

**Processes Controlling Production and  
Transport of Dissolved Organic  
Carbon in Forest Soils**

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## Abstract

Dissolved organic carbon (DOC) leached from the O horizon of forest soils is a major source of soil organic carbon in the mineral soil, where a major proportion of the organic carbon in forest ecosystems is located. The relative contribution of recent litter and humified organic matter to the leaching of DOC from the O horizon is still being debated. In the present work, I studied the sources of DOC leached from the O horizon by manipulating the amounts of litter and humus and measuring DOC concentrations and fluxes, isotopic composition ( $^{13}\text{C}$  and  $^{14}\text{C}$ ) and chemical characteristics (measured by NMR, UV absorbance and fractionation into hydrophilic and hydrophobic compounds). A computer model (DyDOC) was used to simulate the DOC leaching processes. Furthermore, DOC was measured at different soil moisture conditions at three sites along a climate gradient in Sweden. In addition,  $^{14}\text{C}$  measurements of DOC were made at two of these sites to reveal the fate of the DOC leached from the O horizon. I concluded that about half or more of the DOC leached from recent litter is lost during passage through the O horizon. Despite this, both recent litter in the Oi horizon and more humified organic matter in the Oe and Oa horizons contribute significantly to the DOC leaving the O horizon, but with the major proportion coming from the Oe and Oa horizons. To successfully model DOC leaching, the DyDOC model had to be modified to allow DOC to also be leached from recent litter. Measurements along the climatic gradient showed that the concentration and fluxes were highest in the south and lowest in the north. I suggest that these differences can be related to differences in net primary production. Both differences in mean annual temperature and the gradient in nitrogen status from south to north contribute to this effect of net primary production. Soil moisture had no effect on DOC leaching out of the O horizon. The DOC concentration in the B horizon, which is a sink for DOC, is largely governed by the physical and chemical properties of the mineral soil. The  $^{14}\text{C}$  measurements showed that the major proportion of the DOC in the B horizon is derived from the carbon stored in the mineral soil itself, rather than in the O horizon, suggesting extensive exchange of DOC by sorption/desorption processes in the mineral soil.

Keywords: dissolved organic matter, water-extractable organic carbon, Norway spruce, radiocarbon, forest floor, biogeochemistry



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# Appendix

## Papers I-V

The present thesis is based on the following papers, which will be referred to by their Roman numerals:

- I. Fröberg, M., Berggren, D., Bergkvist, B., Bryant C. & Knicker, H. Contributions of Oi, Oe and Oa horizons to dissolved organic matter in forest floor leachates. *Geoderma* 113: 311-322.
- II. Fröberg, M., Berggren Kleja, D., Bergkvist, B., Tipping, E. & Mulder, J. Dissolved organic carbon leaching from a coniferous forest floor – a field manipulation experiment. (Submitted)
- III. Tipping, E. Fröberg, M., Berggren Kleja, D., Mulder, J. & Bergkvist, B. DOC leaching from a coniferous forest floor – modelling a manipulation experiment. (Manuscript)
- IV. Fröberg, M., Berggren Kleja, D. & Hagedorn F. The contribution of fresh litter to dissolved organic carbon leached from a coniferous forest floor. (Submitted)
- V. Fröberg, M., Berggren, D., Bergkvist, B., Bryant C. & Mulder, J. Concentration and fluxes of dissolved organic carbon (DOC) in three Norway spruce stands along a climatic gradient in Sweden. *Biogeochemistry* (In press)

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# Introduction

## Why study DOC?

Dissolved organic carbon (DOC) is one of the most actively cycling soil organic carbon pools and is of significance for transport of nutrients, such as nitrogen, phosphorus and sulphur (Qualls *et al.*, 1991; Kaiser *et al.*, 2001), metals (Tipping & Hurley, 1992) and pollutants (Chiou *et al.*, 1986) in soils. It also plays a key role in the pedology (soil formation) of, for example, podzols (Lundström *et al.*, 2000). Furthermore, DOC is also involved in the biogeochemistry of carbon and redistributes organic carbon with soil depth, which is in the focus of this thesis.

The soil carbon is of interest because it may act as a sink, or source, for carbon dioxide in the atmosphere and hence influence the global warming. World-wide, the amount of carbon in soils is even three times that in aboveground biomass and twice that in the atmosphere (Eswaran *et al.*, 1993). Estimates of carbon stocks in well-drained Nordic forest soils range from 2.4 kg m<sup>-2</sup> in the northern boreal zone to 13.5 kg m<sup>-2</sup> in the nemoral zone of Scandinavia (Liski & Westman, 1997; Callesen *et al.*, 2003). However, the largest amounts of soil organic carbon do not occur in the organic (O) horizon, but rather in the upper part of the mineral soil (Figure 1). In fact, only 20-30% of the total amount of organic carbon to a depth of one metre occurs in the O horizon of Nordic well-drained forest soils (Callesen *et al.*, 2003), the rest being located in the mineral soil. Major sources of soil organic carbon in mineral soils are in particular DOC leached from the O horizon and root litter. DOC is therefore of interest for the amounts of carbon in the forest soils, not because of the amounts of carbon present as DOC, but because of its role as a vehicle for the transport of carbon from the organic horizon, down to the mineral soil, where it gets caught, mainly by physico-chemical processes. The relative significance of roots vs. DOC as the main source of soil organic carbon in mineral soils is poorly known, but undoubtedly DOC contributes with a significant proportion of this carbon pool. Estimates of the contribution of DOC to soil carbon pools range from 25% of the total carbon stock down to 60 cm (Neff & Asner, 2001) to 73-89% of mineral soil carbon (Michalzik *et al.*, 2003).

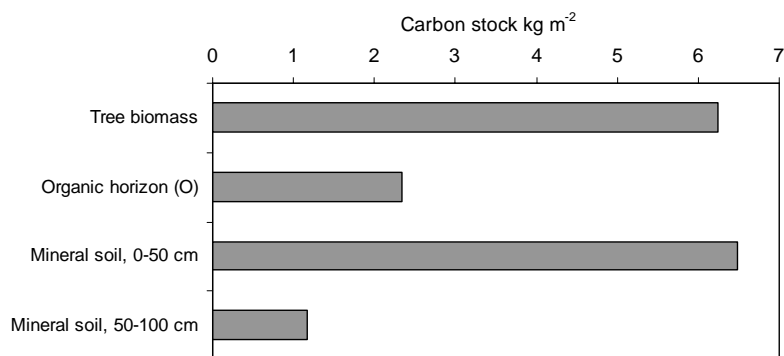


Figure 1. Average carbon stocks (kg m<sup>-2</sup>) at well drained sites at Asa, Southern Sweden. Data from Berggren *et al.* 2004.

## What is DOC?

Dissolved organic carbon is operationally defined as organic molecules of different sizes that pass through a filter of 0.2  $\mu\text{m}$  or 0.45  $\mu\text{m}$ . A minor fraction of the DOC in forest floor leachate consists of chemically well-defined compounds *e.g.* low molecular weight organic acids such as acetic, citric, lactic and oxalic acids (Hongve *et al.*, 2000). However, turnover of these low molecular weight acids is extremely rapid, with half-lives of only some hours in the O horizon (Jones, 1998), which implies that they are of no significance for the soil organic carbon stocks in the mineral soil, even though they may be important for the podsolisation process (Lundström *et al.*, 2000). The major fraction of DOC in soils consists of a polydisperse mixture of complex macromolecules with a typical molecular weight of about 1000 (Berdén & Berggren, 1990). However, a large proportion of these molecules are not in true solution, but are rather colloids, defined as having linear dimensions ranging from 1nm to 1 $\mu\text{m}$ . Colloidal molecules are larger in size than those found in true solutions, but smaller than those found in suspensions.

A key factor for the solubility of organic colloids is their net electrical charge (Tipping & Hurley, 1992). A small size and high charge density favours the solubility of humic organic matter. An increase in electrical charge is generally caused by oxidation, which is driven mainly by microbial processes (Guggenberger *et al.*, 1994). The solubility of organic matter is also dependent on the pH of the soil solution. An increased pH leads to an increased deprotonation of the active groups and with that, an increased net negative charge. This behaviour of increased solubility with increased pH is well known (Andersson *et al.*, 2000; Andersson & Nilsson, 2001) and has been successfully incorporated into computer models that partition humic substances between solid and aqueous phases (*e.g.* Tipping & Woof, 1991). Major constituents of the bulk of DOC are alkyl, carbohydrate, aromatic and carboxylic carbon (Dai *et al.*, 1996; Guggenberger *et al.*, 1998). An operational fractionation based on the chromatographic properties of DOC is often made, with a division into hydrophilic and hydrophobic fractions depending on sorption behaviour on a non-ionic sorbing resin (XAD-8) (Leenheer, 1981).

## Objectives

The work presented in this thesis aimed to contribute to the understanding of processes and factors controlling DOC leaching in typical northern forest soils. In particular, I aimed to quantify the contributions from recent litter and humified organic matter to the leaching of DOC from the O horizon, to investigate the role of abiotic factors (temperature, moisture, water flux) controlling the leaching of DOC in the O horizon and to study the fate of this DOC in the mineral soil. A further aim was to test the concepts of the computer model DyDOC, which simulates soil carbon dynamics, with a focus on DOC.



## Methods

### Overview

Papers I and II are based on data from a field manipulation experiment. The manipulations involved treatments where extra litter was added or subhorizons were removed. Concentrations, chemical characterization and  $^{14}\text{C}$  content of DOC in leachate from the different treatments were used to draw conclusions about the origin of DOC leached at the bottom of the organic horizon. In Paper III, the computer model DyDOC (Michalzik *et al.*, 2003) was tested using data on concentrations and  $^{14}\text{C}$  content of DOC obtained from Papers I and II.  $^{13}\text{C}$  labelled litter was used in Paper IV to obtain information about recent litter as the source of DOC leached from the forest floor. In Paper V, the effects of temperature and soil moisture on concentrations and fluxes of DOC were studied along a climate gradient from southern to northern Sweden.

Table 1. Site characteristics (Berggren *et al.*, 2004)

	Asa	Knottåsen	Flakaliden
Latitude	57°08'N	61°00'N	64°07'N
Longitude	14°45'E	16°12'E	19°27'E
Altitude (m. a. s. l.)	200	320	320
Mean annual temperature (°C)*	5.5	3.4	1.2
Length of vegetation period (days)**	190	160	120
Mean annual precipitation (mm)*	688	613	523
Nitrogen deposition (kg ha <sup>-1</sup> yr <sup>-1</sup> )	10	4	2
Average C/N ratio in O horizon	29.7	34.0	39.6
Major tree species	<i>Picea abies</i>	<i>Picea abies</i>	<i>Picea abies</i>
Stand age (years)	38	38	41
Soil type according to FAO (1990)	Podzols	Podzols	Podzols

\*Long-term averages (1961-1990) from nearest official meteorological station (Asa: Berg; Knottåsen: Åmotsbruk; Flakaliden: Kulbäcksliden)

\*\*Days with average temperature > 5 °C

### The study sites

Field measurements were conducted at three sites in Sweden: Asa, Småland (57°08'N), Knottåsen, Gästrikland (61°00'N) and Flakaliden, Västerbotten (64°07'N). These sites are identical to the experimental field sites used in the LUSTRA (Land Use Strategies for Reducing Net Greenhouse Gas Emissions) research programme, which were chosen with the intention of establishing a climate gradient whilst maintaining other environmental variables as constant as possible. For this thesis, the main work was carried out at the southernmost site, Asa. Papers I-IV are all based on data from Asa only, whereas data from all three sites are used in Paper V. Properties of the sites are summarized in Table 1.

Norway spruce (*Picea abies* (L.) Karst.) is the dominant tree species at all sites and the stands were planted in 1963-1967. All sites are situated on acidic bedrock and the soils are Podzols developed on sandy loamy tills. According to FAO (1990), soils at the moist plots are Gley Podzols and at the mesic and dry plots Haplic Podzols. The O horizon at all sites has a mor-type organic layer, typically with a depth of 3-10 cm. Three subhorizons were identified, the Oi horizon with recent or slightly decomposed litter, the Oe horizon, which contains organic matter under degradation and the Oa horizon with humified organic matter. Estimated mean forest production (total volume over bark from stump to tip) at Asa, Knottåsen and Flakaliden is 10.1, 6.3 and 3.2 m<sup>3</sup> year<sup>-1</sup> ha<sup>-1</sup> respectively (Berggren *et al.*, 2004). Nitrogen deposition (NO<sub>3</sub><sup>-</sup>-N plus NH<sub>4</sub><sup>+</sup>-N) based on the county levels is 10, 4.1 and 2.3 kg ha<sup>-1</sup> yr<sup>-1</sup> at Asa, Knottåsen and Flakaliden respectively (data from IVL, Swedish Environmental Institute, <http://www.ivl.se>).

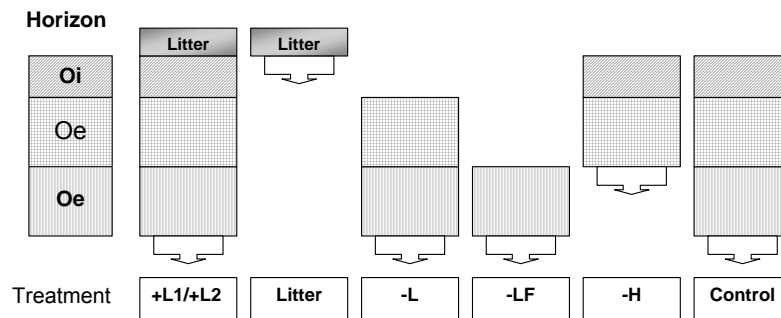


Figure 2. Schematic overview of the different treatments in Papers I and II.

## Experimental design

### Field manipulation study (Papers I, II, III)

The field manipulation experiments in Papers I and II were designed in five randomised blocks. The manipulations involved adding extra litter or removing the subhorizons. Figure 2 shows a diagram of the experimental design. In the *-L* and *-LF* treatments, the Oi and Oi+Oe horizons were removed, respectively. In the *+L1* and *+L2* treatments extra litter was added corresponding to 1.2 and 3 times annual litterfall respectively. The *Litter* treatment contained only litter, the same amounts as in *+L2*, on a lysimeter placed on the ground with no soil on it. In an additional treatment, *-H*, the lysimeter was installed under the Oe horizon, while in the *Control* the lysimeter was installed under the Oa horizon of a intact mor layer. A detailed description of the treatments is found in Paper II. Litter was obtained by shaking branches on trees in the same stand used in the experiment and collecting falling litter on a tarpaulin. Litter was put on the lysimeters the day after collection. To prevent litter from being added to the *-L* and *-LF* lysimeters plots, polyethene (PE) netting was applied and shaken regularly to remove accumulated litter. In the *-LF* treated plots, a 1 cm thick layer of PE pellets was added to mimic natural temperature and moisture conditions. The PE pellets and nets neither released nor adsorbed any DOC according to a pilot study, in which manual

temperature measurements of soil temperature did not reveal any major differences in temperature (0.1 °C on average) between the Oa horizon in the *-LF* treatment and the temperature in the O horizon outside the treatments. Lysimeters were installed in June 2000. Measurements of DOC in soil leachate started in September 2000. Forest floor manipulations were initiated in April 2001. Repeated manipulation of the *+L1*, *+L2* and *Litter* treatments was carried out in May 2002 and May 2003. The manipulations were made on an area covering the lysimeters plus an additional 10 cm perpendicular to the sides of each lysimeter. For calculations of DOC fluxes, the same water flux was assumed in all of the the Control, *+L1*, *+L2* and *-L* treatments. For the *-LF* and *-H* treatments, the losses through transpiration and evaporation were assumed to be half those in the other treatments. For the *Litter* treatment the water flux calculated for throughfall was used.

Statistical analysis to test for differences between treatments in DOC concentration and UV absorptivity was performed using SAS, procedure Mixed. Effects of treatment, block, sampling occasion and the interaction between sampling occasion and treatment were tested. The 'Repeated' statement was used to account for the temporal dependency of successive measurements close in time.

#### *<sup>13</sup>C labelling study (Paper IV)*

<sup>13</sup>C labelled spruce litter was applied to lysimeters installed under the Oe and Oa horizons. The litter was obtained from spruce plants grown in a synthetic atmosphere with a lower <sup>13</sup>C content (Hagedorn *et al.*, 2004). The plants were grown on an acidic loam under N deposition of 7 kg N ha<sup>-1</sup> yr<sup>-1</sup>. Needles were cut from the living trees and then dried and frozen until the day of application. <sup>13</sup>C content in the litter was -41%. An amount of 404.5 g DW m<sup>-2</sup> of <sup>13</sup>C-labelled spruce litter was added to each lysimeter, corresponding to about 2.5 times annual litterfall. The treated area was the lysimeter (30 cm \*30 cm) plus an additional 10 cm around the lysimeter.

The treatments were:

- *Litter*: Only litter added on a lysimeter placed on the ground.
- *Oe13*: Lysimeter installed under the Oe horizon. <sup>13</sup>C-litter added.
- *Oa13*: Lysimeter installed under the Oa horizon. <sup>13</sup>C- litter added.
- *OeC*: Lysimeter installed under the Oe horizon. No <sup>13</sup>C-litter added
- *OaC*: Lysimeter installed under the Oa horizon. No <sup>13</sup>C-litter added.

Treatments for the different lysimeter positions were chosen randomly. Three replicates of the *Litter*, *Oe13* and *Oa13* treatments were installed in June 2002. The <sup>13</sup>C litter was applied in May 2003. The *OeC* and *OaC* lysimeters were installed in June 2000 and were identical to those used in the field manipulation experiments in Papers I and II. Five replicates each of the *OeC* and *OaC* treatments were used. DOC concentrations were measured on samples from individual lysimeters.

### *Measurements along the climate gradient (Paper V)*

Three plots (30 m x 30 m) per moisture class – dry, mesic and moist – were established at each of the three sites along the climate gradient from southern to northern Sweden. When selecting the location of plots, transects along the slopes were selected in order to cover the slope areas. The positions of plots along the transects were selected subjectively based on (i) position along the slope, and (ii) the composition of field and bottom layer vegetation. The species used for indicating dry conditions were reindeer lichens, *Cladonia sp.* (L.) and moist condition sphagnum mosses, *Sphagnum sp.* (L.). Blueberry, *Vaccinium myrtillus* (L.) and lingonberry, *Vaccinium vitis-idaea* (L.) were generally frequent at both dry and mesic plots, but less frequent at moist plots. The denomination of the moisture classes follows the one used by the National Survey of Forest Soils and Vegetation and is based on average depth to the groundwater level during the vegetation period; dry >2 m, mesic 1-2 m and moist <1m.

In each of the nine plots per site, three lysimeters were installed below the O horizon and two below the B horizon, *i.e.* 9 lysimeters below the O horizon and 6 below the B horizon were used per moisture class and site.

All measurements were grouped into three seasons: 'summer' (May-July), 'autumn' (August-November), and 'winter' (Dec-April). For O and B horizon leachate, a statistical evaluation was made with a three-way ANOVA to test for differences between sites, moisture classes and seasons.

### **Sampling of soil leachates**

Sampling of O horizon leachate was carried out with zero tension lysimeters (30 cm squares), made of plexiglass and polyethene (PE) netting. The lysimeters were horizontally installed directly beneath the O horizon with the aim of minimizing the disturbance of the forest floor. Soil solution samples were collected in 1 L polyethene bottles, which were placed in PVC tubes below ground to keep samples cool. In Paper V, the soil solution from the lower part of the B horizon (40-50 cm soil depth) was also sampled, using tension lysimeters (teflon/quartz, Prenart super quartz, vacuum 50 kPa).

### **Chemical analyses**

DOC was measured using a Shimadzu TOC-5000 A analyser, usually within one week of sampling. UV absorbance (285 nm) was determined using a Shimadzu UV-1201 spectrophotometer. DOC fractionation was done according to the method of Leenheer (1981). Solid state  $^{13}\text{C}$  NMR analyses were run at Technische Universität München, while  $^{14}\text{C}$  analyses prepared at NERC Radiocarbon Laboratory and analysed either there or at the NSF-AMS Facility, University of Arizona.  $\delta^{13}\text{C}$  was measured at the Department of Forest Ecology, SLU, Umeå. Further details are given in the different papers.

## Modelling of soil water fluxes

Vertical soil water fluxes were used to get DOC fluxes from the measurements of DOC concentrations. The water fluxes were calculated using the COUP model (Jansson & Karlberg, 2001). The model simulates soil water and heat processes in different types of soils. The calculations of water and heat flows are based on soil properties such as the water retention curve, functions for unsaturated and saturated hydraulic conductivity, the heat capacity including the latent heat at thawing/melting and functions for the thermal conductivity. Air temperature, vapour pressure, wind speed, precipitation, global radiation and net radiation are driving variables in the model. Data on these variables were obtained from the measurements made within the LUSTRA program (Berggren et al. 2004).

## The DyDOC model

The DyDOC model (Michalzik *et al.*, 2003) describes soil carbon dynamics, with the focus on dissolved organic carbon (DOC). The model simulates metabolic transformations, sorption and water transport (Figure 3). The pore space comprises macropores, within which water moves due to gravity, and micropores, within which it is immobile. Incoming water mixes with water already present in the macropores, and macropore water can enter the micropores if they are not filled. Dissolved organic carbon exchanges between the macropores and micropores, governed by an exchange constant,  $D_{\text{exch}}$  (Figure 3). The hydrology sub-model runs on an hourly time step. Organic carbon enters the soil as litter fall and root litter, treated as a single component. In the original version of the model (Michalzik *et al.*, 2003), the litter is transformed into “substrate” or  $\text{CO}_2$ , and the substrate into two humic fractions (Hum-1 and Hum-2) or  $\text{CO}_2$ . In the modified version, presented in paper III, there is also a possibility of direct conversion of litter into Hum-1 and Hum-2 (Figure 3). The humic fractions Hum-1 and Hum-2 may be converted to Hum-3 or  $\text{CO}_2$ . Finally, Hum-3 may be converted back to Hum-1 and Hum-2, or to  $\text{CO}_2$ . The three humic fractions correspond approximately to hydrophilic acids (Hum-1), hydrophobic acids (Hum-2) and humic acid plus aged humin (Hum-3). The substrate and litter pools combined are equivalent to “fresh” humin. The scheme allows Hum-1 and Hum-2 to be both precursors and products of Hum-3. Only Hum-1 and Hum-2 are mobile, being transported downwards as DOC. The metabolic transformations are assumed to be mediated principally by microorganisms, and are described with first-order rate constants and “ $Q_{10}$ ” relationships, according to the general equation

$$\Delta C = -k Q_{10}^{(T/10)} C_{\text{pool}} \Delta t$$

where  $\Delta C$  is the loss of carbon from the relevant pool,  $C_{\text{pool}}$  is size of the carbon pool,  $\Delta t$  is the time,  $T$  is the temperature in  $^{\circ}\text{C}$  and  $Q_{10}$  is a constant. A  $Q_{10}$  value of 2 means that the rate of loss of C doubles for a temperature increase of  $10^{\circ}\text{C}$ . The metabolism sub-model runs on a daily time step.

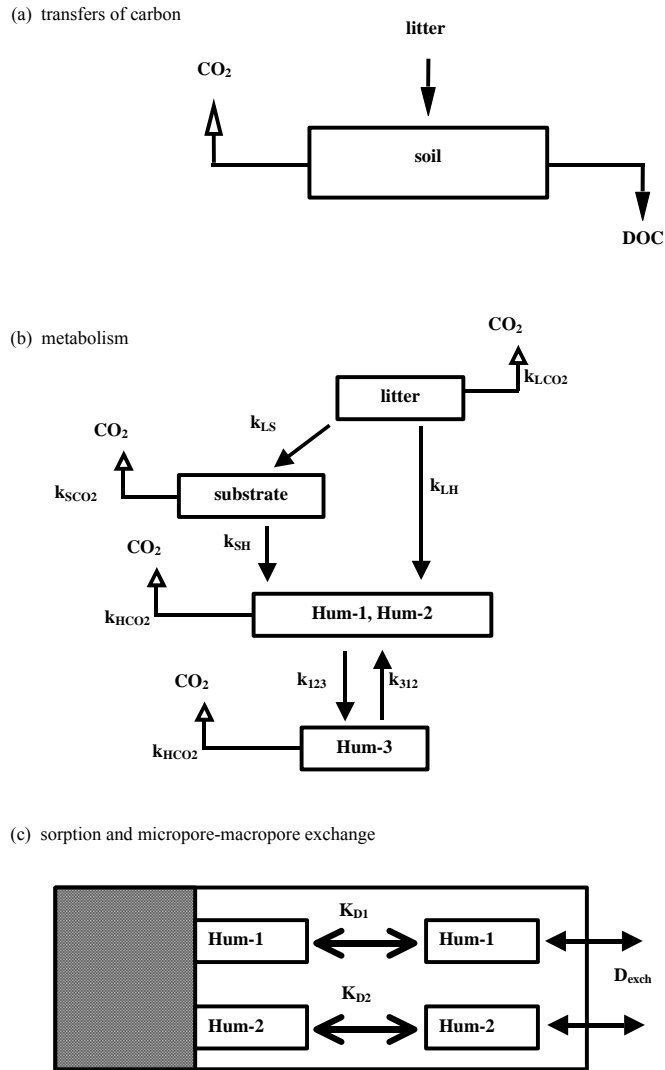


Figure 3. Representation of O-Horizon carbon dynamics in DyDOC.

Humic fractions Hum-1 and Hum-2 adsorb reversibly to the soil solids and become DOC when passing into solution. The tendency to sorb to the soil is described by equilibrium partition coefficients ( $K_D$ ), according to the equation

$$K_D = \frac{\text{g DOC sorbed per g soil}}{\text{solution concentration of DOC}}$$

where the solution concentration refers to the micropore. The value of  $K_D$  for Hum-1 is lower than that for Hum-2, reflecting the lesser tendency of hydrophilic organic solutes to undergo sorption reactions.

The bomb  $^{14}\text{C}$  signal, created by testing of thermonuclear weapons in the late 1950s to early 1960s, which almost doubled the atmospheric  $^{14}\text{C}$  concentration, provides a means to track the processing of C through soils on relatively short time scales and is an important feature of the DyDOC model. Calibration of the model is made with the assumption that the present-day situation represents steady state.

## Sources of DOC

### State of the art

The relative contributions from fresh litter and humified organic matter as the substrate for DOC leaching is still being debated. McDowell & Likens (1988) hypothesized that a major part of the DOC leached out of the O horizon is derived from the large stock of humified organic matter in the forest floor. In contrast, many studies have emphasized the role of recent litter as the source of DOC in the O horizon. In several laboratory studies (*e.g.* Huang & Schoenau, 1996; Magill & Aber, 2000), recent litter was found to have a large potential to produce DOC. Furthermore, in many field studies (Qualls *et al.*, 1991; Huang & Schoenau, 1998; Michalzik & Matzner, 1999) the highest amounts of DOC have been measured under the Oi horizon, with no further increase in DOC concentrations and fluxes in the lower O horizon. However, studies with increasing DOC concentrations and fluxes in the lower O horizon have also been published (Solinger *et al.*, 2001; Park & Matzner, 2003; Kalbitz *et al.*, 2004) Until a few years ago, however, statements about the sources of DOC were mainly based on indices such as leaching rates per gram of carbon from different substrates and measurements of DOC concentrations and fluxes under the different sublayers in the forest floor. In recent years, several studies using isotopic techniques and manipulated systems have placed more emphasis on the role of humified organic matter. Hagedorn *et al.* (2002) studied DOC in open-top chambers in which spruce and beech trees were grown in a  $^{13}\text{C}$ -depleted atmosphere. They concluded that only 5-8% of the DOC collected at 5-10 cm depth was derived from new  $^{13}\text{C}$  labelled carbon, despite 17-22% new carbon in the soil at 0-10 cm depth. In a study using the bomb  $^{14}\text{C}$ , Michalzik *et al.* (2003) observed that DOC was derived mainly from humified organic matter. Based on laboratory studies using soil columns and a field manipulation study, Park *et al.* (2002) and Park & Matzner (2003) suggested that DOM in forest floor leachate should be regarded as a mixture of leachate from both newly added litter and humified organic matter. DOC has been modelled by allowing it to be produced from litter only (Currie & Aber, 1997), from humified

organic matter only (Michalzik *et al.*, 2003) or from both litter and old organic matter (Neff & Asner, 2001).

This uncertainty regarding the origin of DOC achieved attention in reviews of dissolved organic matter by Kalbitz *et al.* (2000) and McDowell (2003), both of which emphasized the relevance of different sources of DOC leaching, such as recent litter and humus, as one of the most important areas for future research on dissolved organic matter in soils.

### **Different composition and origin of water-extractable organic carbon and DOC**

Laboratory data from Paper I showed, in accordance with numerous other studies (*e.g.* Huang & Schoenau, 1996; Magill & Aber, 2000; Moore & Dalva, 2001), that the highest amounts of water-extractable organic matter per gram of carbon were obtained from recent litter. Leaching per gram carbon from the Oi horizon was twice that in the Oe horizon and three times higher than in organic matter from the Oa horizon (Table 2). However, taking the higher carbon stocks of the Oe and Oa horizons into account, the amounts of soluble organic carbon extracted from soil organic matter per m<sup>2</sup> in the three different horizons were approximately the same.

The high potential for DOC leaching from recent litter as suggested by the data on water-extractable carbon has already been shown by other authors and can hardly be doubted. However, water-extractable organic carbon is not a perfect alternative for DOC. A difference in chemical composition between DOC and the water-soluble organic carbon obtained in the extractions was revealed by NMR spectroscopy (Table 3) and by fractionation of DOC and water-extractable organic carbon into hydrophilic and hydrophobic compounds (Figure 4).

Table 2. Concentrations and amounts of water-extractable organic carbon from the Oi, Oe and Oa horizons in Asa

Horizon	Water-extractable organic carbon (mg l <sup>-1</sup> )	Extracted fraction of total C (%)	Extracted amount of C (g m <sup>-2</sup> )
Oi	97 (6)	0.41	2.4
Oe	45 (2)	0.19	3.5
Oa	28 (2)	0.14	2.4

The NMR measurements showed that there was a higher content of O-alkyl (carbohydrates) and lower content of aromatic carbon in the water-extractable organic carbon compared to the DOC collected in the lysimeters. The fractionation showed a lower content of hydrophobic compounds in the DOC from the water extracts compared with the lysimeters. The differences between water extracts and lysimeter water suggest that DOC and water-extractable organic carbon, at least partly, represent two different pools. The water-extractable organic carbon, with its higher content of carbohydrates and lower content of aromatic carbon, bears signs of a younger and more soluble pool of carbon. This was supported by



Hagedorn *et al.* (2002), who obtained a larger fraction of 'new' ( $^{13}\text{C}$  labelled) carbon in water extracts than in DOC collected from lysimeters. DOC and water-extractable carbon both represent the most labile pool of the soil organic matter. One possibility for the differences could be that they are spatially separated, by being situated in different pore systems of the soil. The DOC collected by the zero tension lysimeters is transported by the mobile water, which is not in contact with the whole soil. By sieving and suspending the soil in a solution, soil organic matter that was not in contact with the mobile water in the soil becomes exposed. Furthermore, there could be a relatively large proportion of microorganism-derived carbon in the water extracts. Microorganisms have been found to mainly produce hydrophilic neutrals and bases (Christ & David, 1994) and there was a trend for a higher content of hydrophilic bases in the extracts compared with the DOC from the lysimeters (Figure 4). Water-extractable organic carbon should thus not be used as a substitute for DOC transported through the soil.

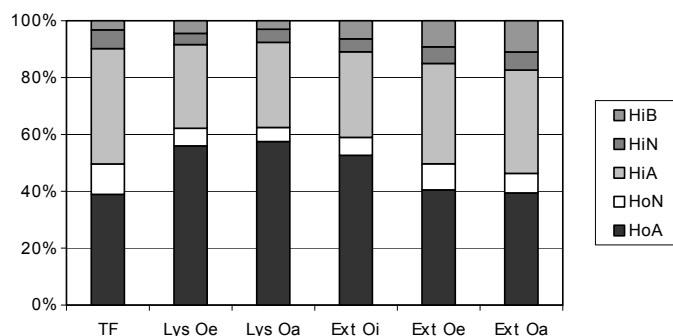


Figure 4. Content of hydrophobic acids (HoA) and neutrals (HoN), hydrophilic acids (HiA) and bases (HiB) in throughfall (TF), extracts (Ext) and lysimeter water (Lys). Average values ( $n=2$ )

Paper IV also presents interesting data regarding water-extractable organic carbon. In the water-extractable organic carbon obtained from  $^{13}\text{C}$  labelled litter, which had been stored in litterbags in the field for 140 days, there was a surprisingly high contribution from native (unlabelled) carbon (Figure 5). The bulk litter from the litter bags had a  $^{13}\text{C}$  signal close to that in the fresh labelled litter,  $-40.6\text{‰}$  and  $-41.1\text{‰}$  respectively. In contrast, there was a clear difference between the water extracts, with a  $\delta^{13}\text{C}$  signal of  $-37.0\text{‰}$  in carbon extracted from the litter stored in the field and  $-41.4\text{‰}$  in that obtained from fresh litter. With a  $\delta^{13}\text{C}$  in the native litter of  $-29.3\text{‰}$ , this implies that about one third of the water-extractable organic carbon in the litter stored in the field was derived from native (non-labelled) carbon. This indicates that there was a small pool of soluble carbon with a high leaching potential, originating from native carbon, which had been added to the carbon in the forest floor. A possible source of this carbon in the microorganism pool was DOC in throughfall, *i.e.* water that had passed through the tree canopies, which has been suggested to be a significant source of easily available carbon for the microorganisms in the O horizon (Zech & Guggenberger, 1996; Michalzik *et al.*, 2001). The large contribution of this native carbon to the water-extractable organic carbon would then again suggest that a large part of the extractable organic carbon is derived from the microbial biomass.

Table 3. Relative signal intensities (%) from solid state  $^{13}\text{C}$  NMR spectroscopy. Average values with standard error within brackets (n=2)

	Soil Oi	Soil Oe	Soil Oa	Ext Oi	Ext Oe	Ext Oa	Lys Oe	Lys Oa	TF
Carbonyl (160-220)	7.7 (0.5)	10.0 (0.0)	13.2 (0.7)	13.5 (0.5)	12.6 (1.6)	11.1 (1.6)	14.8 (3.2)	15.1 (0.7)	8.6
Aromatic (110-160)	18.5 (0.3)	19.7 (0.7)	23.0 (1.5)	15.6 (2.3)	11.3 (1.8)	9.1 (0.0)	16.4 (1.1)	16.0 (0.1)	11.2
O-alkyl (45-110)	52.8 (1.6)	47.2 (0.1)	40.6 (2.4)	47.4 (2.2)	54.6 (2.3)	56.2 (1.4)	43.3 (2.6)	44.4 (0.5)	56.7
Alkyl (10-45)	21.0 (0.8)	23.0 (0.6)	23.1 (0.1)	23.5 (0.6)	21.5 (1.0)	23.5 (0.2)	25.4 (0.5)	24.4 (1.3)	23.6

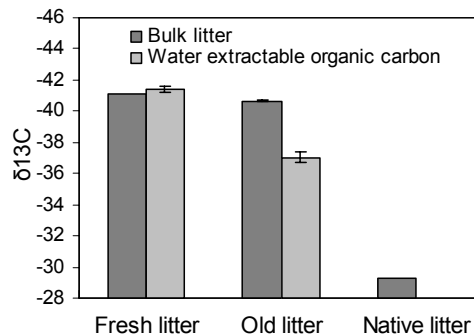


Figure 5.  $\delta^{13}\text{C}$  signals in fresh labelled litter, old labelled litter stored in the field and in native litter from Asa. Error bars represent standard deviation (n=2 or 3)

## DOC from throughfall

The throughfall concentrations and fluxes presented in Paper II correspond to 30% and 35% of concentrations and fluxes in the *Control*, respectively, which is within the typical range for forest ecosystems (Michalzik *et al.*, 2001). However, a large part of this probably does not contribute to the leaching of DOC from the O horizon. According to the NMR data in Paper I (Table 3) and characterization in other studies (*e.g.* McDowell & Likens, 1988; Guggenberger & Zech, 1994) the DOC in throughfall consists of a large fraction of carbohydrates, which is consistent with the fact that DOC from throughfall in incubation studies has been shown to be a labile pool of carbon (Qualls & Haines, 1992; Hongve *et al.*, 2000, Yano *et al.*, 2000). This indicates that a large part of the DOC from throughfall is degraded quickly and does not reach the bottom of the O horizon. Nevertheless, throughfall may play a role in the carbon cycle of the forest floor. Positive effects of throughfall on the DOC leaching from the forest floor due to the high proportion of easily decomposable carbon in throughfall, which can act as a co-substrate or promoter for decomposition, have been proposed by Zech & Guggenberger (1996), based on the observation that degradation of lignin is co-

metabolic in nature and by Michalzik *et al.* (2001) as a possible explanation for a co-variation between DOC fluxes and forest floor leachate.

Similarly to the DyDOC model by Michalzik *et al.* (2003), it was assumed here that DOC in throughfall was rapidly decomposed and did not contribute significantly to the DOC leaching from the O horizon. In some of the calculations it was even assumed that the contribution from throughfall was zero.

### Recent litter as a source of DOC

*Loss of DOC from recent litter during passage through the O horizon is substantial*

The field manipulation experiment in Paper II support the high DOC leaching from recent litter indicated by the laboratory data on water-extractable organic carbon (Table 2). Substantial amounts of DOC were leached from the *Litter* treatment, consisting of applied litter only and no soil. The DOC concentrations in this treatment (51 mg l<sup>-1</sup>) were not even significantly different from the intact O horizon in the *Control* (55 mg l<sup>-1</sup>) and the net increase in DOC concentration compared with throughfall (16 mg l<sup>-1</sup>) was 35 mg l<sup>-1</sup> (Table 4). However, a large proportion of the DOC derived from recent litter was not captured in the +L2 treatment, which contained the same amount of litter but also an intact O-horizon. The increase in DOC flux in the *Litter* treatment compared with throughfall was 50 g m<sup>-2</sup> (Table 4). In contrast, the increase in the +L2 treatment compared with the *Control* was only 28 g m<sup>-2</sup>.

Table 4. Average DOC concentrations and fluxes from April 2001 to December 2003 in the different treatments. Molar absorption coefficient at 285 nm. Standard error of the mean in brackets (n=5) and p-values are given for differences in concentrations compared with the *Control*

	DOC concentration (mg l <sup>-1</sup> )	p	DOC flux (g m <sup>-2</sup> ) (Apr. 2001-Dec. 2003)	Molar absorptivity coefficient (l mol <sup>-1</sup> cm <sup>-1</sup> )	p
+L2	75 (8)	0.003	110	266 (7)	0.82
+L1	69 (7)	0.13	105	267 (7)	0.99
<i>Litter</i>	51 (2)	0.38	79	237 (7)	0.02
-LF	37 (4)	<0.0001	63	302 (11)	<0.001
-L	47 (4)	0.12	65	293 (5)	0.04
-H	65 (8)	0.92	103	263 (7)	0.18
<i>C</i>	55 (4)	-	82	274 (7)	-
<i>TF</i>	16	-	29		

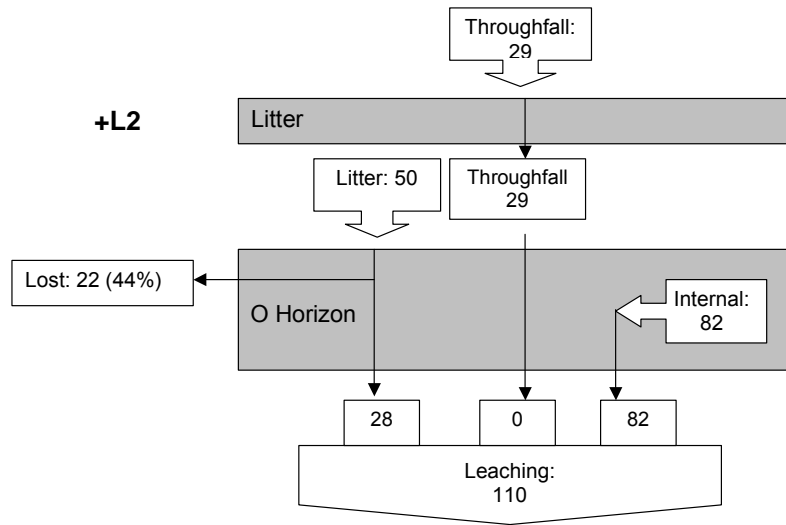


Figure 6. DOC fluxes from April 2001 to December 2003 in the +L2 treatment. 44% of the DOC from litter was lost during passage through the soil.

Assuming no retention of throughfall DOC in the *Litter* treatment and that equal fractions of the throughfall DOC passed through the +L2 and *Control* treatments, there was a 44% loss of the DOC from recent litter during passage through the O horizon, either by sorption or through decomposition (Figure 6). This fraction could be even higher, if there was a loss of throughfall-derived DOC during passage through the applied litter. Despite this loss, the DOC concentration in the +L2 treatment was significantly higher ( $p=0.003$ ) than in the *Control* (Table 4).

The  $^{13}\text{C}$  data in Paper IV also suggest that a large fraction of the DOC derived from recent litter is lost during passage through the O horizon. Despite initially high DOC leaching, with  $177 \text{ mg l}^{-1}$  coming from the added litter in the lysimeter without soil (Figure 7a), the concentrations of DOC from the labelled litter in leachate from the Oe (Figure 7b) and Oa (Figure 7c) horizons were low, only 6-20  $\text{mg l}^{-1}$ . In total, a 94% reduction in the flux of DOC leached from the  $^{13}\text{C}$ -labelled litter was measured during passage through the whole O horizon. This can be compared to the loss of 44% or more suggested by the *Litter* and +L2 treatments. The 94% is probably an overestimate of the reduction in DOC from litter under normal circumstances, however. The litter was collected from the living trees and was dried and frozen before its application as one large dose in the field. This 'pre-treatment' could have had the effect of increasing the initial flush of DOC compared to 'real' litter. The low UV absorptivity of the DOC leached from the added litter suggests that there is a low fraction of hydrophobic compounds (Dilling & Kaiser, 2002) and that this DOC is easily biodegraded (Kalbitz *et al.*, 2003), which could indicate that the loss of DOC from litter was overestimated. On the other hand if sorption is an important first step in the removal process, a low fraction of hydrophobic compounds and a high fraction of hydrophilic fractions could give the opposite effect by underestimating the loss of DOC during

passage through the O horizon. Nevertheless, there would also have been a negligible contribution of litter-derived C to the DOC leached from the Oe and Oa layers with aged 'real' litter because less DOC would have been released from the litter and thus less DOC would have had to be retained in the organic layers.

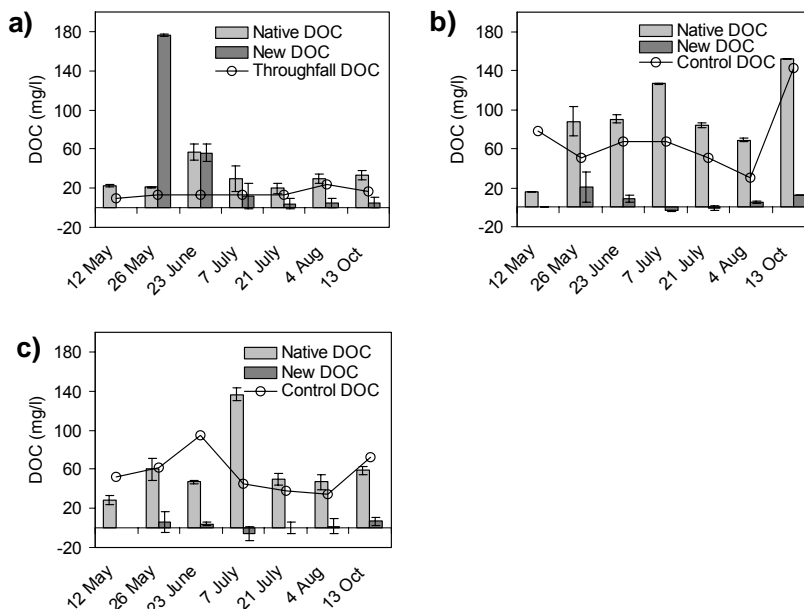


Figure 7. DOC from native and added litter in the  $^{13}\text{C}$  labelling study a) in the treatment with only added litter, b) under the Oe horizon and c) under the Oa horizon.

A 44% or 94% reduction in DOC from recent litter, suggested by the data in Papers II and IV, respectively, is a large span. However, the data agree in the sense that both papers suggest that a large part of the DOC from recent litter is lost during passage through the soil. As discussed above, 44% may be an underestimation and 94% an overestimation. Moreover, the effects of litter additions were monitored continuously over more than two years in Paper II, whereas only the first initial flush of DOC from added litter was studied in Paper IV. The large loss of DOC during passage through the forest floor may, however, be compared with the 10-40% easily decomposed fraction of DOC suggested by Kalbitz *et al.* (2000) after reviewing a large number of incubation studies. Even higher proportions of easily decomposed carbon have been found for DOC derived from only slightly decomposed substrate (Qualls & Haines, 1992; Hongve *et al.*, 2000; Kalbitz *et al.*, 2003). Sorption processes also need to be accounted for, however, which in a short-time perspective might contribute to the removal of DOC from the soil solution. An indication that decomposition alone cannot account for the large loss of DOC is that the transit time of litter-derived DOC through the O horizon was short compared to the time it needed to be decomposed. In a laboratory study, Kalbitz *et al.* (2003) found that as much as

50% of DOC leached from the litter layer of a spruce forest was decomposed during the first 10 days of incubation at 20°C. Transport of solutes through the uppermost forest floor, however, occurs on a time scale of hours (Feyen *et al.*, 1999). As a consequence, decomposition of the labelled litter-derived DOC alone could not account for the loss of DOC from labelled litter. Sorption is probably also involved in this process. Potential sorption mechanisms involve electrostatic attraction or binding, hydrogen bonding and van der Waals forces (Qualls, 2000). Thus, sorption is likely to be an important first step in the removal of DOC in the O horizon. In a longer-term perspective however, mineralization is of course the ultimate fate of the sorbed DOC.

#### *Quantifying the contribution from the Oi horizon to DOC leaching*

In the *-L* treatment (Paper II), *i.e.* the manipulation with the Oi horizon removed, the DOC concentration was not significantly different ( $p=0.13$ ) from the *Control*, but there was a tendency towards lower concentrations, indicating that 20% of the DOC was derived from this horizon (Table 4). This was supported by the fact that there was a significant increase in UV absorptivity in the *-L* treatment compared to the *Control* (Table 5). Accordingly, there must have been a contribution from recent litter to the leachate in the intact O horizon, which affected the composition of the soil solution in a direction towards lower aromaticity. Assuming that the UV absorptivity in leachate from the Oi horizon is equal to that in the *Litter* treatment, the contribution to DOC leaving the O horizon can be estimated at 35%. Thus, recent litter proved to contribute a substantial fraction of DOC leaving the O horizon. However, the Oe and Oa horizons must also be important, since they make up the largest contribution to DOC in O horizon leachate.

### **Humified organic matter as the source of DOC**

#### *A majority of the DOC originates from the Oe and Oa horizons*

As seen above, the data from the field manipulation in Paper II suggested substantial contributions from fresh litter to leaching of DOC from the O horizon, although with the majority of DOC still originating from the lower O horizon. More than half the DOC originated in the Oe and Oa horizons. Furthermore,  $^{13}\text{C}$  data in Paper IV suggest that most of the DOC from recent litter was lost during passage through the O horizon. In addition to this, there is also information from the  $^{14}\text{C}$  data in Paper I (Figure 8) suggesting that the majority of the carbon leached from the O horizon is leached from the Oe and Oa horizons, rather than from recent litter. The DOM in soil leachate from the Oe horizon had a  $^{14}\text{C}$  content that was significantly higher ( $p=0.05$ ) than the  $^{14}\text{C}$  content in soluble organic matter extracted from the Oi horizon, but equal to the  $^{14}\text{C}$  content in the soluble organic matter extracted from the Oe and Oa horizons (Figure 8), suggesting that the main proportion of the DOC in Oe and Oa horizon leachate had its origin in the Oe and Oa horizons themselves. The differences in chemical composition and origin between DOC and water-extractable carbon discussed above may provide scope for another interpretation of the  $^{14}\text{C}$  data, if the isotopic composition in the water-extractable carbon pool and the DOC-generating pools is not the same.

However, data from the field manipulations and the DyDOC modelling also supported an origin of DOC leaving the O horizon mainly in the Oe and Oa horizons.

Note though that a statement about an origin of DOC in a certain horizon may not always be unambiguous. DOC, which has been adsorbed earlier, may be desorbed again and contribute to the leaching of DOC from the horizon being studied. The DOC will in that case represent  $^{14}\text{C}$  signal and molecular constitution of the above lying horizon.

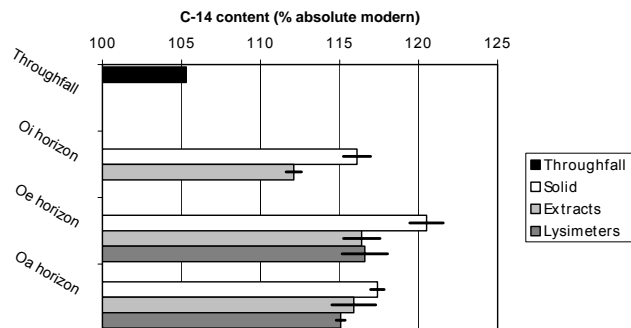


Figure 8.  $^{14}\text{C}$  contents in throughfall and in bulk soil, extracts and lysimeter water from the Oi, Oe and Oa horizons. Error bars represent standard error (n=2)

### *Quantifying the contributions from the Oe and Oa horizons to DOC leaching*

The most important information about the relative contributions from the Oe and Oa horizons are provided by the data in Paper II. It was not possible to draw any conclusions from the  $^{14}\text{C}$  data in Paper I about the relative importance of the Oe and Oa horizons, since the  $^{14}\text{C}$  signals of both bulk soil and DOC in the two horizons were not significantly different from each other (Figure 8). The DOC concentration data presented in Paper I and Paper II, similarly to other studies (*e.g.* Qualls *et al.*, 1991; Michalzik & Matzner, 1999), show that there was no net increase in DOC concentration and fluxes in the Oa horizon (Table 3). However, the *-LF* treatment, with the Oi and Oe horizons and litterfall removed (Paper II), produced substantial amounts of DOC and more than doubled the flux compared with throughfall from 29 to 63 g m<sup>-2</sup> (Figure 9). This shows that the Oa horizon is not inert and also that this horizon is capable of producing significant amounts of DOC. Accounting for a lower water flux through the Oa horizon in an intact O horizon compared with the *-LF* treatment and assuming a loss of about half the DOC flux in throughfall in the *-LF* treatment, there is a contribution from the Oa horizon in the *-LF* treatment corresponding to about 50% of the total flux of DOC in the *Control*. The results from this and other studies showing that there was no net increase in DOC concentration in the Oa horizon should accordingly not be interpreted as showing that this horizon is inert with respect to DOC production and sorption. Another important implication of the observations presented here is

that it is not possible to add the net leaching from the different horizons to get the total leaching.

Some clues to the origin of DOC, either in the Oe or in the Oa horizon, were also obtained from the UV absorptivity data. These showed that there was a higher UV absorptivity in the DOC originating in the Oa horizon (-LF) than in DOC leached from an intact O horizon (*Control*) (Table 4). In contrast, there was a tendency for a lower UV absorptivity in the -H treatment than in the *Control*. Applying a simple end-member mixing model, with the absorptivity in the -H and -LF as the end-members, a 30% contribution from the Oa horizon was obtained.

The approximately 50% contribution from the Oa horizon inferred from the DOC data, together with the estimation of about 20% contribution from the Oi horizon, suggest that the Oi, Oe and Oa horizons contribute 20%, 30% and 50% to the DOC leaching from the O horizon, respectively. There are uncertainties in these figures, but the data presented here undoubtedly show that there is a significant contribution from the Oi horizon, but that the majority of DOC leaving the O horizon has its origin in the Oe and Oa horizons.

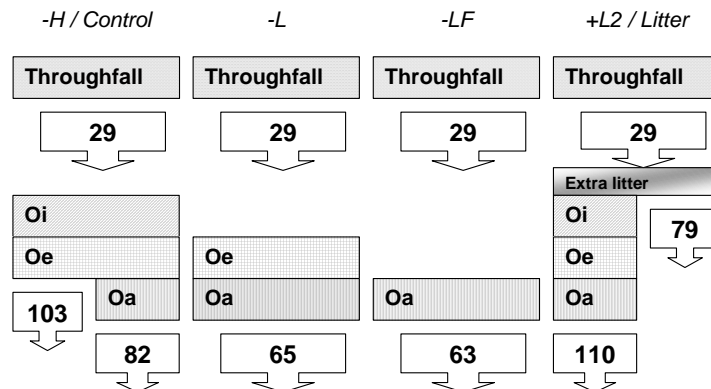


Figure 9. DOC fluxes from the different treatments from April 2001-December 2003.

### DyDOC modelling

The observations of a significant contribution from the Oi horizon to DOC leaching and the majority of DOC originating in the Oe and Oa horizon were supported by the DyDOC modelling in Paper III. The original version of the model (Michalzik *et al.*, 2003) could not cope successfully with the manipulations in Paper II. The model correctly forecast the directions of the responses of the soil to the manipulations, but the quantitative agreement was rather poor. The predicted increases in DOC export following litter addition, and the decrease following litterfall withdrawal and the removal of the Oe layer, were appreciably smaller than the observed responses. This indicated that the processes represented in the model were insufficiently responsive to the changes imposed in the experiments. Specifically, the model could not generate DOC rapidly enough. A straightforward solution to this problem was to allow the direct formation from litter of Hum-1 and Hum-2 (i.e. the components of DOC). The modified version of



DyDOC, presented in Paper III improved the fit between calculations and field measurements significantly (Figure 10). The best fit was obtained with a parameter setting generating 30% of the total DOC flux in the *Control* from the litter pool and 32 and 38% from substrate and Hum-3, respectively. This is good agreement with the experimental results presented above. Thus the results of the litter manipulation experiments suggest that the litter pool is a significant source of DOC leached from the O-horizon. However, this does not imply that DOC is rapidly formed from fresh litter, since the soil litter pool at Asa has a turnover time of 4.6 years. The other two soil carbon pools, substrate and humic matter, have turnover times of 24 and 39 years respectively.

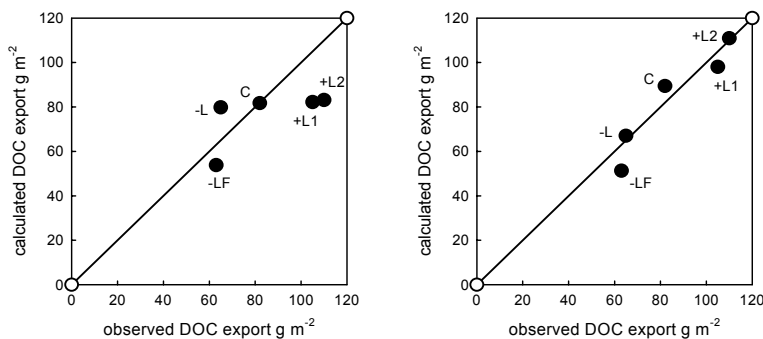


Figure 10 Observed and calculated exports of DOC for the period 19 April 2001 to 10 December 2003 in the manipulation experiments (Table 4). The figure shows the results obtained by fitting the *Control* data with a) the original version of DyDOC (Michalzik *et al.*, 2003) and b) the revised version (Paper III).

## DOC in relation to temperature

### Short-term effects of different temperatures

Temperature may affect DOC concentrations in O-horizon leachate in two ways, either directly via an effect on the microbially-mediated processes governing the production of DOC, or indirectly by affecting the amount of litter (substrate) produced and decomposed in the ecosystem. Most studies on the effect of temperature have focused on the direct effect of temperature on the leaching of DOC and generally show that temperature has a positive effect on DOC concentrations and fluxes. A consistent finding from laboratory studies is that increasing the temperature increases DOC leaching (*e.g.* Christ & David, 1996; Gødde *et al.*, 1996; Andersson *et al.*, 2000; summarized by Kalbitz *et al.*, 2000). This is supported by numerous field studies showing that there are seasonal variations in DOC concentrations in O horizon leachate, with the highest concentrations during summer or autumn (*e.g.* Michalzik & Matzner, 1999; Yano *et al.*, 2000; Solinger *et al.*, 2001; Kaiser *et al.*, 2002). A seasonal variation was also observed in Paper V. However, the highest DOC concentrations did not occur during the warmest time of year, but rather during autumn (Figure 11).

The time lag between temperature and DOC concentration was suggested to be caused by buffering of DOC in the O horizon by sorption/desorption processes. However, this seasonal pattern has not been reported in any other study and was not seen for the lysimeters in the litter manipulation study in Paper II (Figure 12). The variations with time in the lysimeters used in the manipulation study, which represented a longer data record, did not show any pronounced seasonal patterns. This would suggest that at Asa, variables other than temperature are responsible for most of the variations in DOC concentrations with time.

### Long-term effects of different climate

The short-term direct effects of differences in temperature presented so far are easy to study in the laboratory or by observing the seasonal variations in DOC concentrations over the year. In the long-term, an important question is whether increased DOC production at higher temperatures could be maintained. The main control of DOC export may be supply of new material for the decomposition process. To date, however, most studies have focused on the short-term dynamics and relatively little is known about the long-term response to climatic factors such as temperature and precipitation. To my knowledge, the only previous published field study dealing with a variation in concentrations and fluxes of DOC in forest ecosystems along a climate gradient is a comparison between two northern hardwood stands in the USA, where the highest DOC concentration was found at the warmest site (Liechty *et al.*, 1995).

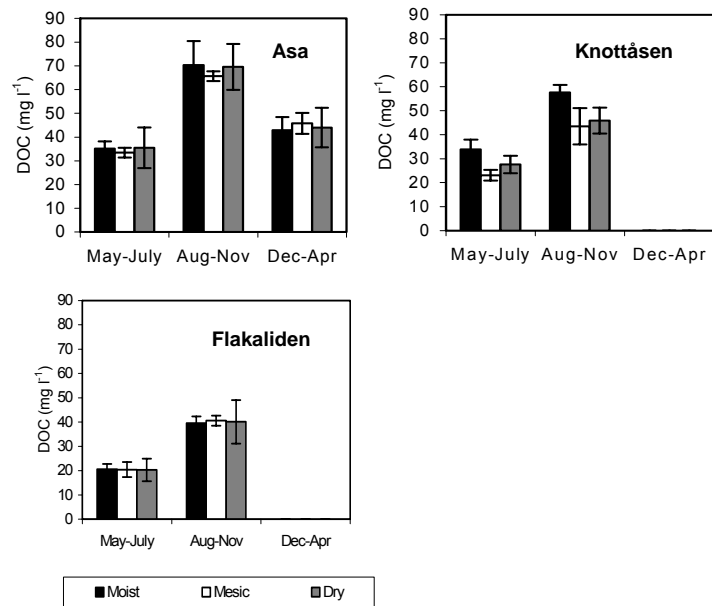


Figure 11. Average DOC concentrations in leachate from the O horizon moist, mesic and dry plots at Asa, Knottåsen and Flakaliden (n=2 for Asa mesic, n=3 for other moisture classes and sites). Error bars represent standard error of the mean.

Along the climate gradient in Paper V, there were statistically significant differences between the three LUSTRA sites in DOC concentration in the O horizon leachate (Table 5). The southernmost site, Asa, had the highest concentration (average 49 mg l<sup>-1</sup>), followed by the site in central Sweden, Knottåsen (average 39 mg l<sup>-1</sup>). Lowest average DOC concentration of the three sites was measured at the northernmost site, Flakaliden (average 30 mg l<sup>-1</sup>). However, the differences in DOC concentration between the three sites could not be attributed solely to a direct effect of temperature. The differences in temperature were too small to provoke the quite substantial differences in DOC concentration. Differences in average temperature between the sites during the vegetation period (average daily temperature >5 °C) were less than 1 °C, which with the temperature sensitivity for DOC production published in the literature (a Q<sub>10</sub> of about 2: Christ & David, 1996; Gödde *et al.*, 1996), would give a less than 10% difference in DOC concentration between the sites. If the difference instead is calculated from the mean annual temperature, the difference is 4.3 °C between Asa in the south and Flakaliden in the north, which, with a Q<sub>10</sub> of 2, would give about half the measured difference in DOC between the sites.

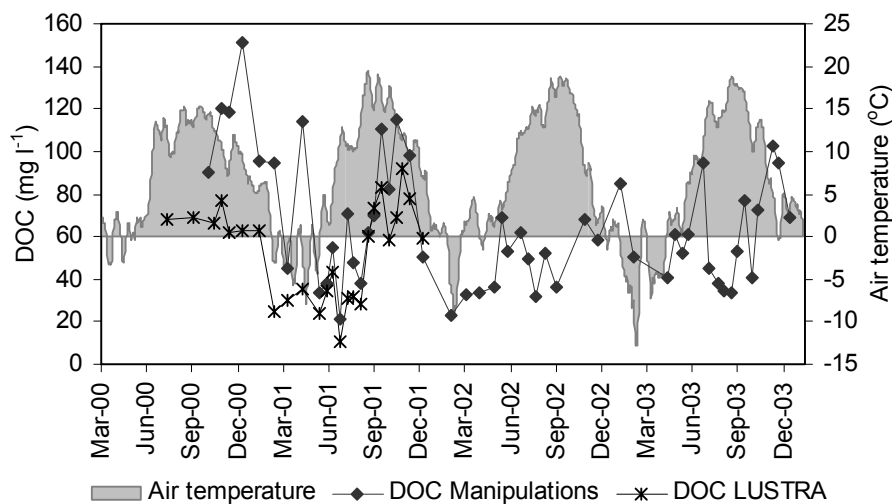


Figure 12. Temporal variations in air temperature at Asa research station, DOC concentrations in the *Control* treatment in the Manipulation study and the average DOC concentrations at the LUSTRA plots in Asa.

In addition, carbon stocks in the O horizon cannot explain the differences between the sites, although there were differences in carbon stocks at the three sites, with largest amounts of carbon in the south and lowest in the north (Table 5). However, there were higher carbon stocks at the moist plots, compared with the dry and mesic, at the LUSTRA sites, but this was not reflected in the DOC concentrations, which were similar for all moisture classes. Furthermore, no correlation between DOC concentration and depth of the O horizon could be found, either at the LUSTRA sites or at the manipulation plots. The manipulations also showed that removal of the O<sub>a</sub> horizon did not change the DOC concentrations and fluxes and that the contributions from different compartments could not simply be added to

get a sum of the total leaching. This all indicates that DOC leaching is not related primarily to the size of the carbon pools of the O horizon.

To explain the gradient in DOC leaching, another explanation apart from the direct effects of mean annual temperature or the size of the carbon stock is needed. I suggest that the net primary production may be a parameter that better explains the differences between the three sites. For boreal ecosystems, the net primary production of the ecosystem is well correlated with mean annual temperature (Gower *et al.*, 2001; Zheng *et al.*, 2004). A higher net primary production results in a higher litter production rate and with that higher amounts of the substrate needed for DOC production. At present, no litterfall data are available for the three LUSTRA sites, but litter production in other studies has been related to the aboveground tree biomass, the latitude and the mean annual temperature (Berg *et al.*, 1999; Berg & Meentemeyer, 2001), which were all in turn correlated with DOC leaching in the present study. Figure 13a shows that aboveground biomass is well correlated with DOC concentration.

Table 5. DOC concentration ( $\text{mg l}^{-1}$ ) in bulk deposition, throughfall and leachate from the O and B horizons grouped by site, season and moisture class. The evaluation for soil leachate was performed with a three-way ANOVA. For throughfall, only site effects were tested ( $n=3$ ). Letters refer to significant differences within each group. Averages and standard errors are based on average concentration per plot and season

Grouped by		Asa	n	Knottåsen	n	Flakaliden	n
Site	Bulk deposition	2.5	1	4.8	1	5.1	1
	Throughfall	15.9 (0.4) a	3	7.7 (3.3) b	3	6.2 (0.7) b	3
	O horizon	49.3 (3.6) a	24	38.6 (3.3) b	18	30.3 (2.9) c	18
	B horizon	5.9 (0.9) a	24	7.0 (2.3) a	18	2.2 (0.2) b	18
Season		May-July		Aug-Nov		Dec-April	
	O horizon	27.6 (1.8) a	26	52.0 (3.1) b	26	44.0 (3.4) b	8
	B horizon	4.4 (1.1) a	26	5.4 (1.4) a	26	6.4 (1.8) a	8
Moisture class		Dry		Mesic		Moist	
	O horizon	40.4 (4.0) a	21	37.4 (3.6) a	18	42.9 (3.8) a	21
	B horizon	3.1 (0.4) a	21	2.4 (0.2) a	18	9.5 (1.9) b	21

\* Data from Asa only.

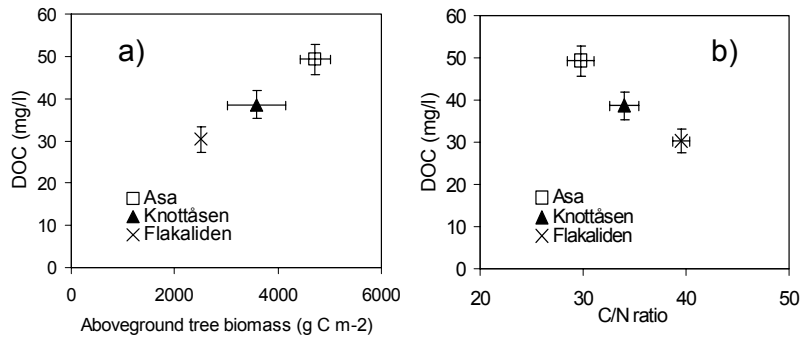


Figure 13. Average DOC concentrations in O horizon leachate (2000-2001) vs. a) aboveground tree biomass and b) C/N ratio of the O horizon. Error bars represent standard errors. Data for aboveground biomass from Berggren *et al.* (2004) (Asa, Knottåsen) and Strömberg (2001) (Flakaliden).

Theoretically, the net primary production seems to be a good explanation. Under steady state, in respect to carbon stocks in the O horizon, the input of litter must equal the losses through mineralization to CO<sub>2</sub> plus DOC leaching. This implies that modelling of DOC leaching under steady state can hypothetically be done using just two parameters – a) the amount of carbon being decomposed and b) the relationship between CO<sub>2</sub> and DOC, as the fate of the decomposed organic matter. If the CO<sub>2</sub>/DOC ratio is held constant, the only parameter governing DOC leaching is the flux of carbon through the system. At the three LUSTRA sites, which were established with the aim of having similar environmental conditions, there is no reason to believe that different environmental factors would greatly affect the CO<sub>2</sub>/DOC ratio. The main differences between the sites are the temperature and nitrogen status, which are not likely to have any major effect. The temperature sensitivity of DOC leaching (*i.e.* the direct effect of temperature) has been found to be similar to that of respiration (Christ & David, 1996; Gödde *et al.*, 1996). Nitrogen effects are discussed below.

In a wider range of ecological conditions, however, the relationships between temperature, net primary production and DOC leaching probably do not hold. In the review by Michalzik *et al.* (2001), covering 42 ecosystem studies performed mainly in Europe and the USA, no correlation was found between mean annual temperature and DOC concentrations or fluxes in soil leachate collected below the O horizon, although mean annual temperature varied between 1-16 °C. Furthermore DOC flux as a fraction of aboveground litter input ranged from 6 to 30%. A reason for the non-existent correlation with mean annual temperature or litter input in the review by Michalzik *et al.* (2001) may have been the large variations in ecological conditions between sites and interactions between different parameters may have masked any effect of *e.g.* temperature. For example, precipitation and temperature may interact, particularly in warmer climates. High temperature combined with low or moderate precipitation may impose water stress on vegetation, limiting tree growth and litter production. Nitrogen effects, as discussed below, may also obscure any effects of factors such as temperature.

## DOC in relation to nitrogen

The effects of nitrogen on DOC leaching were originally beyond the scope of this thesis. It is therefore not an ambition to here solve the enigma of nitrogen effects on the leaching of DOC. However, there was a strong co-variation between mean annual temperature and nitrogen status of the soils and the effects of these two variables could not be separated. Therefore, some discussion about this issue is necessary.

Nutrient status, just like mean annual temperature, influences net primary production, which is of significance for DOC leaching from the O horizon, as suggested above. Nitrogen is of particular interest, because tree growth in northern temperate forests is typically nitrogen-limited (*e.g.* Vitousek & Howarth, 1991; Tamm, 1991). However, both positive and negative net effects of nitrogen on DOC leaching are possible (Figure 14). The positive effect of nitrogen on biomass production is often accompanied in laboratory studies by a hampering effect on decomposition rates of soil organic matter (Nohrstedt *et al.*, 1989; Magill & Aber, 1998), and probably also DOC production (Gödde *et al.*, 1996; Michel & Matzner, 2002). The mechanism behind this observation is not yet known. Chemical stabilisation of organic matter through nitrogen incorporation (Nömmik & Vahtras, 1982), suppressed lignin degradation (Berg & Matzner, 1997) and changes in carbon use efficiency of microorganisms (Ågren *et al.*, 2001) have all been proposed as explanations. In recent reviews (Kalbitz *et al.*, 2000; McDowell, 2003; Chantigny, 2003) it has been concluded that the net effects of the positive and negative influences of nitrogen on DOC in general are still uncertain. Clear effects of nitrogen on DOC are often not reported in field studies (Currie *et al.*, 1996; McDowell *et al.*, 1998; Gundersen *et al.*, 1998; Sjöberg *et al.*, 2003).

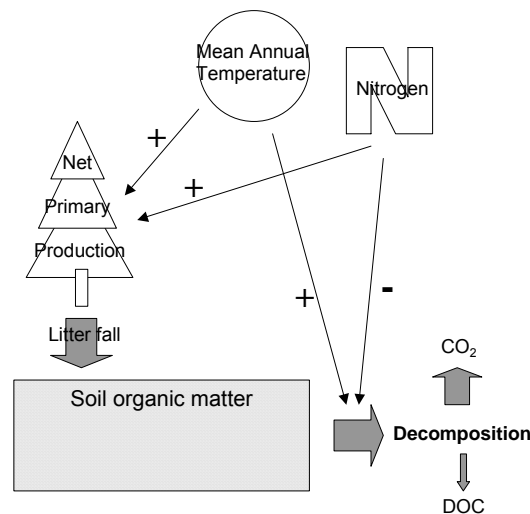


Figure 14. The effects of temperature and nitrogen on soil organic matter and DOC leaching. Under steady state, the input by litterfall must equal the losses by CO<sub>2</sub> and DOC.

However, I suggest that the nitrogen in the ecosystems studied in this thesis had a positive effect on DOC leaching. Nitrogen additions have been found to strongly increase net primary production in spruce forests in both southern and northern Sweden (e.g. Berg *et al.*, 1999). To what extent there is a hampering effect is more uncertain, however. All three LUSTRA sites have low nitrogen status in comparison with nitrogen fertilization experiments and with many areas in central Europe subjected to high loads of nitrogen deposition (MacDonald *et al.*, 2002).

The dual effect of nitrogen, on one hand favouring net primary production in nitrogen-limited ecosystems and on the other reducing soil organic matter decomposition rates, can be an explanation for the negative relationship between the DOC concentration in O horizon leachate and the C/N ratio in the O horizon presented here (Figure 13b), whereas others have found a positive relationship (Aitkenhead & McDowell, 2000) or no relationship (Michalzik *et al.*, 2001) when comparing data from different sites. Thus, in nitrogen-rich ecosystems there might be a decoupling between net primary production and the DOC leaching rate from the O horizon and the results presented here may therefore not be applicable to other environmental conditions with, for example, high nitrogen deposition. This can be illustrated by the long-term nitrogen fertilisation experiment in Stråsan, central Sweden, where nitrogen applications increased tree growth considerably (Tamm, 1991) but DOC concentration in O horizon leachate remained unaffected (Berggren *et al.*, 1997; Sjöberg *et al.* 2003).

## **DOC in relation to soil moisture and water fluxes**

### **No major effect of soil moisture**

Most studies on soil moisture effects on DOC in forest soils have been based on seasonal variations. A consistent finding is that high DOC concentrations occur during rewetting after dry periods (reviewed by Kalbitz *et al.*, 2000). Water content has been found to have a positive influence on DOC concentration (Falkengren-Grerup & Tyler, 1993). However, data on DOC along hydrological gradients, showing the long-term effects of soil moisture conditions, are hard to find.

At the LUSTRA sites, soil moisture regime along the hydrological gradients (Paper V) did not seem to be of any major importance for DOC concentrations in the O horizon. There were no significant differences between the moisture classes (Figure 7, Table 5), despite larger carbon stocks in the moist plots. The differences in carbon stocks between the moisture classes cannot be related to differences in biomass productivity, according to measurements of tree biomass. It is also unlikely that there are any major differences in litter quality between the moisture classes. Spruce is the dominating tree species for all moisture classes. Furthermore, respiration studies from O horizon material from Asa showed that

there was no difference in respiration between Oi horizon material collected from the different moisture classes (Stefan Andersson, pers. comm.). Instead, the differences in C stocks have to be explained by lower turnover rates of the organic matter in the moist plots. The position of the groundwater in the moist plots at Asa was periodically close to the bottom of the O horizon during 2001, suggesting that soil organic matter decomposition was hampered in the mineral soil as well as in the lower part of the O horizon during part of that year. Seasonal variations in DOC concentrations were also the same for all moisture classes, indicating no episodic occurrence of anaerobic conditions, which could change the DOC concentrations during parts of the year in the moist plots. No relationship between TDR measurements of soil moisture and DOC concentrations was found at Knottåsen, the only site where these measurements were available. Altogether, this suggests that soil moisture *per se* does not have any major influence on the DOC leaching from the O horizon. I suggest that DOC production and transport in the moist plots should instead be related to the turnover of SOM in the upper part of the O horizon, which is not severely influenced by a high groundwater level. The lower part of the O horizon – periodically subjected to oxygen-deficient conditions – probably does not contribute substantially to the DOC leaving the O horizon.

### **DOC concentrations are not substantially affected by differences in water fluxes**

In the review by Kalbitz *et al.* (2000), it was concluded that water fluxes does not influence DOC concentrations in the O horizons of forest soil. In published studies, water flux has been found to have either negative (McDowell & Wood, 1984) or no (Michalzik & Matzner, 1999; Solinger *et al.*, 2001; Park & Matzner, 2003; Kalbitz *et al.*, 2004) correlations with DOC concentration. In contrast to these studies, soil water flux was found to be significantly and positively correlated with DOC concentrations during summer in the LUSTRA plots at Knottåsen and Asa. No such correlations were found at Flakaliden and for the autumn or winter periods at Asa and Knottåsen, however. For the field manipulations in Paper II, the correlation between water flux and DOC leaching also seemed to be positive, but was not significant ( $p=0.11$ ). The correlation was not improved by a split of the year into different seasons. A positive relationship with DOC for the summer period in the LUSTRA plots at Knottåsen and Asa should not be over-interpreted based on the data found here. The general picture is that there is no strong connection between water flux and DOC concentrations. However, the positive correlation found could have been caused by re-wetting of dried organic matter, which is known to result in high DOC concentrations (Lindquist *et al.*, 1999; Pechtel *et al.*, 2000; Schaumann *et al.*, 2000).

The more or less insensitive response of DOC concentrations to water fluxes found in this thesis and in many other studies suggest that there is a large pool of potentially soluble organic carbon and that the release of DOC to the percolating soil water is mainly a physico-chemical process, regulated by sorption-desorption mechanisms. DOC concentrations, which are more or less independent of the water fluxes, also imply that the DOC flux is largely a function of the amount of water running through the soil.



## DOC in the mineral soil

### Control of DOC in the mineral soil

A decrease in the DOC concentrations when moving from the O horizon to the mineral soil is a consistent finding in the literature (reviewed by Michalzik *et al.*, 2001) This decrease is generally assumed to be a result of adsorption, rather than decomposition (Kalbitz *et al.*, 2000). DOC retention occurs on a scale of minutes to hours (Guggenberger & Zech, 1992; Kaiser & Zech, 1998), whereas mineralization is much slower, occurring on a scale of days and weeks (Qualls & Haines, 1992; Kalbitz *et al.*, 2003). Thus, a rapid sorption of DOC followed by a slower decomposition is generally thought to be the fate of the DOC in the mineral soil.

There is strong evidence that carbon already sorbed to mineral particles decreases the retention of dissolved organic carbon (Moore *et al.*, 1992; Vance & David 1992; Kaiser & Guggenberger 2003). A positive correlation between C stocks and DOC leaching can therefore be expected for the B horizon. This was also the case for the DOC concentrations under the B horizon in the LUSTRA plots. There were significantly higher DOC concentrations in the moist plots, which had larger carbon stocks compared to the dry and mesic sites, most likely due to slow degradation of organic matter caused by anoxic conditions. There was a significantly lower DOC concentration in B horizon leachate at Flakaliden compared with the other two sites. However, this was only due to a relatively low DOC concentration in the moist plots compared to at Asa and Knottåsen. For the dry and mesic plots, there were no major differences between the sites. Effects of temperature on DOC leaching should not be expected in the B horizon, since the DOC concentration in the mineral soil is mainly governed by physico-chemical processes, rather than biological. The higher carbon stocks in the south compared with the north, both at the LUSTRA sites and generally in Scandinavia (Callesen *et al.*, 2003) could indicate that the DOC concentrations should be higher in the south, but an impact of this effect was not found at the three LUSTRA sites. Nevertheless, the total amount of DOC retained in the mineral soil should be governed by the DOC leaching from the O horizon, since there is a large influx and a small outflux of DOC in the mineral soil (with a smaller variation in absolute numbers).

### Large exchange of DOC in the mineral soil, revealed by <sup>14</sup>C

The <sup>14</sup>C data from dry and mesic plots at Asa and Knottåsen showed that the DOC sampled in the mineral soil mainly had its origin in the B horizon itself and was not derived from DOC leached from the O horizon (Figure 15). There were large differences (13-18 %-units) in <sup>14</sup>C activity between the Oe and Oa horizons on one hand and the B horizon on the other, both for solid soil samples and for DOC (Figure 15). This large difference can be compared with the much smaller differences in <sup>14</sup>C content between solid soil organic matter in the B horizon and DOC obtained from the same horizon (< 5 %-units difference). This suggests that

there is a substantial exchange between the pool of solid old carbon and the incoming 'fresh' DOC and that the carbon leaving the B horizon is different to the DOC transported into this horizon from the horizons above, *i.e.* the DOC in the B horizon had its origin in the mineral soil.

The differences in  $^{14}\text{C}$  between the O and B horizons presented here can be compared with a study by Trumbore *et al.* (1992) who reported  $\text{DO}^{14}\text{C}$  values from a Spodosol in Ontario, Canada, where the radiocarbon values in the O, Ah and B horizons were above 100% modern, with no consistent difference between the horizons, which could indicate a substantial preferential flow in their soil. The  $^{14}\text{C}$ -signal pattern found in the soils at Asa and Knottåsen was, however, in accordance with that found in Podzols at Birkenes, Norway (Michalzik *et al.*, 2003). The high degree of sorption and desorption of DOC in the mineral soil indicated by the  $^{14}\text{C}$ -data implies that characteristics of the mineral soil (content of inorganic Fe and Al precipitates, texture, amounts of carbon already present in the soil, *etc.*) rather than the incoming DOC concentrations are important for the DOC concentration. Thus DOC properties and concentrations at the bottom of the B-horizon and DOC concentration should be regarded more as a function of the soil horizon in which they are measured than as a function of the horizons above.

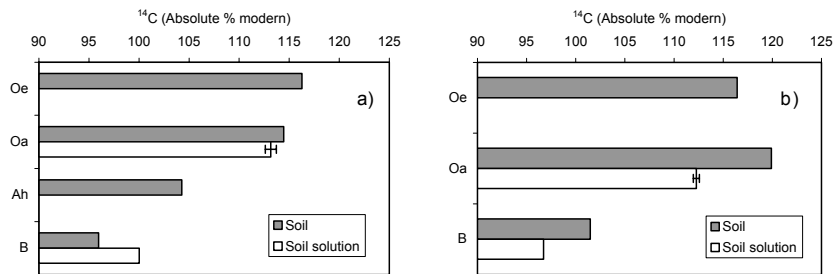


Figure 15.  $^{14}\text{C}$  activity in soil solution and solid soil in different horizons at (a) Asa and (b) Knottåsen. Error bars represent standard error ( $n=3$ ) based on variation between samples.

## Conclusions

A large proportion, half or more, of the DOC from recent litter is retained during passage through the O horizon, probably due to a combination of sorption and biodegradation. Despite this, the Oi horizon still contributes about 20% of the carbon leaving the O horizon. However, the Oe and Oa horizons are the major sources of DOC leached from the O horizon. No net additions of DOC were made in the Oa horizon, but the forest floor manipulations showed that this horizon contributed around half of the carbon in DOC. It is thus not possible to add the contributions from different sublayers in the O horizon to get a total sum of DOC.

Simulations of DOC leaching from the O horizon required recent litter to be allowed to contribute to DOC leaching. In good agreement with the field study,

the best fit was obtained with a parameter set which simulated a 30% contribution to DOC from the litter pool, 32% from 'substrate' and 38% from the humus pool.

Higher DOC leaching in the south compared to the north was measured in the O horizon. I suggest that this can be related to the net primary production of the ecosystems. Soil moisture did not have any effect on DOC concentrations in the O horizon, despite larger carbon stocks in the moist plots compared to the dry and mesic plots.

The content of  $^{14}\text{C}$  in solid organic matter and in DOC collected from the lysimeters revealed that DOC in the B horizon is not derived from the O horizon, but is derived from carbon stored in the mineral soil itself, suggesting extensive sorption and desorption of DOC in the mineral soil.

Water-extractable organic carbon has a different chemical composition to DOC, with a higher content of carbohydrates and lower content of aromatic carbon. Thus, the chemical characteristics of DOC in water extracts should not be used as a substitute for DOC that is being transported in the soil.

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