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Controls on the dynamics of dissolved organic carbon and nitrogen in a Central European deciduous forest

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Abstract Despite growing attention concerning the role of dissolved organic matter (DOM) in element cycling of forest ecosystems, the controls of concentrations and fluxes of both dissolved organic carbon (DOC) and nitrogen (DON) under field conditions in forest soils remain only poorly understood. The goal of this project is to measure the concentrations and fluxes of DON, NH_4^+, NO_3^- and DOC in bulk precipitation, throughfall, forest floor leachates and soil solutions of a deciduous stand in the Steigerwald region (northern Bavaria, Germany). The DOC and DON concentrations and fluxes were highest in leachates originating from the Oa layer of the forest floor (73 mg C L^{-1}, 2.3 mg N L^{-1} and about 200–350 kg C, 8–10 kg N ha^{-1} yr^{-1}). They were observed to be highly variable over time and decreased in the mineral topsoil (17 mg C L^{-1}, 0.6 mg N L^{-1} and about 50–90 kg C, 2.0 to 2.4 kg N ha^{-1} yr^{-1}). The annual variability of DOC and DON concentrations and subsequential DOC/DON ratios was substantial in all solutions. The DOC and DON concentrations in throughfall were positively correlated with temperature. The DOC and DON concentrations did not show seasonality in the forest floor and mineral soil. Concentrations were not related to litterfall dynamics but did correspond in part to the input of DOC and DON from throughfall. The throughfall contribution to the overall element fluxes was higher for DON than for DOC. Concentrations and fluxes of DON were significantly correlated to DOC in throughfall and the Oi layer. However, the correlation was weak in Oa leachates. In addition, seasonal and annual variation of DOC/DON ratios indicated different mechanisms and release rates from the forest floor for both components. The concentrations of DOC and DON in forest floor leachates were in most cases dependent neither on the pH value or ionic strength of the solution, nor on the water flux or temperature changes. As a consequence, the DOC and DON fluxes from the forest floor into the mineral soil were largely dependent on the water flux if annual and biweekly time scales are considered.

Introduction

Dissolved organic matter (DOM), including C (DOC) and N (DON), is generally regarded as a continuum of organic molecules of various sizes and structures. Often the filtration size of < 0.45 μm is used for defining the dissolved fraction. The DOM is known to contribute significantly to the C and N cycle in terrestrial ecosystems (Qualls & Haines 1991; Piirainen et al. 1998; Smith et al. 1998; Campbell et al. 2000), to soil formation (Dawson et al. 1978; Petersen 1976) and pollutant transport (Temminghoff et al. 1997). Only minor proportions of DOC have been chemically identified (Herbert & Bertsch 1995).

A number of studies have addressed the nature and dynamics of DOC under field conditions (e.g. McDowell & Likens 1988; Zech et al. 1994; Liechty et al. 1995; Hagedorn et al. 2000; Hongve et al. 2000) but little information concerning DON is presently available (Kalbitz et al. 2000). The majority of field studies focussed on coniferous forests, whereas deciduous forests have rarely been investigated. In their comparative study on DOC and DON fluxes and concentrations, Michalzik et al. (2001) reported on 40 sites, 26 of which were coniferous sites but only 14 were deciduous sites. Obviously, there is a paucity of studies on DOC and DON dynamics in deciduous ecosystems.

In pristine ecosystems, DON often represents the main form of dissolved N (Fahey et al. 1985; Hedin et al. 1995; Stuanes et al. 1995; Currie et al. 1996; Campbell et al. 2000; Weathers et al. 2000). The canopy and the forest floor have been positively identified as significant sources of DON in forest ecosystems (Qualls et al. 1991; Michalzik & Matzner 1999). The release of DON from the forest floor and its fate in the mineral soil are supposed to be tightly linked to the dynamics of DOC. However, differences in their dynamics can be expected presuming different origins and bioavailability (Michalzik & Matzner 1999; Kalbitz et al. 2000; Prechtel et al. 2000).

Laboratory studies have shown that the release of DOC from organic soil horizons is positively effected by the following factors; (1) pH and sulfate concentration (summarized by Kalbitz et al. 2000), (2) C/N ratio of the solid phase (Gödde et al. 1996; Kalbitz & Knappe 1997), (3) the leaching rate (Christ & David 1996a) and (4) temperature (Christ & David 1996b; Andersson et al. 2000). In contrast, elevated ionic strength (Evans et al. 1988) and increasing metal saturation of DOC (Tipping 1998) had adverse effects on DOC mobilization. Whether these controlling factors are discernable under field conditions and their validity for DON remains open to research and debate (Tipping 1998; Kalbitz et al. 2000).

Seasonal effects on DOC and DON concentration and fluxes were reported in several field studies (summarized by Kalbitz et al. 2000). A few studies have gone further and found seasonal changes in the concentration of DOC and DON in forest floor leachates to be directly related to litterfall inputs (Lundström 1993; Casals et al. 1995; Currie et al. 1996). However, no evaluation has been made with respect to the fluxes. The observed concentration dynamic may be caused by other factors, such as drying and rewetting and/or by elevated temperatures.

The purpose of this project is to quantify the role of DOC and DON in the C and N cycles of a Central European deciduous forest ecosystem. The project's secondary purpose is to identify the dynamics of DOC and DON concentrations and fluxes in throughfall, the forest floor and the upper mineral soil under field conditions with respect to regulating factors. To realize these goals the effects of water fluxes, seasonal temperature changes and the physico-chemical properties of the solutions were critically examined in addition to the organic matter input from throughfall and litterfall.

Materials and methods

Site description and experimental setup

The experiments were carried out at a 1.3 ha long-term research site managed by the Bayreuth Institute for Terrestrial Ecosystem Research (BITÖK). The site is located in the center of the 55 ha Steinkreuz catchment (49°52′20″ N and 10°27′40″ E) in the Steigerwald Nature Park (northern Bavaria, Germany) at an altitude of 400–460 m a. s. l. and is exposed to the southwest. The mean annual precipitation is approximately 775 mm and the average air temperature is 7.5 °C (Welss 1985). The stand is composed of European beech (*Fagus sylvatica* L.) and Sessile oak (*Quercus petraea* (Matt.) Liebl.), both about 130 years old. There are 286 beech stems ha^{-1} with a basal area of 20.5 m^2 and 93 oak stems ha^{-1} with a basal area of 9.5 m^2. Further information concerning the site has been published by Lischeid and Gerstberger (1997).

The forest floor has a mean thickness of 6 cm and is classified as a typical moder containing distinct Oi and Oe layers and a thin and fragmentary Oa layer. The average C and N pools of the forest floor were measured at 12,000 kg C ha^{-1} and 570 kg N ha^{-1}, respectively with a C/N ratio of about 23 (Table 1).

The sandy textured soil is classified as a Dystric Cambisol (FAO) which has developed from the underlying triassic sandstone parent material. The

Table 1. Soil properties at the Steinkreuz site

Horizon	Depth [cm]	TOC[1] %	TON[1] %	TOC/TON	pH (H_2O)	CEC[2] [$\mu mol_c^* kg^{-1}$]	BS[3] [%]
Oi+Oe	6	40.8	1.76	23.2	5.08	n.d.	n.d.
Oa	2	25.4	1.15	22.1	4.19	92.4	74
Ah	0–6	2.46	0.10	24.5	4.15	53.3	58
Bw	40	0.82	0.03	27.3	4.58	31.7	35
C	48	0.20	0		4.62	29.3	38

[1]Total organic carbon and total organic nitrogen (Foss-Heraeus CHN-O-Rapid).
[2]Cation Exchange Capacity measured as the sum of cations in a 0.1n NH_4Cl extract.
[3]Base saturation = (Ca, Mg, K, Na)/CEC.
n.d. not determined.

soil is acidic as indicated both by the pH depth gradients and by the base saturation in relation to the cation exchange capacity (CEC) (Table 1).

Bulk precipitation (BP) was gathered in 3 rain collectors of 314 cm^2 at a clearing about 100 m away from the site, where a meteorological station recorded air temperature. Throughfall (TF) was collected by 12 replicate collectors of equal size installed in a 5 $\times$ 5 m grid. The collectors were equipped with filters to remove large particles. The 12 replicates were pooled to form 4 composite samples in order to reduce analysis labour. Leachates from the forest floor were collected by tension plate lysimeters with a surface of 176 cm^2 at a equi-periodical suction (for 0.5 min every 10 min) of approximately 100–200 hPa. The lysimeters consisted of plastic material with a polyethylene 50 μm pore membrane. The periodical suction ensured that free drainage water was collected in sampling bottles with a minimal loss to evaporation. The relatively large membrane pore size prevented extraction of capillary water from the forest floor. The lysimeter plates were installed at two subplots (each 100 m^2) which were 10 m apart from each other. Six replicates were installed underneath the Oi layer and 15 underneath the Oa layer. Therefore, Oa lysimeter samples included both Oi and Oe leachates. Mineral soil solutions were collected by 9 ceramic suction cups buried at 20 cm depth. All samples were collected biweekly from October 1996 to December 1998. In addition, 4 suction cups were installed at 60 cm depth and were sampled monthly in order to make a rough statistical estimation of DOC and DON concentrations and fluxes in the deeper mineral soil.

Above-ground litterfall was collected in ten 1 m^2 littertraps, located on a transect and sampled at intervals ranging from 2 to 6 weeks, depending on litterfall intensity. Litter samples were air-dried and weighed prior to C and N

analysis, after which they were oven-dried. Below-ground litter was not taken into consideration.

Calculation of fluxes

The element fluxes both in forest floor leachates and in throughfall were calculated utilising measured water volumes and concentrations of each sample on a biweekly basis. Water fluxes through the mineral soil were calculated on a daily basis with a soil hydrological model (Hydrus 2D) based on Darcy flow (Simunek et al. 1996). Parameterisation details are provided by Chang (1999). The saturated hydraulic conductivity was measured (Chang 1999), whereas the transpiration rate was computed using the potential transpiration rate, a reduction function for root water uptake as dependent on soil water tension, and the root distribution. The daily potential evapotranspiration rate was calculated from meteorological data using a simulation program (Manderscheid 1992) based on the Pennman-Monteith equation. Measurements of tree transpiration, soil matrix potential and water content were used to calibrate the model (Chang 1999). Soil matrix potentials simulated by Hydrus 2D were compared with the field data measured by tensiometers at 20 cm depth (Chang 1999) to validate the model. The program successfully simulated the patterns of the matrix potential except during episodes of frost and periods with repeated wetting and drying of the soil (Chang 1999).

Due to technical difficulties, some forest floor leachates and soil solution samples were missing. In order to avoid an underestimation of annual element fluxes, water fluxes for missing forest floor samples were interpolated from throughfall fluxes assuming fluxes of 78% and 75% occurring in the Oi and the Oa layer, respectively. These ratios are derived from the measured mean relations reported in 1997 and 1998. The missing concentrations were interpolated by calculating the mean of the adjoining dates. This interpolation refers to approximately 15% of all flux data.

Chemical analysis

After measurement of pH (WTW pH 323 pH meter with Sentix 50 glass electrode) and electrical conductivity (EC; WTW LF 92 conductivity meter with Tentron 325 electrode), all samples were filtered through pre-rinsed (ultra pure water and sample) 0.45 μm cellulose-acetate filters. The analysis of blank samples did not show a release of carbon and nitrogen from the used filters. Subsequent analysis methods included (1) DOC by infrared detection of CO_2 after persulfate-UV-oxidation (Foss Heraeus Liqui TOC; detection limit: 0.3 mg C L^{-1}, analytical error 1.2%), (2) NH_4^+ by colorimetrical flow injection analysis (Lachat FIA; detection limit: 0.05 mg N L^{-1}, analytical

error 1.5%), (3) NO_3^- by ion chromatography (Dionex 2000i-SP; detection limit: 0.03 mg N L^{-1}, analytical error 1%), and (4) total dissolved N (TDN) by chemoluminiscence detection of NO_x after combustion at 800 °C (Abimed Total N Analyzer TN-05; detection limit: 0.05 mg N L^{-1}, analytical error 2.6%). DON was calculated as the difference between total-N and mineral-N. The lower quantification threshold for DON increased with increasing mineral N background concentrations. Using the calculated error of the DON values (square root of the sum of the squared analytical errors of NH_4-N, NO_3-N and TDN) it was determined that this DON quantification threshold was 0.1 mg N L^{-1} for bulk precipitation, 0.2 mg N L^{-1} both for throughfall and for the Oi layer, 0.4 mg N L^{-1} for the Oa layer and 0.3 mg N L^{-1} for mineral soil solution. Some calculated DON values were found to be below this quantification threshold, especially in bulk precipitation and in mineral soil solution. Those values were replaced by one half of the corresponding detection limit. The same procedure was applied for calculated DON values which were zero or fell below zero (representing 13% of all calculated DON values). The replaced data was not utilized for calculating DOC/DON ratios. The mean holding time prior to DOC and DON analysis was 3 days. The C and N content of litter samples were analyzed by heat-conductance-detection after thermooxidation (Foss-Heraeus CHN-O-Rapid).

Statistics

The concentrations and fluxes of DOC, DON, NO_3-N, and NH_4-N in all solutions were not normally distributed. Therefore, differences between bulk precipitation, throughfall, forest floor and upper mineral soil solution were tested by the parameter-free Kruskal-Wallis-rank-test as an alternative to the variance analysis. In addition, the Mann-Whitney U-test was performed to determine differences between two mean values. Correlations between measured variables were tested with Spearman rank correlations.

Mean concentrations are volumetric weighted means, which are represented in tables and figures. These means were computed for each individual sampling date. Correlations between temperature (mean of the biweekly sampling period) and concentrations as well as between different compartments (e.g. DOC in throughfall and DOC in the Oi layer) were computed from these calculated volumetric weighted means. In these cases data was normally distributed and Pearson correlation coefficients were calculated. Furthermore, volumetric weighted mean concentrations and cumulated mean fluxes were calculated for each season (10 seasons total). Differences between seasonal means were tested using the ANOVA procedure and the Scheffé test. These means were also correlated with the corresponding mean air temperature.

Table 2. Average NO_3-N, NH_4-N, DON and DOC concentrations

	NO_3-N [mg L^{-1}]		NH_4-N [mg L^{-1}]		DON [mg L^{-1}]		DOC [mg L^{-1}]		DOC/DON	
	1997	1998	1997	1998	1997	1998	1997	1998	1997	1998
Bulk precipitation	0.7	0.6	0.7	0.7	0.2	0.2	1.8	2.3	9	11
Throughfall	1.5	1.1	1.9	1.4	1.2	0.8	11.9	16.4	15	19
Oi leachates	1.3	3.3	1.3	1.7	1.0	1.5	27.9	44.0	26	34
Oa leachates	10.4	8.4	2.8	1.2	2.7	2.1	63.1	75.9	27	40
Soil solution 20 cm	10.9	7.0	0.1	0.1	0.7	0.4	14.6	21.0	18	40
Soil solution 60 cm	2.3	1.1	n.d.	n.d.	n.d.	n.d.	3.9	7.5		

n.d.: not detectable.

Results

Concentrations

The mean DOC and DON concentrations increased significantly ($\alpha < 0.001$) in the following order: bulk precipitation < throughfall < Oi layer < Oa layer (Table 2). The DOC and DON concentrations decreased in the upper (20 cm) and deeper mineral soil (60 cm) relative to the forest floor. DON could not be quantified in deeper mineral soil due to the high mineral N component background.

Mineral N compounds dominated in all solutions (Table 2), although the proportion of DON to the Total Dissolved Nitrogen (TDN) increased from 11% in bulk precipitation to 27% in Oi leachates, which then declined to 6% at 20 cm depth. The DON concentrations exceeded those of NH_4-N while NO_3-N became the dominant dissolved N fraction with the transition from throughfall to soil solution, representing >90% of total-N in mineral soil solution samples taken at 20 cm and 60 cm depth.

The mean DOC/DON ratios increased from bulk precipitation to the forest floor leachates and then declined in the mineral soil solution (Table 2). The DON concentrations in soil solution collected at 60 cm depth were below the detectable limit and DOC/DON ratios could not be accurately calculated.

Significant correlations were found between DOC concentrations in throughfall vs. Oi leachates ($r = 0.47$, $p < 0.01$, $n = 45$) and Oi vs. Oa leachates ($r = 0.40$, $p < 0.01$, $n = 45$), although none of these correlations were statistically significant for DON (Table 3).

In throughfall, DOC and DON concentrations showed a distinct seasonal variation (Figure 1). The DOC concentrations were significantly lower in

Table 3. Correlation coefficients between DOC and DON concentrations in forest floor leachates vs. DOC and DON concentrations in throughfall, NH_4-N and NO_3-N concentrations in forest floor leachates, pH, electrical conductivity (EC), waterflux and temperature, Spearman rank (n > 100) or Pearson (n < 100)

	DOC TF [mg L^{-1}]	DON TF [mg L^{-1}]	NH_4-N [mg L^{-1}]	NO_3-N [mg L^{-1}]	pH	EC [μScm^{-2}]	H_2O [mm]	Temp. [°C]
DOC Oi [mg L^{-1}]	0.47** n = 45	0.29 n = 45	0.40** n = 198	0.52** n = 198	–0.18** n = 198	0.73** n = 198	–0.23** n = 183	0.12 n = 44
DON Oi [mg L^{-1}]	0.52** n = 45	0.29 n = 45	0.57** n = 198	0.36** n = 198	0.12 n = 198	0.72** n = 198	–0.31** n = 183	0.07 n = 44
DOC Oa [mg L^{-1}]	0.10 n = 47	–0.27 n = 47	0.17** n = 515	0.18** n = 516	–0.21** n = 516	0.23** n = 514	0.10* n = 469	–0.10 n = 46
DON Oa [mg L^{-1}]	0.75 n = 47	–0.01 n = 47	0.37** n = 514	–0.002 n = 515	0.04 n = 515	0.11* n = 513	0.05 n = 467	–0.02 n = 46

**p < 0.01; *p < 0.05.

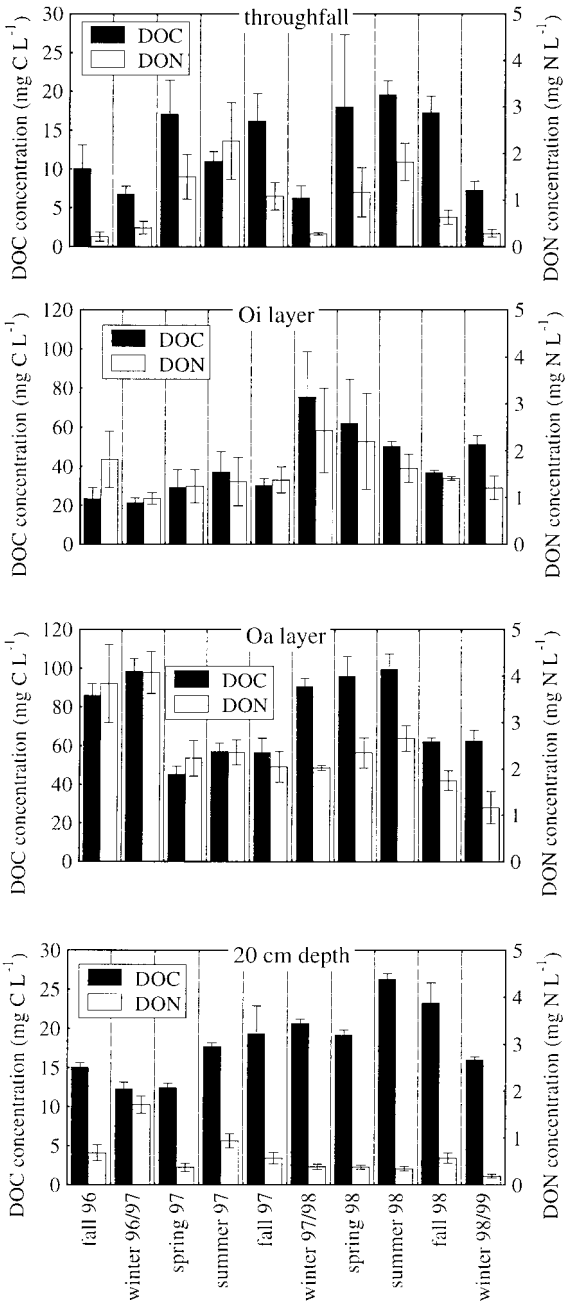

Figure 1. Seasonal mean concentrations of both DOC and DON in throughfall, forest floor leachates (Oi and Oa) and mineral soil solution (20 cm) (mean and standard error of biweekly determined volumetric weighted mean concentrations; seasons: fall: 1 SEP. to 30 NOV., winter: 1 DEC. to 28 FEB., spring: 1 MAR. to 30 MAY., summer: 1 JUN. to 31 AUG.)

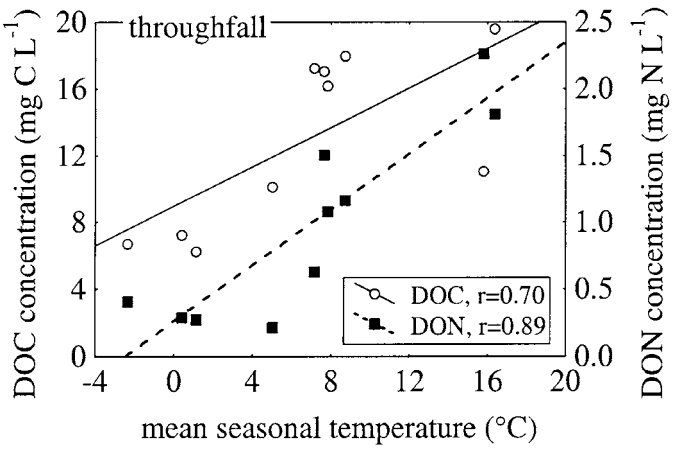

Figure 2. Linear regressions between seasonal mean DOC and DON concentrations in throughfall and the seasonal average mean temperature.

winter than in other seasons. The DON concentrations increased in the following order: winter < fall < spring < summer. In throughfall, DOC and DON were positively correlated to the temperature (DOC: r = 0.42, DON: r = 0.58). This correlation improves with seasonal statistical means of concentration and temperature (Figure 2). When comparing 1998 with 1997, it is evident that only the summer 1998 DOC concentrations were significantly higher. In contrast, DON concentrations tended to be lower during all 1998 seasons than in the corresponding 1997 seasons.

The concentrations in the Oi layer differed drastically between both years. The lowest concentrations of both DOC and DON occurred in winter 1997 in the Oi layer (winter 1996/1997, Figure 1), whereas in winter 1998 the concentrations peaked. The DOC concentrations were generally higher in 1998 as compared to 1997. The highest increase was found in winter 1998 (a factor of 3.5). The DON concentrations also increased in winter 1998 compared to winter 1997 (a factor of 2.5). In contrast to DOC, the DON concentrations were equal during the fall for both years.

Relatively high DOC and DON concentrations were measured in the Oa layer during the fall season 1996 and also during winter 1996/1997. An effect of the installation of the lysimeters (June 1996) can not be excluded as a likely cause. Apart from that, DOC concentrations were higher in 1998 than in 1997 (Table 2, Figure 1). In contrast, the DON concentrations did not deviate much from 1997 to 1998.

No significant correlations between either the DOC or the DON concentrations and temperature were found in either of the forest floor organic layers.

The DOC concentrations of soil solution at 20 cm depth showed a lesser magnitude increase from 1997 to 1998 than that reported for the Oi layer. In contrast, the DON concentrations were higher in 1997 than in 1998. A significant correlation was discovered between the DOC concentration and temperature ($r = 0.46$, $\alpha < 0.001$) at this depth, whereas the DON concentrations did not correlate with temperature.

Summarizing the seasonal effects on DOC and DON concentrations, the most distinct effects were higher DOC concentrations in 1998 than in 1997 in all compartments, whereas NO_3-N, NH_4-N and DON decreased in most cases (Table 2). Consequently, the DOC/DON ratios increased from 1997 to 1998.

The average DOC/DON ratios increased in the following order: bulk precipitation < throughfall < Oi layer < Oa layer. Lower DOC/DON ratios were only found in 1997 in the mineral soil as compared to the forest floor. The average DOC/DON ratios of forest floor leachates (Oi and Oa) were generally higher than the forest floor solid phase C/N ratios (Tables 1, 2).

The Oi leachates' DOC and DON concentrations showed positive correlations to electrical conductivity, NH_4-N, and NO_3-N (Table 3). In comparison, the Oa leachates' statistical correlations of DOC and DON concentrations to electrical conductivity, pH, and mineral N were generally poor, despite significant variation of these parameters. Correlations between DON and NH_4-N in forest floor leachates were positive and better than those between DON and NO_3-N (Table 3). The correlation between water fluxes and DOC or DON concentrations were weak or insignificant in all compartments. The concentrations of DOC and DON in the Oi leachates were correlated with a high confidence ($r = 0.73$, $n = 198$, $p < 0.01$) but the correlation was weaker in the Oa leachates ($r = 0.54$, $n = 513$, $p < 0.01$).

Fluxes

Most of the C and N input to both the forest floor and the mineral soil was provided by litterfall which occurred in the period from the end of October to the beginning of November. In 1996 the total litterfall summed up to 2,613 kg C and 60.5 kg N. In 1997 the litterfall declined to 2,273 kg C and 55.8 kg N. This deviation led to a small decline of total litter C/N from 43.2 to 40.7, while the C/N ratio of leaf litter remained stable at 41.0.

Another significant DOC and DON input to the forest floor was provided by throughfall (Table 4). The DON fluxes in throughfall were often in the same range as those in forest floor leachates (Figure 3). Throughfall DOC

Table 4. Average fluxes of H_2O, NO_3^--N, NH_4^+-N, DON and DOC; in brackets: net release or net retention (negative values)

	H_2O [mm]		NH_4-N [kg*ha^{-1}]		NO_3-N [kg*ha^{-1}]		DON [kg*ha^{-1}]		DOC [kg*ha^{-1}]	
	1997	1998	1997	1998	1997	1998	1997	1998	1997	1998
Bulk precipitation[1]	665	838	4.7	5.9	4.6	4.6	1.2	1.5	11.9	22.0
Throughfall[1]	448	578	8.4 (3.7)	8.0 (2.1)	6.8 (2.2)	6.3 (1.7)	5.3 (4.1)	4.7 (3.2)	53.4 (41.5)	94.6 (72.6)
Oi leachates[1]	309	465	5.3 (–3.1)	8.3 (–0.3)	5.0 (–1.8)	16.4 (10.1)	3.3 (–2.0)	7.4 (2.7)	85.9 (32.5)	208.2 (113.6)
Oa leachates[1]	293	432	8.2 (2.9)	5.9 (–2.4)	38.1 (33.1)	39.6 (23.2)	8.0 (4.7)	9.7 (2.3)	188.7 (102.8)	353.1 (144.9)
Soil solution 20 cm depth[2]	325	475	0.3 (–7.9)	0.3 (–5.6)	39.4 (1.3)	26.4 (–13.2)	2.4 (–5.6)	2.3 (–7.4)	48.1 (–140.6)	93.2 (–259.9)
Soil solution 60 cm depth[2]	202	313	n.d.	n.d.	5.6 (–33.8)	3.2 (–23.2)	n.d.	n.d.	7.7 (–40.4)	26.7 (–66.5)

n.d. not detectable.
[1]measured water fluxes.
[2]calculated water fluxes (Hydrus 2D).

fluxes almost doubled from 1997 to 1998, while DON fluxes declined by 11%. The DOC and DON fluxes in the Oi and Oa layers were about twice as high in 1998 than in 1997, whereas water fluxes increased by a factor of 1.5. In contrast, the DON fluxes remained more or less unchanged.

Based on the annual DOC input from throughfall, the forest floor represented a net source of DOC (Table 4). The highest DOC fluxes were measured beneath the Oa layer, exceeding those in throughfall threefold. In relation to the annual DON input from throughfall, the two forest floor layers showed equivocal features: In 1997, the Oi layer acted as a sink for all N compounds and retained 2.0 kg DON ha^{-1}. This feature changed drastically in 1998, when the Oi layer became a net source of 2.7 kg DON ha^{-1}. The net release of DOC from the Oi layer also increased significantly from 32.5 kg ha^{-1} in 1997 to 113.6 kg ha^{-1} in 1998. In contrast, the Oa layer was a net source of DON during both years. In opposition to the trend in the Oi layer, the DON net release in the Oa layer diminished from 4.7 kg ha^{-1} in 1997 to 2.3 kg ha^{-1} in 1998. The net release of DOC from the Oa layer increased only moderately from 102.8 to 144.9 kg ha^{-1}.

The DOC and DON fluxes decreased with depth in the mineral soil. The DOC fluxes at 20 cm depth were still in the range of those observed in throughfall, but DON fluxes were lower than in throughfall (Table 4, Figure 3). The DOC fluxes doubled from 1997 to 1998, whereas DON fluxes decreased slightly.

The DON concentrations and fluxes at 60 cm depth were below the lower threshold of quantification, while the DOC flux was 7.7 kg C ha^{-1} in 1997 and 26.7 kg C ha^{-1} in 1998.

No statistical correlations were found between temperature and either the DOC or DON fluxes. Seasonal patterns of DOC and DON fluxes were closely related to the water fluxes (Figure 3). Heavy rainfall in fall 1998 resulted in large DOC and DON fluxes.

Discussion

Annual DON and DOC concentrations and fluxes

At the Steinkreuz site the fluxes of N were dominated by NH_4-N in bulk precipitation and throughfall and by NO_3-N in forest floor leachates and soil solutions. Even under these conditions, the DON fluxes in throughfall and forest floor leachates were similar to those of NH_4-N and DON and represented a significant portion of the N turnover. The DOC and DON fluxes in Oa leachates were about 10% of the C and N fluxes in litterfall.

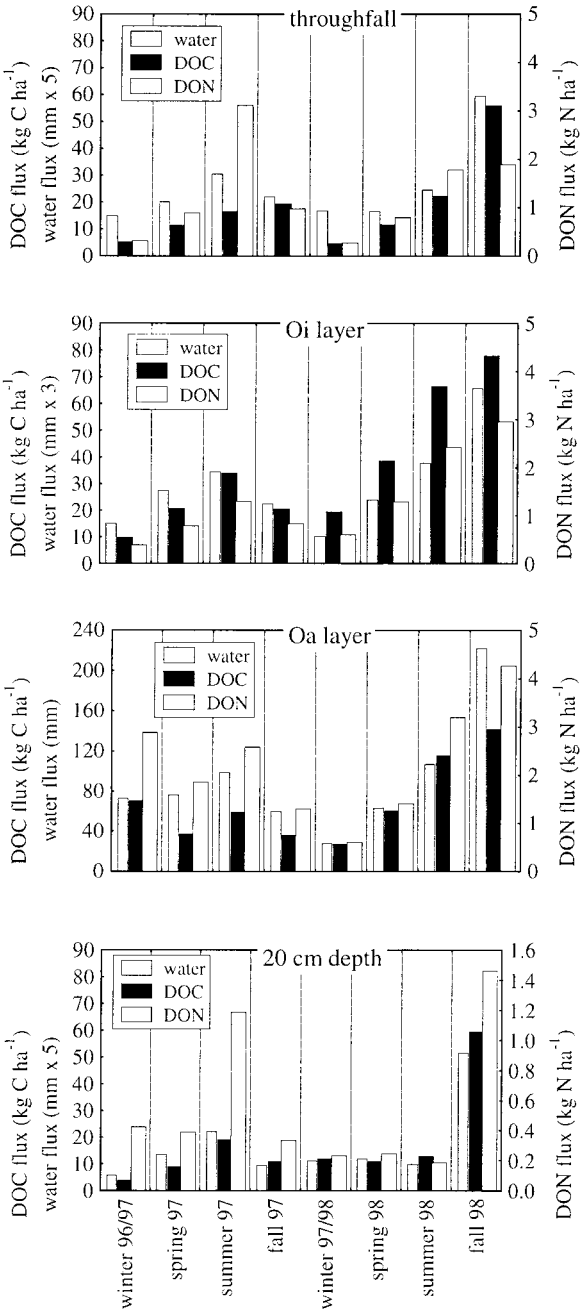

Figure 3. Cumulated DOC and DON fluxes for each season in throughfall, forest floor leachates (Oi and Oa) and mineral soil solution (20 cm) (means of each sampling date were summed over one season).

The 2-year average DON and DOC concentrations and fluxes found in the Oa leachates at the Steinkreuz site are in the upper range of those reported from other deciduous forest ecosystems (summarized by Michalzik et al. 2001).

The DON input from throughfall was in the same range as the net release from the forest floor, whereas the net release of DOC from the forest floor was about twice that of the flux in throughfall. The data compiled by Michalzik et al. (2001) appears to support the greater importance of throughfall DON over throughfall DOC in relation to their fluxes in the forest floor.

In 1997 the Oi layer was a net sink for all dissolved N fractions and retained nearly 40% of DON input from throughfall (Table 4) indicating that fresh litter acts as a N sink during initial stages of decomposition (Staaf & Berg 1982; Aber & Melillo 1982; Berg & Cortina 1995). The following year the Oi layer became an N source and released more DON than the Oa layer. The increase in the DOC net release from 1997 to 1998 was much higher in the Oi than in the Oa layer. This drastic change in Oi layer characteristics might be due to progressing litter decomposition and the eventual subsequent formation of an Oe layer. The strong increase in DOC and DON release from the Oi layer in the second year supports the hypothesis by Zsolnay (1996) and McDowell and Likens (1988). They proposed that partly decomposed organic matter in the forest floor is the major source of DOM rather than fresh litter. This hypothesis is corroborated by higher DOC concentrations and fluxes found in the Oa than in the Oi layer. Thus, these results contradict the findings by Qualls et al. (1991), Casals et al. (1995), Huang and Schoenau (1996, 1998) and Michalzik and Matzner (1999) who identified the Oi layer as the most important DOM source in deciduous and coniferous forests. However, a higher bioavailability of DOM derived from fresh litter could be responsible for the lower DOM fluxes from this part of the forest floor.

The DOC concentrations and fluxes in the upper mineral soil (20 cm) are in the range of those reported for other deciduous stands (summarized by Michalzik et al. 2001). The DON concentrations and fluxes in this soil depth are similar to those reported by Currie et al. (1996) at 60 cm depth. No comparative data was found for any DON concentrations and fluxes in the upper mineral soil of deciduous stands. Annual DON fluxes with streams from upland forest catchments were between 0.9 and 2.4 kg N ha^{-1} yr^{-1} (Campbell et al. 2000; McHale et al. 2000) which are comparable to the DON fluxes found at 20 cm depth.

The sharp decrease of both the DON and the DOC concentrations and fluxes over depth in the mineral soil indicates efficient retention in the mineral soil through adsorption or decomposition. Qualls and Haines (1991) reported rather low decomposition rates of both DON and DOC from hardwood forest

floors in laboratory studies. The sorption of DOC to the solid phase in the mineral soil was shown to be an effective retention mechanism (Qualls & Haines 1992; Kaiser & Zech 1997; Kalbitz et al. 2000). If a similar behaviour for DON is assumed (Kaiser & Zech 2000), sorption would then be the most likely mechanism responsible for DON retention in the mineral soil.

Seasonal effects of temperature, water fluxes, soil solution properties and litterfall

The release of DOC from the forest floor was shown in laboratory experiments to be positively correlated to temperature (Andersson et al. 2000; Kalbitz et al. 2000). In numerous field studies DOC concentrations in the forest floor and soil were higher in summer than in winter (summarized by Kalbitz et al. 2000). As a result DOC release has been often attributed biological controls (McDowell & Likens 1988; Guggenberger & Zech 1994; Guggenberger et al. 1998). Concentration and temperature correlations were found (based on biweekly sampling) between DOC and DON in throughfall and to some extent in the upper mineral soil as well, although no correlation was found in the forest floor. This new evidence directly supports our theory that DOC and DON concentrations in throughfall are to some extent dependent on biological processes occurring in the canopy. At the same site Stadler et al. (2000) emphasized the insect follivore effect on DOC concentrations in throughfall during May and June.

On the annual scale, higher DOC concentrations in 1998 than in 1997 could be related to a higher average temperature in 1998 (8.3 °C) than in 1997 (7.6 °C). The 1996/1997 winter (1 DEC 96 to 28 FEB 97) was 3.4 °C colder than the following winter (Figure 4). Differences between those two years during the other seasons were negligible. The increase in DOC concentrations from 1997 to 1998 began in winter 1997/1998 (Oi layer and at 20 cm depth) or in spring (Oa layer) and was most pronounced during the winter. It is our hypothesis that an enhancement of DOC production in the forest floor and the mineral soil was caused by the warmer winter. Brooks et al. (1999) found a close relationship between the heterotrophic activity and the size of the DOC pool under snow. This increased pool of potential DOM that built up over the winter could be the source of higher DOC concentrations in 1998 than those found in 1997 and would not be easily exhausted in winter or spring. The effect continues into fall. The warmer winter had no apparent effect on DON, which is open to speculation as to why.

Fluxes of DOC and DON in throughfall, forest floor and mineral soil seem to be independent of temperature as reported by Michalzik et al. (2001). The lack of any correlation between these DON and DOC concentrations and water fluxes indicates that the pool of DOM is rather large and is neither

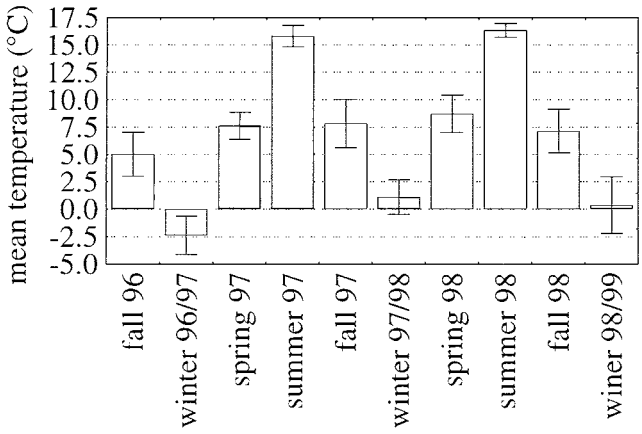

Figure 4. Seasonal average mean air temperatures at the Steinkreuz site.

subjected to concentration nor dilution effects. It is our conclusion that water fluxes control DOC and DON fluxes in throughfall, the forest floor and mineral soil.

A significant correlation was found to exist only in the Oi layer between both the DOC and DON concentrations and the physico-chemical properties of the aqueous phase (electric conductivity, NH_4-N and NO_3-N). The positive correlation between DOC and DON concentrations and the electric conductivity contradicts laboratory findings that increasing ionic strength reduces DOC mobilization (summarized by Kalbitz et al. 2000). This positive relationship and the positive correlations to NO_3-N, NH_4-N (Table 3), and SO_4-S (not shown) supports the relationship between the C-, N- and S cycle in the Oi layer.

The lack of any correlation of the DOC and DON concentrations to either the pH or the electric conductivity in Oa layer leachates contradicts laboratory findings (Chang & Alexander 1984; Cronan 1985; Vance & David 1989; Andersson et al. 2000) but is in consensus with other field studies (summarized by Kalbitz et al. 2000). None of these physico-chemical parameters were identified as a decisive regulative for DON and DOC release under field conditions, given the temporal and spatial resolution of our measurements and the environmental conditions during the sampling period.

The dynamics of DOC and DON in forest floor leachates were found to be independent of the litterfall dynamics, contradicting other field studies reporting a positive response (Lundström 1993; Casals et al. 1995; Currie et al. 1996). However, on a regional scale Michalzik et al. (2001) could not confirm a positive relationship between annual litterfall and annual DOC fluxes in the forest floor.

Dynamics of DOC/DON ratios

The DOC/DON ratios differed temporally and spatially between the compartments, indicating different DOC and DON turnover rates. The DOC/DON ratios of forest floor leachates were higher than the C/N ratios of the forest floor solid phase, indicating either preferential release of DOC and/or preferential retention of DON in the forest floor. In the mineral soil, DOC/DON ratios decreased, supporting the findings by Qualls and Haines (1991), Gu et al. (1995) and Kaiser and Zech (1997) who support preferential sorption of hydrophobic components with a lower N content as compared to hydrophilic components containing a higher N content (Kaiser & Zech 2000).

In 1998 higher DOC/DON ratios were measured in solutions from all compartments as compared to 1997. This occurrence was equally caused by decreased DON concentrations (except for Oi leachates) and increased DOC concentrations. The causes for these differences in DOC and DON concentrations between the observed years could not be identified with the data collected. However, some possible causes have been postulated:

Water fluxes can be excluded as being responsible for a preferred DOC leaching in comparison to DON. This line of reasoning is especially fitting when the period from September 1998 to the end of 1998 is observed, when 50% of the total annual water flux occurred. During the same period about 45% of both the annual DOC and the DON fluxes in forest floor leachates were recorded. Temperature effects (lower winter temperature in 1997 than in 1998) (Figure 4) and aboveground litterfall are incapable of explaining the observed differences in the DOC/DON ratios. As of yet no literature has been published citing a different response of DOC and DON to temperature changes.

Throughfall is an important source of DON (equal to the forest floor) and DOC (half enters the forest floor) to the forest floor of our site. Comparing 1997 to 1998, the DOC flux in throughfall increased by 77% while the DON flux declined by 11%. This divergence of DOC and DON fluxes persisted in all compartments except the Oi layer, which might have undergone exceptional circumstances due to its development towards an Oe layer. The reduced input of DON and mineral N possibly led to an attenuation of DON production and mobilization. Equally, the high DOC input from throughfall in 1998 which consists mainly of easily decomposable compounds (Guggenberger & Zech 1994) might have induced intensified DOC production. Lignin decomposition has been shown to be a key process for DOC mobilization (Zech et al. 1996) and is accelerated by the addition of easily decomposable carbon, especially at low nitrogen contents (Fog 1988; Eriksson et al. 1990). The DON should be less effected because of the low N content of lignin. Thus, the higher input from throughfall DOC would explain a higher DOC release.

Statistically significant positive correlations between DOC and DON fluxes in throughfall and those in forest floor leachates have also been reported by Michalzik et al. (2001) in a variety of field studies.

Conclusions

- The DOC and DON released from the forest floor represents a significant flux of C and N into the mineral soil, even at sites with high fluxes of mineral N compounds.
- Both seasonally and annually varying DOC/DON ratios as well as weak correlations between DOC and DON imply that the mechanism and rates of release from the forest floor are different for DOC and DON. Therefore, a different parameterization of DON release as compared to DOC is required if models of DOM turnover in soils are to be accurately developed (e.g.: Tipping et al. 1995).
- The DOC and DON concentrations are temperature dependent in throughfall but not in the forest floor. It appears that an unusually warm winter accelerates DOC release from the forest floor and the mineral soil.
- Concentrations of DOC and DON in throughfall, the forest floor and mineral soil are not hydrologically controlled. Thus DOC and DON fluxes are mainly driven by water fluxes on annual and biweekly time scales.
- The DOC and DON fluxes in throughfall affect DOC and DON concentrations and fluxes in the litter layer on a biweekly sampling scale. Based on an annual time scale this effect is probably true for the forest floor and the mineral soil as well. Throughfall contributed relatively more DON than DOC to the overall element fluxes.
- The temporal variation of DOC and DON concentrations in the forest floor at the site was not attributable to one distinct environmental factor (e.g. temperature, pH, ionic strength, litterfall). This fact is obviously due to their manifold interaction and interdependence which makes differentiation difficult under field conditions. More emphasis should be placed on plot-scale manipulation experiments in order to identify controlling factors under field conditions.

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