Biogeochemistry (2011) 106:461–473
DOI 10.1007/s10533-010-9526-2

Dynamics of dissolved organic ^{14}C in throughfall and soil solution of a Norway spruce forest

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Received: 28 April 2010 / Accepted: 31 August 2010

Abstract Dissolved organic carbon (DOC) is an important component of the C cycle in forest ecosystems, but dynamics and origin of DOC in throughfall and soil solution are yet poorly understood. In a 2-year study, we analyzed the radiocarbon signature of DOC in throughfall and soil solution beneath the Oa horizon and at 90 cm depth in a Norway spruce forest on a Podzol soil. A two-pool mixing model revealed that throughfall DOC comprised mainly biogenic C, i.e. recently fixed C, from canopy leaching and possibly other sources. The contribution of fossil DOC from atmospheric deposition to throughfall DOC was on average 6% with maxima of 8–11% during the dormant season. In soil solution from the Oa horizon, DO^{14}C signature was highly dynamic (range from −8‰ to +103‰), but not correlated with DOC concentration. Radiocarbon signatures suggest that DOC beneath the Oa horizon originated mainly from occluded and mineral associated organic matter fractions of the Oa horizon rather than from the Oi or Oe horizon. Relatively old C was released in the rewetting phase following a drought period in the late summer of 2006. In contrast, the DO^{14}C signature indicated the release of younger C throughout the humid year 2007. In soil solutions from 90 cm depth, DO^{14}C signatures were also highly dynamic (−127‰ to +3‰) despite constantly low DOC concentrations. Similar to the Oa horizon, the lowest DO^{14}C signature at 90 cm depth was found after the rewetting phase in the late summer of 2006. Because of the variation in the DO^{14}C signatures at this depth, we conclude that DOC was not equilibrated with the surrounding soil, but also originated from overlaying soil horizons. The dynamics of DO^{14}C in throughfall and soil solution suggest that the sources of DOC are highly variable in time. Extended drought periods likely have a strong influence on release and translocation of DOC from relatively old and possibly stabilized soil organic matter fractions. Temporal variations as well as the input of fossil DOC needs to be considered when calibrating DOC models based on DO^{14}C signatures.

Keywords Dissolved organic carbon · Forest soils · Norway spruce · Throughfall · Radiocarbon · ^{14}C

Introduction

Dissolved organic carbon (DOC) plays an important role in the carbon cycle of terrestrial ecosystems and for the transfer of organic C from terrestrial to aquatic systems (Neff and Asner 2001; Cole et al. 2007). The production and leaching of DOC in terrestrial

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ecosystems affects the concentration, composition and age of DOC in aquatic systems (Raymond and Bauer 2001; Sickman et al. 2010; Tipping et al. 2010). The origin and quality of DOC as well as the dynamics of DOC concentrations in terrestrial ecosystems have therefore an impact on DOC concentrations in rivers and lakes (Evans et al. 2007; Roulet and Moore 2006).

As other land use systems, forests are relevant for the quantity and quality of surface water and groundwater. Pronounced seasonal and inter-annual variations of DOC concentrations and fluxes have been reported for different compartments of forest ecosystems (Buckingham et al. 2008; Michalzik and Matzner 1999; Solinger et al. 2001). Leaching of DOC from forest canopies represent a C flux to the soil that is mainly used as C and energy source by microorganisms (Michalzik et al. 2001). Besides precipitation, seasonal pattern of temperature could influence concentration and composition of throughfall DOC since biological, temperature-dependent processes (e.g., budding, pest infection, pollination) affect the production of DOC in the canopy. Fluxes of DOC in organic layers are often larger than throughfall input due to net production of DOC in organic horizons. In contrast, only small concentrations and fluxes of DOC are observed in deeper mineral soil horizons (Michalzik et al. 2001; Hentschel et al. 2007).

The origin, composition and function of DOC in different compartments of forest ecosystems are still a matter of debate. In throughfall, DOC may result from the leaching of organic substances from plant tissues as well as from atmospheric deposition of organic substances. The latter may include marine and terrestrial organic C emissions as well as emissions from the combustion of fossil fuels and biomass (Avery et al. 2006). However, systematic analyses on the origin of DOC in throughfall are not available to our knowledge.

Concentrations and fluxes of DOC in forest soils are the result of multiple factors and processes. Water fluxes are considered as a main driver of DOC fluxes among soil horizons and of DOC output by leaching. DOC concentration, which determines DOC flux resulting from water transport, is partly controlled by sorption/desorption processes (Guggenberger and Kaiser 2003). Further factors controlling DOC concentrations and fluxes are leaching from plant litter, production, immobilization and mineralization of DOC by microorganisms (Kalbitz et al. 2000; Neff and Asner 2001). Recent studies suggest that a large fraction of DOC is sorbed and stabilized by mineral surfaces rather than mineralized by soil organisms (Kaiser and Guggenberger 2000; Sanderman and Amundson 2009). The residence time of sorbed DOC, however, is rather short, i.e. years-decades, unless it is sorbed by juvenile mineral surfaces (Guggenberger and Kaiser 2003).

In soil solution from B and C horizons, the concentration of DOC is relatively low and constant throughout the year (e.g., Borken et al. 1999; Fröberg et al. 2006). An unsolved question is to what extent DOC in these horizons originates from vertical translocation or desorption and production in the respective soil depth. Isotopic signature of DOC can be helpful to answer this question. In a field study with ^{13}C labelled spruce litter, the analysis of DO^{13}C revealed only a minor proportion of litter DOC in percolates below the Oe and Oa horizon of a Podzol in a Norway spruce forest (Fröberg et al. 2007a). Hence, most of the DOC was produced in the respective organic horizons themselves. In the same and another Norway spruce stand on Podzol, the DO^{14}C signature of soil solution below the B horizon was similar to the ^{14}C signature of bulk soil from the B horizon (Fröberg et al. 2006). Despite similar ^{14}C signatures, DOC is not necessarily desorbed from the B horizon alone. Both, DOC and soil organic matter (SOM) comprise a mixture of different constituents of varying ^{14}C signatures. Different results were reported for a Podzol in a forested watershed (Trumbore et al. 1992), and for Mediterranean forest and grassland soils (Sanderman and Amundson 2009). In both studies, DOC from different mineral soil horizons exhibited much younger ^{14}C signatures than the respective bulk soil. In addition to vertical translocation, the difference in the ^{14}C signature of DOC and bulk soil could be caused by equilibration between DOC and specific SOM fractions.

The few studies on DO^{14}C in forest ecosystems have not considered dynamics of ^{14}C signature, but used the ^{14}C signature from single sampling events or even from water extracts. Seasonal and inter-annual changes of DO^{14}C signatures, however, are of relevance for tracing the origin of DOC and for predicting DOC dynamics in soils by simulation models (Michalzik et al. 2003). The goal of this study was to use the temporal pattern of DO^{14}C signatures, concentrations and fluxes of DOC in throughfall and soil solutions in order to improve our understanding of DOC sources and dynamics in a Norway spruce site.

Methods

Site description

The Coulissenhieb II site is a mature Norway spruce forest (*Picea abies* L.) in the German Fichtelgebirge, adjacent to the Coulissenhieb I site which has been subject of long-term biogeochemical studies (Matzner 2004). The mean annual precipitation is about 1,160 mm and the mean annual air temperature is 5.3°C. The soil has a sandy to loamy texture and is classified as Haplic Podzol according to the FAO soil classification (IUSS 2006). The well stratified, mor-like organic layer has a thickness of 7–10 cm, comprising Oi, Oe and Oa horizons (Table 1). The organic layer is almost completely covered by ground vegetation, mainly *Deschampsia flexuosa* (L.) and *Callamagrostis villosa* (Chaix). Soil properties are described by Schulze et al. (2009). In short, organic C content of the soil decreases with increasing depth from 46.6% C in the Oi horizon to 1.3% C in the Bv horizon. The soil stores 3.8 kg C m^{-2} in the organic layer and 11.4 kg C m^{-2} in the mineral soil down to 62 cm depth (Table 1).

About one-third of trees were removed from the study site in 2007 after a partial damage of trees by a storm event in January 2007. Except for three throughfall samplers, the soil and installations (see below) were not damaged by the hurricane. The three damaged throughfall samplers were replaced and installed at similar locations about 1 week after the hurricane. Aboveground litter input was very large (562 g m^{-2}) due to this disturbance. Afterwards, litter fall was reduced by one-third from April to December 2007 (329 g m^{-2}) compared to the respective period in 2006.

Sampling

Three plots each of 400 m^2 were established and equipped on an area of about 1 ha at the Coulissenhieb I site in the summer of 2005. Throughfall and soil solutions were sampled between January 2006 and January 2008. Throughfall was continuously collected in 1 m height with three conical funnels (upper diameter of 20.2 cm) per plot. Each funnel was connected with a 5 l sampling flask and equipped with fine polyethylene fibre to exclude litter input into throughfall solution. Funnels and sampling flasks were replaced every second week. Throughfall solution of each 2-week sampling interval was used for chemical analyses. Prior to chemical analyses, throughfall solution from all nine samplers was merged to one mixed sample per sampling period (i.e., 25 and 23 mixed samples in 2006 and 2007, respectively). The amount of throughfall of all sampling flasks was used for calculation of 4-weekly and annual fluxes of throughfall volume and DOC.

Solution from the organic layer was collected below the Oa horizon using three plate lysimeters per plot. The plate lysimeter was made of a plastic bowl

Table 1 Thickness of soil horizons, bulk density (BD), organic C content, organic C stock and radiocarbon signatures (Δ^{14}C) of bulk soil and density fractions (FPOM = free particulate organic matter, OPOM = occluded organic matter, MAOM = mineral associated organic matter) of a Podzol at the Fichtelgebirge after Schulze et al. (2009)

Horizon	Thickness (cm)	BD (g cm^{-3})	C (%)	C stock (kg C m^{-2})	$\Delta^{14}C_{Bulk}$ (‰)	$\Delta^{14}C_{FPOM}$ (‰)	$\Delta^{14}C_{OPOM}$ (‰)	$\Delta^{14}C_{MAOM}$ (‰)
Oi	2.1 ± 0.1	0.07 ± 0.00	45.8 ± 0.9	0.7 ± 0.1	114 ± 8	n.d.	n.d.	n.d.
Oe	2.2 ± 0.2	0.15 ± 0.02	42.1 ± 6.3	1.4 ± 0.9	162 ± 16	n.d.	n.d.	n.d.
Oa	4.9 ± 0.5	0.25 ± 0.03	21.2 ± 2.3	2.0 ± 0.6	119 ± 13	128 ± 22	49 ± 21	13 ± 34
EA	5.2 ± 0.8	0.60 ± 0.02	8.3 ± 0.9	2.6 ± 1.3	23 ± 68	41 ± 76	−8 ± 54	−16 ± 30
Bsh	5.3 ± 0.6	0.75 ± 0.01	6.0 ± 0.4	2.4 ± 1.2	−14 ± 13	4 ± 27	−22 ± 22	−22 ± 6
Bs	11.4 ± 1.5	0.79 ± 0.02	3.6 ± 0.3	2.7 ± 1.2	−63 ± 11	−82 ± 46	−138 ± 13	−50 ± 11
Bv	30.5 ± 3.0	1.17 ± 0.03	1.4 ± 0.2	4.4 ± 1.9	−145 ± 18	−30 ± 37	−140 ± 39	−176 ± 33

Error bars represent the standard deviation of the mean ($n = 9$, $n = 3$ for radiocarbon analyses, n.d. = not determined) with a 50 µm pore-size polyethylene membrane on top. Each plate lysimeter had a surface area of 176 cm^2 that was connected to a vacuum pump. A suction of −10 kPa was applied for 1 min every 5 min throughout the whole experimental period. Solution of three plate lysimeters was continuously collected in one 2-l plastic flask per plot that was stored in an underground container. Water volume of each flask was measured biweekly and was used for calculation of water fluxes. We cannot exclude that water fluxes were underestimated at few occasions when the 2-l flasks were filled before the 2-week sampling interval. Total solution of the first 2-week sampling interval was stored in a climate chamber at 5°C and then mixed with total solution of the second 2-week sampling interval for chemical analyses. Apart from this scheme, solutions were biweekly analyzed during the snowmelt in April 2006 and after the drought period in 2006. Four-weekly DOC fluxes were calculated from water fluxes and respective DOC concentrations.

Three ceramic suction cups per plot were installed below the rooting zone at 90 cm soil depth. These suction cups were operated at a continuous suction of −25 kPa. The sampling procedure and sampling intervals for soil solution from suction cups and plate lysimeters were identical. Samples from three suction cups per plot were merged to one mixed sample using the same 2-l flasks.

In March 2008, groundwater from a well at 10 m depth and spring water were sampled at three occasions. The well was located about 50 m east from the study site and the spring about 100 m west from the study site. All water samples including throughfall and soil solution were filtered with pre-washed 0.45 µm cellulose-acetate filters and stored at 2°C until chemical analysis.

Chemical analyses

DOC was determined by high temperature combustion and subsequent determination of CO_2 (Elementar, high-TOC). Prior to ^{14}C analyses, volume-weighted subsamples of soil solution were merged to 2–3 months samples per plot ($n = 3$) whereas volume-weighted subsamples of throughfall were merged to one representative sample of the study site per quarter. The ^{14}C signature of groundwater was determined at three dates. Radiocarbon signature of DOC was determined by accelerator mass spectrometry (AMS). Subsamples ($\sim$1 mg C) of freeze-dried DOC were oxidized in 6 mm sealed quartz tubes with 60 mg CuO and 1 cm silver wire for 2 h at 900°C. The resulting CO_2 was purified from water and non-condensable compounds. Afterwards, CO_2 was reduced to graphite using the zinc reduction method (Xu et al. 2007). All preparations took place at the Department of Soil Ecology at the University of Bayreuth. The graphite targets were analyzed by the Keck-CCAMS facility of University of California, Irvine with a precision of 2–3‰. Radiocarbon data are expressed as $\Delta^{14}C$ (‰ deviation from the $^{14}C/^{12}C$ ratio of oxalic acid standard in 1950). The samples have been corrected for a $\delta^{13}C$ value of −25‰ to account for any mass dependent fractionation effects (Stuiver and Polach 1977). Tests of thermonuclear weapons between the 1950s and the early 1960s have almost doubled the ^{14}C content (835‰) of the atmosphere (Levin et al. 1985). The atmospheric ^{14}C level has steadily decreased after a moratorium on atmospheric testing mainly due to combustion of fossil fuels. Bomb ^{14}C is still present in the atmosphere as indicated by a $\Delta^{14}C$ signature of 47‰ in 2007 (Levin et al. 2008). The atmospheric pre-bomb $\Delta^{14}C$ level since the industrialization in 1750 as measured by tree-ring analyses varied between 4.1 and −22.8‰ (Stuiver et al. 1998).

Biogenic and fossil DOC in throughfall

Throughfall may contain DOC from leaching of plant tissues in the canopy (hereafter ‘biogenic DOC’) and DOC from deposition of soot and other organic particles (hereafter ‘fossil DOC’). We assume a mean residence time of 3 years for C in plant tissues after photosynthetic fixation before it is released as biogenic DOC in throughfall. This assumption is based on half live of Norway spruce needles of about 3 years at our study site (Schulze et al. 2009). Consequently, biogenic DOC had ^{14}C signatures of 70‰ in 2006 and of 64‰ in 2007 equivalent to the average ^{14}C signature of CO_2 in the atmosphere at the Jungfraujoch, Switzerland, in 2003 and 2004 (Levin et al. 2008). Provided that biogenic and fossil DOC have different ^{14}C signatures a two-pool mixing model can be used to separate their portion to total DOC.

$$\Delta^{14}C_{\mathrm{sample}} = x \cdot \Delta^{14}C_{\mathrm{fossil}} + (1 - x) \cdot \Delta^{14}C_{\mathrm{biogenic}} \tag{1}$$

where $\Delta^{14}C_{\mathrm{sample}}$ is the measured DO^{14}C signature of throughfall, x the portion of fossil DOC in throughfall, $\Delta^{14}C_{\mathrm{fossil}}$ is the DO^{14}C of fossil fuel carbon depleted in ^{14}C (−1,000‰). We cannot exclude that the portion of biogenic DOC is overestimated at deposition of soluble non-fossil organic particles with ^{14}C signatures >−1,000‰.

Temperature and matric potential

Air temperature was hourly recorded at 2 m above ground. At each plot, soil temperature was automatically recorded in 30 min intervals below the Oa horizon and the Bv horizon using one sensor per horizon. Volumetric water contents 6 cm below the Oa horizon were measured every 30 min with a time-domain reflectometer (TDR probe) and converted into matric potentials using a calibration function for this specific horizon (Zuber 2007). Soil matric potential in 90 cm mineral soil depth was simultaneously recorded using self-constructed and calibrated tensiometers.

Statistical analysis

Statistical analyses were performed using STATISTICA 6.0. Linear regressions were made between DOC concentrations of throughfall and soil solution and throughfall, soil moisture and air temperature. Relationships were further tested by the Spearman correlation.

Results

Throughfall and air temperature

Mean DOC concentration in throughfall was 18.0 ± 2.2 mg l^{-1} in 2006 with a maximum of 60 mg l^{-1} in July (Fig. 1). In 2007, average DOC concentration of throughfall was smaller by 11.5 ± 1.8 mg l^{-1}. As the year 2006 had much less precipitation (868 mm throughfall) than 2007 (1,152 mm throughfall) (Fig. 2a), annual DOC fluxes were almost identical in 2006 (129.5 kg C ha^{-1} a^{-1}) and 2007 (132.5 kg C ha^{-1} a^{-1}) (Fig. 2b).

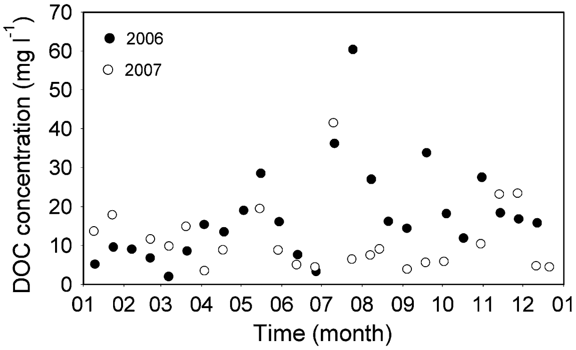

Fig. 1 Concentrations of DOC in throughfall from biweekly sampling intervals during 2006 and 2007

Mean annual air temperature was similar in 2006 (7.1°C) and in 2007 (7.5°C), however, the seasonal pattern of air temperature was different between the years (Fig. 2a). Mean winter air temperature was considerably lower in 2005/2006 (−3.8°C) than in 2006/2007 (1.2°C) whereas the summer of 2006 was warmer (14.1°C) compared to 2007 (12.6°C). DOC concentration in throughfall did not correlate with the amount of throughfall or air temperature (not shown).

DO^{14}C signatures of throughfall varied between −52 and 41‰ throughout the study period (Fig. 2c), indicating a strong variation in the origin of DOC. Negative Δ^{14}C signatures occurred only during the dormant season from October to March and for the period from October to December 2006, representing the dominance of pre-bomb C in throughfall DOC. In contrast, throughfall DOC contained bomb C during growing seasons. Based on Eq. 1, the portion of fossil DOC in throughfall varied between 2 and 11% (Fig. 2d). Largest fluxes of fossil DOC were consequently found for the quarters from October to December 2007 (4.3 kg C ha^{-1}), from January to March in 2006 (2.3 kg C ha^{-1}) and 2007 (3.0 kg C ha^{-1}). On a 2-year average, throughfall DOC comprised about 124 kg biogenic C ha^{-1} a^{-1} and 7 kg fossil C ha^{-1} a^{-1}. The concentration of DOC had no clear influence on its Δ^{14}C signature (Figs. 1, 2c).

Oa horizon

Soil temperature exhibited a strong seasonal pattern with lowest values during soil frost in the cold winter

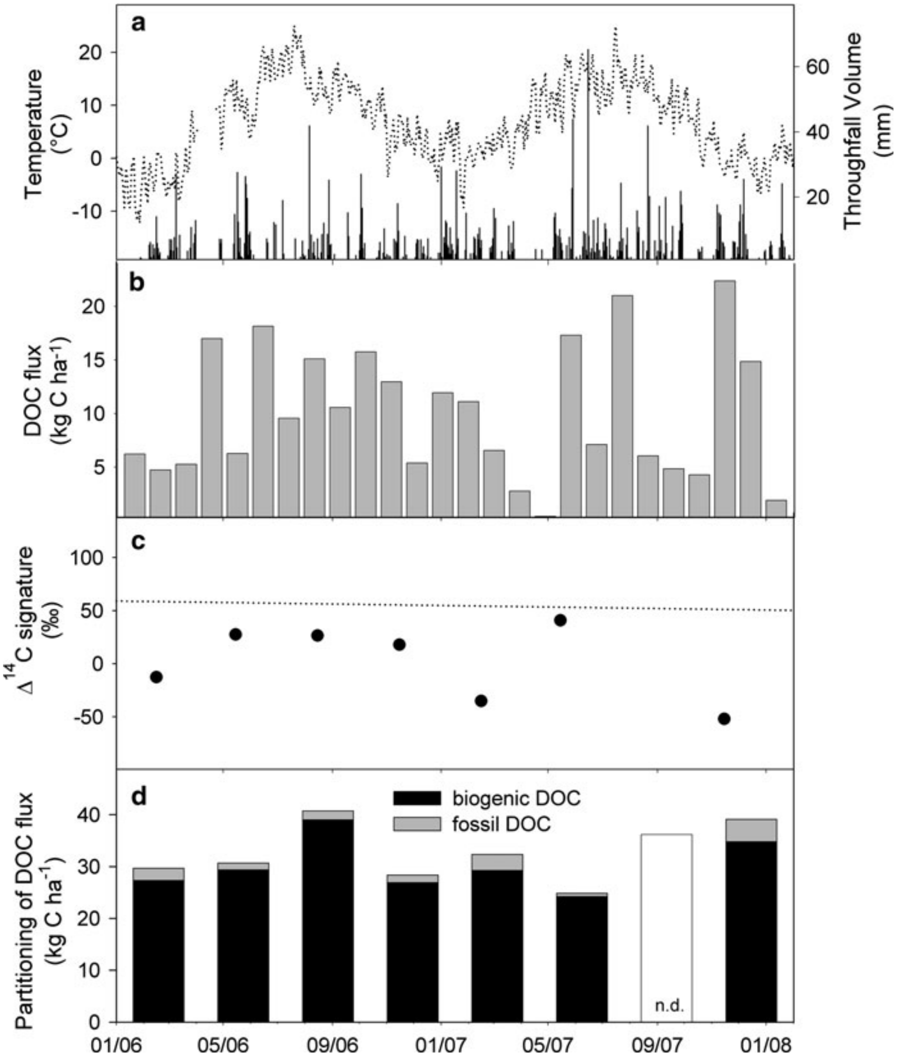

Fig. 2 **a** Daily means of air temperature and throughfall volume, **b** 4-weekly DOC fluxes, **c** mean quarterly radiocarbon signature, and **d** quarterly proportion of biogenic and fossil DOC in throughfall during 2006 and 2007. The *dotted line* indicates the ^{14}C signature of atmospheric CO_2 at the Jungfraujoch (Levin et al. 2008). n.d. = not determined

of 2005/2006. Mean annual soil temperatures were 6.5°C in 2006 and 7.4°C in 2007 (Fig. 3a). The matric potential in the O horizon varied between −22 and −310 kPa throughout the study period, except during a dry period between June and October 2006 where it decreased to a minimum of −2,572 kPa in early August (Fig. 3a).

Mean concentrations of DOC below the organic layer (28.4–79.8 mg l^{-1}) were above those of throughfall concentration (Figs. 2b, 3b). In the cold winter of 2006, DOC concentration decreased from 50–57 mg l^{-1} to a minimum of 28 mg l^{-1} in April after melting of about 40–50 cm snow cover. In the dry summer of 2006, mean DOC concentration increased and peaked at 80 mg l^{-1} in August 2006, but then decreased during autumn and winter to a minimum in March 2007 (32 mg l^{-1}). A similar seasonality was visible in 2007 although matric potential exhibited no seasonal trend (Fig. 2a). A weak correlation was found between DOC concentration and soil temperature ($y = 1.8x + 44$, $r^2 = 0.43$, $p < 0.001$) (not shown).

Annual DOC flux was greater in 2006 (455 kg ha^{-1}) than in 2007 (322 kg ha^{-1}) despite smaller throughfall volume in 2006 (Figs. 3c, 2a). The DOC flux peaked in April 2006 after the snowmelt when the soil was water-saturated. Small DOC fluxes occurred during the drought periods in July 2006 and April/May 2007 and during the frost period in December 2007/January 2008.

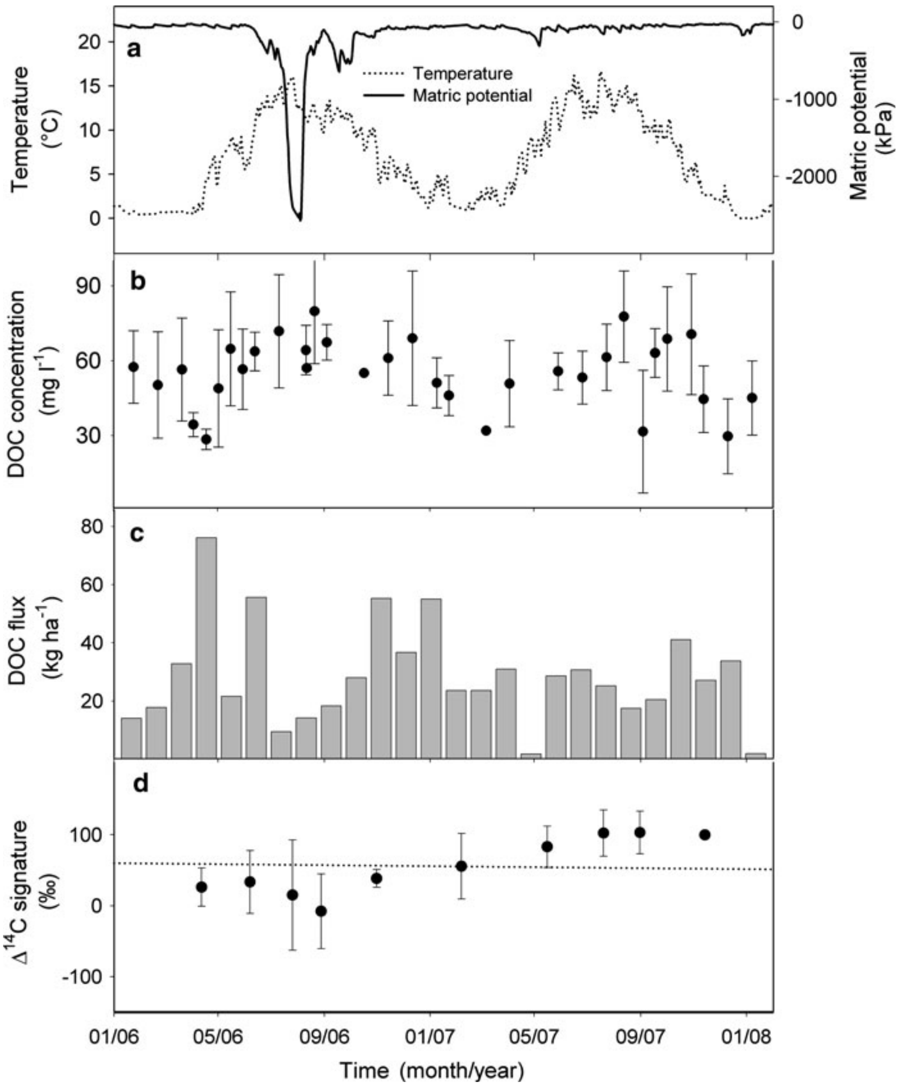

Fig. 3 **a** Daily means of soil temperature and matric potential, **b** 4-weekly mean DOC concentrations, **c** 4-weekly means DOC fluxes, and **d** mean bimonthly radiocarbon signatures of DOC in the soil solution beneath the Oa horizon during 2006 and 2007. The *dotted line* indicates the ^{14}C signature of atmospheric CO_2 at the Jungfraujoch (Levin et al. 2008). *Error bars* represent the standard error of the mean ($n = 3$)

With one exception, positive DO^{14}C signatures indicate bomb C in the range from 15 to 103‰ (Fig. 3d). The only mean negative DO^{14}C signature (−8‰) occurred in the late summer/early autumn of 2006 after rewetting of dry soil. Prior to this minimum, the second lowest DO^{14}C signature (15‰) was found in the dry and warm period from July to September 2006. In the wet year 2007, the DO^{14}C signatures were consistently higher compared to 2006 and partly above the ^{14}C signature of atmospheric CO_2, indicating the release younger DOC in 2007 than in 2008. Again, DO^{14}C signature was not correlated with DOC concentration.

Water samples from 90 cm soil depth, well and spring

Because of the snow cover in the cold winter of 2005/2006 soil temperature reached its minimum of 1.5°C in early April 2006 shortly after snowmelt (Fig. 4a). In the mild winter of 2006/2007, minimum soil temperature of 2.8°C occurred in February of 2007. Mean annual soil temperatures were 6.4°C in 2006 and 7.4°C in 2007. Soil matric potential in 90 cm depth ranged between 6 and −20 kPa and was not significantly reduced during the dry summer of 2006.

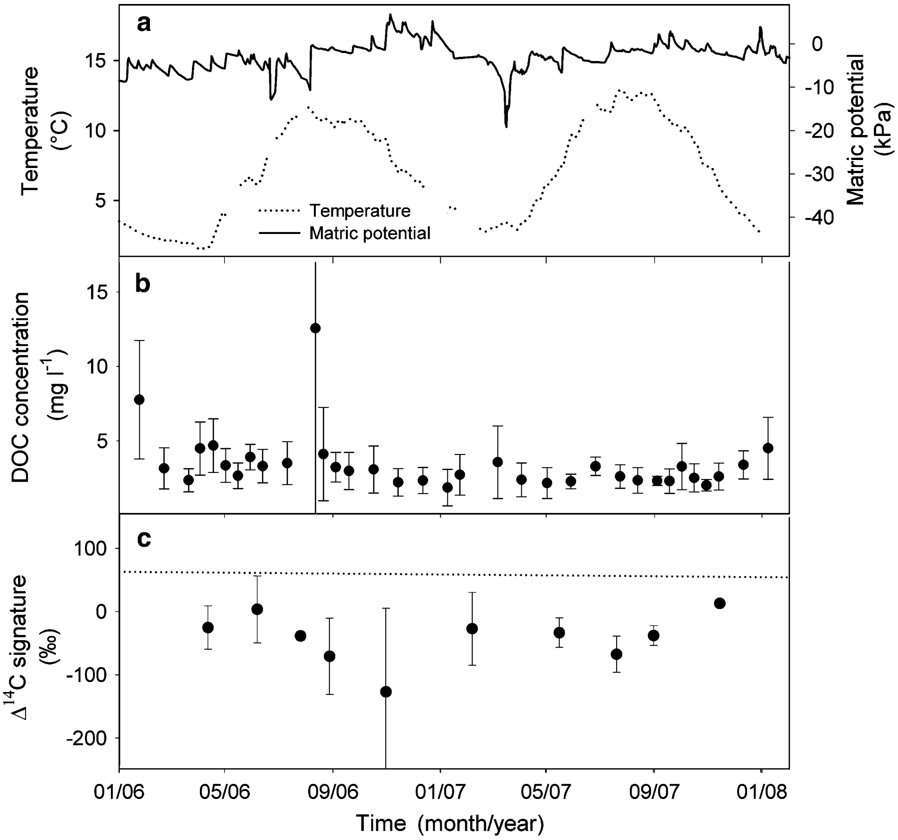

Fig. 4 **a** Daily means of soil temperature and matric potential, **b** 4-weekly means of DOC concentrations, and **c** bimonthly means of radiocarbon signatures of DOC in the solution from the mineral soil at 90 cm depth during 2006 and 2007. The *dotted line* indicates the ^{14}C signature of atmospheric CO_2 at the Jungfraujoch (Levin et al. 2008). *Error bars* represent the standard error of the mean ($n = 3$)

Mean DOC concentration (3.0 ± 0.1 mg l^{-1}) was generally small and showed little variation among the three plots (Fig. 4b). Notable DOC concentrations were measured in August 2006 after rewetting of dry soil. This singular peak coincided with the maximum DOC concentration in the solution from the organic layer. The enhanced spatial variation is attributed to the large DOC concentration (20.2–41.6 mg l^{-1}) of one plot. No correlations were found between DOC concentration in 90 cm soil with soil temperature, matric potential and amount of throughfall (not shown).

DOC in 90 cm depth consisted of much older C with ^{14}C signatures ranging between −127 and 12‰ with no clear seasonal trend (Fig. 4c). Positive ^{14}C signatures were analyzed at two periods from May and July 2006 and from September to December 2007, pointing to the presence of bomb C below the rooting zone. Consistent with solution from the organic layer, lowest DO^{14}C signatures were detected after the dry and warm summer of 2006. However, the lowest value occurred later in the last quarter of 2006. DO^{14}C signature from one plot (−277‰) was mainly responsible for this minimum value and the pronounced spatial variability in 2006. The other two plots had DOC signatures between −53‰ and −21‰ from July to December 2006. Both, spatial and seasonal variability of DO^{14}C signatures were much smaller in 2007. DO^{14}C signatures were positively correlated with ln-transformed DOC concentrations ($y = 86.4 \ln(x) - 136, r^2 = 0.29, p = 0.009$) in 90 cm soil depth (not shown), indicating that the portion of ‘younger C’ increased with DOC concentration.

Groundwater at 10 m depth had a mean DOC concentration of 0.79 ± 0.03 mg l^{-1} and a mean ^{14}C signature of −133 ± 34‰ (data not shown). The difference between the mean DO^{14}C signature of groundwater and soil solution at 90 cm (−41‰ from 2006 to 2007, Fig. 4c) indicate either input of older DOC from other sources than soil solution or preferential decay/sorption of younger soil solution DOC along the pathway below 90 cm. The relevance of DOC decay/sorption during transportation is supported by the difference in DOC concentration between groundwater (0.79 ± 0.03 mg l^{-1}) and soil solution (3.0 ± 0.1 mg l^{-1}).

Spring water had a similar DOC concentration of 0.85 ± 0.09 mg l^{-1} to groundwater (data not shown). The mean ^{14}C signature of −226 ± 52‰ indicates that DOC resides for some thousands years in the soil-groundwater system before it is released by the spring.

Discussion

DOC in throughfall

Our results suggest that the seasonal pattern of DOC concentration in throughfall is not controlled by air temperature or the amount of throughfall. Both, low and high DOC concentrations may occur after periods of light or heavy rainfall. The difference in mean annual DOC concentration between 2006 and 2007 can be attributed to the removal of one-third of all trees after the hurricane in January 2007. Canopy coverage is a main factor of concentrations and fluxes of DOC in throughfall. Clarke et al. (2007) found a decrease of DOC concentrations and fluxes with decreasing litterfall as a proxy for canopy coverage along a chronosequence of Norway spruce stands. Despite consistently lower DOC concentrations in 2007, elevated throughfall water volume in 2007 resulted in annual DOC fluxes being similar between the years. The annual DOC flux of 133 kg C $ha^{-1}a^{-1}$ at our study site is on the upper range of throughfall fluxes (40–160 kg C ha^{-1} a^{-1}) reported for various temperate forests (Michalzik et al. 2001). The DOC flux at our site was relatively large as conifers seem to release more DOC than deciduous trees under same climatic conditions (Borken et al. 2004).

The radiocarbon signatures of DOC in the 1st quarter of 2006 (−13‰) and 2007 (−35‰) as well as in the 4th quarter of 2007 (−52‰) display relatively old carbon that was not alone released by the canopy. We assume that deposition of DOC from combustion of fossil fuels altered the radiocarbon signature of DOC in winter throughfall. According to the mass balance approach, between 5 and 11% or 1.4 and 4.3 kg C ha^{-1} of throughfall DOC originated from combustion of fossil fuels during the dormant seasons in 2006 and 2007. The contribution of fossil fuel was smaller in the 2nd to 3rd quarters, although relevant for annual DOC fluxes. Our estimates are likely biased because deposition of C with a different ^{14}C signature as from the combustion of firewood might represent an additional and unaccounted source of DOC in throughfall. Firewood is increasingly used in Germany as an alternative energy source during recent years. Consequently, the amount of biogenic DOC from the canopy was overestimated by the two-pool mixing model. The contribution of 'firewood DOC' could be estimated by a three-pool mixing model using the isotopic signatures of 'canopy DOC' and of soot particles released by combustion of firewood.

In samples of single rain events, fossil DOC contributed between 4 and 24% to total DOC based on a ^{14}C signature of contemporary living material for biogenic DOC (Avery et al. 2006). According to Avery et al. (2006) the proximity of anthropogenic combustion sources and the wind direction influence the content of fossil fuel DOC in rainwater. The relative portion of fossil DOC is smaller in our quarterly throughfall samples because of the input of biogenic DOC from the canopy that was not reduced after the hurricane in 2007. Total input of fossil DOC, however, is likely greater in throughfall than in rainwater due to dry and wet deposition of organic particles and solutes in the canopy. The change of the DO^{14}C signature in throughfall is possibly not only affected by the input of fossil DOC via rainwater, but also by the leaching of biogenic DOC with different ^{14}C signature. A seasonal shift in the ^{14}C signature could result from predominantly leaching of recently synthesised C during growing season and enhanced leaching of older DOC during dormant season. However, varying biogenic DOC sources and DO^{14}C signatures would have had limited influence on the partitioning of DOC fluxes as fossil DOC is depleted in ^{14}C. For example, the portion of fossil DOC would be less than 27% as long as biogenic DOC has ^{14}C signatures <300‰. Based on the ^{14}C signature of atmospheric CO_2, biogenic DO^{14}C signatures of 300–1,000‰ could only occur if DOC is released from plant tissues that were synthesized between 1962 and 1980 (Levin et al. 1985).

The fate of infiltrating fossil DOC in the soil remains unknown. Despite its age it is not necessarily recalcitrant or accumulates in the soil. However, even small inputs of fossil DOC could potentially affect the ^{14}C signature of DOC in the organic layer or mineral soil.

DOC below the Oa horizon

In agreement with other studies (e.g., Michalzik and Matzner 1999; Solinger et al. 2001; Dawson et al. 2002) DOC concentration below the organic layer exhibited a seasonal pattern with maximum in summer/autumn and minimum in early spring. DOC concentration followed slightly the seasonal pattern of soil temperature, suggesting that temperature has a small effect on the production of DOC. Even soil moisture seems to play a minor role in the control of DOC concentration. The seasonal pattern and level of DOC concentration were similar in both years although water availability in the organic layer was different during the growing season of 2006 and 2007. Release of DOC from particulate soil organic matter by physicochemical processes likely controls the concentration of DOC at different water contents (Fröberg et al. 2006). The amount of water extractable DOC from the organic layer of our study site increased with increasing amount of water (Schulze, unpublished data). Hence, water flux is an important driver of DOC fluxes from the organic layer into the mineral soil. We assume that the hydrological conditions after the snowmelt in 2006 display a specific situation. The DOC flux was much greater in 2006 than in 2007 although throughfall volume was opposite in these years.

The seasonal and interannual variation of DO^{14}C signature demonstrates that DOC originated from different carbon pools. In the late summer of 2006, the DO^{14}C signature decreased to $-8 \pm 30‰$ after some rainfall events which is below the ^{14}C signature of bulk organic C in the Oa horizon (Table 1). A potential source with a considerable effect on the DO^{14}C signature of the organic layer is fossil DOC from throughfall. According to a mass balance approach as given in Eq. 1, fossil DOC input of 1% (is equivalent to 3 kg C ha^{-1} a^{-1}) would reduce the ^{14}C signature of total DOC by $-10‰$. However, the fate of fossil DOC in the soil is unknown and the DO^{14}C signatures of throughfall and the Oa horizon were seasonally decoupled.

Another source of DOC is old C associated with mineral soil. Because of varying thickness of the Oa and Ea horizon it was impossible to separate completely these horizons at the installation of the lysimeter plates. We assume that DOC originated partly from the EA horizon although the amount of the EA horizon should have been small compared to the amount of the organic layer. Density fractionation of the Oa horizon revealed only a negative ^{14}C signature for mineral associated OM in one of three soil pits whereas lighter density fractions as well as mineral associated OM of the two other pits had positive ^{14}C signatures (Schulze et al. 2009). The portion of C in the mineral associated fraction of the Oa horizon was small (3%) compared to C in free particulate (72%) and occluded OM (25%). Nevertheless, it seems that this small fraction or very old occluded organic matter contributed to DOC during the re-wetting period in the summer of 2006. Disruption of soil aggregates due to drying and wetting and add-on desorption of DOC (Lundquist et al. 1999) from the mineral associated organic matter might be the responsible mechanisms for the occurrence of the negative DO^{14}C signature. Isotopic fractionation by microbial decomposition of ‘young’ organic matter or other processes would have enriched the ^{14}C signature towards more positive values. Carbon that was photosynthetically fixed during the past 50 years has more positive ^{14}C values as presently fixed C because of the decline of $^{14}CO_2$ in the atmosphere since terminating atmospheric nuclear bomb tests. Radiocarbon signature of respired CO_2 also provides in some cases evidence of enhanced availability and release of ‘old carbon’ during the natural summer drought in 2006 at our study site (Muhr and Borken 2009) and following artificial re-wetting of a dry forest soil under laboratory conditions (Borken et al. 2006).

One would expect leaching of DOC from the whole organic layer into the mineral soil after some intensive rain events. Soil moisture of the O horizon, however, was not recovered during autumn 2006 despite of 345 mm rain between August and November. Remoistening of the organic layer was incomplete at this site, most likely due to hydrophobicity of organic matter and preferential flow (Bogner, personal communication). These transient changes of physicochemical soil properties have possibly contributed to the leaching of ‘old DOC’ in 2006.

Soil drought could trigger the mobilization/desorption of old, i.e. protected organic matter because of the new spatial orientation of organic molecules under hydrophobic conditions.

Constant soil moisture promotes microbial activity and C mineralization of younger C pools (Christ and David 1996) and perhaps the release of young DOC from live roots. The improved conditions for microbial activity and root turnover in 2007 may explain the rather consistent DO^{14}C signatures (83–103‰) which were closer to the ^{14}C signature of the bulk Oa horizon. Fröberg et al. (2003) also found bomb C in DOC from organic horizons of a Norway spruce stand, where the ^{14}C signatures of DOC were smaller than those of the respective bulk soil. Fresh litter as well as Oi and Oe horizons contribute a minor portion to DOC leached from the Oa horizon (Fröberg et al. 2005, 2007b). Thus, the Oa horizon itself is the main source of DOC beneath the Oa horizon. Specifically, ^{14}C signatures of free particulate and occluded organic matter correspond to the DO^{14}C signatures in 2007.

DOC in 90 cm soil depth

The DOC concentrations in 90 cm soil depth were relatively small and constant throughout the entire study period. In Podzols, DOC is strongly adsorbed by Al and Fe oxides/hydroxides and clay minerals which results in low DOC outputs (Kalbitz et al. 2000). An exceptional increase of DOC concentration was observed after a dry period and some rain events in August 2006. This increase could be an indication of rapid movement of water and DOC from upper soil horizons through the soil profile.

Like the Oa horizon, the DO^{14}C signature in 90 cm depth decreased during the growing season of 2006, indicating the exposure of 'old' DOC. However, in contrast to the Oa horizon, this drought induced isotopic shift cannot be attributed to a specific soil horizon. Besides the drought/rewetting period in 2006, DO^{14}C signatures of −68 to 13‰ suggest that different OM fractions of the Bv and overlaying horizons could have acted as potential source for DOC. Given the dynamics of DO^{14}C signatures the source strength of specific soil horizons and OM fractions varied seasonally and inter-annually. The intensity of summer drought is possibly a factor of inter-annual variations as flow paths of soil water change with soil moisture. Preferential flow along roots and rock surfaces has been identified as a relevant and rapid transport of soil water at our site (Bogner et al. 2008). According to Bundt et al. (2001) roots generate organic compounds and thereby change the composition of DOC along preferential flow paths. Provided that these compounds have ^{14}C signatures similar to fresh litter, roots might influence the DO^{14}C signature in the Bv horizon. Microbial decomposition of dead roots is possibly another source of 'young' DOC in the subsoil.

The small concentration of groundwater DOC indicates that the soil below 90 cm depth is an effective net DOC sink. If the ^{14}C signature (−133‰) of groundwater DOC is consistent throughout the year and representative for this forest stand then there is a substantial change of DOC composition during the passage from the subsoil to the well. Microbial decay and sorption/desorption of DOC may occur down to the well since the bedrock is partly weathered up to 30 m depth in this area.

Conclusion

Combustion of fossil fuels contributed between 5 and 7% to annual throughfall DOC, but the fate of fossil DOC in the soil remains unknown. The temporal variation of the DO^{14}C signature in soil solution beneath the Oa horizon and at 90 cm depth points to different sources within a year and between years. DOC beneath the organic layer originated mainly from the Oa horizon whereas DOC from throughfall, Oi and Oe horizon was quickly decomposed and/or sorbed by the Oa horizon. DOC at 90 cm depth likely represented a mixture of DOC from the surrounding soil and overlaying soil horizons including the Oa horizon. The seasonal and inter-annual variation of the DO^{14}C signature may be attributed to water movement and downward transport of DOC along preferential flow paths. The shift in the DO^{14}C signature beneath the Oa horizon and at 90 cm depth after the dry summer of 2006 provides evidence for desorption of very old C following re-wetting of dry soil. Alternatively, strong preferential sorption or decay of young DOC could also affect the DO^{14}C signature in the deep mineral soil following summer droughts. In conclusion, repeated measurements over longer time periods are required when DO^{14}C is used to calibrate soil C models. Sorption and desorption of DOC with varying $DO^{14}C$ signatures could alter the ^{14}C signature of particulate organic matter, and thus, challenge our understanding of organic C turnover in forest soils.

Acknowledgments This research was financially supported by the *Deutsche Forschungsgemeinschaft* (DFG), Research Unit 562, project BO 1741/3-2. We thank the members of the Central Analytic Department of the *Bayreuth Center of Ecology and Environmental Research* (BayCEER) for chemical analyses of soil solutions and Uwe Hell, Jan Muhr, Gerhard Müller, Andreas Kolb, Petra Eckert and Marta Gerslova for their help in the experimental work.

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