

# Site-to-site variability and temporal trends of DOC concentrations and fluxes in temperate forest soils

WERNER BORKEN\*, BERNHARD AHRENS\*, CHRISTOPH SCHULZ<sup>†</sup> and LOTHAR ZIMMERMANN<sup>†</sup>

\*Department of Soil Ecology, University of Bayreuth, 95440 Bayreuth, Germany, <sup>†</sup>Bavarian Forest Institute, 85354 Freising, Germany

## Abstract

Here, we report site-to-site variability and 12–14 year trends of dissolved organic carbon (DOC) from organic layers and mineral soils of 22 forests in Bavaria, Germany. DOC concentrations in the organic layer were negatively correlated with mean annual precipitation and elevation whereas air temperature had a positive effect on DOC concentrations. DOC fluxes in subsoils increased by  $3 \text{ kg ha}^{-1} \text{ yr}^{-1}$  per 100 mm precipitation or per 100 m elevation. The highest DOC concentrations were found under pine stands with mor humus. Average DOC concentrations in organic layer leachates followed the order: pine > oak > spruce > beech. However, the order was different for mean DOC fluxes (spruce > pine > oak > beech) because of varying precipitation regimes among the forest types. In 12 of 22 sites, DOC concentrations of organic layer leachates significantly increased by 0.5 to  $3.1 \text{ mg CL}^{-1} \text{ yr}^{-1}$  during the sampling period. The increase in DOC concentration coincided with decreasing sulfate concentration, indicating that sulfate concentration is an important driver of DOC solubility in the organic layer of these forest sites. In contrast to the organic layer, DOC concentrations below 60 cm mineral soil depth decreased by  $<0.1\text{--}0.4 \text{ mg CL}^{-1} \text{ yr}^{-1}$  at eight sites. The negative DOC trends were attributed to (i) increasing adsorption of DOC by mineral surfaces resulting from desorption of sulfate and (ii) increasing decay of DOC resulting from decreasing stabilization of DOC by organo-Al complexes. Trends of DOC fluxes from organic layers were consistent with those of DOC concentrations although trends were only significant at seven sites. DOC fluxes in the subsoil were with few exceptions small and trends were generally not significant. Our results suggest that enhanced mobilization of DOC in forest floors contributed to the increase of DOC in surface waters while mineral horizons did not contribute to increasing DOC export of forest soils.

**Keywords:** DOC, forest soils, organic layer, sulfate, tree species

Received 15 October 2010 and accepted 21 November 2010

## Introduction

Dissolved organic carbon (DOC) is an important component of many biogeochemical processes in forest ecosystems. It consists of different compounds with various biological and physicochemical properties, serves as C source for heterotrophic microorganisms, contributes to the sequestration of organic C in mineral soils, and controls the mobilization and speciation of metals in solution. Leaching of DOC represents a relatively small loss of C from terrestrial soils, but a major input to groundwater and surface water.

A growing number of publications highlight the relevance and function of DOC in soils. Nonetheless, little literature is available regarding the variations of DOC concentrations and fluxes among different forest ecosystems. Few studies in adjacent forest stands with the same climate and soil suggest that tree species may

have an effect on DOC fluxes (Smolander & Kitunen, 2002; Borken *et al.*, 2004). Michalzik *et al.* (2001) analyzed data from 16 case studies and showed that the variation of annual DOC fluxes in forest floor leachates among the sites was best explained by the annual amount of precipitation whereas temperature, forest type (coniferous vs. hardwood forests), litterfall and soil organic C stock were neither correlated with concentrations nor with fluxes of DOC. Similarly, Buckingham *et al.* (2008) found no systematic differences among different forest types in UK topsoils. They reported strong regulation of annual DOC fluxes by annual water fluxes. The analysis by Wu *et al.* (2010) supported the strong influence of precipitation on DOC concentrations in forest floor leachates from Norwegian forests. A major problem is the tremendous inter-annual variation of DOC concentrations and fluxes that makes it difficult to generalize controlling factors on the regional scale. Further problems are often differences in the methodology and in the installation depth of sampling devices.

Correspondence: Werner Borken, e-mail: werner.borken@uni-bayreuth.de

In the temperate and boreal zone of the northern hemisphere, DOC concentration of many rivers and lakes has increased during past decades (Driscoll *et al.*, 2003; Evans *et al.*, 2005; De Wit *et al.*, 2007; Hruska *et al.*, 2009). This increase has been attributed to decreasing atmospheric deposition of pollutants and sea salt (Evans *et al.*, 2006; Monteith *et al.*, 2007). The reduction of SO<sub>2</sub> emissions by 73% between 1980 and 2004 was one of the most effective environmental changes in Europe within a relatively short period (Vestreng *et al.*, 2007). While the reductions were small during the 1980s, strongest reductions were achieved between 1990 and 2000. Consequently, sulfate deposition decreased in most European forest ecosystems (Lorenz & Mues, 2007).

Other factors such as increasing litter productivity, land use change, drought periods and rising temperatures could have also contributed to elevated DOC levels in surface waters (Roulet & Moore, 2006). Tranvik & Jansson (2002) argued that the increase of DOC in aquatic systems is triggered by rising temperature and decreasing precipitation. As much of the DOC of rivers and lakes originates from terrestrial ecosystems, it is possible that DOC concentrations and fluxes in soils responded in a similar way to environmental changes. However, in contrast to aquatic systems there is little knowledge on long-term trends of DOC in forest soils. Moreover, trends of DOC could be different in organic layers and mineral soil horizons considering distinct vertical patterns in production and sorption capacities of DOC in forest soils.

In Norwegian spruce and pine stands, DOC concentrations in soil solution at 5 cm depth exhibited no significant trend between 1996 and 2006 because of relatively small changes in atmospheric deposition of sulfate and chloride during this period (Wu *et al.*, 2010). In the same study, concentration of DOC mostly decreased in soil solutions at 15 and 40 cm depth, likely due to decreasing sulfate concentration, and thus, increasing adsorption of DOC. Kalbitz *et al.* (2004) reported a negative trend for DOC concentrations in the mineral soil of a spruce forest, but no trend for a beech forest between 1992 and 2001. Such data analyses of DOC concentrations and fluxes from monitoring sites improve our understanding with respect to the function of DOC for soil processes and its future role for water quality. Because of the gradient in deposition and general climate in the northern hemisphere, variability in soil properties and forest stand species, further analyses are necessary to obtain a more complete picture of temporal and spatial trends in DOC in temperate forests.

The aim of this study was to analyze site-to-site variability and temporal trends of DOC concentrations and fluxes of soil solution from three different soil depths of 22 temperate forest sites in Bavaria, Germany. We analyzed

the influence of air temperature, precipitation, elevation, tree species, humus form, C/N ratio and thickness of organic layers on concentrations and fluxes of DOC. Further, we used concentrations of single ions, ionic strength and pH to examine relationships between temporal trends of these parameters and DOC concentrations.

## Material and methods

### Study sites

The 22 study sites are located in different climatic and geological regions of Bavaria, Germany, and were established between 1990 and 1995 as Level II sites within the International Co-operative Programme on Assessment and Monitoring of Air Pollution Effects on Forests (ICP Forests, 2006). Long-term means of annual air temperature (MAT) range between 5.1 and 9.1 °C and of annual precipitation (MAP) between 659 and 1886 mm (Table 1). Soil types, soil texture, soil depth and chemical properties of soils vary considerably among the sites. The pH (H<sub>2</sub>O) of the A horizons ranges from pH 7.4 on flood plain sediments at LAN to pH 2.9 on weathered phyllite at GOL (Table 1). It is general thought that acid deposition has reduced the pH and base saturation of many forest soils in Central Europe since industrialization. Forests in north-east Bavaria (FLO, GOL) were among the regions in Europe that received particularly high loads of acid rain (STMELF, 2008).

The dominating tree species of the study sites are Norway spruce (*Picea abies* (L.) Karst.) (*n* = 8), European beech (*Fagus sylvatica* L.) (*n* = 5), Scots pine (*Pinus sylvestris* L.) (*n* = 4), oak (*Quercus petraea* (Matt.) Liebl., *Quercus robur* L.) (*n* = 4), and European larch (*Larix decidua* Mill.) (*n* = 1). Most stands comprise different age classes of trees and consist of up to four different tree species. The oak and pine forests generally grow at lower elevation and in regions with higher temperatures and less precipitation as compared with the beech, larch and spruce stands. The beech and oak forests developed mull and moder humus forms, while the pine forests accumulated mor humus forms and the spruce forests only moder humus forms, except at KRE with mull (Table 1).

### Sampling and chemical analyses

Soil solutions were sampled from different soil depths within an area of about 400 m<sup>2</sup> at each study site between 1990 and 2008. DOC concentrations of soil solutions, however, were analyzed starting in 1994 (see Table 2 for site-specific start of DOC analysis). Six plate lysimeters per plot were installed at the boundary between the organic layer and the mineral soil (0 cm) for sampling of leachates from the organic layer. The free-draining plate lysimeters had a surface area of 700 cm<sup>2</sup> and consisted of a conical, trapeze-shaped plastic vessel with a polyethylene gauze on top. Leachates were continuously collected in 2-L glass flasks and sampled every second week. The glass flasks were located in underground containers at 50–60 cm soil depth beside the plate lysimeters. We cannot exclude that DOC in the glass flasks was partly mineralized during the fortnightly sampling period. Leachates of all six

**Table 1** Location, elevation, dominating tree species, stand age, soil type (WRB), humus form, soil texture (USDA classification), soil pH (H<sub>2</sub>O) of the A horizon, mean annual precipitation (MAP), and mean annual air temperature (MAT) of 22 study sites

Site	Location	Elevation(m)	Tree species	Stand age (years)	Soil type	Humus form	Soil texture	Soil pH	MAP (mm)	MAT (°C)
Altdorf (ALT)	49°25'N, 11°19'E	406	<i>Pinus sylvestris</i>	70–100	Haplic Podzol	Mor	Sand	3.7	789	8.0
Altötting (AOE)	48°13'N, 12°45'E	415	<i>Picea abies</i>	45–80	Haplic Alfisol	Moder	Silt loam	3.4	967	7.8
Bad Brückenau (BBR)	50°21'N, 09°56'E	812	<i>Fagus sylvatica</i>	107–127	Eutric Cambisol	Moder	Silt loam	4.0	1041	6.1
Berchtesgaden (BER)	47°35'N, 12°57'E	1500	<i>Larix decidua</i>	118–221	Eutric Leptosol	Mull	Silt loam	6.6	1327	5.1
Bodenwöhr (BOD)	49°17'N, 12°23'E	396	<i>Pinus sylvestris</i>	70–121	Cambic Arenosol	Mor	Sand	3.4	749	7.3
Dinkelsbühl (DIN)	49°07'N, 10°35'E	468	<i>Pinus sylvestris</i>	78–115	Cambic Arenosol	Mor	Sand	3.5	738	7.6
Ebersberg (EBE)	48°07'N, 11°55'E	540	<i>Picea abies</i>	56–76	Haplic Alfisol	Moder	Silt loam	3.4	992	7.7
Ebrach (EBR)	49°46'N, 10°32'E	410	<i>Fagus sylvatica</i>	137–162	Eutric Cambisol	Moder	Silt loam	3.8	780	7.4
Flossenbürg (FLO)	49°56'N, 12°24'E	840	<i>Picea abies</i>	60–103	Haplic Podzol	Moder	Sandy loam	3.3	949	6.1
Freising (FRE)	48°24'N, 11°39'E	508	<i>Fagus sylvatica</i>	130–150	Eutric Cambisol	Mull	Sandy clay loam	4.6	841	8.2
Goldkronach (GOL)	49°58'N, 11°48'E	800	<i>Picea abies</i>	50–97	Dystric Cambisol	Moder	Silt loam	2.9	1171	5.6
Kreuth (KRE)	47°44'N, 11°40'E	1100	<i>Picea abies</i>	> 120	Gleyic Cambisol	Mull	Loam	4.4	1777	6.7
Landau (LAN)	48°42'N, 12°14'E	335	<i>Quercus robur</i>	110	Mollic Fluvisol	Mull	Silt loam	7.4	706	8.7
Mitterfels (MIT)	48°59'N, 12°53'E	1025	<i>Fagus sylvatica</i>	81–131	Dystric Cambisol	Moder	Silt loam	3.3	1357	5.5
Pegnitz (PEG)	49°42'N, 11°30'E	440	<i>Pinus sylvestris</i>	52–95	Haplic Podzol	Mor	Sand	3.6	908	6.8
Riedenburg (RIE)	48°56'N, 11°46'E	475	<i>Quercus petraea</i>	90–110	Eutric Cambisol	Mull	Silt loam, clay	5.2	699	7.9
Rothenkirchen (ROK)	50°27'N, 11°21'E	670	<i>Picea abies</i>	30–52	Dystric Cambisol	Moder	Silt loam	3.2	1084	6.2
Rothenbuch (ROT)	49°59'N, 09°28'E	470	<i>Quercus petraea</i>	71–92	Dystric Cambisol	Moder	Sandy loam	3.5	1023	7.3
Schongau (SOG)	47°53'N, 10°48'E	780	<i>Fagus sylvatica</i>	80–105	Haplic Alfisol	Mull	Loam	3.9	1195	6.4
Sonthofen (SON)	47°34'N, 10°23'E	1170	<i>Picea abies</i>	54–114	Dystric Cambisol	Moder	Sandy loam	3.5	1886	6.0
Würzburg (WUE)	49°43'N, 09°53'E	330	<i>Quercus petraea</i>	79	Dystric Cambisol	Mull	Silt loam, clay	4.2	659	9.1
Zusmarshausen (ZUS)	48°25'N, 10°32'E	515	<i>Picea abies</i>	35–96	Albic Luvisol	Moder	Silt-clay loam	3.3	848	8.2

**Table 2** Annual DOC concentrations (mean  $\pm$  SD) below the organic layer (0 cm), in the top mineral soil (20–30 cm) and the subsoil (60–140 cm) of the 22 study sites

Site	Start year	DOC concentration (mg L <sup>-1</sup> )		
		Organic layer	Topsoil	Subsoil
ALT	1994	65 $\pm$ 15	7.6 $\pm$ 2.2	7.3 $\pm$ 2.8
AOE	1995	54 $\pm$ 15	5.4 $\pm$ 1.0	4.2 $\pm$ 4.1
BBR	1997	33 $\pm$ 7	1.7 $\pm$ 0.3	2.1 $\pm$ 0.4
BER	1995	15 $\pm$ 2	5.2 $\pm$ 1.3	4.0 $\pm$ 2.7
BOD	1996	80 $\pm$ 17	22.7 $\pm$ 6.6	3.9 $\pm$ 2.5
DIN	1995	76 $\pm$ 13	6.2 $\pm$ 0.7	7.2 $\pm$ 2.7
EBE	1995	55 $\pm$ 11	7.5 $\pm$ 2.8	3.6 $\pm$ 0.9
EBR	1995	44 $\pm$ 13	23.1 $\pm$ 4.4	9.9 $\pm$ 4.8
FLO	1995	32 $\pm$ 6	3.3 $\pm$ 0.7	4.3 $\pm$ 1.4
FRE	1995	43 $\pm$ 12	6.6 $\pm$ 7.2	3.0 $\pm$ 1.4
GOL	1995	36 $\pm$ 7	4.9 $\pm$ 0.5	3.0 $\pm$ 0.6
KRE	1997	30 $\pm$ 8	5.2 $\pm$ 1.5	2.4 $\pm$ 0.5
LAN	1995	47 $\pm$ 11	13 $\pm$ 17.9	6.7 $\pm$ 5.2
MIT	1995	19 $\pm$ 3	1.3 $\pm$ 0.4	1.2 $\pm$ 0.5
PEG	1995	50 $\pm$ 9	15.4 $\pm$ 5.0	6.4 $\pm$ 2.9
RIE	1994	46 $\pm$ 6	5.4 $\pm$ 4.2	5.0 $\pm$ 4.8
ROK	1997	52 $\pm$ 15	5.5 $\pm$ 2.8	2.9 $\pm$ 3.2
ROT	1996	48 $\pm$ 12	3.4 $\pm$ 3.2	1.2 $\pm$ 0.4
SOG	1994	27 $\pm$ 4	1.8 $\pm$ 1.3	1.2 $\pm$ 0.3
SON	1994	28 $\pm$ 3	5.8 $\pm$ 1.6	4.7 $\pm$ 3.3
WUE	1997	68 $\pm$ 14	3.0 $\pm$ 0.3	7.7 $\pm$ 4.3
ZUS	1994	69 $\pm$ 10	4.5 $\pm$ 3.8	2.4 $\pm$ 3.6

The sampling periods of DOC vary among sites beginning from the start year to 2008.

plate lysimeters were merged by volume to one mixed sample and then stored in a refrigerator at 4 °C until transportation to the laboratory. A maximum of 26 mixed samples was collected per site and per year.

For solution from the mineral soil, we used ceramic suction cups (5 cm length, 2.5 cm diameter) with a pore size of 1.0  $\mu$ m, consisting of 70% Al<sub>2</sub>O<sub>3</sub> and 30% SiO<sub>2</sub>. Four suction cups were installed per soil depth at 20–30 cm and at the boundary between the subsoil horizon and the C horizon (60–140 cm; see Fig. 5 for specific installation depths). These suction cups were operated at an initial suction of –50 kPa that was applied by a vacuum pump at the beginning of the sampling interval. Soil solutions from the mineral soil were continuously sampled over 1 week every fourth week resulting in up to 13 samples per suction cup and year. The solution of each suction cup was separately collected in 1-L glass flasks which were stored in underground containers. After the sampling interval aliquots of 100 mL solution were stored at 4 °C in a fridge until shipping to the laboratory of the Bayerische Landesanstalt für Wald und Forstwirtschaft, Freising. Immediately after arrival, soil solutions were filtered with pre-washed 0.45  $\mu$ m cellulose-acetate filters (Millipore Corporation, Billerica, MA, USA). Soil solutions were stored at 4 °C and analyzed within 7 weeks after sampling in the field.

DOC and total N in soil solutions were determined by high temperature combustion and subsequent determination of CO<sub>2</sub> and NO<sub>2</sub> (Dima-TOC 2000, Dima-N, DIMATEC Analysentechnik GmbH, Essen, Germany). NH<sub>4</sub><sup>+</sup>, NO<sub>3</sub><sup>-</sup>, Cl<sup>-</sup> and SO<sub>4</sub><sup>2-</sup> were analyzed by ion chromatography (DX-120, Dionex Corporation, Sunnyvale, CA, USA). NH<sub>4</sub><sup>+</sup> was separated from other cations in a H<sub>2</sub>SO<sub>4</sub> eluant system and then determined by measurement of conductivity. An inductively coupled plasma optical emission spectrometer (ICP-OES) (Optima 5300 DV, Perkin Elmer Incorporation, Waltham, MA, USA) was used to determine concentrations of Al, Ca, Fe, K, Mg, Mn, Na, P and Si. The pH of soil solution was measured with low-ionic-strength-electrode (Electrode type N64, pH-Meter Model 220 pH, Schott AG, Mainz, Germany).

Ionic strength (IS) was calculated from the molar concentrations of Ca<sup>2+</sup>, Mg<sup>2+</sup>, Na<sup>+</sup>, K<sup>+</sup>, Al<sup>3+</sup>, Fe<sup>2+</sup>, Mn<sup>2+</sup>, NO<sub>3</sub><sup>-</sup>, NH<sub>4</sub><sup>+</sup>, SO<sub>4</sub><sup>2-</sup>, Cl<sup>-</sup>, H<sup>+</sup> and OH<sup>-</sup>:

$$IS = 0.5 \sum_i c_i Z_i^2 \quad (1)$$

where  $c_i$  is the molar concentration of ion  $i$  and  $Z$  is the charge of ion  $i$ .

Using equivalent concentrations of the ions, the charge balance (CB) was calculated from the difference between the sums of cations and of mineral anions:

$$CB = (2[Ca^{2+}] + 2[Mg^{2+}] + [Na^+] + [K^+] + 3[Al^{3+}] + 2[Fe^{2+}] + 3[Mn^{2+}] + [H^+] + [NH_4^+]) - ([NO_3^-] + 2[SO_4^{2-}] + [Cl^-] + [OH^-]) \quad (2)$$

It was assumed that iron occurs as Fe<sup>2+</sup> and aluminum as Al<sup>3+</sup> in the soil solution. HCO<sub>3</sub><sup>-</sup> was not specifically determined, and thus, IS and CB are incomplete for sites (BER, LAN) with soil pH >5.4 (Table 1).

### Hydrological modeling and DOC fluxes

Water fluxes in different soil depths were calculated for all 22 sites using the same hydrological model BROOK90 (Federer, 1995) modified by Hammel & Kennel (2001). The model calculated potential evapotranspiration, interception, the amount of infiltrating water at the soil surface and soil water fluxes on a daily basis using vapor pressure, precipitation, wind speed, global radiation, minimum and maximum of daily air temperature. Climatic data were obtained from associated weather stations located on non-forested open areas within a distance of <1000 m apart from the forest stands. Retention and conductivity of soil water were derived from soil texture, gravel content, bulk density and organic carbon content of different soil horizons using pedotransfer functions. Retention and conductivity curves were then fitted with functions of van Genuchten (1980) and Mualem (1976). Lateral water fluxes were calculated as additional flow component when sites were situated on mountain slopes or where soils had impermeable horizons. Most soils are well to moderately drained, except the soil at ZUS, an albic Luvisol, that is poorly drained, and thus, strongly influenced by lateral water flow. Impermeable subsoil horizons at EBR, KRE, PEG and SON temporarily caused lateral water flow.

DOC fluxes were calculated by multiplying the mean DOC concentration with the respective cumulative 2-week (0 cm) or 4-week water flux (20–140 cm). We assumed that the DOC concentration of the 1-week sampling period (20–140 cm) is representative for the whole 4-week period. For statistical trend analyses, mean monthly DOC concentrations and fluxes were calculated whereby monthly values based either on one DOC concentration or on two DOC concentrations.

### Statistics

The Seasonal Mann–Kendall test (SMK test) was used to detect monotonic trends in the time series (Hirsch & Slack, 1984), since it can cope with autocorrelation, nonnormality seasonality and missing or censored data. The SMK test calculates the Mann–Kendall statistics  $S_g$  within monthly grouped blocks of the respective time series. Within 1 month  $g$  all possible differences ( $X_{jg} - X_{ig}$ ) are evaluated by a sign function that gives +1 for positive differences, -1 for negative differences and 0 for tied or missing values. The signs for 1 month  $g$  are summed to give the Mann–Kendall statistics  $S_g$ :

$$S_g = \sum_{i < j} \text{sgn}(X_{jg} - X_{ig}). \quad (3)$$

Summing up  $S_g$  over all months gives the seasonal Mann–Kendall statistics  $S$ , which together with its variance  $\text{var}(S)$  is used to calculate the standardized test statistic  $Z$ . While the sign of  $Z$  indicates the direction of the trend, the magnitude of  $Z$  determines the significance of the trend. Trends were considered significant at  $P < 0.10$ .

The magnitude of trend slopes was calculated with the Seasonal Kendall Slope Estimator (Hirsch *et al.*, 1982). Similar to the calculation of  $S_g$  Eqn (3) all slopes  $d_{jig}$  between the years  $j$  and  $i$  within one monthly block  $g$  are calculated:

$$d_{jig} = \frac{X_{jg} - X_{ig}}{j - i}, \quad (4)$$

where  $j > i$ ,  $g$  the monthly blocks from January to December. The Seasonal Kendall Slope Estimator is then determined as the median of all possible combinations of  $d_{jig}$ . This slope estimator is robust against extreme values, skewness and seasonality in the time series. Annual trends of monthly DOC concentrations are given in  $\text{mg L}^{-1} \text{yr}^{-1}$  whereas annual trends of monthly DOC fluxes are given in  $\text{kg ha}^{-1} \text{month}^{-1} \text{yr}^{-1}$ .

In order to detect trend turning points in the time series of DOC concentrations the Sequential Mann–Kendall test was applied after Gerstengarbe & Werner (1999). Generally it is based on the same principle as the SMK test Eqn (3), but without accounting for possible seasonality in the dataset. Normalized values of Kendall's  $\tau$  are calculated progressively based on  $S$  and  $\text{var}(S)$  of  $n-1$  subseries of the original time series  $y_1, y_2, \dots, y_n$ . This means that the first subseries is composed of  $y_1$  and  $y_2$ , the second of  $y_1, y_2$  and  $y_3$ , etc. The  $S$  is then calculated for the  $i$ th of  $n-1$  subseries as:

$$S_i = \sum_{k=2}^{i-1} \sum_{j=k}^i \text{sgn}(Y_j - Y_k). \quad (5)$$

The same procedure is then applied to a retrograde subseries, with  $y_n$  and  $y_{n-1}$  as first and  $y_n, y_{n-1}$  and  $y_{n-2}$  as second

subseries. This results in a progressive and retrograde time series of Kendall's  $\tau$ . Intersection points of the progressive with the retrograde time series of  $\tau$  mark approximate trend turning points within the original time series. The trend turning points can be considered significant when the intersection point is outside a band of  $\tau$  from  $-1.96$  to  $+1.96$  corresponding to a significance level of 0.05.

Linear regression was used to identify relationships between DOC trends or DOC concentrations and fluxes and possible explanatory variables. Comparison of differences between groups like tree species was made using an ANOVA and the least significant difference procedure for post hoc testing. The statistical analysis was performed with R (R Development Core Team, 2010, Version 2.11.0) and its packages Kendall (McLeod, 2009), zyp (Bronaugh & Werner, 2009) for the slope estimator, pheno (Schaber, 2009) for the sequential Mann–Kendall test and agricolae (de Mendiburu, 2010) for multiple comparisons. The Seasonal Mann–Kendall test was performed according to Libiseller (2002).

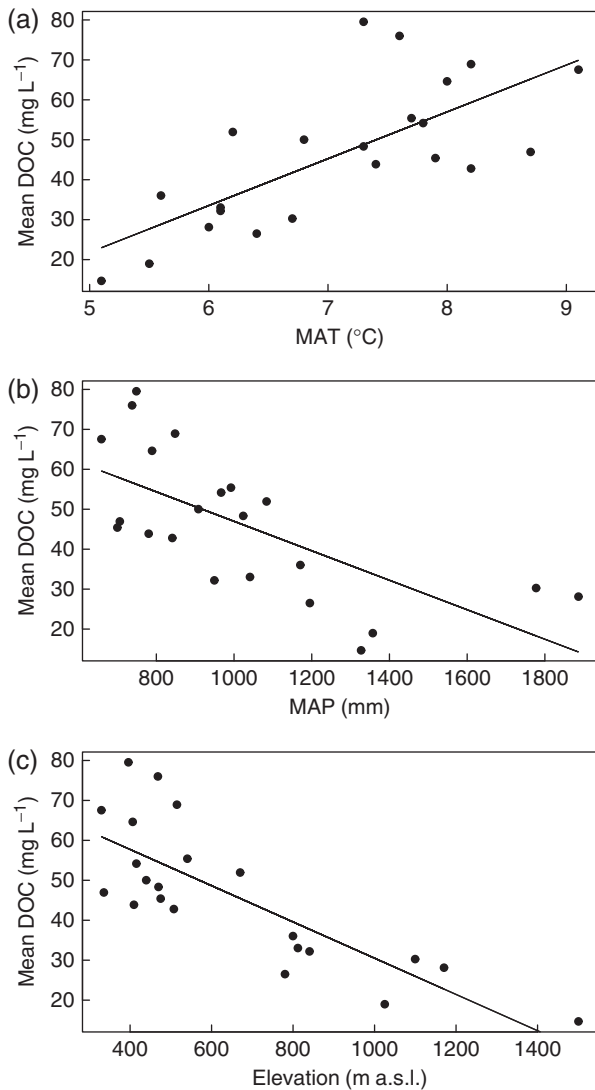
### Results

#### *Effect of climatic parameters on DOC concentrations and fluxes*

Mean annual DOC concentrations of leachates from the organic layer ranged between 15 and 80  $\text{mg CL}^{-1}$  across all 22 forest sites (Table 2). Within a temperature gradient of 5–9 °C, DOC concentrations increased linearly with MAT ( $y = 11.7x - 36.8$ ,  $r^2 = 0.52$ ,  $P < 0.001$ ) (Fig. 1a). Increasing precipitation reduced the mean DOC concentration by 3.7  $\text{mg CL}^{-1}$  per 100 mm MAP ( $y = -0.037x - 84.0$ ,  $r^2 = 0.46$ ,  $P < 0.001$ ) (Fig. 1b). Because of the significant relationship between MAT and MAP along the altitudinal gradient (not shown), DOC concentration decreased with increasing elevation by 4.5  $\text{mg CL}^{-1}$  per 100 m ( $y = -0.045x - 76.0$ ,  $r^2 = 0.63$ ,  $P < 0.001$ ) (Fig. 1c).

Much of infiltrating DOC from the organic layers was retained in the top mineral soils. In 20–30 cm mineral soil depth, mean annual DOC concentrations varied between 1.3 and 23.1  $\text{mg CL}^{-1}$  whereby only four sites had concentrations  $> 8 \text{ mg CL}^{-1}$  (Table 2). These four sites were located at elevations  $\leq 440$  m and had MAP of  $< 910$  mm (Table 1). Without these four sites, DOC concentrations at the 20–30 cm depth were not correlated with MAP, MAT or elevation.

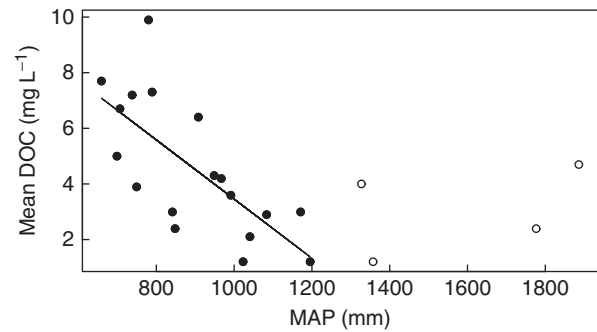
DOC concentrations in the subsoil (60–140 cm) were either further reduced or reached a similar level in the range of 1.2–9.9  $\text{mg CL}^{-1}$  as the respective DOC concentrations in 20–30 cm (Table 2). A remarkable increase from 3.0 in 30 cm to 7.7  $\text{mg CL}^{-1}$  in 110 cm depth was observed at WUE, the stand with the lowest precipitation and highest temperature (Table 1). The effects of MAT and MAP on DOC concentrations in this depth were rather weak compared with 0 cm. In case of MAP, the relation-



**Fig. 1** Relationship between mean DOC concentrations in 0 cm soil depth and (a) mean annual air temperature, (b) mean annual precipitation and (c) elevation of 22 forest sites.

ship was relatively strong ( $y = -0.01 \times -14.1$ ,  $r^2 = 0.51$ ,  $P < 0.001$ ) when sites with MAP > 1200 mm (BER, KRE, MIT, SON) were excluded from the regression analysis (Fig. 2). The relationship indicates that the diluting effect through rising precipitation on mean DOC concentration is limited at a maximum of about 1200 mm.

Mean annual DOC fluxes varied between 156 and 401 kg C ha<sup>-1</sup> yr<sup>-1</sup> in 0 cm and between 8 and 87 kg C ha<sup>-1</sup> yr<sup>-1</sup> in 20–30 cm depth (Table 3). Thus, average DOC flux was reduced by 227 kg C ha<sup>-1</sup> yr<sup>-1</sup> or 87% in topsoils. Neither temperature nor precipitation had a significant effect on DOC fluxes at both depths. Nevertheless, precipitation seems to have an offsetting effect on the variation of DOC concentrations in 0 cm among the forest stands as the variation of DOC fluxes was small



**Fig. 2** Relationship between mean DOC concentrations in the subsoil and mean annual precipitation of 22 forest sites. Sites with MAP > 1200 mm (open circles) were excluded from linear regression.

compared with those of DOC concentrations. In the mineral soil, however, variations of DOC concentrations and fluxes were relatively large.

DOC fluxes in the subsoil varied between 1 and 46 kg C ha<sup>-1</sup> yr<sup>-1</sup> representing an average net retention of 20 kg C ha<sup>-1</sup> yr<sup>-1</sup> between the topsoil and subsoil. MAT had a small negative but significant effect on DOC fluxes ( $y = -5.2x + 50.3$ ,  $r^2 = 0.23$ ,  $P < 0.05$ ) (Fig. 3a). Increasing MAP enhanced DOC fluxes (Fig. 3b), but again the relationship was rather weak ( $y = 0.02x - 6.1$ ,  $r^2 = 0.29$ ,  $P < 0.05$ ). The relationship was weakened by high DOC fluxes in pine stands with sandy soil texture (ALT, DIN, PEG) and a beech stand with silt loam texture (EBR). Sandy textures allowed rapid movement of soil water, and thus, enhanced DOC export at ALT, DIN and PEG whereas the DOC export at EBR was exceptionally great as a result of weak DOC retention in the topsoil. Exclusion of these four sites strongly improved the relationship between mean annual DOC flux and MAP ( $y = 0.03x - 16.7$ ,  $r^2 = 0.60$ ,  $P < 0.001$ ). A slightly stronger relationship was found between DOC flux and elevation ( $y = 0.03x - 8.8$ ,  $r^2 = 0.63$ ,  $P < 0.001$ ) after the same sites (ALT, DIN, PEG, EBR) were excluded (Fig. 3c).

#### *Effects of tree species and organic layer on DOC concentrations and fluxes*

DOC concentrations in leachates from organic layers were highest under pine ( $68 \pm 13$  mg CL<sup>-1</sup>) followed by oak ( $52 \pm 11$  mg CL<sup>-1</sup>), spruce ( $45 \pm 15$  mg CL<sup>-1</sup>) and beech ( $33 \pm 11$  mg CL<sup>-1</sup>) (Fig. 4a). The relative differences of DOC concentrations among the tree species (ratio of (DOC/MAP)<sub>spruce, oak, beech</sub>:(DOC/MAP)<sub>pine</sub>) were even greater per mm precipitation: pine (1.0) > oak (0.81) > spruce (0.49) > beech (0.40). In other words, average DOC concentrations would be 2.5 times greater under pine than under beech at same MAP. As a result of tree species and litter quality, the humus form

**Table 3** Annual DOC fluxes (mean  $\pm$  SD, in  $\text{kg ha}^{-1}\text{yr}^{-1}$ ), trends of monthly DOC fluxes per year ( $\text{kg ha}^{-1}\text{mth}^{-1}\text{yr}^{-1}$ ) and corresponding *P*-values below the organic layer (0 cm), in the top mineral soil (20–30 cm) and the subsoil (60–140 cm) of 22 study sites

Site	Organic layer			Topsoil			Subsoil		
	Flux	Trend	<i>P</i> -value	Flux	Trend	<i>P</i> -value	Flux	Trend	<i>P</i> -value
ALT	258 $\pm$ 111	0.50	ns	21.4 $\pm$ 4.2	−0.03	ns	23.1 $\pm$ 16.2	0.02	ns
AOE	259 $\pm$ 104	1.49	0.01	16.3 $\pm$ 8.0	0.02	ns	2.7 $\pm$ 2.1	0	ns
BBR	199 $\pm$ 67	0	ns	9.7 $\pm$ 2.7	0	ns	10.3 $\pm$ 3.7	0	ns
BER	165 $\pm$ 65	0.81	0.01	61 $\pm$ 8.0	−0.03	ns	34 $\pm$ 15.3	−0.17	ns
BOD	278 $\pm$ 111	0.38	ns	81.6 $\pm$ 37.5	0.34	0.03	6.1 $\pm$ 2.2	0	ns
DIN	288 $\pm$ 81	0.62	ns	19.5 $\pm$ 4.1	0.02	ns	14.9 $\pm$ 5.7	0	ns
EBE	289 $\pm$ 98	0.42	ns	29.2 $\pm$ 12.4	−0.14	0.09	7.1 $\pm$ 5.9	−0.03	ns
EBR	215 $\pm$ 75	0.78	0.08	87.4 $\pm$ 30.0	0.09	ns	23.9 $\pm$ 10.5	0	ns
FLO	156 $\pm$ 57	0.32	ns	12.7 $\pm$ 5.4	0.00	ns	12.2 $\pm$ 6.7	−0.01	ns
FRE	235 $\pm$ 63	0.78	0.07	29.4 $\pm$ 42.7	−0.02	ns	4.6 $\pm$ 1.9	0	ns
GOL	294 $\pm$ 176	0.17	ns	39.1 $\pm$ 19.7	0.07	ns	17.3 $\pm$ 8.3	0.01	ns
KRE	381 $\pm$ 111	1.38	ns	53.3 $\pm$ 23.3	−0.11	ns	18.5 $\pm$ 4.9	−0.06	ns
LAN	194 $\pm$ 42	0.31	ns	30.6 $\pm$ 58.0	0.00	ns	6.8 $\pm$ 6.8	0	ns
MIT	226 $\pm$ 70	−0.02	ns	11.9 $\pm$ 3.0	0.02	ns	10.1 $\pm$ 4.5	−0.03	ns
PEG	283 $\pm$ 89	0.39	ns	81.8 $\pm$ 33.0	0.16	ns	32.9 $\pm$ 24.1	0	ns
RIE	186 $\pm$ 38	0.38	0.05	12.3 $\pm$ 0.9	−0.03	ns	3.1 $\pm$ 2.7	0.03	NA
ROK	401 $\pm$ 146	0.99	ns	30.6 $\pm$ 9.8	0.09	ns	8.5 $\pm$ 0.6	−0.02	ns
ROT	363 $\pm$ 126	1.03	0.08	12.8 $\pm$ 4.4	−0.08	0.05	5.2 $\pm$ 2.3	−0.02	ns
SOG	219 $\pm$ 41	−0.24	ns	14.7 $\pm$ 9.5	−0.03	ns	6.2 $\pm$ 1.7	−0.03	0.01
SON	395 $\pm$ 120	0.64	ns	73.8 $\pm$ 25.5	0.30	0.01	46.7 $\pm$ 32.9	−0.19	0.05
WUE	261 $\pm$ 71	0.87	0.05	7.6 $\pm$ 1.8	0.01	ns	6.3 $\pm$ 3.3	−0.01	ns
ZUS	200 $\pm$ 73	0.02	ns	5.3 $\pm$ 2.8	0.01	ns	0.7 $\pm$ 0.7	0	ns

NA, *P*-value was not estimated; ns, not significant.

also had a significant effect on DOC concentrations (Fig. 4b). Pine forests with mor exhibited a mean DOC concentration of  $68 \text{ mg C L}^{-1}$  whereas moder and mull were not statistically different. The C/N ratio of the organic layer was positively correlated with mean DOC concentration ( $y = 2.28x - 12.9$ ,  $r^2 = 0.31$ ,  $P < 0.01$ ) (Fig. 4c), indicating that increasing N availability reduces DOC concentration in soil solution from organic layers.

Tree species partly explained the variation in DOC fluxes of organic layer leachates as spruce ( $297 \pm 91 \text{ kg C ha}^{-1}\text{yr}^{-1}$ ) and pine stands ( $277 \pm 13 \text{ kg C ha}^{-1}\text{yr}^{-1}$ ) had higher fluxes than oak ( $251 \pm 82 \text{ kg C ha}^{-1}\text{yr}^{-1}$ ) and beech stands ( $219 \pm 13 \text{ kg C ha}^{-1}\text{yr}^{-1}$ ). In the mineral soil, the order was different and pine stands had on average the largest DOC fluxes of  $51 \pm 35 \text{ kg C ha}^{-1}\text{yr}^{-1}$  at 20–30 cm and of  $19 \pm 35 \text{ kg C ha}^{-1}\text{yr}^{-1}$  in the subsoil. Lowest fluxes occurred in the oak stands with  $16 \pm 10 \text{ kg C ha}^{-1}\text{yr}^{-1}$  at 20–30 cm and  $5 \pm 2 \text{ kg C ha}^{-1}\text{yr}^{-1}$  below the rooting zone.

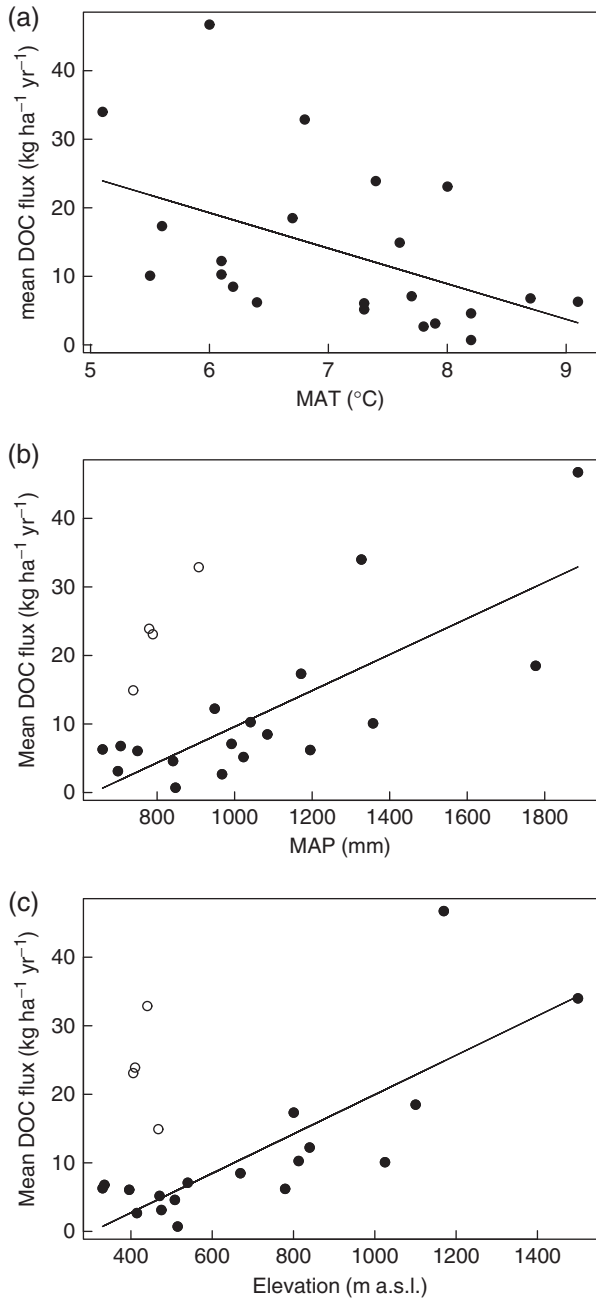
#### Long-term trends of DOC concentrations

DOC concentrations in 0 cm soil depth significantly increased by 0.5 to  $3.1 \text{ mg C L}^{-1}$  per year in 12 of 22 forest sites between 1995 and 2008 (Fig. 5). Further,

three sites (EBR, KRE, ROK) had a significant turning point in the trend between 2002 and 2006, indicating a significant increase in DOC concentrations afterwards (Fig. 6). At these 15 sites, mean DOC concentrations increased between 12% (ROT) and 99% (AOE) comparing the first 3 years with the last 3 years of the respective sampling periods. The strength of positive DOC trends (0 and 20–30 cm) was linearly correlated with mean DOC concentrations ( $y = 0.038x - 0.070$ ,  $r^2 = 0.77$ ,  $P < 0.001$ ) (Fig. 7). Thus, the initial DOC concentrations had a prominent effect on the DOC trends.

Significant DOC trends ( $P < 0.01$ ) were best explained by decreasing  $\text{SO}_4^{2-}$  trends ( $y = -1.49x - 0.38$ ,  $r^2 = 0.96$ ,  $P < 0.01$ ) in some cases (Fig. 8). However, the relationship was not significant when GOL and FLO were included in the regression analysis. These two sites had the strongest negative trends in  $\text{SO}_4^{2-}$  concentrations. Both sites, located in the north-east of Bavaria, were subjected to extreme high atmospheric inputs of  $\text{SO}_4^{2-}$  (data not shown). Relationships between DOC trends and significant trends of other parameters were either not significant or less significant (ionic strength, charge balance, nitrate, pH).

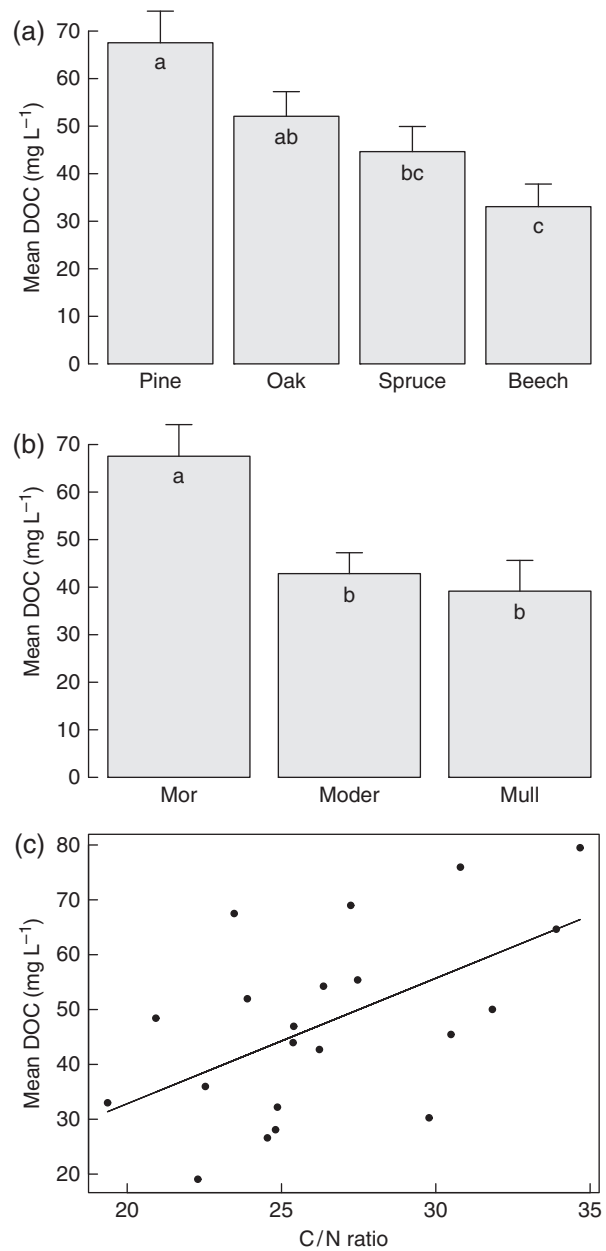
No changes in DOC concentrations were observed for seven sites representing five broadleaf stands (LAN,



**Fig. 3** Relationship between mean annual DOC fluxes in the subsoil and (a) mean annual air temperature, (b) mean annual precipitation and (c) elevation of 22 forest sites. Sites with open circles were excluded from linear regression.

MIT, RIE, SOG, WUE) and two coniferous stands (DIN, ZUS). The level of DOC concentrations in the spruce stand at ZUS were likely affected by a windthrow. While  $\text{SO}_4^{2-}$  concentrations decreased at all sites, DOC concentrations of these stands were controlled by other or additional factors.

Trends of DOC concentrations in the top mineral soil were generally not significant (Fig. 5). Three stands



**Fig. 4** Effect of (a) of tree species, (b) humus form and (c) C/N ratio of the organic layer on mean DOC concentration in 0 cm soil depth.

(BOD, PEG, SON) were characterized by rising DOC concentrations in 0 and 20 cm depth. Opposite DOC trends in the range of  $-0.08$  to  $-0.37 \text{ mg C L}^{-1} \text{ yr}^{-1}$  occurred in the deeper mineral soil (60–140 cm) of 8 sites (Fig. 5). In contrast to 0 cm depth, DOC trends in the mineral soil of all depths were more negative at high mean DOC concentrations ( $y = -0.05x - 0.03$ ,  $r^2 = 0.57$ ,  $P < 0.001$ ) (Fig. 9). Interestingly,  $\text{SO}_4^{2-}$  concentrations decreased in most of these sites, but the strong  $\text{SO}_4^{2-}$  trends of  $-0.1$  (KRE) to  $-2.5 \text{ mg L}^{-1} \text{ yr}^{-1}$  (RIE) and



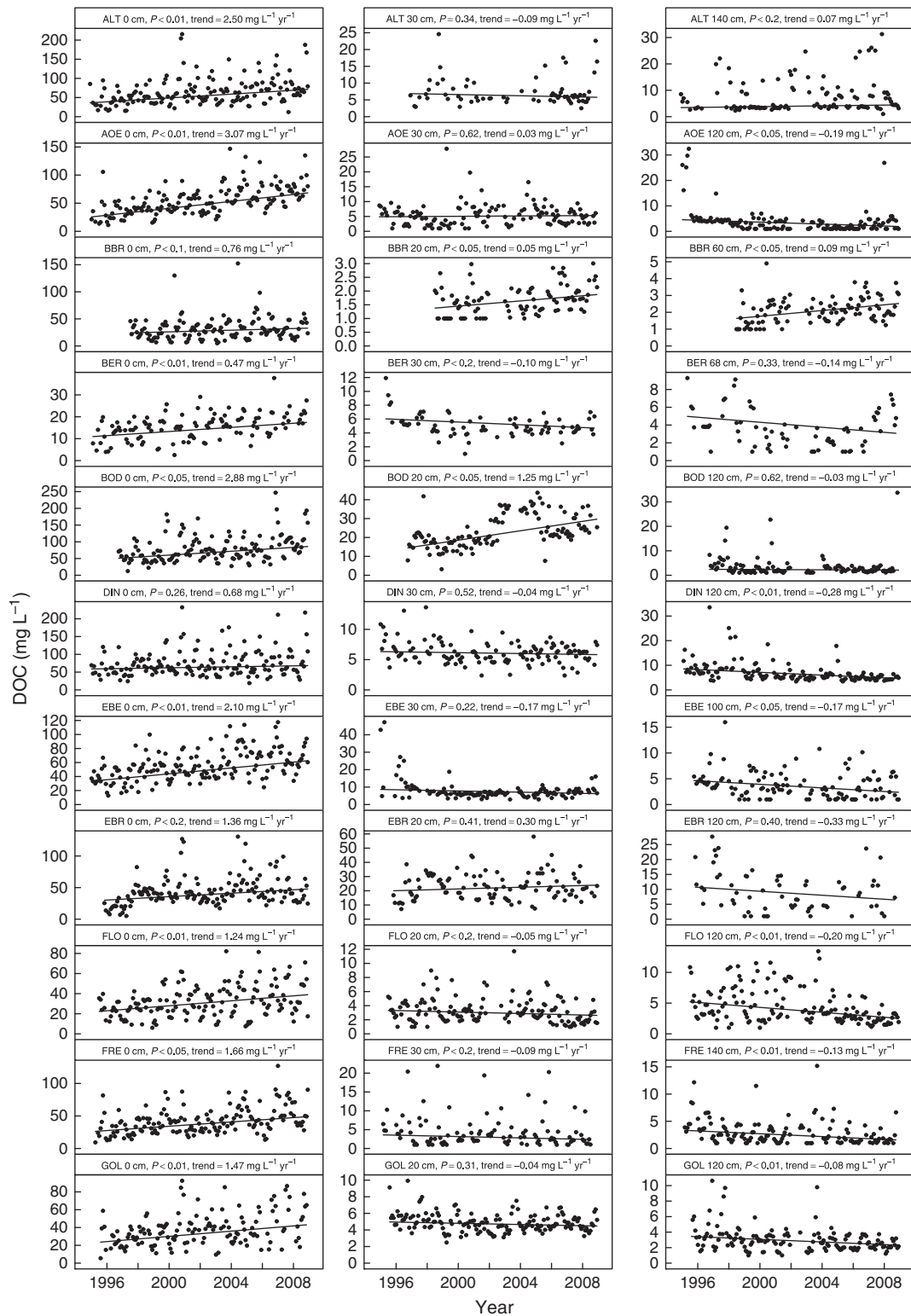


Fig. 5 Time series of monthly DOC concentrations in three different soil depths of 22 forest sites. Scales for DOC concentrations vary with soil depth.

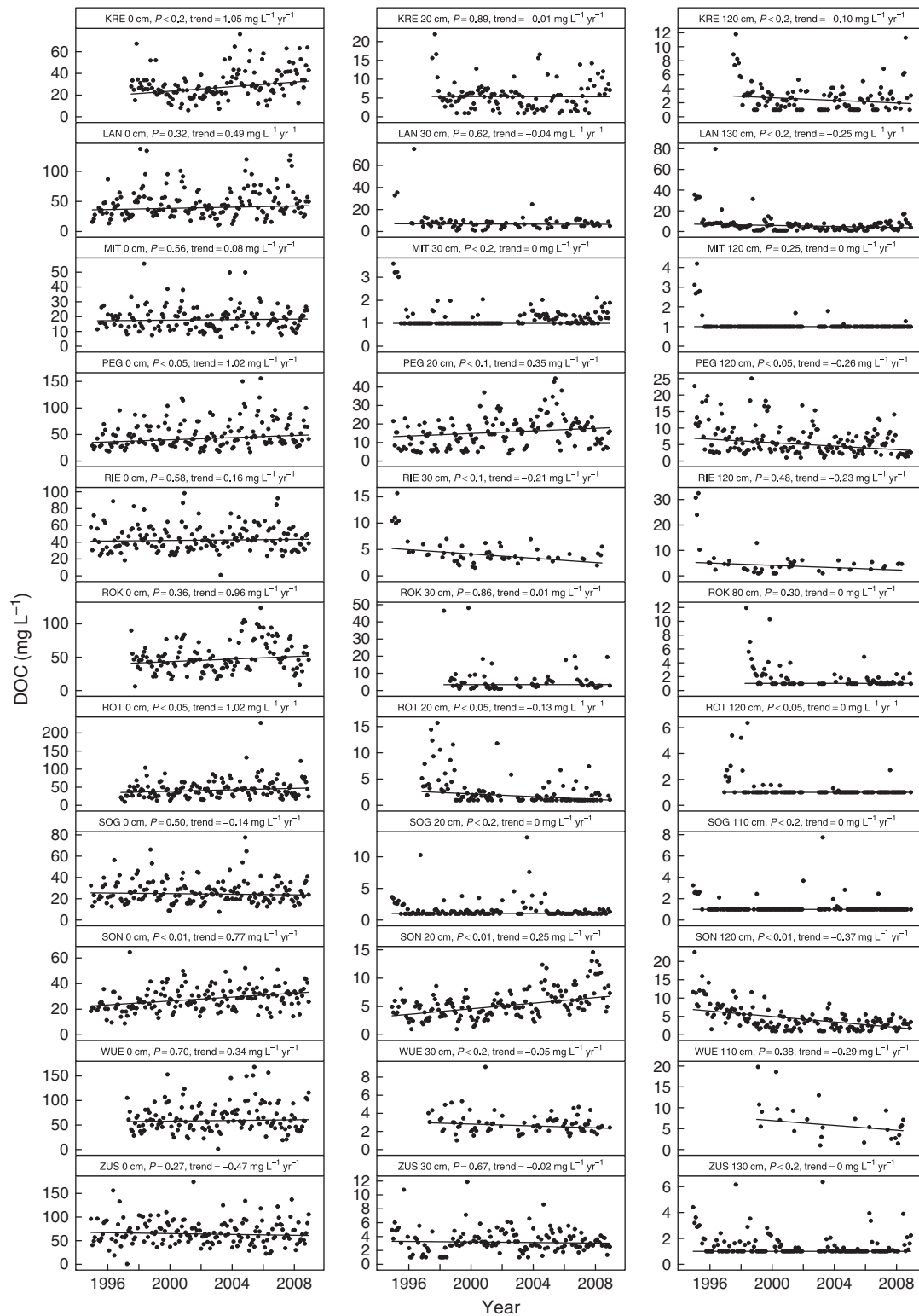
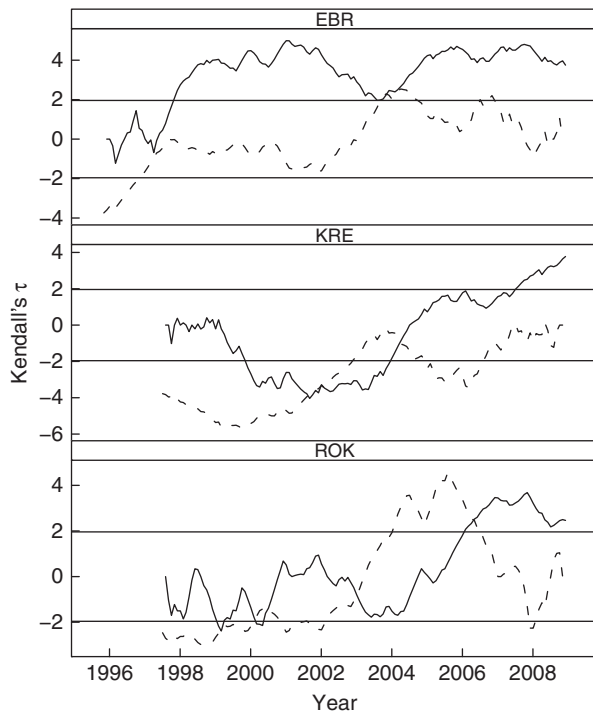


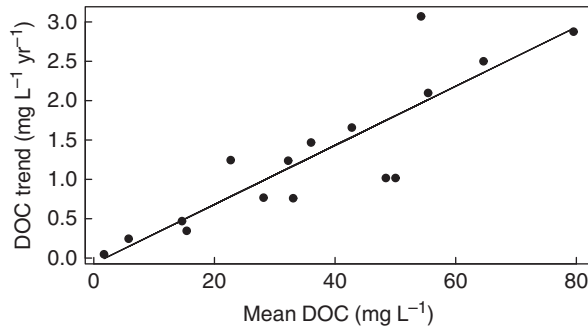
Fig. 5 Continued.

rather weak DOC trends were not correlated. Hence, DOC trends in the mineral soil were triggered by other mechanisms than in 0 cm depth. At the few sites with

elevated Al concentrations (Al > 1.5 mg L<sup>-1</sup>) the best fit was obtained between negative DOC and negative Al trends ( $y = 0.69x + 0.002$ ,  $r^2 = 0.71$ ,  $P < 0.05$ ) (Fig. 10),



**Fig. 6** Study sites with significant turning points in the time series of monthly DOC concentrations in 0 cm soil depth. Results of the sequential Mann-Kendall test: straight lines represent the threshold levels of  $\tau \pm 1.96$ . The solid line represents the progressive and the dashed line the regressive application of the test. Crossing points of the two curves outside the range between  $-1.96$  and  $1.96$  indicate significant turning points.

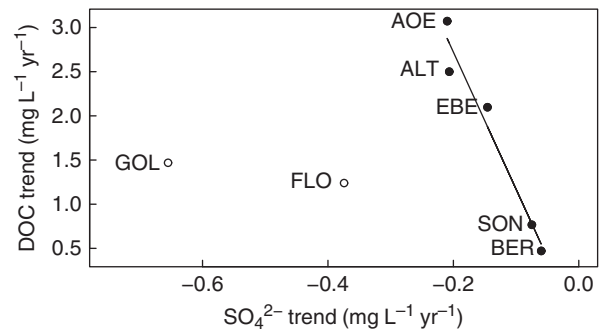


**Fig. 7** Relationship between positive significant DOC trends ( $P < 0.10$ ) and mean monthly DOC concentration in 0 and 20–30 cm soil depth.

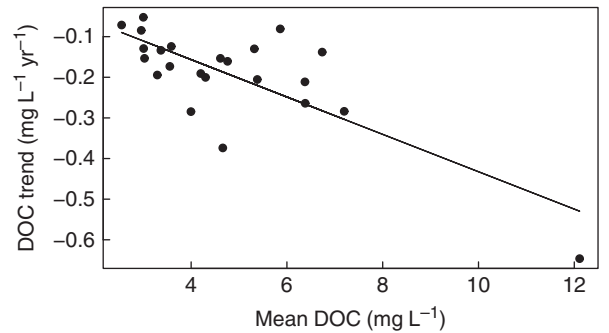
indicating that Al concentration partly controlled DOC concentration in mineral soil solution or vice versa.

*Long-term trends of DOC fluxes*

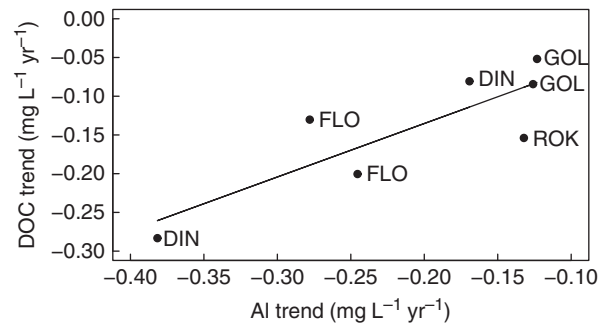
The seasonal Mann-Kendall test revealed significant positive trends for monthly DOC fluxes in organic layers at seven forest sites (Table 3). DOC fluxes of these sites



**Fig. 8** Relationship between significant DOC trends ( $P < 0.01$ ) and significant  $\text{SO}_4^{2-}$  trends in soil solution from 0 cm depth.



**Fig. 9** Relationship between negative significant DOC trends ( $P < 0.10$ ) and mean monthly DOC concentrations in the mineral soil.



**Fig. 10** Relationship between significant DOC trends ( $P < 0.10$ ) and significant Al trends ( $P < 0.10$ ) in soil solution for sites with Al concentrations  $> 1.5 \text{ mg L}^{-1}$  in the mineral soil.

increased in the range of  $0.38$  to  $1.49 \text{ kg ha}^{-1} \text{ month}^{-1} \text{ yr}^{-1}$ . With three exceptions, the slopes although not significant were positive for the other sites. The negative slope at SOG ( $-0.24 \text{ kg ha}^{-1} \text{ month}^{-1} \text{ yr}^{-1}$ ) coincided with an average decrease in water flux ( $-3.2 \text{ mm yr}^{-1}$ ).

The slopes for DOC fluxes in the top mineral soil were weaker and inconsistent. Two sites (BOD, SON) had significant positive trends and two sites (EBE, ROT) had significant negative trends (Table 3). In the sub-

soil, only two sites (SOG, SON) had significant negative trends of  $-0.03$  and  $-0.19 \text{ kg ha}^{-1} \text{ month}^{-1} \text{ yr}^{-1}$ . The site SON had the greatest mean DOC flux ( $46.7 \text{ kg ha}^{-1} \text{ yr}^{-1}$ ) of all sites and a significant, negative trend in DOC concentration (Fig. 5). Interestingly, although not significant, most other sites exhibited no or negative trends of DOC fluxes in the subsoil.

## Discussion

### *Effects of climate parameters on site-to-site variation*

In view of temporal trends it is of relevance that DOC was sampled and measured using uniform methods and during approximately the same time period at all sites. Hence, the considerable variation of long-term mean DOC concentrations and fluxes among the forest sites can be attributed to differences in site characteristics. Similar ranges, vertical gradients and site-to-site variations were reported for other temperate forests (e.g., Buckingham *et al.*, 2008; Michalzik *et al.*, 2001; Wu *et al.*, 2010). Our results suggest that climatic factors, tree species and humus form control DOC concentrations and to a lesser extent DOC fluxes in organic layer leachates. However, most of these factors have little or no clear influence on DOC concentrations and fluxes in the mineral soil.

The positive correlation between MAT and mean annual DOC concentrations in organic layer leachates possibly reflects a direct effect of temperature on biological processes that are involved in the production of DOC. This is consistent with the results of several studies who reported a positive influence of temperature on the seasonal pattern of DOC concentrations (e.g., Kaiser *et al.*, 2001; Solinger *et al.*, 2001; Dawson *et al.*, 2008; Schulze *et al.*, 2011). Moderate temperature sensitivities expressed as  $Q_{10}$  values of 1.5 ( $3\text{--}10^\circ\text{C}$ ) and 2.0 ( $10\text{--}20^\circ\text{C}$ ) were calculated for DOC production in incubated forest floor from red spruce forests (Gödde *et al.*, 1996). However, the effect of temperature on DOC concentration at the site scale remains unclear as it controls the microbial decay of DOC and interacts with soil moisture. Further, temperature indirectly affects DOC production through its influence on plant productivity and soil properties. In a data analysis of different forest sites, there was no relationship between temperature and DOC concentrations in forest floor leachates likely because of interactions with other factors (Michalzik *et al.*, 2001).

The decrease of DOC concentrations in solutions from the organic layer and the subsoil with increasing MAP indicates that infiltrating water diluted the DOC concentration. Surprisingly, DOC concentrations in the interlayer at 20–30 cm depth were not correlated with

MAP. Given the variation of soil types and soil minerals we assume that the differences in the sorption capacity for DOC obscured the influence of MAP on DOC concentration at this soil depth. The strong influence of soil minerals on DOC sorption was shown by Kaiser *et al.* (1996) for many forest soils.

In terms of organic layers, Wu *et al.* (2010) found a similar relationship between DOC concentrations and MAP for coniferous forests in Norway. However, an impact of MAP on DOC fluxes from organic layers cannot be generalized on the regional scale. While DOC fluxes from the organic layer did not increase with rising MAP at our sites and in coniferous forests of Finland (Lindroos *et al.*, 2008), Schmidt *et al.* (2010) reported a positive relationship between DOC fluxes and MAP, considering a precipitation gradient about 500–5000 mm. Despite these differences, it is obvious that infiltrating water has not only a diluting effect, but increases the production of DOC in organic layers. Isotope studies demonstrated that throughfall DOC and fresh litter made a minor contribution to DOC leachates from organic layers, in particular from the Oa horizon (Fröberg *et al.*, 2007; Schulze *et al.*, 2011).

Perhaps one of the most important results of this study is the significant effect of MAP or elevation on DOC fluxes in the subsoil. After exclusion of four sites with an above-average ratio of DOC output to MAP, both relationships indicate that DOC output from the forest soils increases by  $3 \text{ kg ha}^{-1} \text{ yr}^{-1}$  when MAP increases by 100 mm or when elevation rises by 100 m. If this holds true, DOC output will be affected by changes in precipitation whereas rising temperatures will have little impact. Hence, groundwater quality in forested areas could be altered in one or the other direction by changes in precipitation. Considering the remaining four sites, it should be noted that the flow patterns in soils may have a strong effect on the DOC:MAP ratio. Three of the excluded sites have sandy soils, probably with rapid water movement, and exceptionally great DOC fluxes considering MAP.

### *Effects of tree species and organic layer on site-to-site variation*

The effect of tree species on DOC concentrations and fluxes below organic layers is superimposed by MAP and MAT. Pine and oak stands mostly grow in regions with higher temperature and receive less precipitation than spruce and beech stands. These confounding climatic effects are evident from the comparison of DOC concentrations and fluxes. For example, mean DOC concentrations of pine stands are greater than those of spruce stands, but the order of DOC fluxes is reverse, i.e. spruce > pine. When all tree species would grow under

same climatic conditions, DOC fluxes would be of same order as DOC concentrations. Lindroos *et al.* (2008) also found on average slightly greater DOC fluxes at 5 cm depth in spruce forests than in pine forests. Our results suggest that organic layers of coniferous trees produce more DOC than those of deciduous trees. In particular, beech forests were characterized by small DOC concentrations and fluxes. Whether our finding can be generalized for temperate regions remains unclear as Michalzik *et al.* (2001) found no effect of tree species on DOC fluxes. Strong variations among different forest types with no recognizable effect of tree species were also reported by Buckingham *et al.* (2008).

The tree species effect at our sites could result from differences in humus form and in organic matter composition. We partly attribute the high DOC concentrations in the pine and spruce stands to the humus form and the respective thickness of the organic layers. Mor occurred only in the pine stands and moder was with one exception the dominating humus form of spruce forests. It seems that the release of DOC increases with the thickness of the Oa horizon because infiltrating water has more contact and longer contact time to organic matter surfaces. As mentioned before, the Oa horizon makes the largest contribution to DOC leachates from organic layers of spruce forests. In deciduous forests with mull and moder, leachates from the Oe and/or Oi horizon must play the prominent role.

The chemical composition and degradability of organic matter is perhaps of greater importance for DOC concentrations and fluxes as the differences among the spruce and pine or oak and beech stands cannot be explained by the humus form alone. Despite similar humus forms (mull and moder) and less precipitation in the oak stands, DOC concentrations and fluxes were greater under oak than under beech. A laboratory study by Strobel *et al.* (2001) demonstrated that DOC concentrations were highest in organic layers from Norway spruce compared with oak, grand fir and beech, though the concentrations were partly inconsistent within the same tree species. Unlike the differences in the decomposition rate of litter, the chemical composition of DOC was similar for these tree species (Strobel *et al.*, 2001). Only small differences were found with respect to the degradability and chemical composition of DOC in leachates from the Oe and Oa horizons of birch, spruce and pine stands (Kiiikkilä *et al.*, 2006). The differences were remarkable for the litter layer, but the stock is too small compared with the Oe and Oa horizons.

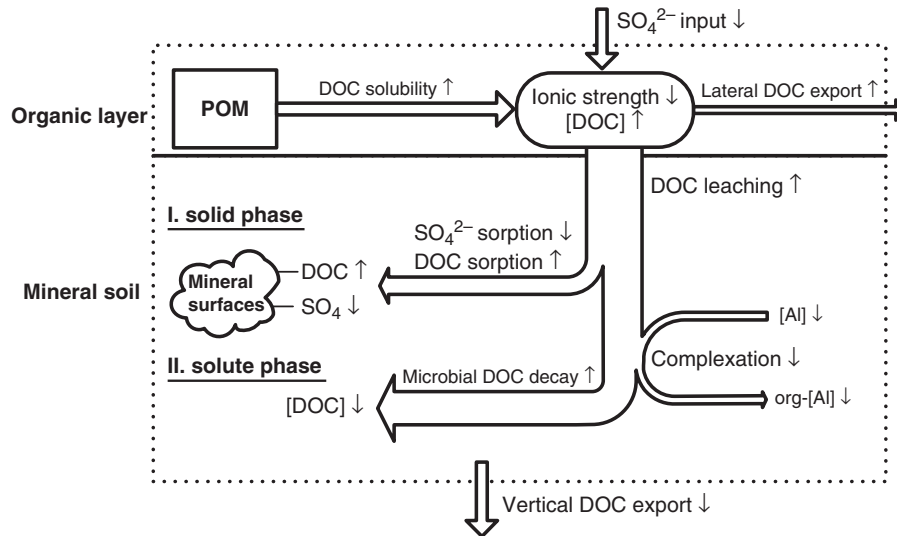
The N availability in organic layers is another factor that could affect DOC concentrations and fluxes. Our results suggest that DOC concentrations decrease with increasing N availability as indicated by the C/N ratios. This is in line with Michel *et al.* (2006) who found

decreasing DOC release from incubated Oa material with decreasing C/N ratio. However, we cannot exclude that the rather weak relationship between DOC concentrations and C/N ratios is skewed by the influence of the humus form or other site factors. The Oi, Oe and Oa horizons have different C/N ratios, and thus, it is problematic to compare average C/N ratios of mull or moder with raw humus. Nonetheless, our result is consistent with results from N fertilization experiments that rising N deposition has no direct relevance for DOC export from soils (Evans *et al.*, 2008).

On average, 87% and 95% of DOC from the organic layers were retained in the top 20–30 cm of the mineral soils and in the underlying subsoils, respectively. Because of the strong retention it is unlikely that tree species have measurable effects on DOC fluxes in mineral forest soils. According to Neff & Asner (2001), hydrology and sorption play the dominant role in regulating DOC losses from terrestrial ecosystems.

#### *Temporal trends of DOC*

Increasing DOC concentrations in surface waters have been reported from many temperate and boreal regions of the northern hemisphere (e.g., Driscoll *et al.*, 2003; Evans *et al.*, 2005; Erlandsson *et al.*, 2008; Oulehle & Hruska, 2009). Several hypotheses have been proposed, but the causes for positive DOC trends are complex given the variety of internal and external factors that control the export of DOC from terrestrial ecosystems (Roulet & Moore, 2006). Recent analyses of DOC trends suggest that the decline of atmospheric deposition is the major driver of increasing DOC concentrations in regions which previously experienced high loads of sulfate or sea salt (Monteith *et al.*, 2007; Clark *et al.*, 2010). In agreement with their findings, the positive trends of DOC concentrations below the organic layer reflect the recovery of forest soils from high loads of sulfuric acid deposition. Here, sulfate trends played a dominant role in soil solution chemistry as concentrations significantly decreased in 21 of 22 forest sites (data not shown). Consequently, sulfate was with few exceptions the only parameter that was correlated with DOC trends. Other studies suggest that changes in the acid–base status of soils as well as ionic strength, pH or charge balance of soil solutions affect DOC solubility in soils (Hruska *et al.*, 2003; Vuorenmaa *et al.*, 2006; De Wit *et al.*, 2007). Reduced input of sulfuric acid may affect the solubility of organic matter through two processes: (1) a decrease in the ionic strength of soil solution and (2) an enhanced dissociation of organic acids (Clark *et al.*, 2006). We assume that the first process largely controlled the DOC solubility at our sites, but we cannot exclude that



**Fig. 11** Conceptual model for opposite changes of DOC concentrations in solutions from the organic layer and the mineral soil. Arrows indicate increasing (↑) or decreasing (↓) process rates, fluxes, concentrations or bindings of DOC, sulfate and aluminum ions.

the latter process also contributed to the increased DOC solubility (Fig. 11).

After a long period of high deposition rates, the input of sulfate strongly decreased in Central Europe beginning in the late 1980s – some years before monitoring of DOC at our sites. This time lag may explain that the DOC trends were generally positive, but not significant at all forest sites. We assume that the response of DOC to decreasing sulfate deposition is site specific as three sites had turning points towards increasing DOC concentrations between 2002 and 2006. This site specific behavior in terms of DOC trends may be attributed to the history of deposition, water fluxes, level of DOC concentrations and soil properties including sulfur stocks. Forest soils have accumulated large amounts of deposited sulfur in organic and inorganic binding forms. Mineralization of organic sulfur as well as desorption of inorganic sulfate represent continuing sources of dissolved sulfate that delays the recovery process of acidified forest soils (Mörth *et al.*, 2005). Because of long-lasting sulfur retention in forest soils the trends of sulfate deposition and sulfate concentrations in soil solution are temporally decoupled (Prechtel *et al.*, 2001). The output of sulfate in forested catchments, however, still exceeds the input of sulfate by deposition as a result of slow mineralization rates of organic sulfur compounds in soils (Mörth *et al.*, 2005; Watmough *et al.*, 2005). In terms of organic layers, we expect no further increase of DOC mobilization in Central European forests because sulfate deposition has reached a low level in past years.

In contrast to leachates from organic layers, trends of DOC concentrations in the mineral soils were inconsis-

tent. Nevertheless, both the positive and negative trends may be explained by decreasing acid deposition. Increasing DOC concentration in the top mineral soils could result from rising DOC input that was leached from organic layers. The sorption capacity of the top mineral soil was likely limited, hindering complete retention of rising DOC inputs. We argue that mineral soils with negative DOC trends generated additional sorption capacity for DOC as presented in the conceptual model (Fig. 11). Accordingly, the adsorption of DOC by Fe/Al oxides and hydroxides increases due to the shift in the competition between DOC and sulfate for binding sites. In other words, decreasing sulfate concentrations by reduced sulfate input and continuing desorption of sulfate enhance the adsorption of DOC, despite rising DOC inputs. Negative DOC trends in the mineral soil were also reported for coniferous forests in Norway for the period between 1996 and 2006 and DOC concentrations were negatively correlated with sulfate and chloride concentrations (Wu *et al.*, 2010). We speculate that the negative DOC trends in the mineral soil will continue as long as the output of sulfate is greater than the input of sulfate.

In a laboratory experiment, where solute sulfate was added to B horizons of forest soils, the retention of DOC was reduced as a result of competing DOC and sulfate ions for adsorption sites (Guggenberger & Zech, 1992). Sorption isotherms indicate a greater affinity of spodic horizons for DOC than for sulfate (Vance & David, 1992) suggesting that the ratio of DOC/sulfate affected the retention and vertical pattern of DOC and sulfate concentrations in our soils. According to Zech *et al.* (1994), competition of DOC with sulfate is one of three mechanisms that increased DOC output from the B

horizons of acidified forest soils. The other two mechanisms are loss of Al and Fe oxides/hydroxides due to buffering processes and elevated DOC release from the forest floor.

Our results suggest that decreasing concentrations of Al ions contributed to decreasing DOC concentrations in the mineral soil. A greater fraction of DOC could be decomposed by microorganisms as decreasing Al concentrations could lessen the stabilization of DOC through complexation with Al ions (Fig. 11). The microbial decay of DOC is partly controlled by the Al/DOC ratio (Schwesig *et al.*, 2003). In their laboratory study, mineralization of DOC was reduced by up to 50% when the Al/DOC ratio was increased to 0.1. However, the role of Al ions for the stabilization of DOC against microbial attack is still unclear under natural conditions. Other factors such as the pH of solution (Scheel *et al.*, 2008), the type of minerals and the composition of soil solution (Mikutta *et al.*, 2007) influence the stability and availability of DOC, and thus, concentrations and fluxes of DOC in mineral soils.

## Conclusions

Climate and tree species are the most important factors of site-to-site variation of DOC concentrations and fluxes in temperate forests. Increasing precipitation increases leaching of DOC from organic layers whereas increasing temperature has an opposite effect. Considering climatic effects, coniferous forests produce more DOC in organic layers than deciduous forests which is associated with the humus form and thickness of the organic layer. Tree species has minor effects on DOC concentrations and fluxes in mineral soils as the composition of minerals and the thickness of mineral soil horizons control the fate of DOC.

Concentrations and partly fluxes of DOC increased in leachates from the organic layer of forest soils following strong reductions of acidic deposition in Central Europe. Changes in sulfate concentration and ionic strength are the main drivers of increased solubility of organic matter. Opposite trends of DOC in the organic layer and the mineral soil seem to be contradictory at first, however, they become reasonable when considering internal soil processes. In the mineral soils, the decrease of acidic deposition and associated changes of soil solution chemistry had no effect or resulted in decreasing DOC concentrations. The lack of negative DOC trends at many sites can be explained by the slow recovery of acidified forest soils and the long-lasting release of retained sulfate that competes with DOC for binding places. The adsorption of DOC by mineral soils will slowly increase in the next decades as more binding places become available for DOC. This postulated ne-

gative DOC trend in mineral forest soils will be accompanied by decreasing Al concentrations because of decreasing stabilization by organo-Al complexes and increasing microbial decay of DOC.

Analyses of time lags concerning changes in soil DOC turnover following reductions in sulfate deposition may require long-term monitoring beyond the 12–14 years period of this study. In conclusion, the widely reported increase of DOC in surface waters of forested catchments cannot be attributed to elevated DOC fluxes from mineral soils, but solely to enhanced leaching from organic layers and perhaps from A horizons.

## Acknowledgements

We like to thank Uwe Blum, Sandra Egger, Constanze Hartmann, Ramona Heinbach, Angelika Hiltmann, Irmgard Kern, Elisabeth Rabenbauer, Monika Riedmaier, Elisabeth Solic, and Angela Zipperer of the Central Laboratory from the Bayerische Landesanstalt für Wald und Forstwirtschaft, Freising, for the comprehensive preparation and chemical analysis of soil solutions since establishment of the Level II sites. The monitoring programme was financially supported by the European Union under the contract No 2152/2003 (Forest Focus) until 2006 and afterwards under No 614/2007 (LIFE +).

## References

- Borken W, Xu Y-J, Beese F (2004) Leaching of dissolved organic carbon and carbon dioxide emission after compost application to six nutrient-depleted forest soils. *Journal of Environmental Quality*, **33**, 89–98.
- Bronaugh D, Werner A (2009). Zyp: Zhang + Yue-Pilon trends package. R package version 0.9-1. Available at: <http://CRAN.R-project.org/package=zyp> (accessed May 2010).
- Buckingham S, Tipping E, Hamilton-Taylor J (2008) Concentrations and fluxes of dissolved organic carbon in UK topsoils. *Science of the Total Environment*, **407**, 460–470.
- Clark JM, Bottrell SH, Evans CD *et al.* (2010) The importance of the relationship between scale and process in understanding long-term DOC dynamics. *Science of the Total Environment*, **408**, 2768–2775.
- Clark JM, Chapman PJ, Heathwaite AL, Adamson JK (2006) Suppression of dissolved organic carbon by sulfate induced acidification during simulated droughts. *Environmental Science & Technology*, **40**, 1776–1783.
- Dawson JJC, Soulsby C, Tetzlaff D, Hrachowitz M, Dunn SM, Malcolm IA (2008) Influence of hydrology and seasonality on DOC exports from three contrasting upland catchments. *Biogeochemistry*, **90**, 93–113.
- De Mendiburu F (2010). *Agricolae*: Statistical Procedures for Agricultural Research. R package version 1.0-9. Available at: <http://CRAN.R-project.org/package=agricolae> (accessed May 2010).
- De Wit HA, Mulder J, Hindar A, Hole L (2007) Long-term increase in dissolved organic carbon in streamwaters in Norway is response to reduced acid deposition. *Environmental Science & Technology*, **41**, 7706–7713.
- Driscoll CT, Driscoll KM, Roy KM, Mitchell MJ (2003) Chemical response of lakes in the Adirondack Region of New York to declines in acidic deposition. *Environmental Science & Technology*, **37**, 2036–2042.
- Erlandson M, Buffam I, Fölster J, Laudon H, Temnerud J, Weyhenmeyer GA, Bishop K (2008) Thirty-five years of synchrony in the organic matter concentrations of Swedish rivers explained by variation in flow and sulphate. *Global Change Biology*, **14**, 1191–1198.
- Evans CD, Chapman PJ, Clark JM, Monteith DT, Cresser MS (2006) Alternative explanations for rising dissolved organic carbon export from organic soils. *Global Change Biology*, **12**, 2044–2053.
- Evans CD, Goodale CL, Caporn SJM *et al.* (2008) Does elevated nitrogen deposition or ecosystem recovery from acidification drive increased dissolved organic carbon

- loss from upland soil? A review of evidence from field nitrogen addition experiments. *Biogeochemistry*, **91**, 13–35.
- Evans CD, Monteith DT, Cooper DM (2005) Long-term increases in surface water dissolved organic carbon: observations, possible causes and environmental impacts. *Environmental Pollution*, **137**, 55–71.
- Federer CA (1995) *BROOK90 – A simulation model for evaporation, soil water and stream flow*. Version 3.24, Computer Freeware and Documentation, USDA Forest Service, Durham, New Hampshire, USA.
- Fröberg M, Berggren Kleja D, Hagedorn F (2007) The contribution of fresh litter to dissolved organic carbon leached from a coniferous forest floor. *European Journal of Soil Science*, **58**, 108–114.
- Gerstengarbe FW, Werner PC (1999) Estimation of the beginning and end of recurrent events within a climate regime. *Climate Research*, **11**, 97–107.
- Gödde M, David MB, Christ MJ, Kaupenjohann M, Vance GF (1996) Carbon mobilization from the forest floor under red spruce in the northeastern USA. *Soil Biology & Biochemistry*, **28**, 1181–1189.
- Guggenberger G, Zech W (1992) Retention of dissolved organic carbon and sulfate in aggregated acid forest soils. *Journal of Environmental Quality*, **21**, 643–653.
- Hammel K, Kennel M (2001) *Charakterisierung und Analyse der Wasserverfügbarkeit und des Wasserhaushaltes von Waldstandorten in Bayern mit dem Simulationsmodell Brook90*. Forstliche Forschungsberichte München, 185.
- Hirsch RM, Slack JR, Smith RA (1982) Techniques of trend analysis for monthly water quality data. *Water Resources Research*, **18**, 107–121.
- Hirsch RM, Slack JR (1984) A nonparametric trend test for seasonal data with serial dependence. *Water Resources Research*, **20**, 727–732.
- Hruska J, Kohler S, Laudon H, Bishop K (2003) Is a universal model of organic acidity possible: comparison of the acid/base properties of dissolved organic carbon in the boreal and temperate zones. *Environmental Science & Technology*, **37**, 1726–1730.
- Hruska J, Kram P, McDowell WH, Oulehle F (2009) Increased dissolved organic carbon (DOC) in central European streams is driven by reductions in ionic strength rather than climate change or decreasing acidity. *Environmental Science & Technology*, **43**, 4320–4326.
- ICP Forests (2006) Manual on methodologies and criteria for harmonized sampling, assessment, monitoring and analysis of the effects of air pollution on forests. Federal Research Centre for Forestry and Forest Products (BFH), Hamburg, Germany. Available at: <http://www.icp-forests.org> (accessed September 2010).
- Kaiser K, Guggenberger G, Zech W (1996) Sorption of DOM and DOM fractions to forest soils. *Geoderma*, **74**, 281–303.
- Kaiser K, Guggenberger G, Haumaier L, Zech W (2001) Seasonal variations in the chemical composition of dissolved organic matter in organic forest floor layer leachates of old-growth Scots pine (*Pinus sylvestris* L.) and European beech (*Fagus sylvatica* L.) stands in northeastern Bavaria, Germany. *Biogeochemistry*, **55**, 103–143.
- Kalbitz K, Zuber T, Park JH, Matzner E (2004) Environmental controls on concentrations and fluxes of dissolved organic matter in the forest floor and in soil solution. In: *Biogeochemistry of Forested Catchments in a Changing Environment, Ecological Studies* (ed Matzner E Vol. 172 (pp. 315–337. Springer-Verlag, Berlin.
- Kiikkilä O, Kitunen V, Smolander A (2006) Dissolved soil organic matter from surface organic horizons under birch and conifers: degradation in relation to chemical characteristics. *Soil Biology & Biochemistry*, **38**, 737–746.
- Libiseller C (2002) MULTMK/PARTMK, a program for the computation of multivariate and partial Mann-Kendall test. Available at: <http://www.mai.liu.se/~cllib/welcome/PMKtest.html>, accessed February 2008.
- Lindroos AJ, Derome J, Mustajarvi K, Nojd P, Beuker E, Helmisari HS (2008) Fluxes of dissolved organic carbon in stand throughfall and percolation water in 12 boreal coniferous stands on mineral soils in Finland. *Boreal Environment Research*, **13**, 22–34.
- Lorenz M, Mues V (2007) Forest health status in Europe. *The Scientific World Journal*, **7**, 22–27.
- McLeod AI (2009). Kendall: Kendall rank correlation and Mann-Kendall trend test. R package version 2.1. Available at: <http://CRAN.R-project.org/package=Kendall> (accessed May 2010).
- Michel K, Matzner E, Dignac MF, Kögel-Knabner I (2006) Properties of dissolved organic matter related to soil organic matter quality and nitrogen additions in Norway spruce forest floors. *Geoderma*, **130**, 250–264.
- Michalzik B, Kalbitz K, Park JH, Solinger S, Matzner E (2001) Fluxes and concentrations of dissolved organic carbon and nitrogen – a synthesis for temperate forests. *Biogeochemistry*, **52**, 173–205.
- Mikutta R, Mikutta C, Kalbitz K, Scheel T, Kaiser K, Jahn R (2007) Biodegradation of forest floor organic matter bound to minerals via different binding mechanisms. *Geochimica et Cosmochimica Acta*, **71**, 2569–2590.
- Mörth CM, Torssander P, Kjønaas OJ, Stuanes AO, Moldan F, Giesler R (2005) Mineralization of organic sulfur delays recovery from anthropogenic acidification. *Environmental Science & Technology*, **39**, 5234–5240.
- Monteith DT, Stoddard JL, Evans CD *et al.* (2007) Dissolved organic carbon trends resulting from changes in atmospheric deposition chemistry. *Nature*, **450**, 537–539.
- Mualem Y (1976) A new model for predicting the hydraulic conductivity of unsaturated porous media. *Water Resources Research*, **12**, 513–522.
- Neff JC, Asner GP (2001) Dissolved organic carbon in terrestrial ecosystems: synthesis and a model. *Ecosystems*, **4**, 29–48.
- Oulehle F, Hruska J (2009) Rising trends of dissolved organic matter in drinking-water reservoirs as a result of recovery from acidification in the Ore Mts., Czech Republic. *Environmental Pollution*, **157**, 3433–3439.
- Prechtel A, Alewell C, Armbruster M *et al.* (2001) Response of sulphur dynamics in European catchments to decreasing sulphate deposition. *Hydrology and Earth System Sciences*, **5**, 311–325.
- R Development Core Team (2010). R: A language and environment for statistical computing. R Foundation for Statistical Computing, Vienna, Austria. ISBN 3-900051-07-0. Available at: <http://www.R-project.org> (accessed May 2010).
- Roulet N, Moore TR (2006) Browning the waters. *Nature*, **444**, 283–284.
- Schaber J (2009). Pheno: Auxiliary functions for phenological data analysis. R package version 1.5. Available at: <http://CRAN.R-project.org/package=pheno> (accessed May 2010).
- Scheel T, Jansen B, van Wijk AJ, Verstraten JM, Kalbitz K (2008) Stabilization of dissolved organic matter by aluminium: a toxic effect or stabilization through precipitation? *European Journal of Soil Science*, **59**, 1122–1132.
- Schmidt BHM, Wang CP, Chang SC, Matzner E (2010) High precipitation causes large fluxes of dissolved organic carbon and nitrogen in a subtropical montane *Chamaecyparis* forest in Taiwan. *Biogeochemistry*, **101**, 243–256.
- Schulze K, Borken W, Matzner E (2011) Dynamics of dissolved organic <sup>14</sup>C in throughfall and soil solution of a Norway spruce forest. *Biogeochemistry*, doi: 10.1007/s10533-010-9526-2, in press.
- Schwesig D, Kalbitz K, Matzner E (2003) Effects of aluminium on the mineralization of dissolved organic carbon derived from forest floors. *European Journal of Soil Science*, **54**, 311–322.
- Smolander A, Kitunen V (2002) Soil microbial activities and characteristics of dissolved organic C and N in relation to tree species. *Soil Biology & Biochemistry*, **34**, 651–660.
- Solinger S, Kalbitz K, Matzner E (2001) Controls on the dynamics of dissolved organic carbon and nitrogen in a Central European deciduous forest. *Biogeochemistry*, **55**, 327–349.
- STMELF (2008) *Waldzustandsbericht 2008*. Bayerisches Staatsministerium für Ernährung, Landwirtschaft und Forsten, München.
- Strobel BW, Hansen HCB, Borggaard OK, Andersen MK, Raulund-Rasmussen K (2001) Composition and reactivity of DOC in forest floor soil solutions in relation to tree species and soil type. *Biogeochemistry*, **56**, 1–26.
- Tranvik LJ, Jansson M (2002) Terrestrial export of organic carbon. *Nature*, **415**, 861–862.
- van Genuchten MT (1980) A closed-form equation for predicting the hydraulic conductivity of unsaturated soils. *Soil Science Society of America Journal*, **44**, 892–898.
- Vance GF, David MB (1992) Dissolved organic carbon and sulfate sorption by Spodosol mineral horizons. *Soil Science*, **154**, 136–144.
- Vestreng V, Myhre G, Fagerli H, Reis S, Tarrason L (2007) Twenty-five years of continuous sulphur dioxide reduction in Europe. *Atmospheric Chemistry and Physics*, **7**, 3663–3681.
- Vuorenmaa J, Forsius M, Mannio J (2006) Increasing trends of total organic carbon concentrations in small forest lakes in Finland from 1987 to 2003. *Science of the Total Environment*, **365**, 47–65.
- Watmough SA, Aherne J, Alewell C *et al.* (2005) Sulphate, nitrogen and base cation budgets at 21 forested catchments in Canada, the United States and Europe. *Environmental Monitoring and Assessment*, **109**, 1–36.
- Wu Y, Clark N, Mulder J (2010) Dissolved organic carbon concentrations in throughfall and soil waters at Level II monitoring plots in Norway: short- and long-term variations. *Water, Air & Soil Pollution*, **205**, 273–288.
- Zech W, Guggenberger G, Schulten HR (1994) Budgets and chemistry of dissolved organic carbon in forest soils: effects of anthropogenic soil acidification. *Science of the Total Environment*, **152**, 49–62.