in Europe the deposition of nitrogen (N) is high and will probably remain so in the foreseeable future (Galloway et al., 2004). Measured N in throughfall indicates unchanged or even slight increases in throughfall inorganic N concentration in the Swedish throughfall monitoring network nationwide during 1996–2008 (Pihl-Karlsson et al., 2011). Prolonged, high N inputs will decrease the decomposition rate of old soil organic matter (SOM) in temperate forest ecosystems (Berg and Matzner, 1997) and litter decomposition is negatively correlated to N enrichment, in particular for low quality substrates (Knorr et al., 2005). Also, there are reports of decreasing C mineralization rates from O horizon material following application of NH_4^+ salts in laboratory studies (Sjöberg et al., 2003). Incomplete decomposition of lignin type SOM induced by high availability of N may be linked to an increase in availability of water soluble, partially decomposed lignin degradation products (Fog, 1988). Guggenberger (1994) found support for increasing dissolved organic carbon (DOC) fluxes and prevalence of products from incomplete lignin degradation in response to elevated deposition of N and sulphur (S) in German spruce forests. After one year of N amendment

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through applying sodium nitrate at 30 kg N ha^{-1} yr^{-1} to a North American deciduous forest stand, water extractable DOC increased and the oxidative enzyme activity in soil was reduced (Sinsabaugh et al., 2004).

However, there is little information on how an elevated supply of N affects long-term leaching of DOM at stand level. In the Harvard Forest experiment in North-Eastern America, Currie et al. (1996) did not find a significant increase in the concentration of DOC in the forest floor after 7 yr of NH_4NO_3 application. Conversely, in mature sugar maple dominated stands, the leaching of DOC through mineral soil increased (more than three times than the control) and leaching of dissolved organic nitrogen (DON) increased (more than six times than the control) after the addition of 30 kg NO_3–N ha^{-1} yr^{-1} for 8 yr (Pregitzer et al., 2004). In the study by Pregitzer et al. (2004), the effect of elevated N deposition on leaching of DOC and DON in mineral B horizon was tested experimentally across a gradient of N availability, temperature and N deposition.

In N addition experiments, the contrasting effects of treatment on DOC might be explained by changes in soil acidity (Evans et al., 2008) because dissociation of functional groups can increase DOC solubility and presence of polyvalent cations limit it. In experiments where N addition probably acidified the soil (e.g. N added as. NH_4SO_4), DOC in soil solution should by this mechanism decrease, whereas, if N addition decreased acidity (e.g. N added as $NaNO_3$), DOC in soil solution should increase.

The leaching of DOC positively correlates with litterfall production in five coniferous forests across Europe (Gundersen et al., 1998). In a laboratory experiment the amount of substrate C increased the amount of extractable DOC (Park et al., 2002). However, the extent to which soil carbon and nitrogen stocks influence the concentration of DOC or DON is unclear (Kalbitz et al., 2000). As long term N addition might influence net primary productivity (NPP) of the ecosystem, indirect effects of N addition, resulting from changes to soil C and N stocks, might affect soil solution DOC and DON concentration.

In the present study, a Norway spruce (*Picea abies* (L.) Karst.) forest stand in Central Sweden, E26A Stråsan (Tamm et al., 1974), was fertilized annually with

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ammoniumnitrate, NH_4NO_3, since 1967. The aim was to contrast the effect of long-term (> 40 yr), intermediate intensity N addition (37 kg N ha^{-1} yr^{-1}) to shorter duration (24 yr), high intensity N addition (73 kg N ha^{-1} yr^{-1}) on soil solution concentration of DOC and DON in O and B horizon soil solution. The properties of the DOM, as determined by fractionation based on hydrophobicity and acidity (Leenheer, 1981) and UV absorbance at 254 and 280 nm, were studied. The hypothesis was that N addition increased the formation of partially decomposed lignin degradation products found in O horizon, resulting in increased DOC concentrations in O and B horizon leachates. This increase in DOC should be linked with higher abundance of aromatic moieties of the DOM, indicated by increased specific UV absorption (at 254 and 280 nm) and an increased hydrophobicity of the DOM.

2 Materials and methods

2.1 Site description

The field site E26A Stråsan (Tamm et al., 1974) is an experimental spruce forest located 350 m a.s.l. in Central Sweden (60° 55′ N, 16° 01′ E). The soil type is classified as a haplic podzol (Berggren et al., 1997). Parent material consists of glacial till, with medium and fine sand as dominating fractions and a normal to high frequency of stones. Roots are present down into the mineral B horizon. Average horizon depths were 10 cm (O horizon), 6 cm (E horizon) and 14 cm (B1 horizon) in 2011.

The experiment was designed as a randomized block experiment with two blocks. Plots were 30 m × 30 m, with measuring plots of 25 m × 25 m. Measurements were taken in the control and N fertilized plots to which ammonium nitrate, NH_4NO_3, had been added at average rates of 35 (N1) and 73 (N2) kg ha^{-1} yr^{-1} (Table 1). The N addition in the N1 treatment was of lower intensity, but longer duration (43 yr), than the N2 treatment, which was of higher intensity and shorter duration (24 yr). Although the N additions were terminated in the N2 treatment in 1990, the N2 plots received a larger

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cumulative amount of N than the on-going N1 treatment by 2009. The NH_4NO_3 salt was spread manually in May once a year. In 2009, manual application of ammonium nitrate was on 12 May but for 1995, no application date was recorded.

Until the middle of the 1950s, the experimental area was covered with old Norway spruce-dominated (*Picea abies* (L.) Karst.) forest. Trees were felled in 1956 and the site was subjected to burning in the early summer of 1957. Norway spruce seedlings were planted in the spring of 1958.

At a nearby meteorological station of the Swedish Hydrological and Meteorological Institute (60° 57′ N, 16° 26′ E), the mean annual precipitation and temperature were 584 mm yr^{-1} and 4.3 °C for the period 1995 to 2009. The effective temperature sum (accumulated daily mean temperatures in excess of 5 °C) was 1163 °C days in 1995 and 1209 °C days in 2009. The annual precipitation was 729 mm in 1995 and 733 mm in 2009 (data from SMHI, Swedish Hydrological and Meteorological Institute, http://www.smhi.se). Based on data for the period 1961 to 1990, snowmelt was usually complete by mid April. The wet deposition of inorganic N at Stråsan was approximately 5.1 kg N ha^{-1} yr^{-1} in 1995/96 and 3.2 kg N ha^{-1} yr^{-1} in 2009/10 (data from IVL, Swedish Environmental Institute, http://www.ivl.se).

2.2 Installation of lysimeters and sampling of soil solution

Zero-tension lysimeters (ZTL) were installed below the O horizon at 6 locations per plot to sample the water moving freely under the act of gravity. The ZTL (Bio-Konsult, Skanör, Sweden) consisted of a Plexiglas trough (30 cm × 30 cm) with two layers of polyethylene nets (mesh sizes 2 mm and 0.5 mm) on top. The lysimeters were connected by silicone tubing to a borosilicate glass bottle. In addition, Rhizon-type lysimeters (R) were installed at the bottom of the O horizon, six in each plot, to sample the meso- and micropore soil water through tension: the Rhizon-type lysimeters were only sampled during 1995.

In the lower B horizon (~ 50 cm depth), tension lysimeters (TL) were installed at four locations in each plot. The TL consisted of poly(tetrafluoroethene) porous cup

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lysimeters (Prenart Equipment Aps, Frederiksberg, Denmark) with a pore size of 4 µm: poly(tetrafluoroethene) cups are chemically inert with respect to DOC (Beier and Hansen, 1992). Solutions were collected in borosilicate glass bottles. Both the TL cups and Rhizon lysimeters were operated at transient vacuum with an initial tension of −70 kPa.

All lysimeters were installed in the outer part of the projection of tree crowns to obtain a similar influence of throughfall on the lysimeter solutions. Collecting bottles were placed below ground in PVC tubes (50 cm) vertically installed in the soil. A lid consisting of styrofoam ensured that solutions were kept cool and dark during the sampling periods. The TL were installed in June 1994 and the ZTL in September/October 1994.

The soil solution was sampled during 2 yr: 20 June 1995 to 21 November 1995 and 8 June 2009 to 12 November 2009. For both years, the sampling interval was two weeks. The soil solution was sampled twelve times per year. Two sets of bottles were used for the solutions collected by ZTL; these were used alternatively to enable bottles to be cleaned in the laboratory (rinsing with de-ionized water and burning at 200–250 °C) before each sampling period. The bottles for TL lysimeters were rinsed in the field with de-ionized water on each sampling occasion.

During 1995, samples from each lysimeter were analyzed separately, but for samples taken during 2009 so-called "pooled samples" were analyzed. Pooled samples were obtained by pouring the samples gathered by all lysimeters from the experimental plot into a large container from which a composite sample was taken and analyzed. Pooling of samples thus renders volume weighted concentrations per plot. If a lysimeter had a larger volume than 1 dm^3, only a 1 dm^3 sample from that specific lysimeter was added to the bulk sample. Samples from 1995 were calculated as volume weighted concentrations by plot and sampling occasion.

2.3 Chemical analyses of soil solution

Samples were filtered through a 0.2 µm filter and analyzed for pH, total organic carbon (TOC), NO_3^- (aq.), NH_4^+ (aq.), metals (Al, Fe, Mn, Ca, K, Mg, Na), anions (Br, Cl, PO_4,

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SO_4) and total nitrogen (TN). The samples were stored at +2 °C until analysis. DON was calculated by subtracting nitrogen content in inorganic nitrogen species (NO_3-N and NH_4-N) from the TN concentration. In 1995, DOC was fractionated into hydrophobic acids (HoA) and neutrals (HoN), and into hydrophilic acids (HiA), neutrals (HiN) and bases (HiB) with an adsorption chromatographic technique according to Leenheer (1981). In 2009, UV absorbance at 254 and 280 nm was measured. Specific UV absorbance, SUVA, was calculated by dividing UV absorbance (m^{-1}) by DOC concentration ($mg\,l^{-1}$).

An aliquot for TOC analysis was filtered through 0.2 µm filters (Acrodisc PF, Gelman Sciences, MI) and acidified to pH 3 with HCl. In 1995, TOC measurements were made with a Shimadzu TOC-500 analyzer (Shimadzu Corporation, Kyoto, Japan), a Shimadzu TOC-VCPH analyzer was used in 2009. Analyses were usually performed within 1 week of sampling.

In 1995, TN samples were treated to persulphate oxidation (10 g $K_2S_2O_8$ in 1 l of 0.15 M NaOH) by mixing of equal volumes and boiling under pressure (14 kPa) for 25 min. Before analysis of NO_3^- by Flow Injected Analysis (FIA), 0.25 ml of 1.44 M H_2SO_4 was added. Determination of TN was performed with a Shimadzu TNM-1 TN analyzer (Shimadzu Corporation, Kyoto, Japan) in 2009.

Anions (Br, Cl, PO_4, SO_4, and NO_3^-) were analyzed by ion chromatography using a Dionex 2000i/SP column in 1995 and a Metrosep A Supp 5 column in 2009. NH_4^+ was analyzed by a FIAStar 5000 analyzator (FOSS, Hilleroed, Denmark) in 2009. The limit of detection (LOD) for NO_3^- and NH_4^+ were 0.01 $mg\,l^{-1}$. Values below detection limit were set to half LOD.

Metals (Al, Fe, Mn, Ca, K, Mg, and Na) were analyzed by a mass spectrometer ELAN 6000 analyzer and an OPTIMA 3000 DV torch (Perkin Elmer, Waltham, USA). The pH of leachate solutions was measured with a microprocessor ionalyzer/901 (Orion Research, Beverly, MA) using a combination glass electrode (Radiometer model PHC2002-8). UV absorbance was determined on a UV VIS spectrofotometer Lambda 11 (Perkin Elmer, Waltham, USA) using a 10 mm cuvette.

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As a measure of the potentially induced acidity of the experimental N additions, ANC forcing (Evans et al., 2008) was calculated according to Eq. (1):

$$\text{ANCforcing} = \Delta NH_4^+ - \Delta NO_3^- \quad (1)$$

where ΔNH_4^+ is the difference between treatment and control in mean annual soil solution concentration ($\mu eq\,l^{-1}$) of NH_4^+ and ΔNO_3^- is the difference between treatment and control in mean annual soil solution concentration ($\mu eq\,l^{-1}$) of NO_3^-.

2.4 Sampling and analyses of soils

Samples from the O_i and O_{e+a} horizon were taken in august 2010 with stainless steel cylinders (Ø 49 mm). Six composite samples, each consisting of 25 subsamples, were taken from a grid in the measuring plots (25 m × 25 m). Samples were weighed and then passed through a 4 mm sieve to remove coarse fragments and to homogenize the samples. Dry weights were determined after drying at least 24 h at 105 °C. The C and N contents were determined from ground samples with a LECO elemental CNS-2000 analyzer (LECO Instruments, St. Joseph, USA).

For estimating the C and N stock in O_{e+a} horizon, the volume occupied by stones and boulders was corrected with the rod penetration method of Viro (1952). The percentage of stones and boulders in the O_{e+a} horizon was assumed equivalent to the percentage of penetrations that hit a stone on the surface or within the O_{e+a} horizon at a depth of less than half the mean depth of the O_{e+a} horizon. Data on C and N stock estimates made in 1996 were obtained from Andersson et al. (2002).

2.5 Estimates of standing stem volume

Trees were calipered in the experimental plots in both 1997 and 2010. The measurements were made in inner plots measuring 20 m × 20 m centered in the net plots which were 25 m × 25 m. The standing stock volume was estimated by the use of stand volume

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functions for Norway spruce, *Picea abies*, (Brandel, 1990): standing dead trees were not included in the estimates. Total stemwood production was estimated by including data for thinned volumes, i.e. the volumes of trees cut down and removed for benefit of the remaining stand. Data on diameter at breast height and height in 1997 were obtained from a database hosted by the Unit for Field-based Forest Research (Swedish University of Agricultural Sciences).

2.6 Statistical analyses

Treatment effects on the concentrations of DOC, DON, and properties of the DOM were analyzed as a randomized block experiment on time-series soil solution data. Autocorrelation of any lag in time series data was not significant ($p > 0.05$). Moreover, the data indicated strong cross-correlation between time series of the different treatments. For analysis of soil solution data of DOC and DON during the years 1995 and 2009, a multiple linear model was fitted according to:

$$y_{ijkl} = \mu + \alpha_i + b_j + d_{ij} + t_k + m_l + e_{ijkl} \quad (2)$$

where

y_{ijkl} = dependent variable
μ = overall mean
α_i = treatment effect
b_j = random block effect
d_{ij} = treatment × year effect
t_k = effect of date of sampling
m_l = effect of year
e_{ijkl} = random error

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Treatment, block, year, and date of sampling were treated as factors. The data were log-transformed prior to model evaluation in order to improve approximation to normality. Data on Leenheer fractionation (analyzed in 1995) and SUVA (analyzed in 2009) were treated in a similar model, but without year as a factor. The linear model was interpreted by analysis of variance (ANOVA). If significant treatment effects were indicated, analyses were continued with Tukey honest significant difference (HSD) method.

The control plots repeatedly displayed soil solution NO_3^- and NH_4^+ below the detection limit; this was the reason these variables were not treated in the time-series analysis. Instead, seasonal means were used. For data on non-time series (NO_3^-, NH_4^+, pH, ionic strength, soil C and N, and standing tree volume), a linear model with treatment, block and year as factors was used. The linear model was interpreted by ANOVA. If significant treatment effects were indicated, post-hoc analyses were made with the Tukey HSD method.

3 Results

3.1 Soil C and N

The C and N stocks in the O_i and O_{e+a} horizons were larger in the N treated plots than control (Table 2). In 1996, the C stock in $O_i + O_{e+a}$ in treatment N1 ($42.6 \pm 8.9\,\mathrm{t\,C\,ha^{-1}}$) and N2 ($48.7 \pm 4.4\,\mathrm{t\,C\,ha^{-1}}$) were more than double the C stock found in control (19.4 ± 3.3 $\mathrm{t\,ha^{-1}}$). Although N addition was ended in treatment N2 by 1991, the C stock was not significantly different from that in the on-going N treatment, N1, in 2010. The largest increase in C stock (relative to control) was in the O_i horizon in 1996 and in the O_{e+a} horizon in 2010 for both N treatments. Soil carbon in O_{i+e+a} horizon increased by 19.3 ± 4.6 and $16.6 \pm 0.6\,\mathrm{kg\,C\,ha^{-1}\,yr^{-1}}$ per added $\mathrm{kg\,N\,ha^{-1}\,yr^{-1}}$ in treatments N1 and N2 in 1996: corresponding figures were 16.5 ± 4.6 and $15.1 \pm 0.3\,\mathrm{kg\,C\,ha^{-1}\,yr^{-1}}$ per added $\mathrm{kg\,N\,ha^{-1}\,yr^{-1}}$ in 2010.

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The N stock in $O_i + O_{e+a}$ in 1996 was, similarly to C stock, more than double the control ($0.57 \pm 0.09\,t\,N\,ha^{-1}$) in both N treatments ($1.57 \pm 0.31$ and $1.92 \pm 0.19\,t\,N\,ha^{-1}$ in N1 and N2 respectively). The O_{e+a} horizon C and N stocks presented the largest relative change in the on-going N1 treatment during the period 1996 to 2010, although the difference between years was not significant ($p > 0.05$).

The C/N-ratio in the O_{e+a} horizon was $33\,g\,g^{-1}$ for the control and $28\,g\,g^{-1}$for N1 in both 1996 and 2010. The C/N-ratio in O_{e+a} horizon in the N2 treatment increased slightly, from $25\,g\,g^{-1}$ in 1996 to $27\,g\,g^{-1}$ in 2010. The C/N-ratio in the O_{e+a} horizon was lower than control in both N treatments. The C/N-ratio was higher in O_i than in O_{e+a} regardless of treatment. The lowest C/N-ratio in O_i horizon was found in the on-going N1 treatment in 1996 (N1: $28\,g\,g^{-1}$).

3.2 Tree stand development

There were large increases in stemwood production in the fertilized plots by 1997 (Table 3). For treatments N1 and N2, stem volume increased by approximately 65 %, compared to control. The difference between the N1 and N2 plots was not significant ($p > 0.05$). In 2010, after an additional 13 yr of N addition in the N1 treatment, the increase in growth was less: 49 % for N1 treatment (corresponding figure for N2 was 55 %). This was partly explained by more thinned volumes in the N1 plots and that the standing tree volume in control plots increased from 163.5 to $286.2\,m^3\,on\,bark\,ha^{-1}$ between 1997 and 2010.

By assuming a tree wood density of $500\,kg\,m^{-3}$ and a C content of 50 % (by mass), standing stemwood increased by 21.0 ± 0.1 and $15.7 \pm 0.3\,kg\,C\,ha^{-1}\,yr^{-1}$ per $kg\,N\,added\,ha^{-1}\,yr^{-1}$ in treatments N1 and N2 in 1997: corresponding figures were 21.4 ± 0.8 and $22.1 \pm 3.5\,kg\,C\,ha^{-1}\,yr^{-1}$ per $kg\,N\,added\,ha^{-1}\,yr^{-1}$ in 2010.

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3.3 Soil solution chemistry

3.3.1 Dissolved organic carbon and nitrogen

Soil solution DOC concentrations were highly variable in O horizon leachates throughout the growing season, ranging 10 to 90 mg l^{-1} (Fig. 1): however, no clear seasonal pattern could be distinguished in either year in data from ZTL-, nor R-, type lysimeters. The addition of N did not affect DOC in O horizon leachates in ZTL or R-type lysimeters (Table 4). DOC annual mean concentration in both the N1 and N2 plots was slightly higher than in control plots in 2009, but the effect was not significant. Regardless of treatment, DOC in ZTL lysimeter leachates was higher in 2009 than in 1995 ($p < 0.05$).

In contrast, there were treatment effects in B horizon leachates for both years: during both 1995 and 2009, DOC in the low-intensity ongoing N1 treatment was higher than in the control, and the DOC concentrations in the N2 treatment was higher than in N1. In comparison to O horizon leachates, mineral B horizon leachates were less variable. Moreover, DOC concentrations below the B horizon were generally an order of magnitude smaller than below the O-horizon, indicating the large capacity for sorption/precipitation of DOM in the mineral soil. DOC in TL leachates was higher during 2009 than 1995 ($p < 0.05$) in all treatments. The annual means of DOC in both O horizon ZTL and B horizon TL leachates were correlated to the standing tree volume of individual plots (Fig. 3).

In 1995, DON concentrations in O horizon R-type lysimeter leachates were elevated in the N1 treatment, compared to both the control and N2. By 2009, O horizon ZTL leachate DON was higher in both N1 and N2 than in control plots ($p < 0.05$). Both N1 plots displayed elevated DON concentrations (> 6 mg DON l^{-1}) during early summer 2009 and DON in mineral B horizon leachates were elevated approximately one month later.

In B horizon leachates, DON in N1 plots were elevated in 2009 but not in 1995, similarly to ZTL leachates. By contrast, DON concentrations in N2 plots differed from

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control plots only in 1995. The difference in DON in B horizon leachates between 2009 and 1995 was not significant ($p > 0.05$).

DOC and DON concentrations in O horizon leachates were positively correlated with sampled water volume across sample collection dates ($p < 0.05$ for both) but with low explained variance (DOC $R^2 = 0.07$ and DON $R^2 = 0.01$). In B horizon lysimeters, DOC concentrations were positively correlated with sampled water volume ($p < 0.05$; $R^2 = 0.36$), but DON concentrations were not ($p = 0.29$). ZTL- and R-type lysimeter leachates did not correlate with respect to either DOC ($p = 0.19$) or DON ($p = 0.11$) on time series data, indicating that the two lysimeter types sampled different kind of soil waters.

As O horizon leachate DOC concentration was unchanged but DON concentration increased in the N1 treatment, the DOC/DON-ratio decreased. In 1995 the DOC/DON-ratio on annual mean concentrations in O horizon leachates was 70 % of control in both N treatments (Fig. 2). In 2009, the DOC/DON-ratio in the N1 treatment was 41 % of control: corresponding figure for the N2 treatment was 78 %. The annual mean DOC/DON in ZTL leachates did not show a 1 : 1 relationship with C/N in the O horizon (Fig. 2). Especially N1 plots DOC/DON were low in 2009, because DON was elevated. The response of SOM and DOM to long-term N addition thus differed, at least in time lag.

3.3.2 Hydrophobicity, acid-base and UV absorbance of leachate DOM

No effect of treatment on the hydrophobicity or acidity of DOM was observed in O horizon leachates, estimated by Lenheer fractionation (Table 5). Hydrophobic and hydrophilic acids were the dominating fractions of the DOM (> 90 % by mass) in leachates from both R-type lysimeters and ZTL. Thus, neutrals and bases constituted low proportions of the DOM (< 10 %).

$SUVA_{254\,nm}$ and $SUVA_{280\,nm}$ did not reveal any treatment effects in O horizon leachates in 2009 (Table 6), which confirmed the results from Lenheer fractionation. However, in the mineral B horizon, $SUVA_{254\,nm}$ was higher ($p < 0.05$) in N1 and N2 plots compared to control. $SUVA_{280\,nm}$ was only elevated in the N2 plots ($p < 0.05$).

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3.3.3 Ionic strength and acidity

Ionic strength in the O-horizon soil solution recovered in ZTL leachates was higher in N1 than in the control in both 1995 and 2009 (Table 7): N2 plots did not display higher ionic strength than control plots in ZTL leachates. In mineral B horizon, the ionic strength of sampled soil solution was not higher than the control in both the N1 and N2 plots ($p > 0.05$).

The concentration of NO_3^- and NH_4^+ recovered in ZTL leachates was higher in the N1 plots than control and N2 in 1995 and 2009 (Table 7). This resulted in ANC forcing in the range −250–50 $\mu eq\,l^{-1}$ in O horizon and −54–3 $\mu eq\,l^{-1}$ in B horizon leachates for N1 and N2. However, ANC forcing showed no linear correlation with relative change of DOC (%) in N treated plots in O or B horizon leachates ($p = 0.24$ and $p = 0.35$ respectively). Significant treatment effects on pH were only present in R lysimeter leachates (lower pH in N1 plots). Accordingly, there was no support for acidity as a driver of DOC at Stråsan (Fig. 4).

4 Discussion

To the contrary of our initial hypothesis, the concentration and the quality of DOC sampled in O horizon leachates did not change in response to long-term addition of mineral N at the Stråsan experimental forest. This finding was in accordance with some lysimeter studies (Currie et al., 1996; Raastad and Mulder, 1999) but stood in contrast to others (Guggenberger, 1994; Pregitzer et al., 2004). The variability in response of DOC to N addition has not been uniformly explained. Acid/base effect of N fertilizer (Evans et al., 2008) and ecosystem-specific response of the microbial community (Waldrop and Zak, 2006) have been proposed to explain between-site differences of DOC response to N addition.

Fröberg et al. (2006) identified a positive correlation between O horizon leachate mean annual DOC concentration and aboveground biomass across a gradient of

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climate and primary productivity in Sweden. We observed a similar relationship in our study (Fig. 3), although we are aware of temporal pseudoreplication. The standing tree volume is a major determinant of litterfall production in Norway spruce forests stands (Saarsalmi et al., 2007) and litter is a significant source of DOC in O horizon soil solution (Fröberg et al., 2005). An indirect positive effect of N addition on DOC in O horizon, through the production and subsequent decomposition of aboveground litter, thus seemed likely. The fact that year was a significant factor in our ANOVA ($p < 0.05$) complimented this observation (Table 4), as well as the fact that amount of precipitation and the effective temperature sums at a nearby weather station were similar in 1995 and 2009 (see Sect. 2.1). As we did not observe treatment effects on DOC in O horizon leachates the direct effect of N addition on DOC in O horizon at Stråsan was inhibitory per unit substrate C (soil C and litterfall production). This was corroborated by the fact that standing tree volumes and O_i and O_{e+a} horizon C stocks increased in N1 and N2, but O horizon DOC was similar in control and N amended plots in both 1995 and 2009. The same effect was found for ZTL and R lysimeters although they sampled different soil water. Data on soil water content at 0.2 and 0.5 m depth in the control and N1 plots (sampled during April–July, 2012) did not indicate changes to the soil moisture sufficient to cause a concentration effect (M. O. Rappe-George, unpublished data). Moreover, there is support that water flux through the soil does not greatly affect DOC concentration, even at high rates (Fröberg et al., 2006; Kalbitz et al., 2007; Schmidt et al., 2010).

In accordance with our hypothesis regarding DOC concentration in mineral B horizon, DOC approximately doubled in both sampling years in response to both N treatments, N1 and N2. These findings were in accordance with other reports on the effects of N addition on mineral horizon DOC across a range of ecosystem types (Guggenberger, 1994; Pregitzer et al., 2004). As there were no treatment effects in O horizon leachates, the increased DOC in mineral soil requires an explanation other than increased leaching of DOC from the overlying O horizon. We found no support that changes to acidity or ionic strength explained the increase in DOC concentration in

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the N treated plots (Table 7). A decrease in either ANC forcing or ionic strength would have been needed. Ionic strength increased slightly in N1 and N2 plots, but the effect was not significant (p = 0.27). The seasonal means of DOC appeared to correlate with the standing tree volume also in B-horizon leachates (Fig. 3). A larger standing tree biomass was likely to have increased root biomass (Cairns et al., 1997) and thus litter input to mineral soil via root litter and/or rhizodeposition. This might be a relatively easily available C source that stimulated decomposition of more recalcitrant SOM found in the mineral soil (Kuzyakov, 2002), resulting in increased DOC. Moreover, the $SUVA_{254\,nm}$ increased in mineral B horizon leachates in the fertilized plots, indicating that the DOM contained more aromatic moieties (Dilling and Kaiser, 2002) which are important for long-term sorptive preservation of OM in mineral soil (Kaiser and Guggenberger, 2000). Dissolved organic carbon in boreal forest B horizon is mainly old C, originating from C found in the mineral solid phase (Fröberg et al., 2006). Taken together, this suggests that a significant source of the increased DOC in N1 and N2 mineral soil leachates was mobilization of old SOM into solution. However, in mineral B horizon leachates, the terminated N treatment, N2, had the highest DOC, not the ongoing N1 treatment, which demonstrated that ongoing N addition did not fuel DOC but that DOC was more related to the accumulated amount of added N. The elevated DOC concentrations in B horizon TL leachates could have consequences for water quality as DOC is known to be a transporter of several metals and radionuclides (Tyler, 1981; Marley et al., 1993).

In O horizon, R lysimeter leachate DON was elevated in the N1 plots in 1995. In contrast, elevated DON in the N amended plots was observed in ZTL leachates only in 2009. McDowell et al. (1998) report increased soil water DON flux sampled beneath the forest floor by a factor of two in a N amended Pine forest stand in Massachusetts, US. DON in O horizon soil solution at Stråsan increased in response to N addition up to a factor of four (N1 plots in O horizon 2009). Both N1 plots at Stråsan displayed elevated DON concentrations (in excess of 6 mg DON l^{-1}) during early summer 2009: elevated DON concentrations in early summer were not apparent in 1995 (Fig. 1). The first sampling in 2009 took place 27 days after the application of ammonium nitrate.

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Seasonality of DON with high concentrations during early summer is reported for a coniferous forest (McDowell et al., 1998) and a grassland altitudinal gradient (Farrell et al., 2011). Stråsan represented a highly N limited ecosystem at the beginning of N treatments in 1967 (Tamm et al., 1974). The internal cycling of N, determined as net-mineralization, at Stråsan increased by a factor of ten in N1 plots by 1996 (Andersson et al., 2001) and these conditions appeared to have been exacerbated in the N1 plots by 2010 with NO_3^- as a major N species in O horizon leachates (Table 7). This indicates a move towards N saturation in the N1 plots. Although N addition was terminated in the N2 treatment by 1991, DON was not elevated in 1995, but in 2009.

DON in mineral B horizon leachates was elevated in N2 plots in 1995 and in N1 plots in 2009. By 2009, DON in N2 plots in mineral soil leachates was still elevated but did not differ significantly from the control: thus DON in mineral soil leachates appeared to be driven by the continuous supply of mineral N. Both N2 (in 1995) and N1 (in 2009) approximately doubled DON in mineral B horizon. In a study by Pregitzer et al. (2004), DON leaching from mineral soil increased by a factor of six in response to 8 yr of N addition in a North American deciduous forest, although the sites in this study were possibly not N limited (C/N in O_{e+a} ranging 17–21). Mineral soil DON in the N1 plots were elevated in the middle of summer 2009, approximately one month after DON concentrations peaked in the above-lying O horizon, which suggests that O horizon ZTL is indicative of DON fluxes from O horizon into the mineral soil.

The dynamics of C/N stochiometry differed between solid and dissolved organic matter: the DOC/DON in O horizon was more responsive to long-term addition of mineral N and termination of N addition than C/N of O-horizon SOM (Fig. 2). Moreover, the annual mean DOC/DON-ratio in the N treatments showed contrasting temporal patterns in O horizon ZTL leachates. The decrease in DOC/DON of N1 plots between 1995 and 2009, as well as increased NO_3^-, corroborates development towards N saturation. Although O horizon DON was elevated in the N2 treatment in 2009 compared to control, the DOC/DON of N2 approached control levels in 2009, indicating recovery from long term N addition.

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The results we present here also demonstrate that long-term N addition to a boreal forest sequestered C (only stemwood and O_{i+e+a} horizon C considered) at rates of 37.9 ± 5.4 (N1 in 2010) and $32.3 \pm 1.0\,\mathrm{kg\,C\,ha^{-1}\,yr^{-1}}$ per added $\mathrm{kg\,N\,ha^{-1}\,yr^{-1}}$ (N2 in 1997). These estimates, although conservative, are in the interval 20–40 $\mathrm{kg\,C\,ha^{-1}\,yr^{-1}}$ per $\mathrm{kg\,N\,ha^{-1}\,yr^{-1}}$ reported by de Vries et al. (2009) across non-N-saturated European forests. Increased soil C in O_{i+e+a} horizon contributed little less than half of this sequestered C, ranging 37–53 % over both N treatments and years. This was caused by increased production of litter and unchanged, or even decreased per unit substrate, DOC. Moreover, respiration rates from O horizon material were suppressed in the N treated plots at Stråsan in an incubation study (Sjöberg et al., 2003). The effect of long-term N addition on mineral soil C balance was unclear: increased DOC originating from old SOM was to an unknown degree countered by altered production of litter belowground and CO_2 evasion. N deposition in Swedish forests has not declined since mid 1990s, in contrast to S deposition which has declined substantially (Pihl-Karlsson et al., 2011). The N2 treatment had elevated mineral B horizon DOC 19 yr after termination of N addition. This indicates that recovery from heavy N addition may be very slow even at sites originally strongly N limited: a finding with implications for the effect of N deposition on C balance of terrestrial ecosystems. Generally, mycorrhizal abundance decreases in response to N addition (Högberg et al., 2003; Treseder et al., 2006). Thus, changes to the soil microbial community composition and its function were likely in the N1 and N2 treatments. Detailed studies of the regulating function of soil biology on C and N cycling at Stråsan are needed to improve our understanding of these systems in the context of biogeochemical cycles and global change, e.g. terrestrial C balances and anthropogenic N deposition.

5 Conclusions

The effect of long-term addition of N on O horizon DOC concentration is a balance between direct and indirect effects. We present support for a positive influence of litterfall

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production on DOC in O horizon at Stråsan. There is no direct positive effect of long term N addition on O horizon DOC: on the contrary, a negative effect per unit substrate C (soil C and litterfall production) is shown. This brings about an enhanced C sequestration in forest floor O horizon. Elevated O horizon DON and NO_3^- in the on-going N treatment, N1, indicates development towards N saturation. DON in O horizon leachate is elevated 19 yr after termination of N addition, although the DOC/DON approaches DOC/DON of control.

Long-term N addition approximately doubles leachate concentration of DOC and DON in mineral B horizon at Stråsan. This could have consequences for water quality as DOC is known to be a transporter of several metals and radionuclides. Increased aromaticity of the sampled DOM in both the ongoing and terminated N treatment indicates that old SOM in the mineral soil is a source of the increased DOC in B horizon. 19 yr after termination of N addition, DON returns to control levels, but DOC remains elevated. These effects appear not to be driven by acidity but rather by biology. Future work at Stråsan should aim to link changes to soil C and N cycling with detailed studies of soil biology, addressing processes in both O and mineral B horizon explicitly.

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Table 1. Nitrogen addition rates ($kg N ha^{-1} yr^{-1}$) and total amount of N added 1967–2009 ($kg N ha^{-1}$) at Stråsan.

Year	Duration	Control	N1	N2
1967–1969	3 yr	0	60	120
1970–1976	7 yr	0	40	80
1977–1990	14 yr	0	40	60
1991–2009	19 yr	0	30	0
Total 1967–2009	43 yr	0	1590	1760

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Table 2. Soil carbon and nitrogen pools in 1996 and 2010 (tons C and N ha^{-1}, respectively). Values are mean ± range (n = 2). Superscripts denote significant differences at p = 0.05 (Tukey HSD test). Within rows, values followed by the same letter were not significantly different. Data from 1996 are from Andersson et al. (2001).

	1996			2010		
	Control	N1	N2	Control	N1	N2
Carbon						
O_i	1.2 ± 0.1^{a}	3.6 ± 0.1^{b}	4.0 ± 0.4^{b}	2.4 ± 0.2^{c}	4.3 ± 0.3^{b}	$3.7 \pm < 0.1^{b}$
O_{e+a}	18.2 ± 3.2^{a}	39.0 ± 8.8^{b}	44.7 ± 4.1^{b}	20.2 ± 2.6^{a}	45.1 ± 10.0^{b}	45.5 ± 3.2^{b}
Total	19.4 ± 3.3^{a}	42.6 ± 8.9^{b}	48.7 ± 4.4^{b}	22.6 ± 2.7^{a}	49.4 ± 10.2^{b}	49.2 ± 3.3^{b}
Nitrogen						
O_i	$0.03 \pm < 0.01^{a}$	0.13 ± 0.01^{bc}	0.16 ± 0.02^{b}	$0.06 \pm < 0.01^{ad}$	$0.12 \pm < 0.01^{bc}$	$0.10 \pm < 0.01^{cd}$
O_{e+a}	0.54 ± 0.09^{a}	1.44 ± 0.30^{b}	1.77 ± 0.17^{b}	0.60 ± 0.07^{a}	1.60 ± 0.34^{b}	1.75 ± 0.17^{b}
Total	0.57 ± 0.09^{a}	1.57 ± 0.31^{b}	1.92 ± 0.19^{b}	0.66 ± 0.07^{a}	1.73 ± 0.34^{b}	1.85 ± 0.17^{b}

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Table 3. Standing tree volume, thinned and total production of stemwood (m^3 on bark ha^{-1}) at Stråsan. Values are mean ± range (n = 2). Superscripts denote significant differences at p = 0.05 (Tukey HSD test). Within columns, values followed by the same letter were not significantly different. Data on diameter at breast height and height in 1997 were obtained from the Unit for Field-based Forest Research database (Swedish University of Agricultural Sciences).

	1997			2010		
	Standing tree volume	Thinned volume	Total production	Standing tree volume	Thinned volume	Total production
Control	163.5 ± 2.5[a]	7.6 ± 0.5	171.1 ± 2.0[a]	286.2 ± 17.7[c]	9.7 ± 2.8	295.9 ± 14.9[c]
N1	267.0 ± 2.0[b]	46.2 ± 2.3	313.2 ± 0.3[b]	424.7 ± 12.7[d]	16.0 ± 8.2	440.6 ± 4.5[d]
N2	274.5 ± 0.5[b]	39.7 ± 13.3	314.2 ± 13.8[b]	442.1 ± 7.0[d]	1.1 ± 1.1	443.2 ± 5.9[d]

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Table 4. Means (95 % confidence intervals) of concentrations of dissolved organic carbon (DOC) and dissolved organic nitrogen (DON) in O and B horizon leachates in 1995 and 2009 at Stråsan (n = 24). Both DOC and DON are in mg l^{-1}. Superscripts denote significant differences at p = 0.05 (Tukey HSD). Within lysimeter type and variable, values followed by the same letter were not significantly different. Significant interaction treatment × year found for DON in ZTL and TL.

Horizon		Control	N1	N2
O	Zero tension lysimeters			
	DOC			
	1995	28.7 (19.1–43.2)^{a}	29.2 (19.4–44.1)^{a}	27.4 (18.2–41.3)^{a}
	2009	41.3 (33.5–50.9)^{b}	55.5 (45.1–68.3)^{b}	53.0 (43.0–65.4)^{b}
	DON			
	1995	0.9 (0.6–1.2)^{a}	1.1 (0.8–1.6)^{ab}	0.9 (0.6–1.3)^{a}
	2009	1.0 (0.7–1.4)^{a}	3.4 (2.4–4.9)^{c}	1.9 (1.3–2.7)^{b}
O	Rhizon lysimeters			
	DOC			
	1995	51.3 (44.2–59.5)^{a}	46.5 (40.1–53.9)^{a}	51.6 (44.5–59.8)^{a}
	DON			
	1995	1.1 (0.8–1.4)^{a}	3.1 (2.3–4.2)^{b}	1.3 (1.0–1.7)^{a}
B	Tension lysimeters			
	DOC			
	1995	1.5 (1.2–2.0)^{a}	2.1 (1.6–2.7)^{b}	3.4 (2.7–4.5)^{c}
	2009	2.3 (1.7–3.1)^{b}	3.3 (2.5–4.5)^{c}	4.7 (3.5–6.3)^{d}
	DON			
	1995	0.07 (0.05–0.09)^{a}	0.11 (0.09–0.14)^{abc}	0.14 (0.11–0.18)^{bc}
	2009	0.08 (0.06–0.12)^{ad}	0.19 (0.13–0.27)^{b}	0.11 (0.08–0.15)^{cd}

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Table 5. Lenheer fractionation of O horizon leachates at Stråsan experimental forest measured in 1995. Data from Zero tension lysimeters (ZTL) and rhizon lysimeters (R) are shown. Values are mean ± 95 % confidence interval (n = 4). Superscripts denote significant differences at p = 0.05 (Tukey HSD). Within column and lysimeter type, values followed by the same letter were not significantly different.

		Hydrophobic		Hydrophilic		
Lysimeter	Treatment	Acids	Neutrals	Acids	Neutrals	Bases
ZTL	Control	48.4 ± 8.8^{a}	5.9 ± 2.2^{a}	37.0 ± 4.4^{a}	4.4 ± 2.6^{a}	4.3 ± 1.9^{a}
ZTL	N1	48.9 ± 8.7^{a}	8.1 ± 2.2^{a}	34.9 ± 4.4^{a}	3.9 ± 2.7^{a}	4.3 ± 2.0^{a}
ZTL	N2	45.6 ± 9.3^{a}	9.5 ± 2.5^{a}	49.6 ± 4.9^{a}	1.7 ± 2.8^{a}	4.4 ± 2.1^{a}
R	Control	58.2 ± 5.2^{a}	2.5 ± 2.7^{a}	36.2 ± 5.5^{a}	2.1 ± 1.2^{a}	1.1 ± 1.0^{a}
R	N1	60.2 ± 6.0^{a}	2.6 ± 2.9^{a}	33.0 ± 6.2^{a}	2.8 ± 1.4^{a}	1.4 ± 1.1^{a}
R	N2	55.9 ± 5.2^{a}	2.9 ± 2.8^{a}	36.6 ± 5.4^{a}	2.8 ± 1.2^{a}	1.9 ± 1.3^{a}

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Table 6. Specific UV absorbance at 254 ($SUVA_{254\,nm}$) and 280 nm ($SUVA_{280\,nm}$) at Stråsan experimental forest in O horizon and B horizon leachates. Both $SUVA_{254\,nm}$ and $SUVA_{280\,nm}$ are in $l\,mg^{-1}\,m^{-1}$. Values are mean ± 95 % confidence intervals ($n = 24$). Superscripts denote significant differences at $p = 0.05$ (Tukey HSD test). Within column and soil horizon, values followed by the same letter were not significantly different.

Horizon	Treatment	$SUVA_{254\,nm}$	$SUVA_{280\,nm}$
O	Control	4.2 ± 0.2^{a}	3.1 ± 0.2^{a}
O	N1	4.1 ± 0.3^{a}	3.1 ± 0.2^{a}
O	N2	4.0 ± 0.3^{a}	3.0 ± 0.2^{a}
B	Control	1.1 ± 0.2^{a}	0.8 ± 0.2^{a}
B	N1	1.3 ± 0.2^{b}	0.9 ± 0.2^{a}
B	N2	1.9 ± 0.3^{c}	1.3 ± 0.2^{b}

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Table 7. Nitrate (NO_3), ammonium (NH_4) both in $mg\,l^{-1}$, pH and ionic strength ($mmol\,l^{-1}$) at Stråsan in 1995 and 2009. Values are mean ± range ($n = 2$). Superscripts denote significant differences at $p = 0.05$ (Tukey HSD test). Within lysimeter type and variable, values followed by the same letter were not significantly different.

	Control	N1	N2
Zero tension lysimeters			
NO_3			
1995	$0.02 \pm < 0.01^{a}$	2.0 ± 0.63^{b}	0.38 ± 0.11^{a}
2009	0.04 ± 0.02^{a}	4.1 ± 0.71^{b}	0.12 ± 0.09^{a}
NH_4			
1995	$0.29 \pm < 0.01^{a}$	2.2 ± 1.0^{b}	0.55 ± 0.01^{a}
2009	0.35 ± 0.15^{a}	2.0 ± 0.19^{b}	0.95 ± 0.35^{a}
pH			
1995	4.39 ± 0.11^{a}	4.34 ± 0.06^{a}	4.31 ± 0.12^{a}
2009	4.12 ± 0.02^{b}	3.98 ± 0.06^{b}	3.97 ± 0.01^{b}
Ionic strength			
1995	$0.06 \pm < 0.01^{a}$	0.14 ± 0.04^{b}	$0.09 \pm < 0.01^{ab}$
2009	$0.16 \pm < 0.01^{c}$	0.38 ± 0.05^{d}	0.24 ± 0.09^{cd}
Rhizon lysimeters			
NO_3			
1995	$< 0.01 \pm < 0.01^{a}$	5.3 ± 2.5^{a}	$0.12 \pm < 0.01^{a}$
NH_4			
1995	$0.07 \pm < 0.01^{a}$	1.6 ± 1.3^{a}	0.21 ± 0.03^{a}
pH			
1995	4.07 ± 0.03^{a}	3.83 ± 0.03^{b}	3.93 ± 0.01^{a}
Ionic strength			
1995	0.07 ± 0.02^{a}	0.22 ± 0.08^{a}	0.08 ± 0.02^{a}
Tension lysimeters			
NO_3			
1995	$< 0.01 \pm < 0.01^{a}$	0.20 ± 0.07^{a}	$< 0.01 \pm < 0.01^{a}$
2009	$0.01 \pm < 0.01^{a}$	0.47 ± 0.28^{a}	$0.01 \pm < 0.01^{a}$
NH_4			
1995	$0.01 \pm < 0.01^{a}$	$0.01 \pm < 0.01^{a}$	$0.01 \pm < 0.01^{a}$
2009	$0.01 \pm < 0.01^{a}$	$< 0.01 \pm < 0.01^{a}$	$< 0.01 \pm < 0.01^{a}$
pH			
2009	5.35 ± 0.05^{a}	5.36 ± 0.14^{a}	4.94 ± 0.01^{a}
Ionic strength			
2009	0.16 ± 0.05^{a}	0.23 ± 0.03^{a}	$0.23 \pm < 0.01^{a}$

BGD
9, 12433–12467, 2012

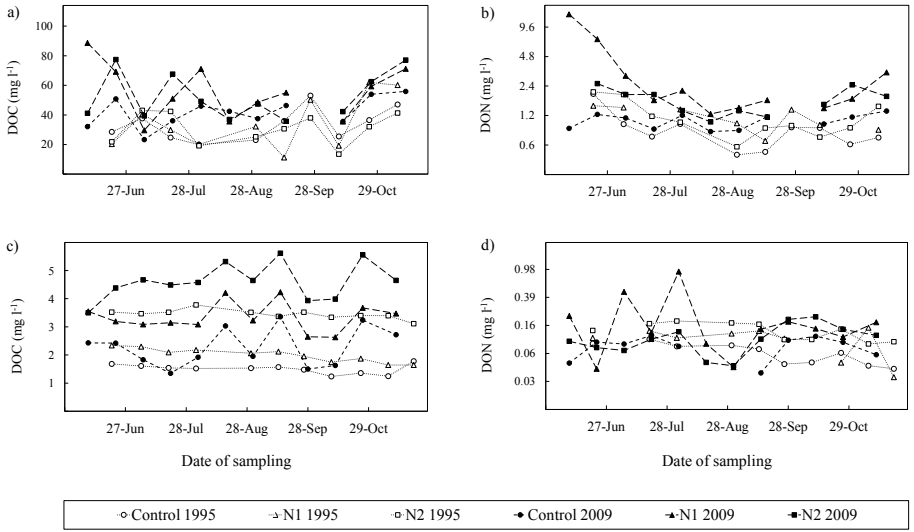

Fig. 1. Concentrations of dissolved organic carbon, DOC, **(a, c)** and dissolved organic nitrogen, DON, **(b, d)** in O horizon ZTL **(a, b)** and mineral B horizon TL **(c, d)** leachates during the growing season of 1995 and 2009. Both DOC and DON are in $mg l^{-1}$. Note that the scales on y-axis are logarithmic in both **(b)** and **(d)**.

BGD
9, 12433–12467, 2012

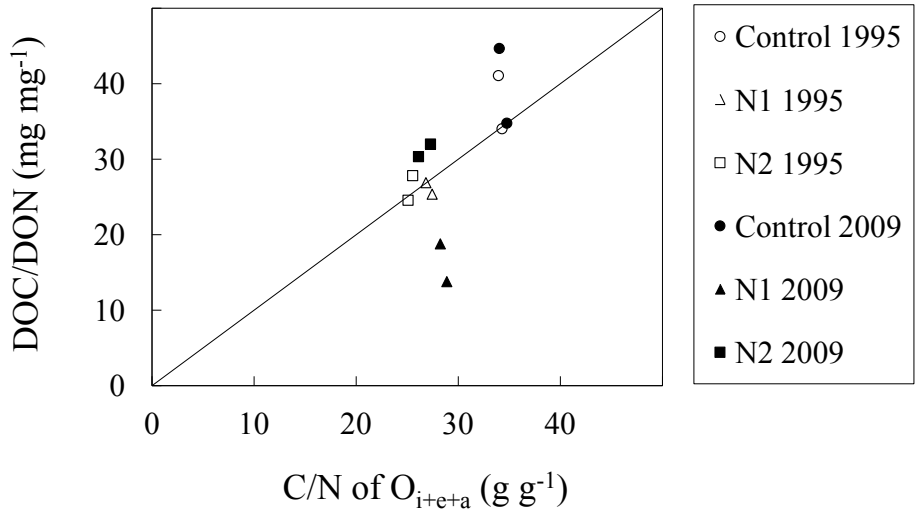

Fig. 2. Dissolved organic carbon/dissolved organic nitrogen, DOC/DON, ($mg\,mg^{-1}$) of annual means per plot in O horizon ZTL leachates and carbon/nitrogen, C/N, ($g\,g^{-1}$) of O_{i+e+a} at Stråsan. O_{i+e+a} horizon carbon and nitrogen were determined in 1996 and 2010.

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9, 12433–12467, 2012

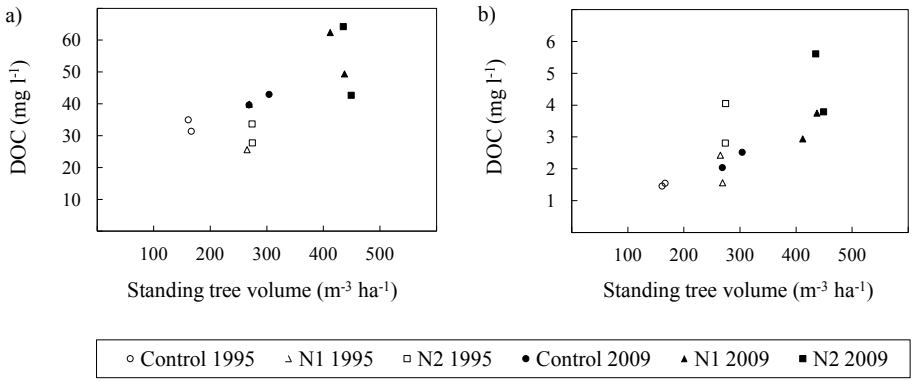

Fig. 3. Annual means of dissolved organic carbon, DOC, concentration ($mg l^{-1}$) in O horizon ZTL **(a)** and mineral B horizon TL **(b)** and standing tree volume ($m^3 ha^{-1}$) at Stråsan. Standing tree volume was determined in 1997 and 2010.

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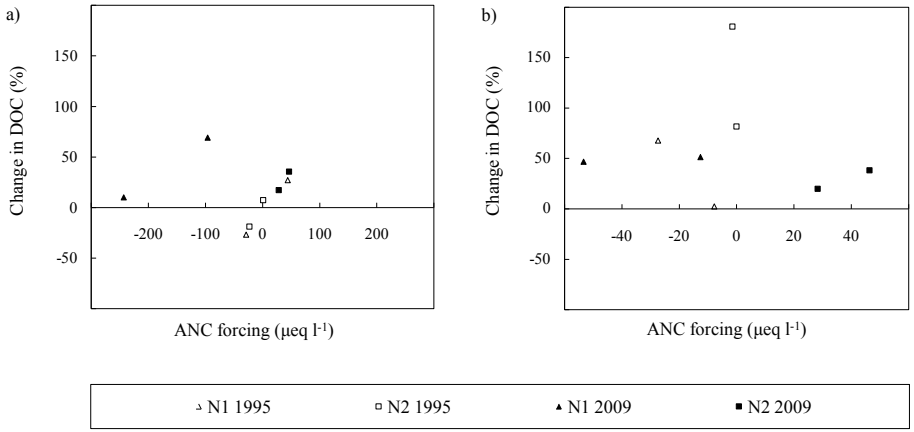

Fig. 4. Change in dissolved organic carbon, DOC, by treatments N1 and N2 (change in % of annual mean of control) in O horizon ZTL **(a)** and mineral B horizon TL **(b)** and ANC forcing in $\mu eq l^{-1}$ (Evans et al., 2008) at Stråsan.

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