

## Dissolved organic carbon leaching from a coniferous forest floor – a field manipulation experiment

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**Abstract.** Leaching of dissolved organic carbon (DOC) from the O layer is important for the carbon cycling of forest soils. Here we study the role of the Oi, Oe and Oa horizons in DOC leaching from the forest floor in field manipulations carried out in a Norway spruce forest stand in southern Sweden. The manipulations involved the addition and removal of litter and the removal of Oi, Oe and Oa horizons. Our data suggest that both recent litter and humified organic matter contribute significantly to the leaching of dissolved organic matter from the O layer. An addition of litter corresponding to four times annual litterfall resulted in a 35% increase in DOC concentrations and fluxes although the specific UV absorbance remained unchanged. The removal of litterfall and the Oi horizon resulted in a decreased DOC concentration and in a significant increase in the molar UV absorptivity. The DOC concentration under the Oa horizon was not significantly different from that under the Oe horizon and there were no increase in DOC flux, but rather a decrease, from the bottom of the Oe horizon to the bottom of the Oa horizon, suggesting that there is no net release of DOC in the Oa horizon. However, significant leaching of DOC occurred from the Oa horizon when litterfall and the Oi and Oe horizons were removed. This indicates that there is both a removal of DOC from the Oi and Oe horizons and a substantial production of DOC in the Oa horizon. Quantitatively, we suggest that the Oi, Oe and Oa horizons contributed approximately 20, 30 and 50%, respectively, to the overall leaching of DOC from the O layer.

### Introduction

Dissolved organic carbon (DOC) leached from the organic layer of forest soils is a significant source of carbon stored in the mineral horizons (McDowell and Likens 1988; Qualls et al. 1991; Neff and Asner 2001; Solinger et al. 2001), where a major part of soil organic carbon in forested ecosystems of northern latitudes is found (Callesen et al. 2003). DOC also accounts for a substantial loss of carbon from the forest floor (Qualls et al. 1991; Vance and David 1991; Park and Matzner 2003). Both climate change and forest management practices influence inputs and outputs of soil organic matter and therefore most likely also DOC fluxes. Knowledge of processes involved in DOC production and the abiotic and biotic factors

controlling these processes is crucial in understanding of how stocks and fluxes of soil organic carbon in forest soils are influenced by a changing climate and different forest management practices. However, as pointed out in recent reviews on DOC by Kalbitz et al. (2000) and McDowell (2003), too little is known about the mechanisms and factors regulating DOC leaching out of the O layer of forest soil.

The contributions of various DOC sources under field conditions, particularly the relative contributions from fresh litter and humified organic matter, are still under debate. Many laboratory studies emphasize the role of recent litter, due to its high capacity for DOC production compared with old humified organic matter (e.g. Huang and Schoenau 1996; Magill and Aber 2000). This is supported by observations from several field studies (Qualls et al. 1991; Huang and Schoenau 1998; Michalzik and Matzner 1999), where 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 layer. In contrast, McDowell and Likens (1988) hypothesized that a major part of the DOC leached out of the O layer is derived from the large stock of humified organic matter in the forest floor. Recent studies using  $^{13}\text{C}$  (Hagedorn et al. 2002) and  $^{14}\text{C}$  (Fröberg et al. 2003) isotope techniques have lent support to this view. A litter manipulation experiment in a hardwood stand in Bavaria, Germany, suggested that DOM in forest floor leachates originated from both the litter layer and the pool of humified organic matter (Park and Matzner 2003).

Field manipulation experiments have a great potential in assessing the role of different substrate qualities in the leaching of DOC from the O layer. In contrast to laboratory experiments, the soil microflora, including roots and their associated mycorrhiza, can be left more or less intact. Furthermore, the soil structure does not need to be disturbed, and the soil is exposed to realistic abiotic conditions, including rainfall amounts and intensities, temperature and freezing-thawing cycles. Despite these advantages, very few field manipulation experiments have been reported in the literature apart from the work by Park and Matzner (2003). To our knowledge, no litter manipulation experiment has previously been carried out in a coniferous ecosystem. In the present work, we performed a field manipulation study in a Norway spruce forest with the overall aim of improving our knowledge regarding the role of recent litter and humified organic matter in DOC leaching from the O layer. The experiment also aimed to provide information on the effects of increased litter production on the rate of leaching of DOC from the O layer. The manipulations involved the addition of litter and the removal of the Oi, Oe and Oa horizons. By measuring concentrations, fluxes and chemical characteristics of DOC leached from these manipulated O layers, we attempted to investigate the contributions from organic matter in the Oi, Oe and Oa horizons to the leaching of DOC from the O layer in a typical Norway spruce stand in southern Sweden.

## Methods

### *Site description*

Measurements were made in a 40-year-old Norway spruce (*Picea abies* (L.) Karst) stand at Asa experimental forest, Southern Sweden (57°08' N, 14°45' E). The stand is situated in the area of the common field site of the LUSTRA (Land Use Strategies for Reducing Net Greenhouse Gas Emissions) research programme (Berggren et al. 2004). Annual mean temperature is 5.5 °C and annual mean precipitation 688 mm. Bulk deposition of nitrogen and sulphur is 9 and 5 kg ha<sup>-1</sup> yr<sup>-1</sup> (2001), respectively. Field vegetation is sparse with patches of mosses, such as *Pleurozium schreberi* (Brid.), *Polytrichum commune* (Hedw.) and *Hylocomium splendens*. (Hedw.) The area was clear-cut in 1966 and the present stand was planted in 1967 with 4-year old Norway spruce seedlings. The soil is a Haplic Podzol, developed on a sandy till. The average depth of the O layer measured at the experimental site was 6 cm. Three horizons 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. Carbon stocks and characteristics of the different horizons are given in Table 1. For more information on site characteristics and history, see Berggren et al. (2004).

### *Experimental design*

The experiment was designed with five randomized blocks. The manipulations involved treatments where extra litter was added or different parts of the O layer (Oi, Oe, Oa horizons) were excluded (Figure 1, Table 2). In the *-L* and *-LF* treatments the Oi (Litter) and Oi + Oe (Litter and Fibric) horizons, respectively, were removed. In the *+L1* and *+L2* treatments extra litter was added. The *Litter* treatment contained only litter in a lysimeter installed in the O layer, but with no soil in it. In treatment *-H*, (Humic horizon excluded) the lysimeter was installed under the Oe horizon and in *Control* under the Oa horizon. Litter was obtained by shaking branches on trees in the same stand as used in the experiment and collecting the falling litter on a tarpaulin. Litter was added to the *Litter*, *+L1* and *+L2* treatments the day after collection. The litter was kept in place by a wall of polyethylene (PE) netting enclosing the

Table 1. Soil properties of the Oi, Oe and Oa horizons.

Horizon	C stock (kg m <sup>-2</sup> )	C content (%)	C/N-ratio	pH (H <sub>2</sub> O)
Oi	0.6 (0.0)	49.3 (0.3)	32.6 (0.6)	4.2
Oe	1.9 (0.2)	48.9 (0.2)	29.7 (0.7)	3.8
Oa	1.8 (0.3)	41.6 (0.8)	33.0 (1.0)	3.7

Average values, with standard error of the mean in brackets ( $n = 5$ ).

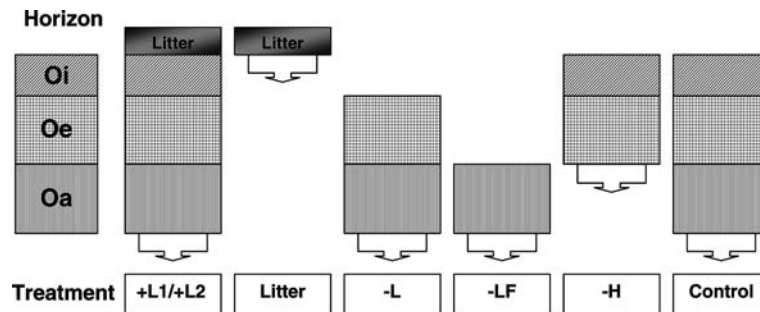


Figure 1. Schematic overview of the different treatments.

Table 2. Detailed description of the different treatments.

	Treatment	Description
Control	Litter	Control. Lysimeter under the Oa horizon
Litter added	+ L1	Lysimeter under the Oa horizon. 320 g litter added annually, corresponding to a total litter input of 2.2 times estimated annual litterfall
	+ L2	Lysimeter under the Oa horizon. 800 g litter added annually, corresponding to a total litter input of 4 times estimated annual litterfall
	Litter	Lysimeter only (no soil) with 800 g litter added, corresponding to a total litter input of 4 times estimated annual litterfall
Subhorizons removed	-LF	Lysimeter under the Oa horizon. Oi and Oe layers removed
	-L	Lysimeter under the Oa horizon. Litter layer (Oi) removed
	-H	Lysimeter under the Oe horizon

treated area. In the  $-L$  and  $-LF$  treatments the Oi and Oi + Oe horizons were carefully removed. The manipulations were carried out on an area covering the lysimeters plus an additional 10 cm perpendicular to the sides of each lysimeter. To prevent litter being added to the  $-L$  and  $-LF$  lysimeters plots, PE netting was placed on the ground 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 in the Oa horizon of the  $-LF$  treatment and of an unmanipulated area did not reveal any major differences (on average 0.1 °C). Lysimeters were installed in June 2000. Measurements of DOC in soil leachates started in September 2000 to check for differences between treatments before the manipulations started. Forest floor manipulations were initiated in April 2001. Repeated additions of litter in the +L1, +L2 and Litter treatments were made in May 2002 and May 2003.

Soil leachate was collected bi-weekly using zero-tension lysimeters (30 cm square, made of Plexiglass and PE-netting). The lysimeters were horizontally installed directly beneath the Oe and Oa horizons with the aim of minimizing the disturbance of the soil above. Soil solution samples were collected in PE-bottles, which were placed in PVC containers below ground to keep the contents cool and dark. Ten collectors of throughfall (20 cm in diameter) were randomly distributed below the canopy but  $> 1$  m away from tree trunks. The samples were stored cold until analysis. All samples were filtered through Acrodisc 0.2  $\mu\text{m}$  polysulphone membrane filters prior to analyses. DOC was measured using a Shimadzu TOC-5000 A analyser, usually within one week of sampling. UV absorbance at 285 nm was determined on samples in 2002–2003 using a Shimadzu UV-1201 spectrophotometer. The Na, K, Ca, and Mg contents were measured by ICP-MS, anions by ion chromatography and  $\text{NH}_4$  with a Flow Injector Analyzer (FIA Star 5010, Tecator).

Litterfall was measured using 20 litter traps, each covering an area of 0.25 m<sup>2</sup>. An estimate of the annual root litter production was obtained from the standing root biomasses in the O layer of the dry and mesic LUSTRA plots described in Berggren et al. (2004), assuming different lifetimes of roots in different size classes (1 year for roots 0–1 mm in diameter, 2 years for 1–2 mm and 4 years for 2–4 mm; Hooshang Majdi pers. comm.) The total amounts of litter supplied during the measurement period to the soil in the different treatments are given in Table 3.

### *Statistical analysis*

Statistical analysis to test for differences between treatments in DOC concentration and UV absorptivity was performed using SAS, procedure Mixed. Due to differences in variance (heteroscedasticity), all DOC concentrations were log-transformed before statistical analysis. 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

*Table 3.* Total carbon stocks and amounts of applied litter and natural litterfall from April 2001 to December 2003.

	Carbon stock (kg C m <sup>-2</sup> )	Applied litter (kg C m <sup>-2</sup> yr <sup>-1</sup> )	Above ground litterfall (kg C m <sup>-2</sup> yr <sup>-1</sup> )	Root litter (kg C m <sup>-2</sup> yr <sup>-1</sup> )
+L2	4.3	0.39	0.13	0.032
+L1	4.3	0.16	0.13	0.032
Litter	0.0	0.39	0.13	0
-LF	1.8	0	0	0.016
-L	3.7	0	0	0.032
-H	2.5	0	0.13	0.016
Litter	4.3	0	0.13	0.032

dependency of successive measurements close in time. Unequal time intervals were accounted for using the spatial power structure for covariance. Testing for significant differences between the *Control* and any treatment was performed using Dunnett's multiple comparison test.

#### *Water fluxes*

Vertical soil water fluxes were calculated using the COUP model (Jansson and Karlberg 2001). The model simulates soil water and heat processes in different types of soils. The calculations of water fluxes 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 and measurements of these variables were made at towers used for micrometeorological measurements (Berggren et al. 2004).

For the +L1, +L2 and -L treatments, the same water flux as for *Control* was used. For the -LF and -H treatments, where approximately half the soil and roots had been removed, the losses thorough transpiration and evaporation were assumed to be half those in the *Control*, i.e. the calculated water fluxes were approximately 18% higher in these treatments than in the *Control*. For the *Litter* treatment, the throughfall water flux was used. Because the lysimeters were believed to collect representative concentrations of DOC, but not to collect all the water passing through the soil, DOC fluxes were calculated by combining the DOC concentrations measured in the lysimeters with water fluxes calculated using the COUP model.

## **Results**

#### *Effects of adding litter*

When extra litter was added, the DOC concentrations in the +L1 and +L2 treatments were generally higher than those in the *Control*, but with the same seasonal variations (Figure 2). These concentrations are within the typical ranges for forest ecosystems, reported in the review by Michalzik et al. (2001). The *Litter* treatment, with only litter and no soil on the lysimeter, showed that fresh litter has a great potential for producing DOC. Average DOC concentration in this treatment was 51 mg l<sup>-1</sup>, not significantly different from the DOC concentration in the *Control*. Furthermore, it was 35 mg l<sup>-1</sup> higher than the DOC concentration in throughfall, suggesting that the major proportion was derived from the added litter (Table 4). High DOC concentrations were recorded in the *Litter* treatments on some occasions during the first months after application, but the concentration remained high throughout the whole year in this treatment too.

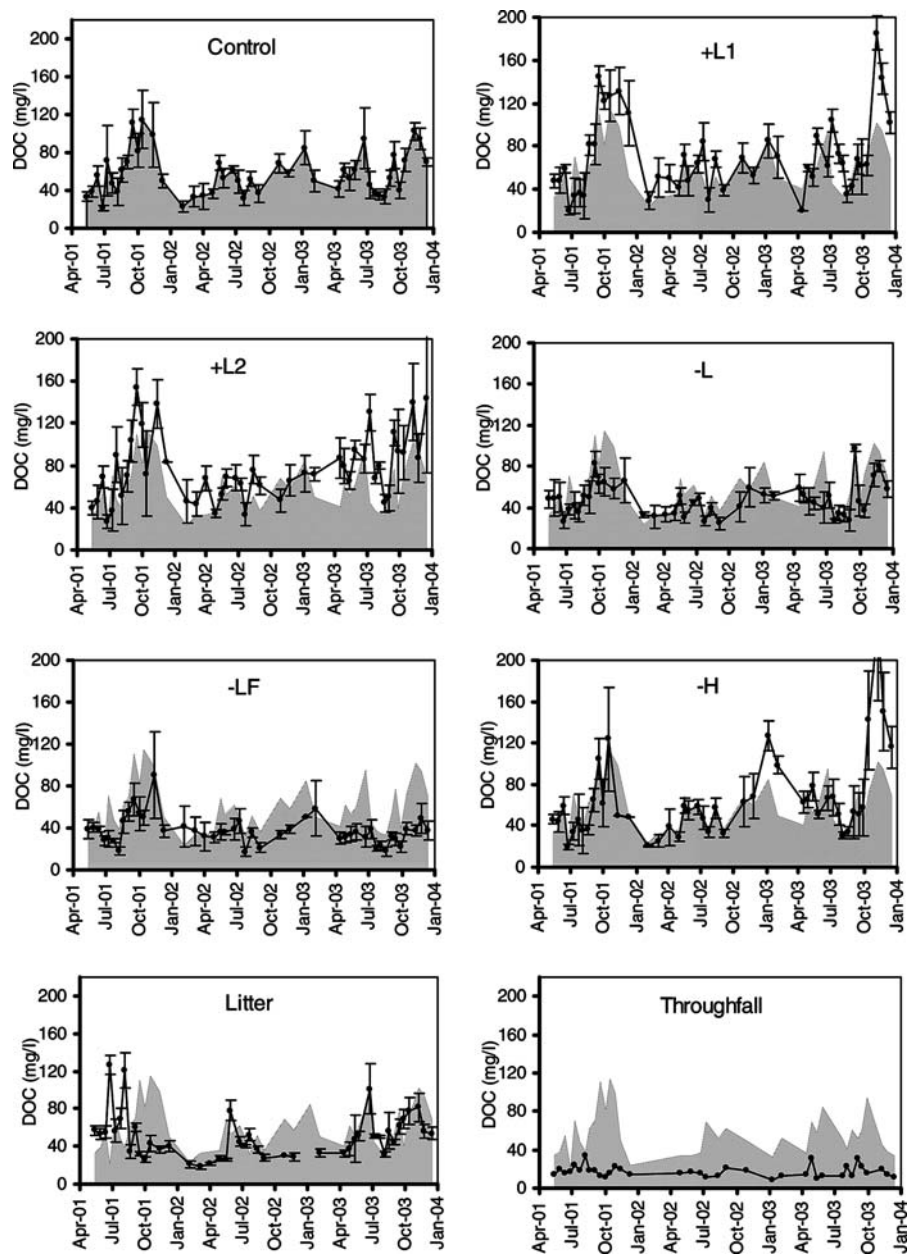


Figure 2. Average DOC concentrations ( $\text{mg l}^{-1}$ ) in the different treatments from April 2001 to December 2003. Error bars represent standard error of the mean ( $n = 5$ ). The shaded area represents the concentration in the *Control* treatment.

Table 4. Average DOC concentrations and fluxes from April 2001 to December 2003 in the different treatments.

	DOC Concentration		DOC fluxes
	mg l <sup>-1</sup>	<i>p</i>	April 2001–December 2003 (g m <sup>-2</sup> )
+L2	75 (8)	0.003	110
+L1	69 (7)	0.13	105
Litter	51 (2)	0.38	79
-LF	37 (4)	<0.0001	63
-L	47 (4)	0.12	65
-H	65 (8)	0.92	103
Litter	55 (4)	–	82
Throughfall	16	–	29

Standard error of the mean in brackets ( $n=5$ ) and *p*-values are given for differences in concentrations compared with the Litter.

The average concentration of DOC increased significantly in the +L2 treatment compared to the *Control*, from 55 to 75 mg l<sup>-1</sup> (Table 4). The +L1 treatment with doubled litter input also had a tendency for a higher DOC concentration (average 69 mg l<sup>-1</sup>), but it was not significantly different from the *Control*. The treatment effects increased with time, as indicated in Figure 3. For individual years, only the treatment effect for +L2 during the last year was significant.

The DOC fluxes during the whole period (31 months) are reported in Table 4. The flux increased from 82 g m<sup>-2</sup> in the *Control* to 105 g m<sup>-2</sup> in the +L1 treatment and 110 g m<sup>-2</sup> in the +L2 treatment. The DOC flux from the lysimeters with fresh litter only (*Litter*) was 79 g m<sup>-2</sup>. The corresponding DOC flux in throughfall was 29 g m<sup>-2</sup>. The annual flux of DOC in the *Control* corresponded to 19% of the litterfall (above ground and below ground). This is in the upper range of the values usually reported for O layers of forest soils, which normally range between 9–18% of the total litter input (Qualls et al. 1991, Solinger et al. 2001; Park and Matzner 2003; Michalzik et al. 2003). The DOC flux in the *Litter* treatment corresponded to about 5% of the total amount of carbon added as litter (including natural litterfall).

Specific UV absorbance was significantly lower in the *Litter* treatment, indicating a lower content of aromatic compounds in leachate from fresh litter compared to that from humified organic matter (Chin et al. 1994; Kalbitz et al. 2003). Despite the elevated DOC concentrations in the +L1 and +L2 treatments (Table 4), the specific UV absorbance was not significantly different from the *Control* (Table 5).

The pH values for soil leachate in the different treatments were similar (Table 6), and the temporal variations in pH also followed the same pattern between treatments. For most of the time, the pH was about 4.5, except for the *Litter* treatment, where it was slightly higher (Table 6). However, the leachate from the fresh litter did not affect pH in the O layer, as indicated by the fact



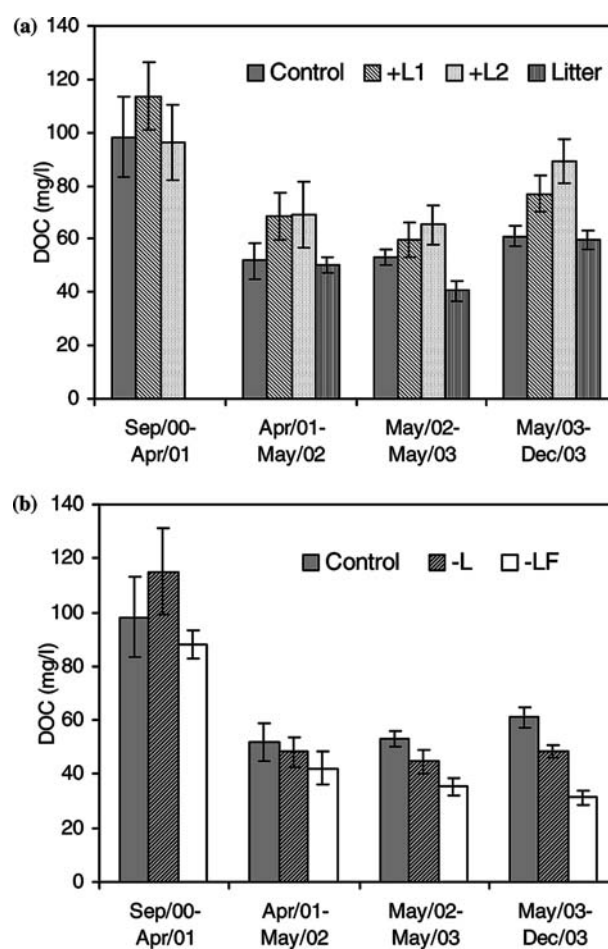


Figure 3. Average DOC concentrations ( $\text{mg l}^{-1}$ ) during the different years in the treatments where (a) litter was added and (b) O horizons were removed. Note that September 2000–April 2001 represents the time before manipulations started.

Table 5. Molar absorption coefficient at 285 nm.

	Molar absorptivity coefficient ( $\text{l mol}^{-1} \text{cm}^{-1}$ )	<i>p</i>
+L1	266 (7)	0.82
+L2	267 (7)	0.99
Litter	237 (7)	0.02
-LF	302 (11)	< 0.001
-L	293 (5)	0.04
-H	263 (7)	0.18
Litter	274 (7)	–

Mean with standard error ( $n=5$ ) in brackets and *p*-values for differences compared with the Control.

Table 6. pH and concentration of macro-ions, mg l<sup>-1</sup> in the different treatments.

	pH	Cl <sup>-</sup>	NO <sub>3</sub> <sup>-</sup> -N	NH <sub>4</sub> <sup>-</sup> -N	SO <sub>4</sub> <sup>2-</sup> -S	K <sup>+</sup>	Na <sup>+</sup>	Mg <sup>2+</sup>	Ca <sup>2+</sup>
+L2	4.88 (0.13)	3.7 (0.7)	0.4 (0.2)	4.3 (0.7)	0.9 (0.1)	4.0 (1.0)	2.6 (0.6)	0.5 (0.1)	1.0 (0.3)
+L1	4.90 (0.19)	3.0 (0.3)	0.5 (0.1)	3.5 (1.1)	0.9 (0.2)	3.2 (0.4)	2.1 (0.2)	0.6 (0.1)	1.3 (0.3)
-L	4.82 (0.10)	3.2 (0.4)	0.2 (0.0)	2.4 (0.8)	0.8 (0.1)	2.3 (0.3)	2.1 (0.2)	0.4 (0.0)	0.7 (0.1)
-LF	4.82 (0.10)	2.8 (0.3)	0.3 (0.1)	1.7 (0.5)	0.8 (0.1)	2.8 (0.3)	1.2 (0.1)	0.3 (0.1)	0.5 (0.1)
-H	5.04 (0.23)	3.0 (0.3)	0.3 (0.1)	3.2 (0.5)	1.1 (0.0)	5.9 (2.8)	2.0 (0.4)	0.7 (0.2)	1.9 (0.6)
Litter	4.81 (0.04)	4.4 (0.9)	0.1 (0.0)	1.9 (0.5)	1.0 (0.1)	4.4 (0.7)	2.6 (0.4)	0.6 (0.1)	1.3 (0.3)
Litter	5.85 (0.03)	2.6 (0.3)	0.8 (0.2)	1.2 (0.3)	0.9 (0.1)	5.4 (0.6)	1.3 (0.1)	1.0 (0.1)	2.5 (0.3)

Average ± Standard error ( $n=5$ ).

that pH values in the *Control* and +L2 treatments were the same. For inorganic cations and anions, no major effect of the litter additions was observed (Table 6).

#### *Effects of litterfall and/or removal of O horizons*

The concentrations of DOC decreased when litterfall and the Oi horizon (-L treatment) were removed (Figure 2). This decrease was even more pronounced when litterfall and both the Oi and Oe horizons were removed (-LF treatment). DOC concentrations followed the seasonal pattern of the *Control*, but the amplitude in variations was smaller. In the treatment with the Oa horizon excluded from the measurements (-H treatment), there was no decrease in DOC concentrations, but instead a tendency for increased concentrations during periods with high concentrations of DOC (Figure 2).

Considering the whole treatment period, there was a significant treatment effect on the DOC concentration in the -LF treatment, but not in the -L treatment (Table 4). The average DOC concentration in -LF was 37 mg l<sup>-1</sup> compared with 55 mg l<sup>-1</sup> in the *Control*, whereas it was 47 mg l<sup>-1</sup> in the -L treatment. The treatment effect in -LF increased with time during the three years (Figure 3b). During the first year, the decrease in DOC concentration was 10 mg l<sup>-1</sup> (not significant), whereas it decreased by 18 mg l<sup>-1</sup> ( $p < 0.001$ ) during the second year and by 30 mg l<sup>-1</sup> ( $p < 0.0001$ ) during the third year. There was no significant difference in concentrations measured below the Oe horizon (-H treatment) and the Oa horizon (*Control*) (Table 4), indicating no net release of DOC in the Oa horizon. However the increase in DOC concentration in the -LF treatment (37 mg l<sup>-1</sup>) compared with throughfall concentration (16 mg l<sup>-1</sup>) indicates a potential capacity of the Oa horizon to produce DOC.

Expressed as DOC fluxes, the amounts leaving the -LF and -L treatments during the experimental period were 63 and 65 g m<sup>-2</sup>, respectively, which can be compared to 82 g m<sup>-2</sup> in the *Control* (Table 4). The small difference in

DOC fluxes between the  $-LF$  and  $-L$  treatments compared to the difference in DOC concentrations (Table 4) was due to the slightly higher water flux in the  $-LF$  treatment. The DOC flux below the Oe horizon ( $-H$ ) was  $88 \text{ g m}^{-2}$ .

The  $-L$  and  $-LF$  treatments had a significantly higher specific UV absorbance than the *Control* (Table 5), indicating a significant contribution of DOC low in aromatic carbon in the Oi and Oe horizons to the leaching of DOC from the Oa horizon. The specific UV absorptivity of the  $-H$  treatment was not significantly different from the *Control*, but with a tendency to be lower.

Removing the Oi horizon, or the Oi horizon plus the Oe horizon did not affect the pH in the soil leachate (Table 6). There was a small tendency in the  $-H$  treatment for a higher pH, reflecting a relatively higher pH in the upper part of the Oi and Oe horizons compared with the Oa horizon (Table 6). The concentrations of K, Na, Mg and Ca were slightly lower in the  $-L$  and  $-LF$  treatments, whereas the concentrations of  $\text{NH}_4^+$  and  $\text{NO}_3^-$  were the same as in the *Control*.

## Discussion

The *Litter* treatment showed that large amounts of DOC are leached from recent litter, which is in accordance with previous findings in laboratory experiments (Huang and Schoenau 1996; Magill and Aber 2000) and in field studies (e.g. Qualls et al. 1991; Michalzik and Matzner 1999). The average concentration of DOC in the *Litter* treatment was equal to that in the *Control*, and the flux was  $50 \text{ g m}^{-2}$  higher than the flux in throughfall (Table 4). However, not all of the DOC leached from recent litter was caught at the bottom of the O layer in the  $+L2$  treatment, which had the same amounts of litter added. Figure 4a shows an attempt to quantify the fluxes of DOC in the O layer in the  $+L2$  treatment. The difference in DOC flux between the  $+L2$  treatment ( $110 \text{ g m}^{-2}$ ) and the *Control* ( $82 \text{ g m}^{-2}$ ) was  $28 \text{ g m}^{-2}$ . Assuming that no degradation of throughfall DOC occurred in the layer of added litter, the net release of DOC from the applied litter was  $50 \text{ g m}^{-2}$ . Using this figure, 44% of the DOC derived from litter was sorbed/mineralized in the O layer. Both these figures would be higher if some of the throughfall DOC was degraded in the layer of added litter; at maximum  $79 \text{ g m}^{-2}$ , corresponding to a loss of 65%, if it is assumed that all of the throughfall DOC was mineralized in the added litter layer. The contribution of the O layer to the net leaching of DOC is also dependent on the assumed fate of throughfall DOC. The figure  $82 \text{ g m}^{-2}$  represents a situation where all throughfall DOC was mineralized in the O layer. Considering the fact that 44–65% of the DOC leached from recent litter was lost during passage through the O layer, we believe this to be a realistic assumption. The DOC in throughfall is a highly labile pool of carbon with a large fraction of carbohydrates (e.g. McDowell and Likens 1988; Fröberg et al. 2003) and has even higher degradation rates than DOC from the Oi horizon (Qualls and Haines 1992). Michalzik et al. (2003) also assumed DOC

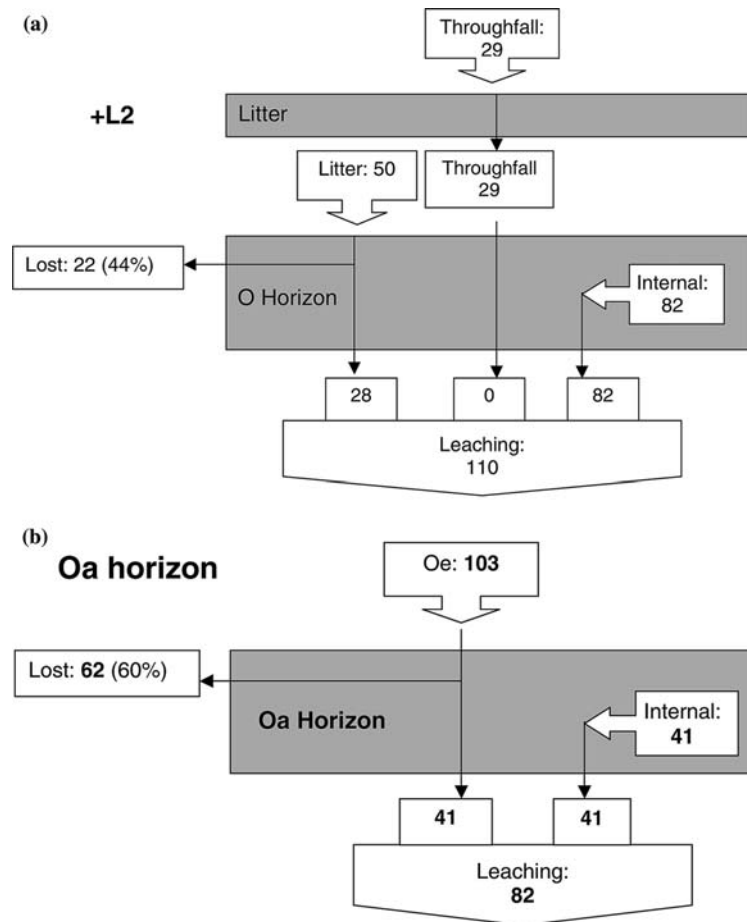


Figure 4. DOC budgets,  $\text{g m}^{-2}$ , in (a) the +L2 treatment and (b) the intact Oa horizon. See text for assumptions and calculations.

in throughfall to be rapidly decomposed and not to contribute to the DOC leaching from the O layer when they applied the DyDOC model on a similar forest ecosystem to that in Asa.

The UV absorptivity data in the leachate from the *Litter* and +L1/+L2 treatments (Table 5) are in accordance with the observations made from the concentrations and fluxes of DOC in the same treatments, i.e. they indicate a qualitative change in DOC as water percolates through the O layer. The DOC in leachate from the added litter (*Litter* treatment) had a lower UV absorptivity than that in leachate from the +L1 and +L2 treatments, indicating that a significant fraction of the low-UV absorbing C was lost in the O layer. The UV absorptivity of DOC in the +L1 and +L2 treatments was not significantly different from the *Control* (Table 5). The UV absorption is strongly related to

the hydrophobic fraction of DOC, which contains almost entirely the aromatic moieties of dissolved organic matter (Dilling and Kaiser 2002). It is not possible to say from our data whether the hydrophilic fraction of DOC in the litter leachate was lost selectively during its passage through the O layer, but this is possible. As mentioned above, the hydrophilic component of DOC is known to be mineralized faster than the hydrophobic component (Qualls and Haines 1992; Kalbitz et al. 2003). On the other hand, the hydrophobic component is known to be sorbed more strongly to the soil matrix than the hydrophilic component (Tipping and Woof 1991; Kaiser et al. 1996).

It is important to note that despite the substantial loss of litter-derived DOC in the O layer, there was a significantly higher DOC concentration in the +L2 treatment than in the *Control* (Table 4). This suggests that recent litter is of significance for DOC leaching from the O layer, which is in accordance with the litter manipulation experiment in a hardwood stand by Park and Matzner (2003). Furthermore, the data on DOC leaching from the treatments with extra litter applications showed that high concentrations in +L1, +L2 and *Litter* occurred over the whole year (Figure 2), supporting the observation by Qualls et al. (1991) that litter is leached gradually over long periods.

The data from the -L treatment, with litterfall and the Oi horizon removed, also indicate that litter is involved in the leaching of DOC from the O layer. Although the -L treatment was not significantly different from the *Control*, there was a tendency for lower concentrations and fluxes, indicating that 20% of the DOC leached from the O layer had its origin in the Oi horizon (Table 4). This is 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 be a contribution from recent litter to the leachate in the intact O layer, which affects the composition of the soil solution in a direction towards lower aromaticity. Thus, recent litter contributes to DOC leaching from the O layer, but the major fraction of DOC originates in the Oe and Oa horizons.

To separate the individual contribution of the Oe and Oa horizons to the leaching of DOC from the Oa horizons was not entirely straightforward, because it was not possible to add the net leaching from the different horizons to get the total leaching. There seemed to be a substantial turnover of DOC leached from the Oe horizon in the Oa horizon. Judging from concentrations and fluxes, which were similar below the Oe and Oa horizons, there was no significant net retention or release in the Oa horizon (Table 4). This is in accordance with results obtained in many other field investigations (Qualls et al. 1991; Huang and Schoenau 1998; Michalzik et al. 2001). However, as shown in the -LF treatment, the Oa horizon produced substantial amounts of DOC and more than doubled the flux compared with throughfall; from 29 to 63 g m<sup>-2</sup>. Figure 4b quantifies the contribution of the Oa horizon to the net leaching of DOC from an intact O layer. The flux of DOC into and out of the Oa horizon was 103 and 82 g m<sup>-2</sup>, respectively (Table 4). In order to obtain an estimate for the contribution from the Oa horizon we assumed that dissolution of DOC from the Oa horizon is not dependent on the DOC concentration in

the soil solution coming into this horizon. Furthermore we assumed that the loss of DOC in throughfall was 100% in the intact O layer and 50% in the Oa horizon in the *-LF* treatment. This gave a net leaching of DOC from the Oa horizon of  $48.5 \text{ g m}^{-2}$  (63 minus  $14.5 \text{ g m}^{-2}$ ). Accounting for the lower water flux through the Oa horizon in an intact O layer compared to that in the *-LF* treatment, a contribution from the Oa horizon of  $41 \text{ g m}^{-2}$  was obtained (Figure 4b), i.e. 50% of the total flux of DOC leaving the O layer. Thus, the major fraction (60%) of the DOC leached from the Oe horizon was sorbed/mineralized in the Oa horizon.

Some clues to the origin of DOC, either in the Oe or in the Oa horizon, can also be found in the UV absorptivity data. These data showed that the DOC originating in the Oa horizon (*-LF*) was significantly richer in UV-absorbing (aromatic) moieties than DOC leached from an intact O layer (*Control*) (Table 5). In contrast, there was a tendency to 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. However, as mentioned above, some qualitative fractionation of DOC might have occurred in the Oa horizon, e.g. a preferential sorption in the Oa horizon of the UV-absorbing hydrophobic fraction in the Oe leachate would result in an overestimate of the contribution of DOC originating in the Oe horizon. Possible experimental artefacts due to the manipulation also have to be considered. Changes in pH or the chemical composition of the soil leachate induced by the treatments might influence the solubility, and thus flux, of DOC. However, no such effects were recorded (Table 6). Rather, the low concentrations of  $\text{NH}_4^+$  and  $\text{NO}_3^-$  in the *-H* and *-LF* treatments indicated the presence of an active root/mycorrhiza system. Furthermore, the soil temperature in the Oa horizon in the *-LF* treatment was about the same as in the *Control* (see above).

Few attempts have been made previously to quantify the contribution from the different O horizons to DOC leaching under field conditions. According to the litter and throughfall manipulation experiment by Park and Matzner (2003), both recent litter and humified organic matter contributed to DOC leaching from the O layer in a deciduous forest stand. However, they did not make measurements below the Oe horizon. Our data are also in agreement with the  $^{14}\text{C}$  measurements made previously on leachate from the *Control* and *-H* treatments (Fröberg et al. 2003), which suggested that the major fraction of DOC leaving the O layer was leached from the Oe and Oa horizons. The DOC losses of 50% or more during passage through the O layer can be compared with the conclusion of Kalbitz et al. (2000), who reviewed the large number of incubation studies made on DOC and found that about 10–40% of DOC may be easily decomposed by microbes. The figure can be even higher for throughfall and DOC from moderately decomposed substrate (Qualls and Haines 1992; Hongve et al. 2000; Kalbitz et al. 2003). Large amounts of DOC leached from the Oe horizon seem to be lost in the Oa horizon. In a short-term perspective, sorption might contribute to that removal, because sorption of

DOC to organic horizons is known to occur (Tipping and Woof 1991; Qualls 2000). However, in a longer term perspective (months–years), the removal must be due to mineralization by microorganisms.

### Conclusions

The data in this study identify both recent litter and humified organic matter as the sources of DOC. Large amounts of DOC were leached from recent litter during the whole year, suggesting a high DOC leaching potential. However, 44% or more of the DOC leached from recent litter in the +L2 treatment was lost during passage through the O layer by sorption/mineralization. The contribution from recent litter and the Oi horizon to the leaching of DOC from the untreated O layer was estimated to be approx. 20%. Thus, management practices or changes in climate resulting in increased litter production will probably increase leaching rates of DOC from the O layer.

The Oe and Oa horizons contributed the major proportion of DOC leached from the O layer. As in several other studies, no net increase in DOC concentrations and fluxes occurred in the Oa horizon. However, the manipulation with litterfall and the Oi and Oe horizons removed showed that there was a significant net production of DOC in the Oa horizon. The contribution of the Oa horizon to the overall leaching from the O layer was estimated to be approx. 50%.

Quantitatively, we suggest that the Oi, Oe and Oa horizons contributed approximately 20, 30 and 50%, respectively, to the overall leaching of DOC from the O layer.

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