

# Concentrations and fluxes of dissolved organic carbon in an age-sequence of white pine forests in Southern Ontario, Canada

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Received: 29 May 2007 / Accepted: 6 June 2007 / Published online: 3 August 2007  
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**Abstract** We determined concentrations and fluxes of dissolved organic carbon (DOC) in precipitation, throughfall, forest floor and mineral soil leachates from June 2004 to May 2006 across an age-sequence (2-, 15-, 30-, and 65-year-old) of white pine (*Pinus strobus* L.) forests in southern Ontario, Canada. Mean DOC concentration in precipitation, throughfall, leachates of forest floor, Ah-horizon, and of mineral soil at 1 m depth ranged from ~2 to 7, 9 to 18, 32 to 88, 20 to 66, and 2 to 3 mg DOC L<sup>-1</sup>, respectively, for all four stands from April (after snowmelt) through December. DOC concentration in forest floor leachates was highest in early summer and positively correlated to stand age, aboveground biomass and forest floor carbon pools. DOC fluxes via precipitation, throughfall, and leaching through forest floor and Ah-horizon between were in the range of ~1 to 2, 2 to 4, 0.5 to 3.5, and 0.1 to 2 g DOC m<sup>-2</sup>, respectively. DOC export from the forest ecosystem during that period through infiltration and groundwater discharge was estimated as ~7, 4, 3, and

2 g DOC m<sup>-2</sup> for the 2-, 15-, 30-, and 65-year-old sites, respectively, indicating a decrease with increasing stand age. Laboratory DOC sorption studies showed that the null-point DOC concentration fell from values of 15 to 60 mg DOC L<sup>-1</sup> at 0 to 5 cm to <15 mg DOC L<sup>-1</sup> at 50 cm. Specific ultraviolet light absorption at 254 nm (SUVA<sub>254</sub>) increased from precipitation and throughfall to a maximum in forest floor and decreased with mineral soil depth. No age-related pattern was observed for SUVA<sub>254</sub> values. DOC concentration in forest floor soil solutions showed a positive exponential relationship with soil temperature, and a negative exponential relationship with soil moisture at all four sites. Understanding the changes and controls of DOC concentrations, chemistry, and fluxes at various stages of forest stand development is necessary to estimate and predict DOC dynamics on a regional landscape level and to evaluate the effect of land-use change.

**Keywords** Afforestation · Carbon flux · Chronosequence · Dissolved organic carbon · Sorption · Specific ultra-violet absorbance index (SUVA) · Temperate pine forests

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## Introduction

Dissolved organic carbon (DOC) is an important component of forest ecosystem carbon (C) and nutrient cycling. Although DOC import to and export

from forest ecosystems is small compared to other C fluxes, the internal DOC cycle plays an important role in nitrogen (N) and phosphorus (P) dynamics and acts further as a major control on soil formation processes, mineral weathering and pollutant transport (Kalbitz et al. 2000; Neff and Asner 2001; Mattson et al. 2005).

The DOC pathway through a forest stand results from DOC input via precipitation and throughfall, leaching through forest floor and mineral soil, and eventually export from the forest ecosystem via groundwater discharge. Several studies have quantified DOC concentration and fluxes in cool and moist forests (e.g., Dalva and Moore 1991; Michalzik et al. 2001; Fröberg et al. 2006). Generally, DOC concentrations of 1 to 8 mg DOC L<sup>-1</sup> in precipitation increase during throughfall and leaching through forest floor, with maximum concentrations reaching up to 90 mg DOC L<sup>-1</sup> in forest floor leachates, owing to DOC release from forest canopy and forest floor organic matter (e.g., Michalzik and Matzner 1999; Moore 2003; Starr and Ukonmaanaho 2004). DOC concentrations in subsoil solutions decrease with depth because of sorption, reaching 10 to 20 mg DOC L<sup>-1</sup> in the B-horizon and 2 to 10 mg DOC L<sup>-1</sup> in the C-horizon (Michalzik et al. 2001). DOC input and export from forest ecosystems have been reported in a range of 1 g DOC m<sup>-2</sup> year<sup>-1</sup> and 1 to 50 g DOC m<sup>-2</sup> year<sup>-1</sup>, respectively (Aitkenhead and McDowell 2000; Moore 2003). Moore (2003) reported differences in DOC sorption ability of mineral soils between dry, sandy, and wet, clayey upland forests in a boreal landscape. However, less information is available on DOC concentrations and fluxes in temperate forests growing on dry, sandy soils. Dosskey and Bertsch (1997) suggested that the transport of organic matter through sandy soil is limited due to strong sorption processes and thus, despite greater leaching rates, DOC fluxes are not larger than in other forests.

Much uncertainty still exists about the controls on DOC concentrations and fluxes, mainly due to contrasting results from both laboratory and field studies (Kalbitz et al. 2000). Furthermore, the controls on DOC result from both physical and biogeochemical factors whose contribution changes with changing environmental conditions, resulting in difficulties in determining the main controls and thus predicting DOC production and consumption (Kal-

bitz et al. 2000; Neff and Asner 2001). Some of the key controls on DOC dynamics include soil temperature and moisture, availability of N, iron (Fe) and aluminum (Al), soil pH, C/N ratio, amount and quality of organic matter, as well as land use and management effects (Kalbitz et al. 2000; Michalzik et al. 2001; Neff and Asner 2001).

Little attention has been given to the question of how DOC concentrations, fluxes and chemistry vary with the successional development of a forest stand. Khomutova et al. (2000) reported that DOC production was smaller in agricultural land as compared to forested land. Quideau and Bockheim (1997) found that DOC concentrations in soil solution increased after afforestation of former prairie land, whereas Kalbitz et al. (2000) reviewed contrasting results on changes in DOC concentrations following afforestation. Forest characteristics such as aboveground biomass, leaf area index (LAI), litterfall and forest floor biomass are known to change throughout stand development and may thereby cause significant alterations to DOC concentration and flux dynamics. Therefore, we need more information to understand the changes in DOC dynamics through various stand development stages (forest age-sequences) to be able to estimate DOC dynamics at a regional landscape level (Michalzik et al. 2001; Mattson et al. 2005).

The objectives of this study were: (a) to determine DOC concentrations and fluxes from precipitation through to subsoil seepage in an age-sequence of white pine forests, (b) to assess the effect of stand age and environmental controls on seasonal and annual patterns of DOC concentration and fluxes, (c) to determine the DOC sorption capacity and DOC null-point (DOC<sub>np</sub>) of subsoil horizons in a laboratory sorption experiment with a leachate of the forest floor, and (d) to test whether there are differences in DOC chemistry through the determination of specific ultra-violet absorbance index (SUVA), suggested as an index of the aromaticity of the DOC (Weishaar et al. 2003).

## Materials and methods

### Site description

The study was conducted at the Turkey Point Flux Station, located ~12 km south east of the town of

Simcoe, close to Lake Erie in southern Ontario, Canada. It consists of a white pine (*Pinus strobus* L.) chronosequence that includes a 2-year-old, a 15-year-old, a 30-year-old, and a 65-year-old stand. All four stands are located within 20 km of each other and experience similar climatic conditions. The region has a temperate climate with a 30-year mean annual temperature of 7.8°C and an annual precipitation of 1,010 mm of which 438 mm fall from May to September (Environment Canada Norms from 1971 to 2000 at Delhi, ON). Mean annual snowfall is 133 cm. The mean annual frost-free period is 160 days, and mean length of the growing season is about 212 days (Presant and Acton 1984). The stands are located on lacustrine sandy plains. Soils in this region are commonly well-to-imperfectly drained, with low-to-moderate water holding capacity (Presant and Acton 1984). A detailed description of soil and stand characteristics is given in Peichl and Arain (2006) and summarized here in Table 1. All four stands were planted on either cleared oak-savannah land (in case of two older stands) or former agricultural lands. Despite differences in land use prior to afforestation, all four sites have similar soil conditions with small concentrations of soil N (<0.05%) and soil organic C (<1.5%). Although soil pH-values are higher at the two younger sites (former agricultural land), we cannot attribute this to land use history, as acidic needle input over decades in the two older sites without agriculture may have caused their soil pH to decline as a natural consequence of stand development. Thinning was conducted at the 65-year-old forest in 1983 and since then the stand has achieved near-full canopy closure. The thinning practices may be considered as part of forest management strategies and thus may not necessarily need to be considered as a disruption of forest development. Therefore, in this study we assume that changes in DOC concentrations and fluxes resulted primarily from successional changes of aboveground biomass, forest productivity, LAI, litterfall, and forest floor biomass accumulation caused by forest ecosystem development.

#### Sample collection and analysis of DOC concentrations and fluxes

Samples for DOC analysis were collected at monthly intervals from the end of May to the end of

November 2004 and at bi-weekly intervals from early April to November 2005 and April to mid-May 2006. Bulk precipitation and throughfall was collected in plastic buckets equipped with a 10 cm-radius funnel whose neck was filled with glass wool in order to avoid contamination from litter-fall and insects. The glass wool in bucket collectors was replaced and buckets were cleaned from algae and organic material build-up on every sampling date. At the 65-year-old site, two precipitation buckets were placed on top of the 28-m high meteorological tower. At the three younger sites, two buckets were installed on the ground in forest clearings that were large enough (>10 m radius) to collect precipitation. The comparison of rainfall data measured with buckets to rainfall data from the tower rain gauges at the 2-year-old and the 65-year-old sites showed strong correlation (slope = 1.04 and 0.88,  $r^2 = 0.97$  and 0.95 at the 65-year-old and 2-year-old site, respectively) to accept bucket measurements representative of precipitation at all four sites. Six buckets were installed along a transect on the forest floor at each of the three older sites in order to collect throughfall. No throughfall buckets were installed at the 2-year-old site as interception and canopy impact on DOC concentrations from the tree seedlings were considered negligible. On rare occasions during very warm periods in the summer, the volume collected from bulk precipitation buckets was less than from the throughfall buckets due to evaporative losses. In these cases, data from the tower rain gauges was used to fill in the amount of precipitation. Bucket volumes were converted into mL per area.

Litter leachates ( $n = 4$ ) from underneath the forest floor (LFH-layer) and leachates from underneath the organic-rich Ah-horizon ( $n = 4$ ) were sampled at all four sites by zero tension lysimeters which consisted of 20 × 20 cm plastic trays, covered with a metal mesh and window screen, and equipped with an outlet at the bottom from which soil solution was captured via a plastic tube into plastic sampling bottles. The litter zero tension lysimeters were subject to disturbance by animals, resulting in occasional missing data.

Sampling of mineral soil solution was attempted with porous cup suction lysimeters at 25, 50, and 100 cm depth ( $n = 3$  for each depth class). However, due to the dry, sandy, and well-draining nature of the soils, samples could only be obtained from the

**Table 1** Significant characteristics of the four Turkey Point sites

Characteristics	65-year-old	30-year-old	15-year-old	2-year-old
Location	42, 42', 35.20"N 80, 21', 26.64"W	42, 42', 24.52"N 80, 20', 53.93"W	42, 46', 27.91"N 80, 27', 31.59"W	42, 39', 39.37"N 80, 33', 34.27"W
Previous land use + management practices	Oak savanna cleared for afforestation; thinned in 1989	Oak savanna cleared for afforestation; no thinning	Agricultural land; no cropping for few years prior to afforestation, no thinning	Agricultural land; no cropping for few years prior to afforestation
Dominant tree species	<i>Pinus strobus</i>	<i>Pinus strobus</i>	<i>Pinus strobus</i>	<i>Pinus strobus</i>
Major understory and ground vegetation species	Understorey: <i>Quercus vultina</i> , <i>Abies balsamifera</i> , <i>Prunus serotina</i>	Understorey: <i>Quercus vultina</i>	Understorey: <i>Quercus vultina</i>	Understorey: none
Groundcover:	<i>Rhus radicans</i> , <i>Rubus</i> spp., <i>Maianthemum canadense</i> , <i>Polytrichum</i> spp., <i>Pteridium aquilinum</i>	Groundcover: scattered patches of moss ( <i>Polytrichum</i> spp.)	Groundcover: none	Groundcover: Herbs, grasses ( <i>Conyza canadensis</i> , <i>Digitaria sanguinalis</i> , <i>Trifolium repens</i> )
Mean tree height (m)	22	12	9	1
Mean tree diameter at DBH (cm)	35	16	16	2.5 (tree base)
Stem density (trees ha <sup>-1</sup> )	429	1,492	1,242	1,683
Aboveground tree biomass (g C m <sup>-2</sup> )	8,416	4,488	3,236	22
Forest floor (LFH) (g C m <sup>-2</sup> )	1,211	545	745	83
Forest floor (LFH) thickness (cm)	2.5	2.0	3.0	0.5
Fine root biomass (<5 mm) in 0–15 cm depth (g m <sup>-2</sup> )	390	465	405	23
Max. LAI (m <sup>2</sup> m <sup>-2</sup> )	8.0 <sup>a</sup>	5.9 <sup>a</sup>	12.8 <sup>a</sup>	1.0
Litter-fall in 2004 (g m <sup>-2</sup> year <sup>-1</sup> )	400	290	520	na
Litter-fall in 2005 (g m <sup>-2</sup> year <sup>-1</sup> )	340	220	440	na
Soil type	Brunisolic luvisol	Brunisolic luvisol	Gleyed brunisolic luvisol	Brunisolic luvisol
Soil texture	Fine sandy	Fine sandy	Fine sandy loam	Fine sandy
Soil pH (upper 20 cm)	5.5	5.5	6.2	7.4
Soil C in 0–15 cm (A-horizon) (g C m <sup>-2</sup> )	1,950	1,420	1,850	1,740

<sup>a</sup> Corrected for clumping factor from Chen et al. (2006)

15-year-old site where the deeper mineral soil appeared to be water-saturated for longer periods after heavy rainfall events. Samples were filtered through a glass fiber paper (<0.45  $\mu\text{m}$  nominal pore diameter) and stored at 4°C until analyzed for DOC concentration on a Shimadzu 5050 Analyzer.

Dissolved organic carbon flux in precipitation, throughfall, and through forest floor and Ah-horizon was calculated by multiplying the average amount of water flux in each profile layer with the respective average amount of DOC concentrations for the spring, summer, and autumn seasons. DOC fluxes within the forest soil were assumed to be zero in winter when soil was frozen. Snowmelt in spring was accounted for in spring flux calculations. To estimate the export of DOC from the ecosystem via groundwater leaching, the DOC flux below 1 m depth of mineral soil was calculated by assuming the water flux below 1 m depth to be the difference between precipitation minus ecosystem evapotranspiration. Evapotranspiration was estimated using a closed-path eddy-covariance system (IRGA LI-7000; Li-Cor, Lincoln, NE, USA) which was installed on top of the meteorological tower (Restrepo and Arain 2005). Runoff at these flat, sandy sites was considered zero. Because the majority of roots are within the upper 50 cm (Peichl 2005), water uptake by roots below 1 m was also considered zero. The volume of water from days on which the daily amount of precipitation exceeded evapotranspiration were summed and grouped into the spring, summer, and autumn seasons (winter DOC flux below 1 m depth was assumed zero) to determine the seasonal and annual leaching rates. Seasonal water leaching rates were multiplied with the null-point DOC concentration ( $\text{DOC}_{\text{np}}$ ) at 1 m depth.  $\text{DOC}_{\text{np}}$  is the DOC concentration of soil solution at which mineral soil neither absorbs nor releases DOC from or into the soil solution and thus represents the concentration of DOC that is subject to leaching loss.  $\text{DOC}_{\text{np}}$  was determined in the laboratory experiment described below.

Determination of SUVA (specific ultra-violet absorbance index)

Samples collected in 2005 were analyzed for SUVA at 254 nm by a spectrometer (GENESYS 10UV scanning). SUVA has been suggested as an index of the aromaticity of DOC and changes with differences

in the chemical composition of DOC.  $\text{SUVA}_{\text{wI}}$  is defined as the UV absorbance at 254 nm measured in inverse meters ( $\text{m}^{-1}$ ) divided by the DOC concentration measured in milligrams per liter ( $\text{mg DOC L}^{-1}$ ) (Weishaar et al. 2003).

Laboratory DOC sorption experiment

Because of a lack of mineral soil solution samples, we assessed the ability of mineral subsoils to release and absorb DOC in a laboratory sorption experiment. Mineral soil samples were collected from two locations at each site at 5, 25, 50, and 100 cm depth, air-dried and sieved through a 2-mm mesh.

A DOC stock solution was prepared by soaking organic forest floor samples collected from the 65-year-old site in distilled water for 48 h. The extract was filtered through 0.45  $\mu\text{m}$  glass fiber paper and stored at 4°C. The stock dilution was further diluted with distilled water to obtain five solutions ranging from 0 to 59  $\text{mg DOC L}^{-1}$  representing the range of DOC concentrations commonly found in these soils. The pH and electric conductivity (at 22°C) of the solutions ranged from 4.8 to 5.0 and from 14.3 to 90.7  $\mu\text{S cm}^{-1}$ , respectively. About 30 mL of each initial DOC solution was added to 3 g of each soil, and the suspensions were shaken slowly for 24 h at 4°C. Afterwards, the suspensions were filtered through 0.45  $\mu\text{m}$  glass fiber paper and analyzed for the DOC concentration in the filtrate. The null-point of DOC ( $\text{DOC}_{\text{np}}$ ), the concentration at which the solution neither gained nor lost DOC, was determined from the intercept of the sorption isotherm with the  $x$ -axis from the linear regression between the DOC concentrations of the filtrates and the initial DOC concentration in the solutions (Moore et al. 1992). The SUVA at 254 nm of all samples treated with the initial solution #3 ( $\sim 22 \text{ mg DOC L}^{-1}$ ) was determined to compare changes in sorption processes throughout the soil profile with changes in aromaticity of DOC.

The pH of each soil sample (<2 mm) was determined in 0.01 M  $\text{CaCl}_2$  using a soil : solution ratio of 1:1 and soil samples were analyzed for total C on a Carlo Erba NC-2500 elemental analyzer.

Environmental controls

Daily averaged soil temperature at 2 cm depth and soil moisture at 5 cm depth were calculated from half

hourly data which was continuously measured by the weather stations at each site.

Litterfall traps ( $n = 9$ ) were placed close to the DOC experiment location and emptied on every DOC sample collection date from September until the end of November 2005 in order to determine the effect of fresh litter input on DOC concentrations in litter and Ah-horizon leachates at the three older sites. Annual and seasonal DOC concentrations and fluxes were also compared to annual and seasonal litterfall during 2004 and 2005.

Correlation of annual and seasonal DOC concentrations and fluxes was further assessed with net ecosystem productivity (NEP) determined by the eddy-covariance technique (Arain and Restrepo-Coupe 2005), forest aboveground biomass C pools, stem density, fine root biomass (<5 mm), the amount of forest floor C, and soil C in the Ah-horizon (Peichl and Arain 2006). The average seasonal LAI values measured with a LAI-2000 from 2002 to 2004 were used to determine the effect of canopy development on DOC concentration and fluxes throughout the growing season.

## Results

### DOC concentrations

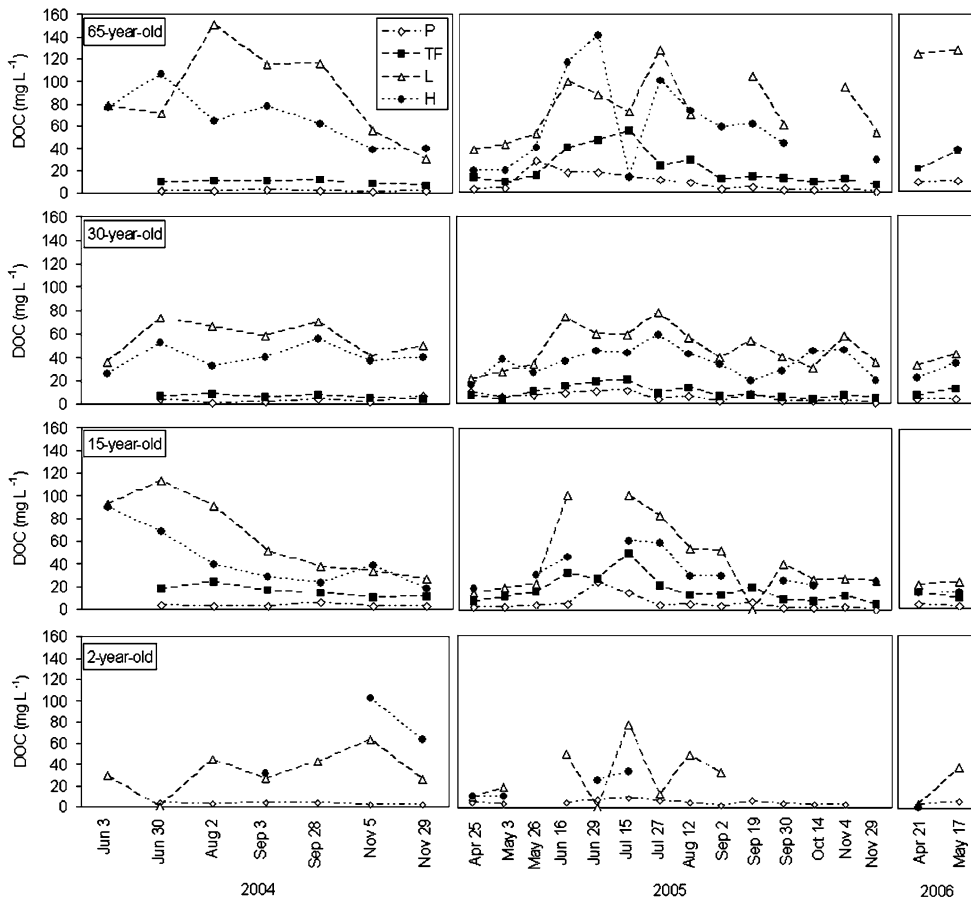
From June 2004 to May 2006, DOC concentration in precipitation ranged between 1 and 5 mg DOC L<sup>-1</sup> except for the early summer in 2005 when high-values occurred at all four sites reaching up to 25 mg L<sup>-1</sup> at the 15-year-old site (Fig. 1). DOC concentration slightly increased within throughfall to about 7 to 15 mg DOC L<sup>-1</sup>. No seasonal pattern was observed during 2004. Dissolved organic carbon concentrations were highest in forest floor leachates commonly ranging from 15 to 50 mg DOC L<sup>-1</sup> during spring and late autumn to between 60 and 120 mg DOC L<sup>-1</sup> during the summer months. Highest values occurred between early June and late August at the three older sites. At the youngest site, however, the limited number of samples retrieved did not confirm this seasonal trend. No consistent seasonal pattern was observed for DOC concentrations in leachates of the Ah-horizon, which were smaller than the forest floor leachates, typically

ranging between 20 and 60 mg DOC L<sup>-1</sup>, except for the 65-year-old site where high values of up to 100 mg DOC L<sup>-1</sup> were observed during the early summer months.

Dissolved organic carbon concentrations in precipitation and throughfall were higher in 2005 than in 2004, whereas DOC concentrations in forest floor and Ah-horizon leachates were higher in 2004 than 2005 (Table 2). This indicates that DOC concentrations in forest floor and organic soil solutions were independent of DOC input from precipitation and throughfall. Throughfall DOC concentrations were larger at the 15-year-old site than the two older sites, possible because the LAI is greatest at that site (see Table 1). The only age-related pattern was observed for forest floor leachates which showed increased DOC concentrations with increasing stand age. DOC concentrations of mineral subsoil retrieved at the 15-year-old site decreased with depth from about 18 mg DOC L<sup>-1</sup> at 20 cm depth to 2.2 mg DOC L<sup>-1</sup> at 1 m depth. Average DOC concentrations increased from precipitation to a maximum in the forest floor and thereafter decreased throughout the soil profile (Fig. 2). Thus, forest canopy and forest floor were large DOC sources whereas sorption or microbial consumption processes in mineral soil decreased DOC concentrations.

### DOC fluxes

Annual water and DOC fluxes estimated from bucket and zero-tension lysimeters are presented in Table 3. DOC fluxes increased from 0.9 to 2.4 g DOC m<sup>-2</sup> in precipitation to about 2 to 4 g DOC m<sup>-2</sup> in throughfall and forest floor solution. Deeper in the mineral soil, the DOC flux decreased to about 0.5 to 2 g DOC m<sup>-2</sup> which was close to the DOC input flux via precipitation. Overall, DOC fluxes were quite similar in both years for each profile layer. However, the water flux and thus DOC fluxes through forest floor and Ah-layer are likely to be underestimated because of drainage problems with the zero-tension lysimeters. Assuming leaching rates as the difference between precipitation and evapotranspiration (as shown and discussed further below), DOC fluxes through both forest floor and Ah-horizon layers may be expected to be higher than suggested from zero-tension lysimeters.



**Fig. 1** Concentrations of DOC in precipitation (*P*), throughfall (*TF*), forest floor litter (*L*), and Ah-horizon (*H*) layers at the four Turkey Point sites from June 2004 to May 2006.  $n = 2$  for *P*, six for *TF*, and four for *L* and *H*

### Specific ultraviolet light absorption (SUVA)

Specific ultraviolet light absorption<sub>254</sub> increased from a range of about 1.3 to 2.0 L mg DOC<sup>-1</sup> m<sup>-1</sup> in precipitation to 2.7 to 3.6 L mg DOC<sup>-1</sup> m<sup>-1</sup> in forest floor leachates (Table 4). SUVA<sub>254</sub> at the 15-year-old site showed a decrease throughout the mineral soil profile from 2.5 to 0.9 L mg DOC<sup>-1</sup> m<sup>-1</sup>. No age-related pattern was observed for SUVA<sub>254</sub>-values.

### DOC sorption in mineral soil

The sorption study on samples from the four profiles showed a very strong linear relationship between the initial DOC concentration and the amount of DOC adsorbed or released, with  $r^2 > 0.90$ ,  $P < 0.05$ ,  $n = 5$  (Table 5). The sorption regression slopes ranged from 0.14 to 0.54, with a mean of 0.29, and the intercept

value (DOC released when distilled water added) ranged from  $-0.3$  to  $-8.5$  mg DOC L<sup>-1</sup>, with an average of  $-3.4$  mg DOC L<sup>-1</sup>. DOC<sub>np</sub> decreased rapidly from about 15 to 60 mg DOC L<sup>-1</sup> in the Ah-horizon (0 to 5 cm depth) to less than 25 mg DOC L<sup>-1</sup> at 25 cm depth at the three older sites, whereas at the seedling site a slight increase from 16 to 19 mg DOC L<sup>-1</sup> was observed (Fig. 3a). DOC<sub>np</sub> of the Ah-horizon was especially high at the 15- and 65-year-old sites compared to the two other sites. Below 25 cm depth, DOC<sub>np</sub> decreased with increasing soil depth to less than 15 mg DOC L<sup>-1</sup> at 50 cm depth at all four sites. DOC<sub>np</sub> values at 1 m depth were slightly higher than at 50 cm depth, except for the 65-year-old site which had the lowest DOC<sub>np</sub> value at a depth of 1 m. This suggests that the maximum sorption capacity at these sites was reached at a depth of 50 cm.

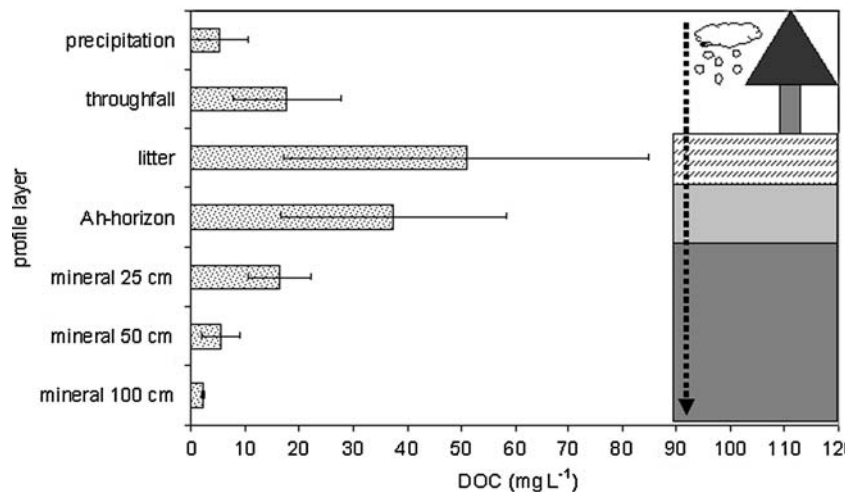
**Table 2** Mean DOC concentration ( $\text{mg DOC L}^{-1}$ )  $\pm$ SD in precipitation, throughfall, forest floor and Ah-layer leachates at the 2-, 15-, 30-, and 65-year-old sites from snowmelt to the end of November in 2004 and 2005

	65-year-old		30-year-old		15-year-old		2-year-old	
	2004	2005	2004	2005	2004	2005	2004	2005
Precipitation <sup>a</sup>	$1.8 \pm 0.6$	$6.7 \pm 6.2$	$3.3 \pm 2.1$	$5.6 \pm 3.2$	$3.3 \pm 1.2$	$6.1 \pm 6.6$	$2.8 \pm 1.0$	$4.3 \pm 2.0$
Throughfall	$9.8 \pm 1.9$	$16 \pm 11.6$	$6.1 \pm 1.5$	$9 \pm 5.5$	$15.7 \pm 5.2$	$17.7 \pm 12.1$	ND	ND
Forest floor	$88.3 \pm 40.9$	$56.4 \pm 20.6$	$56.2 \pm 14.7$	$47.4 \pm 17.7$	$46.8 \pm 34.5$	$32.1 \pm 32.7$	$33.2 \pm 19.6$	$31.4 \pm 26.2$
Ah-layer	$66.5 \pm 23.8$	$44.8 \pm 30.9$	$40.3 \pm 10.6$	$35.4 \pm 12.4$	$43.6 \pm 26.1$	$35 \pm 15.7$	$65.3 \pm 35.4$	$19.8 \pm 11.3$
Mineral soil 25 cm	ND	ND	ND	ND	$18.4 \pm 7.0$	$14.2 \pm 4.8$	ND	ND
Mineral soil 50 cm	ND	ND	ND	ND	ND	$3.7 \pm 0.5$	ND	ND
Mineral soil 100 cm	ND	ND	ND	ND	2.2	$2.3 \pm 0.4$	ND	ND

ND—Not determined

<sup>a</sup> Higher DOC concentrations in precipitation during 2005 resulted from few unusual high summer values which may have been caused by either evaporation of bucket water, or from accumulation of organic matter (i.e., pollen, insects, plant litter, and volatile organic matter) or by contamination from long-range transport of industrial air pollution in the region

**Fig. 2** Mean DOC concentration throughout the forest profile layer at the 15-year-old site between June 2004 and May 2006. Error bars indicate SD



Upon reaction of the  $22 \text{ mg DOC L}^{-1}$  solution with the soils, the  $\text{SUVA}_{254}$ -values decreased from about  $4.5 \text{ L mg DOC}^{-1} \text{ m}^{-1}$  in the upper 5 cm Ah-horizon layer to a minimum at 25 to 50 cm depth, and increased at 1 m depth (Fig. 3b). A considerable increase in SUVA at 1 m depth occurred at the 15- and 30-year-old sites, where SUVA exceeded twice the values of the upper 5 cm layer. This may be related to iron, which may cause interference (Weishaar et al. 2003).

Mineral soil C concentration was small at all four sites with values between 0.5 and 1% C in the upper 5 cm soil layers and decreasing with depth to about 0.1 to 0.3% C at 25, 50, and 100 cm depth (Fig. 3c). Soil

pH increased from the upper 5 cm down to 1 m depth at the three oldest sites, whereas little change with soil depth was observed at the 2-year-old seedling site (Fig. 3d). Soil pH decreased with increasing stand age from an average of about 6 at the 2-year-old site, which was recently under arable crops, to about 5 at the 15-year-old site and about 4.5 at the 30- and 65-year-old sites. This may be a result of increased needle litter accumulation over time that caused acidification especially of the upper 5 cm soil horizon.

When data from all sites and soil depth classes were pooled, the DOC sorption intercept ( $c$ ) was negatively related to soil C, whereas  $\text{DOC}_{\text{np}}$  showed a positive relationship with soil C (Fig. 4). However,

**Table 3** Estimated mean fluxes of water ( $L m^{-2}$ ) and DOC ( $g DOC m^{-2}$ ) from snowmelt to the end of November in 2004 and 2005

Water flux ( $L m^{-2}$ )	65-year-old		30-year-old		15-year-old		2-year-old	
	2004	2005	2004	2005	2004	2005	2004	2005
Precipitation	499 (469–529)	451 (445–458)	489 (460–518)	521 (490–552)	412 (401–423)	445 (433–456)	419 (413–426)	475 (437–514)
Throughfall	384 (313–456)	361 (278–445)	337 (280–394)	340 (280–399)	247 (191–302)	288 (201–374)	NA	NA
Forest floor	25 (13–37)	29 (12–45)	65 (25–104)	47 (28–65)	47 (28–66)	32 (21–45)	9 (2–16)	13 (5–26)
Ah-layer	15 (7–23)	18 (10–25)	40 (30–62)	39 (21–56)	21 (15–27)	13 (9–17)	3 (0.1–6)	3 (0.3–5)
DOC flux ( $g DOC m^{-2}$ )	2004	2005	2004	2005	2004	2005	2004	2005
Precipitation	0.9 (0.5–1.4)	2.4 (1.7–3.1)	1.4 (1.0–1.8)	2.0 (1.4–2.5)	1.3 (0.9–1.7)	1.7 (1.2–2.2)	1.1 (0.7–1.6)	1.9 (1.4–2.4)
Throughfall	3.8 (0.7–7.9)	4.7 (0.7–10.9)	2.0 (1.2–3.1)	2.6 (1.3–4.2)	3.8 (2.9–6.4)	4.5 (1.8–8.5)	NA	NA
Forest floor	2.0 (0.8–3.9)	1.5 (0.5–3.5)	3.5 (0.7–8.2)	2.2 (1.1–4.2)	3.4 (1.4–6.2)	1.6 (0.8–2.9)	0.3 (0.01–0.8)	0.5 (0.1–1.3)
Ah-layer	1.0 (0.3–1.9)	0.9 (0.4–1.6)	1.8 (0.8–3.1)	1.5 (0.5–2.9)	0.7 (0.4–1.1)	0.5 (0.3–0.7)	0.3 (0.01–0.9)	0.1 (0.01–0.2)

NA—Not applicable, numbers in parentheses represent estimated minimum to maximum range

soil C was not able to explain differences among sites within each depth class for neither the DOC sorption intercept nor  $DOC_{np}$ , which indicates that soil C did not act as sole control.

#### DOC export from forest ecosystems

We estimated water flux and DOC export below 1 m soil depth from the difference between precipitation and evapotranspiration (Restrepo and Arain 2005) and the  $DOC_{np}$  as the DOC concentration of soil solution at 1 m depth (Table 6). Despite including snowmelt into spring flux calculations, the highest water and DOC flux occurred during the autumn due to heavy rainfall events. DOC export during spring and summer seasons ranged between 0.3 and  $2 g m^{-2}$  within each season, DOC export during autumn ranged from about 1 to  $3 g m^{-2}$ . The total annual DOC export from the ecosystem decreased with increasing stand age from about  $7 g m^{-2}$  at the 2-year-old seedling site to about 4, 3, and  $2 g m^{-2}$  at the 15-, 30-, and 65-year-old sites, respectively. This age-dependent pattern was consistent for both years 2004 and 2005. The comparison of DOC export estimates with estimates of DOC input via precipitation from Table 3 suggests that the DOC input and output at the two older sites was somewhat in balance whereas the DOC export exceeded the DOC input via precipitation at the younger 15- and 2-year-old sites by two and five times, respectively.

#### Correlations of DOC concentrations with environmental controls

Dissolved organic carbon concentration of forest floor leachate was not related to throughfall DOC concentration at the two oldest sites suggesting that forest floor is a DOC source which is generally independent of DOC input via throughfall. However, at the 15-year-old site DOC concentration of forest floor leachate showed a relationship with throughfall DOC concentration ( $r^2 = 0.58$ ,  $P < 0.001$ ), indicating that higher LAI and higher throughfall DOC concentration at this site compared to the other sites may have had an effect on the DOC concentration of forest floor leachates. DOC concentration of forest floor leachate was also affected by the amount of DOC input from throughfall DOC flux at the 65-year-old site ( $r^2 = 0.27$ ,  $P < 0.05$ ) and at the 15-year-old site ( $r^2 = 0.34$ ,  $P < 0.01$ ).

**Table 4** Mean SUVA ( $\pm$ SD) in precipitation, throughfall, forest floor and Ah-layer leachates at 2-, 15-, 30-, and 65-year-old sites and at 25, 50, and 100 cm depth in the subsoil at the 15-year-old site, during 2005

	65-year-old	30-year-old	15-year-old	2-year-old
Precipitation	1.27 $\pm$ 0.69	1.94 $\pm$ 0.54	2.42 $\pm$ 1.13	2.00 $\pm$ 0.83
Throughfall	2.07 $\pm$ 0.65	2.05 $\pm$ 0.63	2.36 $\pm$ 0.57	ND
Forest floor	3.15 $\pm$ 0.76	3.59 $\pm$ 0.88	2.69 $\pm$ 0.80	2.83 $\pm$ 0.55
Ah-layer	3.04 $\pm$ 0.68	3.26 $\pm$ 0.97	2.53 $\pm$ 1.43	3.73 $\pm$ 2.19
Mineral soil 25 cm	ND	ND	2.17 $\pm$ 0.14	ND
Mineral soil 50 cm	ND	ND	1.33 $\pm$ 0.25	ND
Mineral soil 100 cm	ND	ND	0.90 $\pm$ 0.67	ND

ND—Not determined

**Table 5** Linear regression analysis for determination of DOC<sub>np</sub>;  $\text{DOC}_{\text{np}} = -\frac{c}{m}$ 

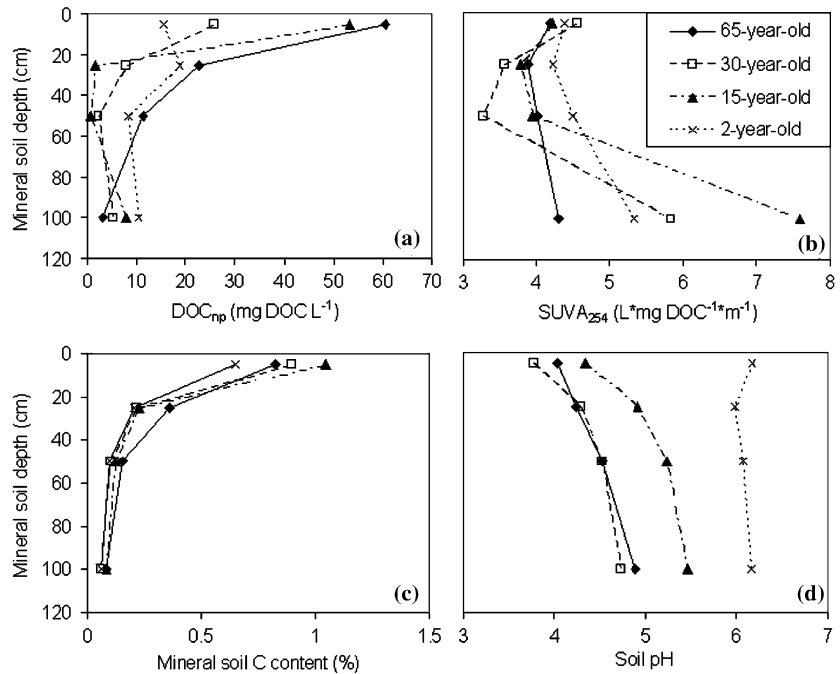
Site	Depth (cm)	DOC <sub>np</sub> (mg DOC L <sup>-1</sup> )	SEE of DOC <sub>np</sub>	<i>c</i>	SE ( <i>c</i> )	<i>m</i>	SE ( <i>m</i> )	<i>r</i> <sup>2</sup>	SEE	Sig. ( <i>P</i> )
65-year-old	5	60.4	4.18	-8.535	0.474	0.141	0.017	0.959	0.603	<0.001
	25	22.6	1.99	-4.797	0.333	0.212	0.012	0.991	0.423	<0.01
	50	11.4	5.58	-2.423	0.972	0.213	0.035	0.926	1.237	<0.01
	100	3.3	4.00	-0.793	0.762	0.238	0.027	0.962	0.970	<0.01
30-year-old	5	25.7	4.41	-6.194	0.863	0.241	0.031	0.954	1.089	<0.01
	25	7.8	1.38	-4.200	0.649	0.535	0.031	0.994	0.738	<0.01
	50	2.3	0.98	-1.089	0.401	0.466	0.019	0.997	0.456	<0.01
	100	5.4	3.10	-1.925	0.994	0.359	0.047	0.967	1.131	<0.05
15-year-old	5	53.4	3.91	-7.790	0.409	0.136	0.012	0.979	0.547	<0.01
	25	1.6	4.41	-0.881	1.260	0.373	0.036	0.973	1.684	<0.01
	50	0.6	3.15	-0.558	0.855	0.373	0.024	0.988	1.143	<0.01
	100	7.9	4.51	-3.144	1.207	0.348	0.034	0.972	1.613	<0.01
2-year-old	5	15.5	2.85	-4.578	0.634	0.296	0.018	0.989	0.847	<0.001
	25	18.8	8.70	-2.659	0.971	0.141	0.027	0.899	1.297	<0.05
	50	8.3	2.85	-1.868	0.431	0.225	0.012	0.991	0.576	<0.001
	100	10.4	4.00	-3.397	0.993	0.328	0.028	0.979	1.327	<0.01
Min				-8.54		0.141		0.899		
Max.				-0.33		0.535		0.997		
Mean				-3.38		0.294		0.969		

Dissolved organic carbon concentrations of forest floor and Ah-horizon leachates were not affected by the amount of water flux via rainfall, throughfall, forest floor, or mineral soil solution fluxes at all four sites, indicating that water flux intensity had no dilution effect on DOC concentration of forest floor and Ah-horizon leachates.

Dissolved organic carbon concentrations of forest floor leachates showed a positive exponential relationship with soil temperature and a negative exponential relationship with soil moisture at the

three older sites in 2005 (Fig. 5). The effect of soil temperature and moisture was less pronounced in 2004, possibly because of longer sampling periods (1-month intervals as compared to bi-weekly sampling in 2005) which may have caused other variables to interfere. At the 2-year-old site, the relationships of DOC concentrations in forest floor leachates with soil temperature and moisture showed similar trends but were not statistically significant due to the limited data obtained from that site.

**Fig. 3** Change in Null-point DOC concentration ( $DOC_{np}$ ) (a), in SUVA associated with sorption of DOC in the soils (b), mineral soil C (c), and soil pH (d) in mineral subsoil layers of the 2-, 15-, 30-, and 65-year-old sites



We observed a similar trend of a positive exponential relationship with soil temperature and a negative exponential relationship with soil moisture for Ah-horizon leachates as well, however this relationship was only significant at 15- and 30-year-old sites in 2005 (data therefore not shown).

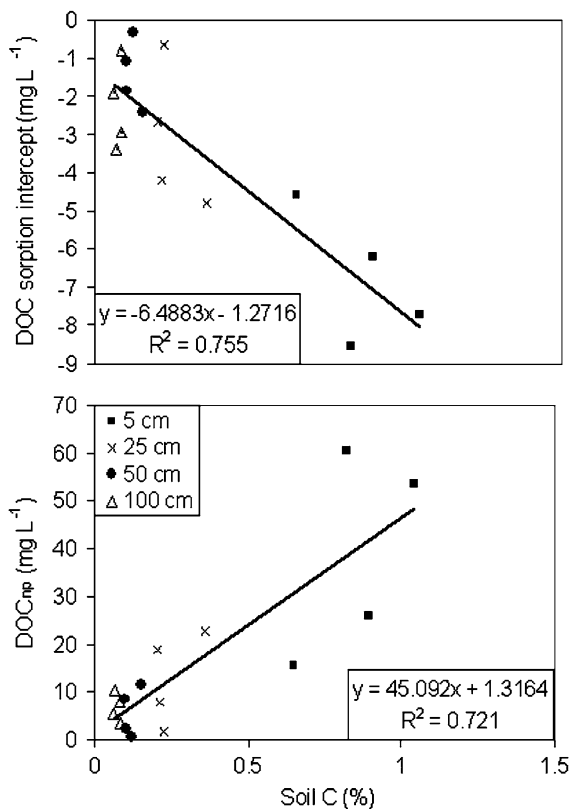
Dissolved organic carbon concentration in Ah-horizon leachates showed a linear relationship with DOC concentration of forest floor leachates ( $r^2 = 0.37, 0.46, 0.71$ ;  $P < 0.01, 0.001, 0.001$  at the 65-, 30-, and 15-year-old sites, respectively) and with DOC flux through forest floor ( $r^2 = 0.27, 0.31$ ;  $P < 0.05, 0.05$  at the 65- and 15-year-old sites, respectively) indicating that DOC concentration in the Ah-layer may have been highly affected by the amount of DOC that was transported down from the litter layer as the major source of DOC production rather than by in situ release and adsorption within the Ah-horizon.

Correlations of DOC concentrations with forest stand characteristics

The mean annual DOC concentration of forest floor leachates did not show any correlation with the amount of annual litter-fall. Our bi-weekly mea-

surements of both litterfall and DOC concentration of forest floor leachate during autumn 2005 revealed contrasting results about the sensitivity of forest floor DOC to fresh litterfall input. Figure 6 shows that during the sampling period of the last 2 weeks in October in which highest litterfall occurred, DOC concentrations of forest floor leachate were up to twice as high than before and after that intense litterfall period at the two oldest sites. In contrast, the large amount of freshly fallen litter did not affect the DOC concentration of forest floor leachates at the 15-year-old site. The limited number of samples retrieved during that period precluded testing for statistical significance of the observed trends.

Higher DOC concentration in throughfall during the summer of 2005 was unlikely to be a result of changes in LAI. Even though maximum DOC concentration in throughfall coincided with maximum LAI in summer, DOC concentrations did not correlate with changes in LAI throughout autumn (Fig. 7). This suggests that DOC concentration in throughfall was mostly determined by DOC concentration in precipitation or by other factors such as flower dust or exudation from needles during the summer months.



**Fig. 4** Relationship between DOC sorption intercept (a) and  $\text{DOC}_{\text{np}}$  (b) with soil C across the mineral soil profile as mean from all four sites

Mean annual DOC concentrations of forest floor leachate were positively correlated with aboveground biomass and forest floor C pools, and negatively

correlated with stand stem density (Fig. 8). The correlations were stronger in 2004 than 2005. The increase of DOC concentration in forest floor leachate with decreasing stem density may be an artifact rather than a real correlation as both may be primarily a result of increasing stand age. No correlation was observed between DOC concentration and NEP, fine root biomass, or soil C pools.

## Discussion

### Concentrations and fluxes of DOC in forest ecosystems

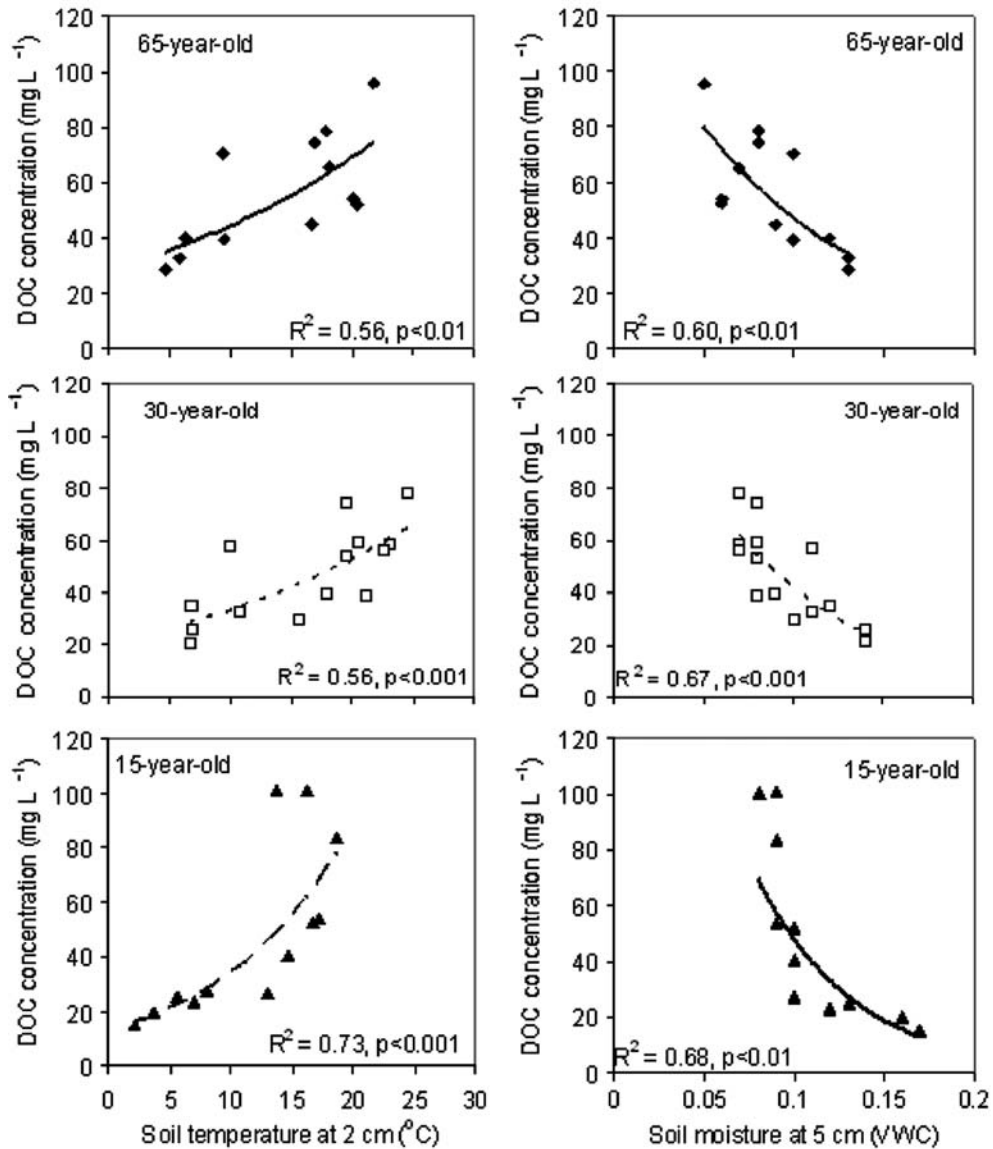
Dissolved organic carbon concentrations in precipitation, throughfall, forest floor, Ah-layer, and subsoil leachates measured in our study were similar to those reported in a review by Michalzik et al. (2001) for coniferous forests in temperate regions, except for few high values in precipitation in early summer of 2005. These high DOC concentrations in precipitation could have been caused either by contamination of the samples, by evaporation or from air pollution, though we have no clear evidence.

Overall, our estimated DOC fluxes in precipitation and throughfall were also similar to estimates for coniferous forests as reported by Michalzik et al. (2001). However, our DOC fluxes through forest floor ( $1\text{--}5 \text{ g DOC m}^{-2} \text{ year}^{-1}$ ) and Ah-layer ( $0.5 \text{ to } 2.0 \text{ g DOC m}^{-2} \text{ year}^{-1}$ ) were considerably less than their reported range of 10 to 40 and 15  $\text{g DOC m}^{-2}$

**Table 6** Estimate of DOC export via groundwater leaching ( $\pm$ SD). Leaching rate below 1 m depth was calculated as the difference between precipitation ( $P$ ) and evapotranspiration ( $ET$ ) as the sum of days on which  $P > ET$  and grouped into seasons

Water leaching (mm)	65-year-old		30-year-old		15-year-old		2-year-old	
	2004	2005	2004	2005	2004	2005	2004	2005
Spring	140 $\pm$ 28	94 $\pm$ 19	88 $\pm$ 18	86 $\pm$ 17	137 $\pm$ 27	122 $\pm$ 24	267 $\pm$ 53	122 $\pm$ 24
Summer	112 $\pm$ 22	187 $\pm$ 37	113 $\pm$ 23	193 $\pm$ 39	115 $\pm$ 23	117 $\pm$ 23	159 $\pm$ 32	229 $\pm$ 46
Autumn	265 $\pm$ 53	320 $\pm$ 64	262 $\pm$ 52	282 $\pm$ 56	263 $\pm$ 53	191 $\pm$ 38	282 $\pm$ 56	259 $\pm$ 51.8
Total	517 $\pm$ 103	601 $\pm$ 120	453 $\pm$ 91	561 $\pm$ 112	515 $\pm$ 103	429 $\pm$ 86	708 $\pm$ 142	610 $\pm$ 122
DOC export ( $\text{g DOC m}^{-2}$ )	2004	2005	2004	2005	2004	2005	2004	2005
Spring	0.47 $\pm$ 0.12	0.31 $\pm$ 0.8	0.47 $\pm$ 0.46	0.46 $\pm$ 0.45	1.08 $\pm$ 0.49	0.96 $\pm$ 0.44	2.77 $\pm$ 1.05	1.26 $\pm$ 0.48
Summer	0.37 $\pm$ 0.10	0.62 $\pm$ 0.16	0.61 $\pm$ 0.56	1.03 $\pm$ 1.01	0.91 $\pm$ 0.41	0.92 $\pm$ 0.42	1.65 $\pm$ 0.62	2.38 $\pm$ 0.90
Autumn	0.88 $\pm$ 0.23	1.07 $\pm$ 0.28	1.40 $\pm$ 1.37	1.51 $\pm$ 1.48	2.09 $\pm$ 0.95	1.51 $\pm$ 0.69	2.93 $\pm$ 1.11	2.69 $\pm$ 1.02
Total	1.72 $\pm$ 0.45	2.00 $\pm$ 0.52	2.48 $\pm$ 2.43	3.01 $\pm$ 2.94	4.08 $\pm$ 1.86	3.40 $\pm$ 1.55	7.34 $\pm$ 2.78	6.33 $\pm$ 2.40

Null-point DOC at 1 m depth was taken as the DOC concentration of exported soil solution



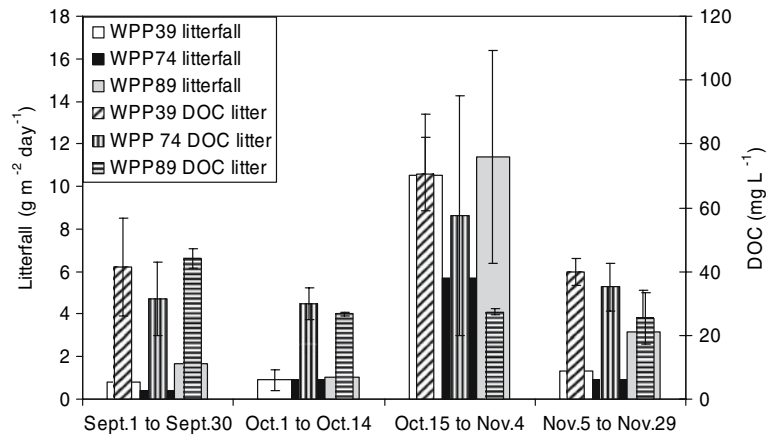
**Fig. 5** Relationship between forest floor DOC concentration with soil temperature and soil moisture at the 15-, 30-, and 65-year-old-sites

year<sup>-1</sup> for forest floor and Ah-layer, respectively, reported by Michalzik et al. (2001). Neff and Asner (2001) reported DOC flux in 0 to 20 cm mineral soil in the range of 1 to 5 g DOC m<sup>-2</sup> year<sup>-1</sup> which is closer to our estimates for the Ah-layer. Our low estimate may result from an underestimation of water flux as zero-tension lysimeters were sometimes clogged and possibly overflowed. Furthermore, our estimates do not cover a full year, as we did not collect data from December to March.

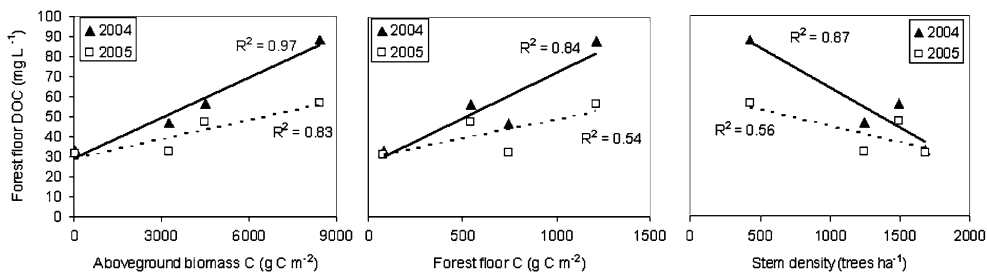
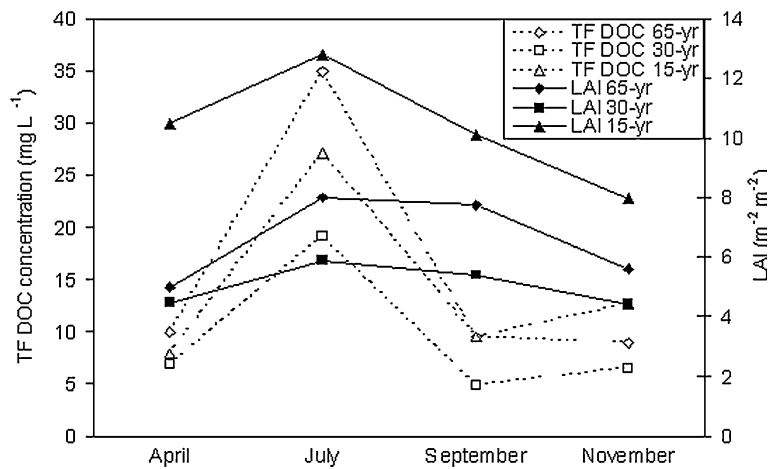
#### Sources and sinks of DOC in forest ecosystems

Forest canopy functioned as a DOC source by increasing incoming DOC concentrations and fluxes from precipitation by two to five times. DOC production from forest canopy might be closely related to LAI, but we found contrasting patterns of DOC concentrations in throughfall for the years 2004 and 2005. In 2004, no seasonal pattern was observed for DOC concentrations in throughfall, whereas a rise

**Fig. 6** Relationship between DOC concentration in forest floor litter and litterfall during autumn 2005 at the 15-, 30-, and 65-year-old sites. Error bars indicate SD



**Fig. 7** Changes of LAI and DOC concentration in throughfall at the 15-, 30-, and 65-year-old sites throughout the growing season



**Fig. 8** Relationship between forest floor DOC concentration with aboveground biomass C pools, forest floor C pools, and stem densities in 2004 and 2005 across the age-sequence

and peak during the early summer was observed in 2005. We showed that this pattern was not consistent with the development of LAI during autumn; therefore, the effect of LAI on DOC concentrations in throughfall cannot be confirmed in our study. We have been unable to find studies on DOC versus LAI

relationships, but this might be a fruitful method of converting the large amount of LAI data for forests into DOC concentrations and fluxes from canopies.

The forest floor (LFH-layer) was the major source of DOC in this forest ecosystem as well as in others (Hongve 1999; Michalzik and Matzner 1999;

Michalzik et al. 2001; Moore 2003; Starr and Ukonmaanaho 2004). The primary origin of DOC production in the forest floor has been attributed to the litter layer (e.g., Michalzik and Matzner 1999; Fröberg et al. 2005) whereas other studies found that DOC is primarily released from stable humified organic matter (Kalbitz et al. 2000). Fröberg et al. (2005) found in a simulation study that forest floor DOC concentrations increased after the addition of litter. In our study, however, mean DOC concentrations of forest floor leachates were not correlated with annual litterfall. DOC concentrations increased in our 30- and 65-year-old stands but did not change in our 15-year-old stand during the autumn litterfall. Thus, other factors than the amount of fresh litter input may control DOC concentrations such as forest floor thickness, cycles of wetting and drying, and mineralization and decomposition processes (Kalbitz et al. 2000; Smolander and Kitunen 2002; Chow et al. 2006). The lack of DOC response of our 15-year-old stand to autumn litterfall may be related to the thicker forest floor compared to the 30- and 65-year-old stands.

We observed an age-related trend in DOC concentration of forest floor leachates which may result from correlation of forest floor DOC concentrations to aboveground biomass and forest floor C. An increase in forest floor C can be expected to provide a greater C supply for decomposition processes and DOC leaching. Thus, changes in forest tree biomass and forest floor C throughout the development of forest ecosystems may have considerably affected DOC concentrations and fluxes.

In our study, the soil Ah-layer was a sink for DOC rather than a source. In contrast, Yano et al. (2004) found that the Ah-layer functioned as a greater source of DOC than the organic layer in coniferous old-growth stands. In general, studies have concluded that DOC concentrations in Ah-layer decrease through adsorption processes, particularly in sandy soils (e.g., Dosskey and Bertsch 1997; Kalbitz et al. 2000; Michalzik et al. 2001). We also found that DOC concentration of the Ah-layer was affected by DOC input from the forest floor, which suggests that DOC concentrations in the Ah-layer did not primarily result from production in the Ah-layer itself. This is in agreement with Fröberg et al. (2006) who used  $C^{14}$  measurements to show a substantial sorption and desorption of DOC from the forest floor and soil C in the mineral soil.

We observed the strongest adsorption capacity (minimum  $DOC_{np}$ ) in our sandy soils at around 50 cm depth, probably due to a combination of low soil C concentrations and the presence of Fe and Al sorption sites, though we did not determine these. The mineral soils at these sites contain about  $5 \text{ kg C m}^{-2}$ , based on bulk density and C concentration measurements. Assuming our estimated difference in DOC flux between the forest floor and soils at a depth of 1 m ranging between  $3 \text{ and } 15 \text{ g m}^{-2} \text{ year}^{-1}$  are caused by adsorption of DOC, then this amount of soil C could be generated by adsorption alone in 300 to 1,700 years, which is much less than the age of these soils (forest floor) and ecosystems. This suggests that much of the adsorbed DOC can be remineralized back to carbon dioxide, as has been suggested by Moore (1989) for New Zealand forested soils.

Environmental controls on DOC production, transport and retention

Seasonal variability in both DOC concentration and fluxes observed in our study may be explained by changes in environmental parameters. Higher DOC concentrations in leachates from the forest floor and the Ah-layer during the summer months may result from the warmer temperatures observed at our sites. Soil temperature has been suggested as a major control on DOC (Dalva and Moore 1991; Guggenberger et al. 1998; Kalbitz et al. 2000), but there is still some uncertainty about its full effects. For instance, Kalbitz et al. (2000) reported that a well-drained soil often showed a negative relationship between soil temperature and DOC concentration. The dependence of DOC concentration on soil temperature in our study was especially pronounced in the forest floor. Michalzik and Matzner (1999) also found a strong temperature dependence of forest floor DOC in a spruce forest, and Guggenberger et al. (1998) suggested that microbial activity in response to temperature changes controls DOC production in the upper soil layers. Laboratory studies have suggested  $Q_{10}$ -values between 1.2 and 2.0 (Christ and David 1996; Göttsche et al. 1996).

Our negative relationship between DOC concentration and soil moisture content is in disagreement with field and laboratory studies that have reported either a positive or no relationship (Christ and David 1996; Kalbitz et al. 2000; Fröberg et al. 2006). Most studies conclude that increasing soil moisture

enhances microbial activity, especially in well-drained soils, and thus increases DOC concentrations (summarized by Kalbitz et al. 2000). We did not observe any dilution effect on DOC concentrations resulting from increased rainfall intensity. Smaller DOC concentrations have been observed for heavy rainfall periods (Michalzik and Matzner 1999; Kalbitz et al. 2000), though Dosskey and Bertsch (1997) reported no dilution effect of rainfall in sandy soils. Drainage of water via macropores in sandy soils may not allow enough contact time between water and soil to release and flush out a substantial amount of DOC.

Our observed DOC flux estimates were mainly driven by the amount of water percolating through the forest ecosystem rather than the actual DOC concentration. Michalzik and Matzner (1999) also suggested that water input was the driving factor for DOC fluxes in forest ecosystems. Thus, factors that control water input and transport, such as storm frequency, canopy interception, snowmelt, and leaching rate, may be more significant than controls on the actual DOC concentration with regards to the amount of DOC cycling and export from forest ecosystems.

#### Changes in DOC chemistry

Based on the SUVA<sub>254</sub> method, our results suggest that there is an increase in the aromatic proportion of DOC as water passes from precipitation to throughfall and the forest floor, though the range in SUVA<sub>254</sub>-values was modest, ranging from 2 to 3 (Weishaar et al. 2003). This is to be expected, as the contribution to DOC comes from decomposed organic matter. The field subsoil DOC samples and the laboratory DOC sorption study both showed a decline in SUVA<sub>254</sub> as water passed through the mineral soil, suggesting a preferential adsorption of the aromatic DOC fraction by the mineral soils, which has been confirmed in other studies (Kaiser and Guggenberger 2000).

#### DOC flux as part of the overall C cycle in forest ecosystems and land use change

Carbon input, transport, and output via DOC fluxes in this forest ecosystem were very small compared to other C pathways. DOC input via precipitation was estimated to be <1% of NEP (Arain and Restrepo-Coupe 2005). DOC transport from canopy to forest

floor was about 1% of C allocation via litterfall and DOC export via leaching was estimated to be 1% or less of the soil respiration as CO<sub>2</sub>-C. DOC may function as substrate for microbial decomposer activities and influence nutrient cycling and thereby affect forest stand productivity and the overall C cycle to a larger extent than just C fluxes.

In eastern North America large areas have undergone land-use change through forest regeneration and recently through afforestation of marginal agricultural land which may affect ecosystem C dynamics (Quideau and Bockheim 1997; Khomutova et al. 2000; Mattson et al. 2005). We observed an increase of DOC concentrations in forest floor and Ah-layer solution with the passage of time after stand establishment, which is correlated with the accumulation of tree and forest floor biomass. Despite higher DOC concentrations in soil solution of older stands, our study suggests that the loss of C by groundwater DOC export may be decreased by up to four times at a stand age of 65 years, compared to a recently established forest. This may be explained by a general decrease in water loss due to increased water uptake by tree roots and by a stronger DOC sorption capacity of the subsoils.

Similarly, Quideau and Bockheim (1997) found that afforestation of prairie land with red pine caused an increase in DOC concentration in soil solution and Khomutova et al. (2000) found in a laboratory leaching experiment that DOC production was higher in a pine plantation soil compared to a pasture soil. In Finland, Mattson et al. (2005) showed that DOC export at the landscape level increased with increasing percentage of agricultural land. They suggested that this resulted from the application of fertilizer and observed a negative correlation between DOC export and percentage of forested land, which is in agreement with our findings. In contrast, Piirainen et al. (2002) suggested that forest-clear cutting of a boreal spruce forest did not significantly alter ecosystem DOC export, probably because of a strong DOC sorption capacity of the subsoil. Understanding the effect of land-use change of DOC concentrations and export is imperative to predict large-scale C dynamics and changes in landscape ecosystem C budgets.

**Acknowledgments** We gratefully acknowledge the financial support of grants from the Strategic Projects Program and Discovery Grants of the Natural Sciences and Engineering Research Council (NSERC) of Canada and BIOCAP Foundation, Canada. Support from the Canadian Foundation

for Innovation, the Ontario Innovation Trust, McMaster University, the Ontario Ministry of Natural Resources and Norfolk County is also acknowledged in establishing Turkey Point sites. Trees at the 2-year-old site were provided by Ontario Power Generation and planted by the Long Point Recreation and Conservation Authority with the help of many other supporting partners. We are grateful to Frank Bahula and Bruce Whitside and their families for providing access to their private properties (2-year and 15-year old forest sites, respectively) to conduct this research. We thank Dolly Kothawala for assistance with the sorption study.

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