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Dissolved organic matter under native Cerrado and *Pinus caribaea* plantations in the Brazilian savanna

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Abstract. The transformation of native Cerrado into *Pinus caribaea* Morelet plantations changes the DOM dynamics including changed rates of mineralisation, denitrification, and C export to the groundwater. To examine the differences in quantity, temporal dynamics, and quality of DOM between Cerrado and Pine plantations we collected rainfall, throughfall, stemflow, litter leachate (under pine only) and soil solution at 15, 80, and 200 cm depth in weekly intervals during the rainy seasons 1997/98 and 1998/99. We determined total dissolved organic carbon (DOC) concentrations and assessed DOM quality by separating hydrophilic and hydrophobic fractions and by NMR analysis of organic layer extracts. The rainfall had a mean DOC concentration of 2.6 mg L^{-1}. The mean concentrations of DOC in the throughfall of the pine plantations (5.0–10.5 mg L^{-1}) were significantly above those of Cerrado (2.6–4.9 mg L^{-1}). During the first part of the rainy seasons (October–December), the concentrations of DOC in the soil solution (15–200 cm depth) under Cerrado and pine did not differ significantly. During the second part of both rainy seasons (January–April), the concentrations of DOC in the soil solution under Cerrado (4.4–5.1 mg L^{-1}) exceeded those under PI (1.4–2.7 mg L^{-1}). Possible explanations of the latter include higher DOM input into the Cerrado soil and a stronger retention and/or faster mineralisation of the pine DOM than of the Cerrado DOM in the mineral soil. As the structural composition of DOM extracted from the organic layer under Cerrado and pine did not differ significantly, faster mineralisation was the most likely explanation for partly lower DOC concentrations in the soil solution under pine than under Cerrado. This assumption was supported by increasing contributions of hydrophobic DOM to total DOM with increasing depth under pine while, under Cerrado, the DOM composition did not change with depth. The reason for DOM mineralisation under pine was probably the higher N availability because total N concentrations were 11–23 times higher under pine than under Cerrado.

Introduction

Dissolved organic matter (DOM) serves as a link between terrestrial and aquatic ecosystems because of its mobility (Thurman 1985). It is an important carrier of metals (Mokma and Evans 2000) and hydrophobic organic compounds (Murphy and Zachara 1995). Parts of DOM serve as a source of C and energy for microorganisms (Jandl and Sollins 1997). Furthermore, DOM contributes to the cycling and leaching of N, P, and S because these plant nutrients form part of many DOM molecules (Qualls and Haines 1991; Nilsson et al. 2001).

The dynamics of DOM in forests of the temperate regions has been intensively studied (e.g., Cronan and Aiken (1985) and McDowell and Likens (1988), Vance and David (1991)). Generally, the soil organic layers and the mineral topsoils are the most important sources for DOM while most subsoils retain DOM effectively. The highest concentrations and fluxes of DOM usually occur in late summer or autumn (Kalbitz et al. 2000; Michalzik et al. 2001). Few studies have been conducted in tropical regions. Frangi and Lugo (1985) and McDowell and Asbury (1994), McDowell (1998) concluded from their observations in a Puerto Rican rain forest that the DOM dynamics under tropical climate is comparable to that of temperate regions. However, the soils in Puerto Rico were developed from relatively young nutrient-rich volcanic parent material which are not typical for tropical regions with strongly weathered Ultisols and Oxisols such as the Brazilian savanna.

In the Brazilian savanna, open woodland with 15–40% tree canopy cover, the Cerrado, dominates (Goodland 1971; Archibold 1995; Ribeiro and Walter 1998). Under Cerrado vegetation, Lilienfein et al. (2001a) reported lower total organic C (TOC) concentrations (filtered $< $ ca. 1 μm) in the soil solution (ca. 5 mg L^{-1}) between 15 and 200 cm depth than usually found in soils of temperate forests (10–20 mg L^{-1}, Michalzik et al. (2001)). In the course of the agricultural exploration of the Cerrado region during the last three decades, about 2000 km^2 of the Brazilian savanna have been transformed into *Pinus* plantations (Espirito Santo 1995). This resulted in the formation of thick organic layers on top of the mineral soils that may serve as a large source of DOM for the mineral soil (Wilcke and Lilienfein 2002). However, Lilienfein et al. (2001a) even observed lower TOC concentrations in the soil solution under *Pinus* than under Cerrado. Furthermore, TOC concentrations dropped between litter leachate and 15 cm soil depth by a factor of almost 10 which is uncommon for temperate forests where similar DOC concentrations are found in litter leachates and soil solution of the A horizons (Cronan and Aiken 1985; Guggenberger et al. 1998). Thus, there were marked differences in the dynamics of DOC between temperate soils and the studied tropical Oxisols.

The characterisation of the chemical DOM quality might help to elucidate the reasons for the above observations. One common method to assess DOM quality consists of the separation of DOM into hydrophilic and hydrophobic compounds according to the XAD-8 fractionation procedure (Leenheer 1981). Hydrophobic DOM is largely refractory (Qualls and Haines 1992; Boissier and Fontvieille 1993) and tends to sorb effectively to the mineral soil (Qualls and Haines 1991; Kaiser and Zech 1997). Hydrophilic DOM sorbs little to soil (Qualls and Haines 1991; Kaiser and Zech 1997) but is partly prone to microbial degradation (Grøn et al. 1992; Jandl and Sollins 1997).

To improve the understanding of the DOM dynamics in soils under tropical climate and to assess the effects of the transformation of native Cerrado into *Pinus caribaea* plantations we studied the seasonal course of the concentrations of total DOC and hydrophilic and hydrophobic DOM in rainfall, throughfall, stemflow, litter leachates, and soil solution between 15 and 200 cm depth under three replicate

Cerrado and *Pinus caribaea* stands near the Brazilian city of Uberlândia. In addition, we assessed the chemical composition of water-soluble organic matter from Cerrado and pine litter, the major source of DOC in the study soils, by liquid-state ^{13}C nuclear magnetic resonance (NMR) spectroscopy.

Material and methods

Study area

The study area is located southeast of Uberlândia (State of Minas Gerais, about 400 km south of Brasília, Brazil). We selected three spatially separated plots (minimum distance > 300 m) of native savanna (Cerrado, CE) and of *Pinus caribaea* Morelet plantations (PI). The inclination in the area was < 1°. For details on the study area see Lilienfein et al. (2000).

Mean annual temperature in Uberlândia between 1981 and 1990 was 22 °C with only small variations between the coldest (June, July: 19 °C) and the warmest months (February: 24 °C). Mean annual precipitation during this period was 1550 mm with 130 mm during the dry season (May–September) and 1420 mm during the rainy season between October and April (Rosa et al. 1991). Due to ″El Niño″, the dry season 1997 was wetter than in typical years and therefore the soil was moist a the beginning of the study in October 1997. The second monitored rainy season (1998/99) was also different from typical climatic conditions because in February, usually the month with highest rainfall, almost no rain fell.

Details on composition and biomass of the Cerrado vegetation on plot CE1 are given in Lilienfein et al. (2001b). Briefly, the studied typical Cerrado was an open grassland with a 15–40% cover of 3–5 m high trees (Goodland 1971). The tree density at the study site was about 6500 ha^{-1} with only 600 trees ha^{-1} taller than 2 m. All woody plants with one single stem beginning at the soil surface were considered as trees. Dominant tree species in the layer > 2 m were *Pouteria torta* (Mart.) Radlk., *Ouratea spectabilis* (Mart.) Engl., *Roupala montana* Aubl., *Bysonima coccolobifolia* H.B. et K., *Dalbergia miscolobium* Benth., *Kielmeyera coriacea* Mart., and *Caryocar brasiliense* Cambess. These 7 species represented 70% of the biomass in the > 2-m layer. Of the numerous species in the 0.5–2 m tree layer *Ouratea hexasperma* (St.-Hil.) Baill. was most abundant representing 33% of the biomass. Dominant shrub species were *Miconia holosericea* DC., *Hortia brasiliana* Vand. ex DC., *Myrcia rostrata* DC., *Parinari obtusifolia* Hook. f., and *Campomanesia velutina* Blume, contributing 93% to the total shrub biomass. Among grass species *Andropogon Minarum* Kunth, *Axonopus barbigerus* (Kunth) Hitchc., *Tristachya chrysothrix* Nees, and *Echinolaena inflexa* (Poir.) Chase were most frequently found; among the herbaceous species, members of the families *Asteraceae*, *Rubiaceae*, *Fabaceae*, and *Mimosaceae* were most abundant.

To establish the *Pinus caribaea* Morelet plantations natural savanna vegetation was cleared by harvesting the trees including their large roots. Pine trees were planted in 1977 and fertilised with about 33 kg Ca, 13 kg P, and, 20 kg S ha^{-1} at the time of plantation. The soils were not plowed, weeds were not controlled and no further fertiliser was applied. At the study time (1997–1999), there were about 950 trees ha^{-1} with an average height of 21 m.

The soils were very-fine isohyperthermic Anionic Acrustoxes (Soil Survey Staff 1998). Table 1 lists some of their properties. Under PI, there was a 10 cm thick organic layer consisting of Oi, Oe, and Oa horizons. In CE, only a discontinuous Oi horizon was found. Results of Lilienfein et al. (1999) indicated that there were no differences in soil properties between the soils under CE and PI prior to the establishment of the *Pinus* plantations.

Experimental setup and sampling

On each of the 6 plots, a 10 × 10 m area was fenced and equipped with 5 funnels (115 mm diameter) connected to sampling bottles to collect throughfall 30 cm above the ground. Rainfall was sampled on adjacent pastures with 5 replicate collectors. On each plot, 5 replicate suction cups were installed at 15, 80, and 200 cm depths in March 1997. Suction cups were placed representatively near and between the trees. Details are given in Lilienfein et al. (2000). Soil solution was sampled using permanent under-pressure. The vacuum was regulated weekly according to measured soil matric potential at the respective depth (Lilienfein et al. 1999). The soil solutions collected with 5 suction cups per depth and plot were combined for analysis. Under PI, zero-tension lysimeters were additionally installed beneath the organic layer to sample litter leachate. They consisted of 16 × 16 cm plastic boxes that were covered with a polyethylene net. We did not install litter lysimeters under CE because there was only a thin, discontinuous Oi horizon. In October 1997, 5 tall trees were equipped with stemflow collectors in each of the CE and 3 trees in each of the PI plots (slightly modified from Likens and Eaton (1970)). In October 1998, after determination of dominant tree and shrub species of CE, 4 dominant tall tree (*Pouteria torta*, *Ouratea spectabilis*, *Roupala montana*, *Byrsonima coccolobifolia*), the dominant small tree (*Ouratea hexasperma*), and the dominant shrub species (*Miconia holosericea*) in plot CE1 were additionally equipped with stemflow collectors. Thus, in the rainy season 1998/99 stemflow was collected from the 4 most abundant tall trees, one small tree, and one shrub species in threefold replication. Solution samples were collected weekly during the rainy season 1997/98 and 1998/99 (14 October 1997–28 April 1998 and 14 October 1998–28 April 1999).

The samples were transported to the laboratory and frozen at −18 °C within less than 10 h after sampling. For the analysis, aliquots of the weekly samples were combined into monthly samples. For extraction of water-soluble organic matter, we sampled the Oi, Oe, and Oa horizons under PI and the Oi horizon under CE in April 1999. Half of the material was frozen immediately to conserve conditions at the end of the rainy season. The rest was air-dried and stored for six month to simulate the effect of the dry season on the production of soluble organic matter.

Table 1. Selected soil properties of the study area (Lilienfein et al. 2000, 2001a). OC = organic Carbon; CECeff = effective cation exchange capacity; Fed = citrate–dithionite–bicarbonate-soluble iron; Alo, Feo = oxalate-extractable aluminum, iron. Standard deviations of the three replicate plots in brackets.

Depth	pH (H_2O)	pH (KCl)	OC	CEC_{eff}	Fe_d	Al_o	Fe_o	Texture			Bulk density
								<2 μm	2–200 μm	>200 μm	
[cm]			[g kg^{-1}]	[$mmol_c$ kg^{-1}]	[g kg^{-1}]						[Mg m^{-3}]
Cerrado											
0–15	4.8	4.2	22.0 (1.3)	6.8 (1.6)	32 (9)	2.8 (0.2)	1.8 (0.2)	705 (78)	88 (69)	207 (22)	0.88 (0.07)
80–120	5.3	5.4	8.4 (0.8)	7.1 (1.2)	32 (9)	2.6 (0.2)	0.7 (0.1)	688 (92)	129 (93)	183 (3)	0.84 (0.02)
120–200	5.4	5.8	6.4 (0.2)	6.6 (2.1)	31 (9)	2.5 (0.1)	0.6 (0.1)	684 (62)	134 (64)	182 (3)	0.82 (0.02)
P. caribaea											
0–15	4.6	4.0	21.9 (1.4)	6.0 (0.4)	31 (4)	3.4 (0.2)	1.6 (0.2)	733 (78)	96 (64)	171 (14)	0.82 (0.02)
80–120	4.7	5.1	8.3 (0.4)	4.7 (0.6)	30 (5)	2.7 (0.3)	0.7 (0.1)	746 (93)	105 (78)	169 (14)	0.84 (0.04)
120–200	4.8	5.6	6.9 (0.2)	5.0 (1.4)	29 (4)	2.6 (0.2)	0.6 (0.1)	748 (85)	101 (67)	151 (19)	0.79 (0.03)

Extractions and chemical analyses

Litter-derived water-soluble organic matter was extracted by mixing 400 g of each of the frozen-stored and air-dried samples from PI and CE with 4 L of deionised water. The suspensions were stirred with a glass stick, stored at room temperature, and, after 24 h, filtered through glass fibre filters (pore size ~ 0.7 μm; Whatman GF; Whatman Int. Ltd.; Maidstone, UK). Preliminary tests showed that further filtration with 0.45-μm filters did not affect the concentration of DOC in solution. Thus, the organic matter in the solution passing the glass fibre filters was considered to be dissolved and not particulate.

The monthly samples of precipitation, throughfall, stemflow, and soil solution were filtered through 0.45-μm membrane filters (Supor-450 Pall Gelman Science, Ann Abor MI, USA). Before filtration, the filters were intensively rinsed with deionised water.

The samples (precipitation, throughfall, stemflow, and soil solution) and the water extracts of the organic layers were adjusted to pH 2 with 1 *M* HCl and fractionated using Amberlite XAD-8 resin (Rohm & Haas, Philadelphia, PA, USA) according to Raastad and Mulder (1999). The proportion of DOM which is retained by the resin represents the so-called hydrophobic fraction whereas hydrophilic DOM passes the column (Leenheer 1981). For NMR analysis an aliquot of the effluent of the extracts of the Oi materials was freeze-dried without further treatment. The XAD-8 resin was eluted with 0.1 *M* NaOH. Mass-balance calculations showed that $\geqslant$ 93% of the C in the hydrophobic fraction was recovered. This suggests that the hydrophobic neutral fraction of DOM was rather low for the studied solutions. For NMR analysis, the cations in the effluent were exchanged against protons using a strongly acidic cation exchange resin AG-MP 50 (Bio-Rad Laboratories, Hercules, CA, USA) prior to freeze drying. The freeze-dried samples were homogenised by grinding. In contrast to the original procedure of Leenheer (1981), the hydrophilic and hydrophobic fractions were not split into acids, bases and neutrals, because of insufficient solution volumes (Raastad and Mulder 1999).

All samples were purged with CO_2-free synthetic air to remove inorganic C before analyses of DOC in bulk solutions and extracts and their hydrophilic fractions (TOC-analyser 5050, Shimadzu Corporation, Tokyo, Japan). Carbon in the hydrophobic fraction was calculated as the difference between total and hydrophilic DOC.

Liquid-state ^{13}C-NMR spectra of organic matter extracted from frozen-stored and air-dried Oi material were recorded on an Avance DRX 500 spectrometer (Bruker Analytik GmbH, Karlsruhe, Germany) operating at a frequency of 125.77 MHz. We dissolved 150 mg of freeze-dried material in 3 mL 0.5 *M* NaOD in a 10-mm NMR tube and accumulated at least 15,000 scans at a pulse angel of 45° and inverse-gated decoupling. The signal-to-noise ratio was improved by using a line-broadening of 100 Hz. Chemical shifts were given relative to the resonance of tetramethylsilane and signal assignments were made according to the literature (Wilson 1987; Orem and Hatcher 1987).

Data evaluation

In order to compare the data, the arithmetic mean concentration of DOC was computed from the results of the monthly samples for the ″first part″ (October–December) and the ″second part″ (January–April) of the rainy season. This was done because we assumed that the processes in soil at the beginning of the rainy season (during re-wetting of soil) differ from those during the second part of the rainy season (when soil is uniformly moist, Lilienfein et al. (1999)). We did not calculate volume-weighted means, because water fluxes in soil remained unknown.

Statistical analyses were conducted with STATISTICA 5.0 (Statsoft Inc., Tusla, OK, USA). To compare the DOC concentrations between the two vegetation types and the two rainy seasons observed, the Kruskal-Wallis-Test was chosen. To test the differences in the concentrations of DOC among the various soil depths we used the Wilcoxon Matched Pairs-Test. Significance was set at $p < 0.05$.

Results and discussion

Rainfall

The mean concentration of DOC in rainfall was 2.6 mg L^{-1}. This value exceeded that reported for a Puerto Rican rain forest (~ 1 mg DOC; McDowell (1998)). Likens et al. (1983) found mean concentrations of 1.1 mg DOC L^{-1} and 1.9 mg DOC L^{-1} in rainfall above mixed forests in New Hampshire and New York (USA), respectively. In contrast, the mean concentrations of DOC in bulk precipitation of the Fichtelgebirge (Germany) exceeded the concentrations found in the study region significantly (4.0–7.6 mg L^{-1}; Guggenberger and Zech (1993)). The difference in DOC concentrations among forest sites may be related with human activity. In areas with a high population density, emissions from traffic and industry, such as volatile organic compounds or chlorinated organic compounds, contribute to the DOC in rainfall (Hoffman et al. 1980; Chebbi and Carlier 1996). In the intensively agriculturally used study area, agrochemicals may also contribute to increased DOC concentrations in rainfall. The study areas of Likens et al. (1983) and McDowell (1998) are, in contrast, situated at remote locations far away from industry or intensive agriculture.

The DOC concentrations in rainfall did not vary much in the course of the rainy seasons (Figures 1 and 2). However, there was a negative correlation between the volume of rainfall and the concentration of DOC ($r^2 = 0.62$). Similarly, Hoffman et al. (1980) and Andreae et al. (1988, 1990) reported increasing concentrations of DOC in rain water during drier periods. Higher DOC concentrations at lower rainfall volumes may be attributable to a concentration effect or to the deposition of dust containing soluble organic matter that is favoured by dry conditions because the used rain samplers also collected the coarse dry particulate deposition.

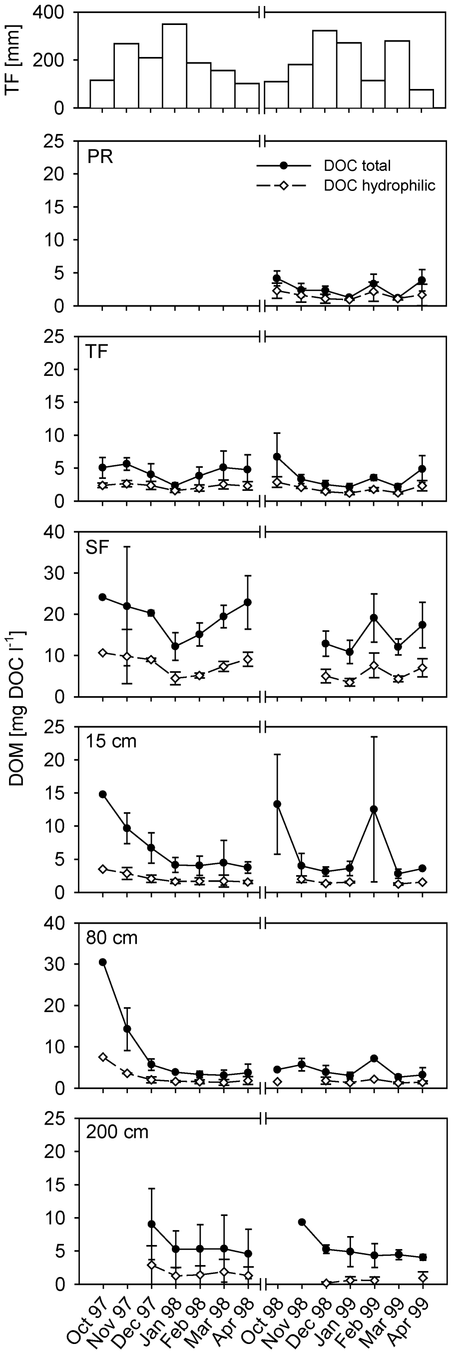

Figure 1. Temporal course of concentrations of total and hydrophilic dissolved organic carbon (DOC) in Cerrado during the rainy seasons of 1997/98 and 1998/99. PR = precipitation; TF = throughfall; SF = stemflow; 15 cm, 80 cm, 200 cm = soil solutions at 15, 80, 200 cm depth. Error bars represent standard deviations of three replicate plots.

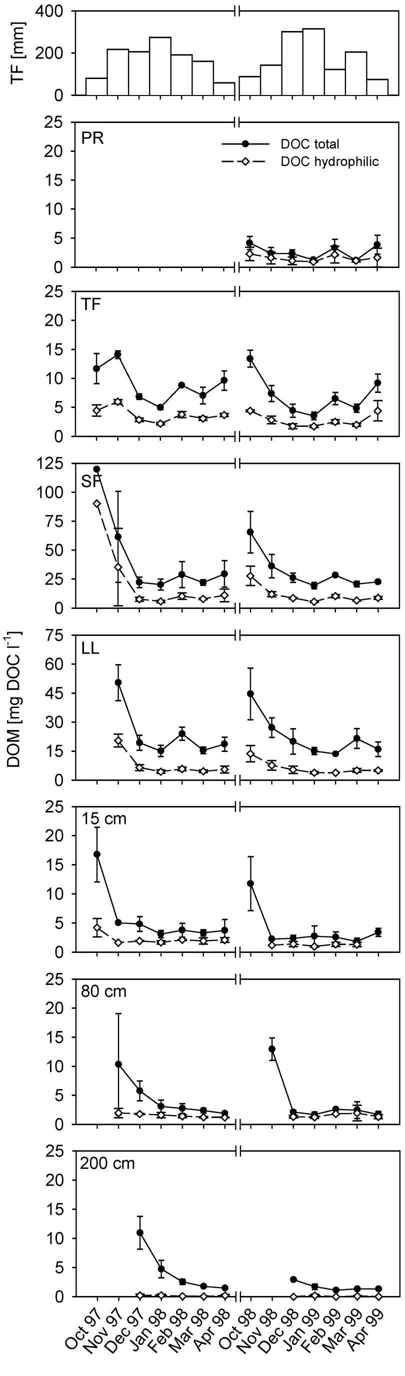

Figure 2. Temporal course of concentrations of total and hydrophilic dissolved organic carbon (DOC) in *Pinus caribaea* plantation during the rainy seasons of 1997/98 and 1998/99. PR = precipitation; TF = throughfall; LL = litter leachate; SF = stemflow; 15 cm, 80 cm, 200 cm = soil solutions at 15, 80, 200 cm depth. Error bars represent standard deviations of three replicate plots.

The largest part of the DOM in rainfall was hydrophilic (Figures 1 and 2) because atmospheric DOM mainly consists of low molecular substances < 1000 Dalton (McDowell and Likens 1988) falling almost completely into the hydrophilic fraction (e.g., Guggenberger and Zech (1993)). Water-soluble substances can only persist in the atmosphere when they are (i) volatile and (ii) resistant against photochemical degradation (Chebbi and Carlier 1996). These prerequisites are met by low molecular weight acids such as formic, acetic, or pyruvic acid (Chebbi and Carlier 1996). However, the mean concentration of DOC (2.6 mg L^{-1}) in the rainfall samples was substantially higher than reported concentrations of low molecular weight acids in rain water of tropical ecosystems. Mean concentrations of formate-C in rain water ranged from 80 to 110 μg L^{-1} and those of acetate-C from 100 to 230 μg L^{-1} in the Venezuelan savanna (Sanhueza et al. 1992). In the Amazon basin, the mean concentration of formate-C in rainwater was 215 μg L^{-1} and that of acetate-C was 274 μg L^{-1} (Andreae et al. 1988, 1990). During the rainy season, the mean concentrations decreased to 61 μg formate-C L^{-1} and 72 μg acetate-C L^{-1}. We conclude that the major part of the DOC in our samples was derived from the dissolution of deposited particles.

Throughfall

The mean DOC concentrations in throughfall ranged from 2.6 to 6.7 mg L^{-1} in CE and from 5.0 to 11 mg L^{-1} in PI (Table 2). These values were at the lower end of the range of concentrations in throughfall of temperate forests (3–35 mg DOC L^{-1}; Michalzik et al. (2001)) but compare well to mean DOC concentration in throughfall of a Puerto Rican rain forest (6.2 mg DOC L^{-1}; McDowell (1998)). In throughfall, DOC concentrations were significantly higher than in rainfall (Figures 1 and 2). This results from dissolution of (i) soluble organic material deposited on the surface of the plants (Hoffman et al. 1980), (ii) soluble animal or microbially-derived organic material produced in the canopy (Whitehead et al. 1983), and (iii) leaching of leaves or needles (Tukey 1970).

The temporal course of the DOC concentrations in throughfall of CE and PI was comparable to that in rainfall (Figures 1 and 2). Highest concentrations occurred during the first rain events after the dry season because soluble organic material that accumulated during the dry season was washed from the plants. The accumulated material probably resulted from deposited dust and degraded biological material. As there were several rain events during the dry season 1997, less material accumulated in the canopies. Therefore, the flush at the beginning of the rainy season was less pronounced in 1997 than in 1998.

The throughfall in both forests had higher concentrations of hydrophobic DOC compared with rainfall (Figures 1 and 2). Furthermore, the hydrophobic DOC contributed more to total DOC in throughfall than in rainfall. This can be explained by leaching of hydrophobic compounds from the surface tissue of leaves and of lipophilic plant excreta. Some of the leached material may be microbially altered before solubilisation (McDowell and Likens 1988; Qualls and Haines 1991; Colina-Tejada et al. 1996). The proportion of DOC in the hydrophobic fraction in PI (55–

Table 2. Mean DOC concentrations in Cerrado and *Pinus caribaea* plantation. Standard deviations of the three replicate plots are given in brackets.

Sample	Cerrado								*P. caribaea* plantation							
	Oct–Dec 97		Oct–Dec 98		Jan–Apr 98		Jan–Apr 99		Oct–Dec 97		Oct–Dec 98		Jan–Apr 98		Jan–Apr 99	
	[mg L^{-1}]															
TF tot	4.9	(1.4)	4.2	(2.7)	4.1	(1.9)	2.6	(0.8)	10.5	(3.5)	8.4	(4.1)	7.5	(2.0)	5.0	(1.5)
TF hi	2.5	(0.5)	2.1	(0.8)	2.1	(0.6)	1.4	(0.3)	4.2	(1.4)	3.0	(1.2)	3.4	(1.2)	2.1	(0.4)
TF ho	2.4	(1.1)	2.1	(2.0)	2.0	(1.3)	1.2	(0.5)	6.2	(2.1)	5.4	(2.9)	4.1	(1.2)	2.9	(1.1)
SF tot	21.5	(8.5)	12.9	(3.1)	16.9	(5.1)	14.9	(5.2)	53.0	(42.0)	42.6	(20.6)	25.2	(8.3)	22.9	(3.9)
SF hi	9.6	(3.9)	5.0	(1.7)	6.3	(2.1)	5.5	(2.5)	31.4	(35.2)	16.1	(9.9)	8.8	(3.4)	7.9	(2.2)
SF ho	12.0	(4.6)	7.9	(1.5)	10.6	(3.2)	9.5	(3.1)	21.6	(8.3)	26.5	(11.1)	16.5	(5.5)	15.0	(2.7)
LL tot									34.9	(18.2)	30.6	(13.5)	17.8	(4.3)	17.3	(4.5)
LL hi	n.i.								13.5	(8.1)	8.9	(4.6)	5.0	(1.2)	4.5	(0.9)
LL ho									21.4	(10.2)	21.7	(9.0)	12.8	(3.3	12.7	(3.8)
15 tot	9.1	(3.5)	3.6	(1.4)	4.1	(1.7)	3.3	(0.9)	10.0	(6.9)	2.4	(0.5)	3.4	(0.9)	2.4	(1.1)
15 hi	2.6	(0.8)	1.7	(0.5)	1.6	(0.5)	1.4	(0.2)	2.9	(1.6)	1.3	(0.4)	1.9	(0.4)	1.2	(0.3)
15 ho	6.5	(2.7)	1.9	(1.0)	2.5	(1.3)	1.8	(0.7)	7.1	(5.5)	1.0	(0.2)	1.5	(0.7)	0.8	(0.4)
80 tot	12.7	(10.0)	4.0	(1.4)	3.5	(1.2)	3.4	(1.7)	7.6	(5.2)	2.5	(0.8)	2.5	(0.8)	2.0	(0.9)
80 hi	3.4	(2.2)	1.7	(0.6)	1.6	(0.6)	1.4	(0.3)	1.8	(0.4)	1.4	(0.2)	1.4	(0.3)	1.5	(0.8)
80 ho	9.2	(7.9)	2.3	(0.8)	1.9	(0.6)	2.0	(1.3)	5.8	(4.8)	0.8	(0.2)	1.2	(0.5)	0.5	(0.2)
200 tot	9.0	(5.4)	5.3	(0.6)	5.1	(3.4)	4.4	(1.5)	11.0	(2.8)	2.9	–	2.7	(1.5)	1.4	(0.4)
200 hi	3.6	(2.9)	1.8	(0.2)	2.2	(1.3)	1.9	(0.6)	1.9	(0.2)	1.5	–	1.1	(0.2)	0.9	(0.2)
200 ho	5.4	(2.5)	3.5	(0.5)	2.9	(2.2)	2.5	(1.2)	9.1	(3.0)	1.5	–	1.5	(1.3)	0.5	(0.3)

n.i. = not installed; TF = throughfall; SF = stemflow; LL = litter leachate; 15, 80, 200 = sampling depth of soil solution in cm; tot = total DOM; hi = hydrophilic DOM; ho = hydrophobic DOM

64% of total DOC) agreed well with findings for deciduous and coniferous forests of temperate climates (Qualls and Haines 1991; Easthouse et al. 1992; Guggenberger and Zech 1993). The throughfall of CE contained less DOC (46–50%) in the hydrophobic fraction.

The differences in concentration and composition of DOM in throughfall between the two forests were attributable to the different structure of the vegetation canopy. The PI canopy was more homogeneous than that of CE. Furthermore, the PI canopy covered a higher surface area than the CE canopy. The higher homogeneity of the PI than of the CE canopy was reflected by the fact that the variation in the concentrations of DOC among the replicate plots (as indicated by the error bars in Figures 1 and 2) was smaller in PI than in CE. Consequently, water passing through the PI canopy has a more intensive contact with the plant surfaces than water passing through the CE canopy. This resulted in a stronger increase in DOC concentrations and in a larger contribution of hydrophobic DOM in throughfall of PI than of CE.

Stemflow

The DOC concentrations in stemflow exceeded significantly those in throughfall and were highest among the studied solutions (Table 2). The concentrations in stemflow at the study sites (13–53 mg DOC L^{-1}) were at the lower end of the range of mean concentrations in the stemflow of forests in temperate and cold climates (23 to 356 mg DOC L^{-1}, Moore (1989) and Dalva and Moore (1991), Koprivnjak and Moore (1992), Hinton et al. (1998)) probably because of different forest structure and climatic conditions. Frangi and Lugo (1985) reported mean DOC concentrations of 9.2 mg L^{-1} in stemflow of a subtropical Puerto Rican palm forest being less than two thirds of the mean concentrations in CE during the second part of the rainy season (14.9 and 16.9 mg L^{-1} for 1997/98 and 1998/99, respectively). This is probably attributable to a pronounced dilution of the Puerto Rican stemflow because of the higher annual rainfall of 3725 mm (vs. 1550 mm at the study sites). The strong enrichment of DOC in stemflow compared with throughfall, particularly in PI, indicated that organic material was leached from the trunks although a contribution of the dissolution of organic matter from dry deposition may not be ruled out. The increase in DOC concentrations in stemflow was related to the height of the trees. The ca. 20-m high pine trees provided a longer pathway for the stemflow than the at most 6-m high Cerrado trees and thus a better opportunity for leaching.

Highest DOC concentrations in stemflow occurred at the beginning of the rainy season (120 mg L^{-1} in PI and 25 mg L^{-1} in CE, Figures 1 and 2). During the second part of the rainy season, the concentrations in the PI stemflow dropped to 25 mg DOC L^{-1}. Thus, there was a similar initial flush as for throughfall. In contrast to the temporal course of the DOC concentrations in the PI stemflow, the DOC concentrations of the CE stemflow did not show a clear seasonal trend possibly because of the low stem density resulting in a higher frequency of wetting and drying of the bark of the Cerrado trees and consequently several minor first-flush events.

At the beginning of the rainy season 1997/98, about 75% of the DOC in the stemflow in PI were in the hydrophilic fraction whereas in the second part of the rainy season most of the DOC was in the hydrophobic fraction. A similar but less pronounced trend was observed in the rainy season 1998/99 (Figures 1 and 2, Table 2). As wood releases mainly soluble lignin degradation products falling into the hydrophobic fraction of DOM (Guggenberger et al. 1994), stemflow usually is dominated by hydrophobic compounds (Qualls and Haines 1991). High proportions of hydrophilic DOM as observed in PI in October 1997 may therefore result from atmospheric deposition or may have been released by microoganisms.

Litter leachate

Litter leachate was only collected in PI where a continuous organic layer was present which was not the case in CE. The mean DOC concentrations in the PI litter leachate (Table 2) were at the lower end of the range of values reported for temperate forests (20–90 mg L^{-1}; Michalzik et al. (2001)). Lower DOC concentrations in the PI litter leachate than in temperate forests were unexpected because in a laboratory experiment, DOM release from spruce Oa material increased by a factor of 1.7 to 2.0 when temperature was increased by 10 °C (Christ and David 1996). Field studies also show a positive correlation between temperature and production of DOM. For example, in temperate regions the production of DOM in organic horizons is higher in summer than in winter (e.g., Scott et al. (1998) and Tipping et al. (1999)). The increased production of DOM in soil organic layers at higher temperature is attributed to increased microbial activity. Although DOM itself can serve as a substrate for microorganisms and thus might be susceptible to mineralisation, field and laboratory experiments show that the amount of DOM released from litter material is positively correlated with the microbial activity (Kalbitz et al. 2000). Gödde et al. (1996), however, state that an increase in temperature from 3 to 10 °C results in a stronger increase in the production of DOC and CO_2 from spruce Oa material than rising the temperature from 10 to 20 °C. Under some experimental conditions, they could not observe any increase in the production of DOC when rising the temperature from 10 to 20 °C while the production of CO_2 still increased. As the temperature in the study area averages 23 °C, faster and more complete degradation of organic matter than in temperate regions might take place resulting in a relatively low production of DOC.

In both rainy seasons, the concentrations of DOC in the PI litter leachate followed the course of the concentrations of DOC in throughfall and stemflow (Figure 2). They decreased significantly from > 30 mg L^{-1} during the first part of the rainy season to about 17 mg L^{-1} during the second part. Increased concentrations of DOC in litter leachate after dry periods, as observed at the beginning of the rainy season or in February 1999, have been reported by numerous other authors (e.g., Mitchell and McDonald (1992) and Scott et al. (1998)). During dry periods, DOC is concentrated because of the evaporation of water (Lundquist et al. 1999). However, the composition of DOM changes after rewetting of litter material (Christ and David 1994, 1996) and chloride in litter leachate increases less than DOC (Scott et al. 1998). Therefore the reduced water content cannot be the only reason for the higher DOC concentration in litter leachate after drying and rewetting. Lundquist et al. (1999) observed in field and laboratory experiments increased production of DOM when samples went through wet–dry cycles compared with samples that were kept at a constant moisture. During drying, part of the microbial population dies thereby producing large amounts of readily soluble hydrophilic organic compounds (Christ and David 1994; Guggenberger et al. 1998). The dissolution of this material during rewetting contributes to increased DOC concentrations in the litter leachate after dry periods.

Except at the beginning of the rainy season 1997/98, the hydrophilic fraction comprised less than 30% of the total DOC on most sampling dates (Figure 2, Table 2). The dominance of the hydrophobic fraction is typical for leachates from coniferous litter (Guggenberger and Zech 1993; Hongve 1999; Kaiser et al. 2001). This is attributable to the production of soluble degradation products of lignin (Guggenberger et al. 1994; Kaiser et al. 2001). However, the mean contribution of the hydrophobic fraction to total DOC (~ 75%) exceeded the values reported for temperate coniferous and deciduous forests (50–65%; Cronan and Aiken (1985) and Qualls and Haines (1991), Guggenberger and Zech (1993)). In temperate regions, increasing concentrations of DOC in solution draining organic soil material often coincide with an increase in the proportion of hydrophilic DOM (Vance and David 1991; Scott et al. 1998). This can be explained by increased biological activity at warmer periods and subsequent production of hydrophilic microbial metabolites. Under tropical conditions, labile hydrophilic compounds might be rather consumed than leached from the organic layers. Incubation studies suggested that the preferential microbial decay of hydrophilic compounds results in an accumulation of the hydrophobic, more refractory fraction of DOM (Qualls and Haines 1992; Jandl and Sollins 1997).

Chemical composition of litter-derived DOM

In the water extracts of the CE Oi material, ~ 70% of the DOC belonged to the hydrophilic fraction which is similar to leachates of the Oi horizon in European beech (*Fagus sylvatica* L.) forests (Kaiser et al. 2001). This suggested that DOC infiltrating the CE soil is mainly hydrophilic. The DOC concentrations in the extract of field-fresh frozen samples (~ 270 mg L^{-1}) were slightly lower than in the extract of the air-dried samples (~ 300 mg L^{-1}). However, the distribution of DOC between the two DOM fractions was not significantly different between the two treatments. Thus, the effect of air-drying was less pronounced than expected from literature (e.g., Christ and David (1994)).

The water extracts of field-fresh frozen samples of the Oi, Oe, and Oa horizons in PI contained less DOC than those in CE. The concentrations were highest in the Oi extract (163 mg DOC L^{-1}) and lowest in the Oa extract (90 mg DOC L^{-1}, Figure 3). The decrease in extractable organic matter with increasing organic layer

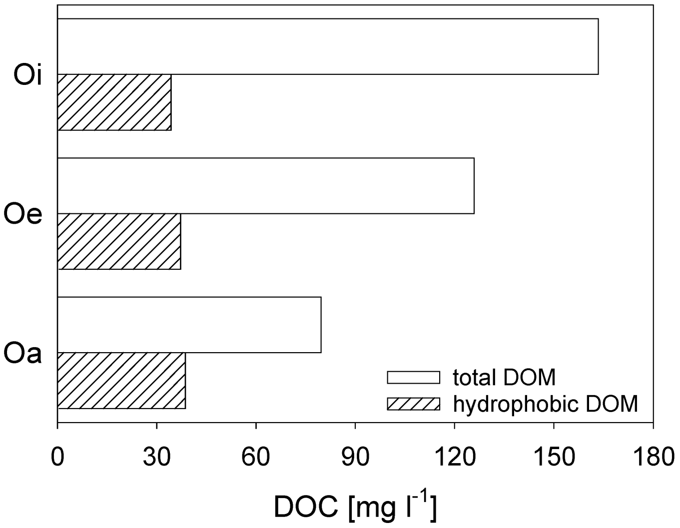

Figure 3. Chemical composition of dissolved organic matter (DOM) extracted from different organic horizons in the *Pinus caribaea* plantation.

depth was mainly due to a strong decrease in the concentrations of hydrophilic DOM while the concentration of hydrophobic DOM remained constant. The decrease in the concentration of the hydrophilic DOM followed the gradient of increased decomposition within the soil organic layer. This suggested that the hydrophilic fraction was microbially degraded in the organic layer while the hydrophobic fraction seemed to be refractory. This agrees well with the results of incubation studies with DOM (Qualls and Haines 1992; Boissier and Fontvieille 1993; Jandl and Sollins 1997). Air-drying increased the concentrations of DOC in the water extracts by ~30%, however, again the distribution of DOC between the two DOM fractions remained almost unchanged.

Similar to the results of the fractionation, the ^{13}C-NMR spectra showed only little influence of storing conditions on the composition of hydrophilic and hydrophobic fractions of DOM obtained from extractions of the organic horizons in PI and CE (Figure 4). The spectra of hydrophilic DOM were dominated by signals in the O-alkyl region (70–80 ppm) which indicates that these fractions were largely composed of carbohydrates (Orem and Hatcher 1987). The second largest signals were by alkyl C (0–55 ppm). Ketone (190–220 ppm), carboxyl (160–180 ppm), methoxyl (55–60 ppm), C-substituted aromatic (105–145 ppm), and especially phenolic C (145–160 ppm) were hardly detectable (Figure 3). Thus, lignin-derived compounds did not seem to contribute to hydrophilic DOM. These results are in agreement with previous results from temperate forests (Dai et al. 1996; Kaiser et al. 2001).

The hydrophobic DOM contains less O-alkyl C than the hydrophilic DOM, whereas the signals of alkyl, carboxyl, phenolic, and C-substituted aromatic C were several times larger than in the spectra of hydrophilic DOM. Ketone C was found

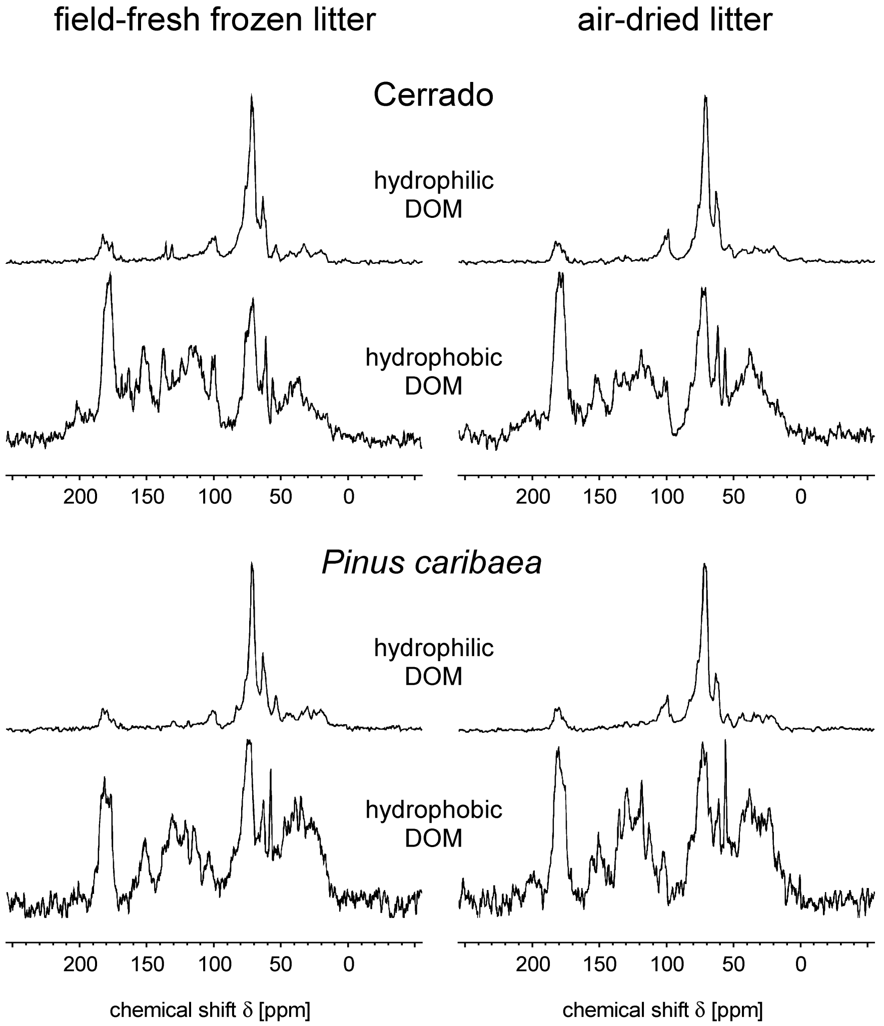

Figure 4. ^{13}C-NMR spectra of dissolved organic matter (DOM) from soil organic layer material. CE = Cerrado; PI = *Pinus caribaea* plantation; ad = air dry; df = deep frozen. tot = total DOM; hi = hydrophilic DOM; ho = hydrophobic DOM.

exclusively in the hydrophobic DOM. The hydrophobic fractions of all samples showed signatures that are typical for lignin-derived compounds with peaks at 115, 135, 150 and 56 ppm (Wilson 1987; Preston et al. 1994). The strong signals of carboxyl C indicate oxidative transformation by microorganisms. Broad signals between 20 to 50 ppm are representative for a heterogeneous mixture of long, branched chains of alkyl compounds (e.g., Preston et al. (1994)).

Air-drying of organic horizon samples collected at the end of the rainy season can be considered as a simulation of the effect of the dry season. From the fact that air-drying only little changed the DOM composition in the extracts it may be concluded that DOM leached from the organic layers has a relatively constant chemical composition in the course of the rainy seasons. As the chemical composition of DOM controls its sorption to minerals (McKnight et al. 1992; Kaiser et al. 1997) and degradation by microorganisms (Qualls and Haines 1992; Jandl and Sollins 1997) this implies a uniform reactivity of DOM leached from the organic layers throughout the rainy season at both sites.

Soil solution

In both forests, the DOC concentrations in the soil solution at 15 cm depth ranged between 3 and 15 mg L^{-1} and at 80–200 cm depth between 1.4 and 11 mg L^{-1} (Figures 1 and 2, Table 2). Again, the concentrations found here were at the lower end of the range of values reported for temperate forest soils (4.6–74 mg L^{-1} in A horizons and 2–35 mg L^{-1} in subsoil horizons, Michalzik et al. (2001)). In Puerto Rican Ultisols, McDowell (1998) found mean DOC concentrations of 2.4 mg L^{-1} at 80 cm depth which was similar to the DOC concentrations at 80 to 200 cm soil depth in PI (1.4–2.7 mg L^{-1}) and lower than in CE (3.4 and 5.1 mg L^{-1}). Higher DOC concentrations in CE than in PI may be attributable to the predominance of broadleaf trees in CE. Hongve (1999) examined leachates from litter of broadleaf and coniferous trees for one year. During this period, litter from broadleaf trees released 6.2 times more DOC than needle material. At the study sites, the mean annual litterfall in PI was only 3.7 times larger than in CE (7.8 vs. 2.1 Mg $(ha\ a)^{-1}$; Wilcke and Lilienfein (2002)). If the production of DOC in the study area was comparable to that in the study of Hongve (1999), the input of DOC into the mineral soil might be higher in CE than in PI resulting in higher DOC concentrations in the CE than in the PI soil solution. The higher extractability of C by water in CE litter compared with PI litter confirms this assumption.

In the first part of the rainy season (October–December), the DOC concentrations in the soil solution at 15 cm depth were between 12 and 15 mg L^{-1} in both forests (Figures 1 and 2). In the second part, they decreased significantly to 3–5 mg DOC L^{-1} (Figures 1 and 2, Tables 2 and 3). The only exception was February 1999 when in CE the soil solution at 15 cm depth contained 14 mg DOC L^{-1}. In the first part of the rainy season, there were only few significant differences in DOC concentrations of the soil solution between CE and PI. In contrast, in the second part of the rainy season, the DOC concentrations in PI soil solution were significantly lower than in CE (Tables 2 and 3). Possible reasons for higher DOC concentrations in the soil solution at 15 cm depth in the first part of the rainy season include the production of soluble organic matter from microbial debris that accumulated during the dry season and the infiltration of DOC-rich litter leachates. Furthermore, drying can enhance the detachment of organic substances sorbed to mineral surfaces (Greenland 1971). These processes might also caused the peak DOC concentration in February 1999 when almost no rain fell during the first weeks.

The DOC concentrations in CE soil solution were comparable in both monitored rainy seasons while in PI, the 1997/98 soil solutions often had significantly higher

Table 3. Results of the statistical analysis of the data given in Table 2. 3a) Comparison of DOM in Cerrado and *Pinus caribaea* plantation; 3b) comparison of both monitored rainy seasons within the same forest type; 3c) comparison of first with second part of the rainy seasons.

(a)	Oct–Dec		Jan–Apr		(b)	Cerrado		*Pinus caribaea*		(c)	Cerrado		*Pinus caribaea*	
	1997	1998	1998	1999		Oct–Dec	Jan–Apr	Oct–Dec	Jan–Apr		1997/98	1998/99	1997/98	1998/99
TF tot	*	*	*	*	TF tot	n.s.	n.s.	n.s.	*	TF tot	n.s.	n.s.	n.s.	n.s.
TF hi	*	n.s.	*	*	TF hi	n.s.	*	n.s.	*	TF hi	n.s.	*	n.s.	n.s.
TF ho	*	*	*	*	TF ho	n.s.	n.s.	n.s.	*	TF ho	n.s.	n.s.	*	*
SF tot	*	*	*	*	SF tot	n.s.	n.s.	n.s.	n.s.	SF tot	n.s.	n.s.	n.s.	*
SF hi	n.s.	*	*	*	SF hi	*	n.s.	n.s.	n.s.	SF hi	*	n.s.	n.s.	*
SF ho	*	*	*	*	SF ho	n.s.	n.s.	n.s.	n.s.	SF ho	n.s.	n.s.	n.s.	*
LL tot	–	–	–	–	LL tot	–	–	n.s.	n.s.	LL tot	–	–	*	*
LL hi	–	–	–	–	LL hi	–	–	n.s.	n.s.	LL hi	–	–	n.s.	*
LL ho	–	–	–	–	LL ho	–	–	n.s.	n.s.	LL ho	–	–	*	*
15 tot	n.s.	*	n.s.	*	15 tot	*	n.s.	*	*	15 tot	*	n.s.	*	n.s.
15 hi	n.s.	n.s.	n.s.	n.s.	15 hi	*	n.s.	*	*	15 hi	*	n.s.	*	n.s.
15 ho	n.s.	n.s.	*	*	15 ho	*	n.s.	*	*	15 ho	*	n.s.	*	n.s.
80 tot	n.s.	n.s.	*	*	80 tot	*	n.s.	*	n.s.	80 tot	*	n.s.	*	n.s.
80 hi	n.s.	n.s.	n.s.	n.s.	80 hi	n.s.	n.s.	n.s.	n.s.	80 hi	*	n.s.	*	n.s.
80 ho	n.s.	*	*	*	80 ho	*	n.s.	*	*	80 ho	*	n.s.	*	n.s.
200 tot	n.s.	–	*	*	200 tot	–	n.s.	–	*	200 tot	n.s.	–	n.s.	–
200 hi	n.s.	–	*	*	200 hi	–	n.s.	–	*	200 hi	n.s.	–	n.s.	–
200 ho	n.s.	–	n.s.	*	200 ho	–	n.s.	–	*	200 ho	n.s.	–	n.s.	–

TF = throughfall; SF = stemflow; LL = litter leachate; 15, 80, 200 = soil depth in cm. tot = total DOM; hi = hydrophilic DOM; ho = hydrophobic DOM; — = no data or data insufficient for statistical analyses; n.s. = not significant; * = significant at $p < 0.05$

DOC concentrations than those of 1998/99. In the dry season 1997, that had several rainfall events (Lilienfein et al. 1999), microbial activity and degradation of organic material may have continued during the dry season. As the volume of rain water was probably too small to induce water fluxes, organic metabolites were not leached but accumulated at the place of production, the smaller water-filled soil pores. Flushing of this DOC-enriched pore water after the first rainfall events may explain the partly higher DOC concentrations in the CE soil solution at the beginning of the rainy season in 1997/98 than in 1998/99.

Because of delayed rewetting of the subsoils at the beginning of the rainy seasons, no or insufficient solution could be sampled from 80 and 200 cm depth. For example, in CE only one sample was obtained in October 1997 which showed the highest DOC concentration of all sampled soil solutions (30 mg L^{-1}). Consequently, statistical analyses of changes in the concentrations of DOC with depth were restricted to the second part of the rainy season (Table 4). During this period, the DOC concentrations in CE changed little (1997/98) or increased (1998/99) with increasing soil depth. In PI, there was a significant decrease of the DOC concentrations at the transition between the organic layer and the mineral soil and a partly significant further decrease with increasing depth of the mineral soil in the second part of the rainy season (Table 4).

A simple explanation for the strong decrease of the concentrations of DOC at the transition between the organic layer and the mineral soil in PI (Figure 2) is sorption of DOM by sesquioxides (Jardine et al. 1989; Gu et al. 1994). The topsoils of the study area are rich in Fe oxides and hydroxides and relatively poor in organic C (Neufeldt et al. 1999). These are conditions that favour retention of DOM in soil (e.g., Kaiser et al. (1996)). Another possible reason for the decrease in DOC concentrations at the transition of the organic layer and the mineral soil is precipitation of organic Al and Fe complexes (Buurman 1985). However, the concentrations of strongly complexing metals such as Al (not detected to 23 μmol L^{-1} at 15 cm soil depth) and Fe (not detected) were very low in the studied soil solutions (Lilienfein et al. 2001a). Also the Ca concentrations (2.8–39 μmol L^{-1} at 15 cm soil depth) were too low to explain the decrease in DOC in the uppermost mineral soil. Therefore, we consider removal of DOC from solution by precipitation of metal complexes as unlikely.

Increasing DOC concentrations with increasing depth in CE could be a concentration effect because of water use of the vegetation. However, Lilienfein et al. (1999) found significantly lower matric potentials in PI than in CE. As the soil water characteristic of all study soils is similar because they do not differ significantly in texture, mineralogy, or organic C concentration, matric potentials are directly proportional to water content. So, the concentration effect should be more pronounced in the dryer PI soils than in the CE soils. This suggests that concentration cannot explain the differences in the depth distribution of DOC concentrations in PI and CE soils. Nevertheless, plant water uptake from the subsoil may have contributed to increased DOC concentrations with increasing soil depth in CE while in PI, this effect was possibly overcompensated by another process. Furthermore, input of litter and topsoil-derived DOM by preferential flow through macropores into

Table 4. Statistical analyses of differences in DOC concentrations within the depth profiles; (a) and (b) Cerrado; (c) and (d) *Pinus caribaea* plantation.

(a)	Tot	hi	ho	tot	hi	ho
	Oct–Dec 1997			Oct–Dec 1998		
TF-SF	*	*	*	–	–	–
SF-15	*	*	*	–	–	–
15-80	–	–	–	–	–	–
80-200	–	–	–	–	–	–
(b)	Jan–Apr 1998			Jan–Apr 1999		
TF-SF	*	*	*	*	*	*
SF-15	*	*	*	*	*	*
15-80	n.s.	n.s.	n.s.	*	n.s.	*
80-200	n.s.	n.s.	n.s.	n.s.	n.s.	n.s.
(c)	Oct–Dec 1997			Oct–Dec 1998		
TF-SF	*	*	*	*	*	*
SF-LL	n.s.	*	n.s.	n.s.	*	n.s.
LL-15	–	–	–	–	–	–
15-80	–	–	–	–	–	–
80-200	–	–	–	–	–	–
(d)	Jan–Apr 1998			Jan–Apr 1999		
TF-SF	*	*	*	*	*	*
SF-LL	*	*	n.s.	n.s.	*	n.s.
LL-15	*	*	*	*	*	*
15-80	*	*	n.s.	n.s.	n.s.	n.s.
80-200	n.s.	*	n.s.	n.s.	*	n.s.

TF = throughfall; SF = stemflow; LL = litter leachate; 15, 80, and 200 indicate mineral soil depth in cm; – = no data or data insufficient for statistical analyses; n.s. = not significant; * = significant at $p < 0.05$

the subsoil as found for a watershed in Tennessee (USA; Jardine et al. (1990)) may have contributed to the elevated concentrations of DOC in the CE subsoil because the fast macropore transport limits the interaction with sorbing surfaces. The less dense CE canopy favours preferential flow as compared with PI where the dense canopy had a larger capacity to intercept precipitation.

In the first part of the rainy season, > 75% of the total DOC in the soil solution at 15 cm depth was in the hydrophobic DOM fraction at both sites. The percentage of DOC in the hydrophobic fraction was significantly larger at the beginning of the rainy season 1997/98 than 1998/99. This may have the same reasons as the higher total DOC concentrations in soil solution at the beginning of the rainy season 1997/98 than 1998/99. While drying and rewetting increases the proportion of DOC in the hydrophilic fraction (Christ and David 1994), in stagnant water the degradation of the hydrophilic DOM fraction will dominate and increase the proportion of hydrophobic DOM (Jandl and Sollins 1997). Furthermore, fungi such as the basidiomycetes, the most important decomposers of lignin (Worrall et al. 1997), are active at much lower matric potentials than bacteria (Gregorich and Janzen 2000) producing hydrophobic lignin degradation products (Guggenberger et al. 1994). Thus preferential decay of hydrophilic compounds in remaining, immobile porewater and production of soluble lignin degradation products can explain the accumulation of DOC in the hydrophobic fraction at the beginning of the rainy season 1997/98.

In most cases, decreased DOC concentrations of the soil solution coincided with increasing proportions of DOC in the hydrophilic fraction of DOM. The maximum contribution of the hydrophilic fraction to total DOC was $\sim 45\%$ in CE and $\sim 70\%$ in PI. Along with the decrease in DOC there was a shift from predominantly hydrophobic DOM in litter leachate to mainly hydrophilic DOM in soil solution at the transition between the organic layers and the mineral soil. This indicates preferential sorption of hydrophobic DOM as shown before in numerous field studies (Cronan and Aiken 1985; Qualls and Haines 1991; Guggenberger and Zech 1993) and laboratory experiments with soils and pure minerals (Kaiser et al. 1996; Kaiser and Zech 1997). At 80–200 cm depth, the hydrophilic fraction of the DOM in soil solution comprised in both forests between 25 and 60% of the total DOC. In CE, the composition of DOM in the soil solution below 15 cm depth did not change significantly, except for an increase in DOC in the hydrophobic fraction between 15 and 80 cm in the second part of the rainy season 1998/99. In PI, in contrast to CE, the concentrations of hydrophilic DOC below 15 cm depth decreased significantly with increasing soil depth in the second part of the rainy seasons while those of hydrophobic DOC did not change (Table 4). Although the concentrations of hydrophobic DOC decreased strongly upon contact with the mineral soil, it remained constant in the mineral soil with depth. Possible reasons for this are that hydrophobic DOM is largely refractory against microbial decay (Boissier and Fontvieille 1993; Jandl and Sollins 1997) and that those hydrophobic compounds remaining in solution after passage through the uppermost mineral soil do not sorb to mineral surfaces at all.

The selective decrease in hydrophilic DOC concentrations with increasing soil depth in the second part of both rainy seasons in the PI mineral soil can be caused by microbial degradation. Uptake of DOM by roots only plays a minor role (Baldock and Nelson 2000). Sorption to the soil matrix is not likely to occur since the affinity of hydrophilic DOM to soil is low (e.g., Kaiser et al. (1996)). Because hydrophilic DOC mainly consisted of carbohydrates (Jandl and Sollins 1997; Kaiser et al. 2001) it should be a suitable C source for microorganisms. Several studies showed, that hydrophilic DOM is, at least partly, biodegradable (Qualls and Haines 1992; Jandl and Sollins 1997). Furthermore, Lilienfein et al. (2001a) noted that, in PI, NO_3-N concentrations decreased from approximately 1.6 mg L^{-1} at 80 cm to 0.8 mg L^{-1} at 200 cm soil depth. The simultaneous decrease of the concentrations of nitrate and hydrophilic DOM with increasing depth in the PI soil suggested that hydrophilic DOM served as source of energy for denitrification (Zsolnay 1996). In CE, the NO_3-N concentrations in soil solution were < 0.2 mg L^{-1} throughout the whole soil (Lilienfein et al. 2001a). In laboratory experiments, Jandl and Sollins (1997) showed that microbial decomposition of hydrophilic DOM can be initialised by the addition of inorganic N. This agrees with the finding that microbial activity is not limited by the energy source but by the availability of N (Wang and Bakken 1997). Thus, it is possible that limited availability of nitrate impedes microbial degradation of hydrophilic DOM in the CE soil.

Conclusions

The concentrations of DOM in all solutions of the two studied tropical forest ecosystems were at the lower end of the concentrations usually found in temperate forests indicating lower DOM production and/or faster mineralisation in tropical than in temperate forests.

The DOM input into soils of Cerrado and *Pinus caribaea* plantations consisted of wet and dry deposition from the atmosphere, leaching of leaves and trunks, and microbial release of soluble organics from litter material. Dissolved organic matter that entered the topsoil was strongly retained mainly because of the sorption of the hydrophobic DOM fraction in the A horizons. This is different to most temperate forests where only little DOM sorption occurs in the topsoil. The result indicates that the sorption sites even of the topsoil are far from being saturated with organic matter implying that there is a large potential to sequester C.

The depth distribution of DOC concentrations in soil during the second part of the rainy seasons when enough solution could be extracted from all depths was markedly different between CE and PI. Dissolved organic C concentrations were similar at all studied soil depths in CE or even tended to increase with depth while DOC concentrations decreased with depth in PI. In both forests, hydrophobic DOM that was not retained in the topsoil was almost not sorbed during its further passage through the soil. Thus, changes in concentration and composition of DOM in the subsoil could only be explained by microbial degradation of hydrophilic DOM. As the decrease of DOM in the PI soil solution was accompanied by decreasing concentrations of nitrate, it is likely that this part of DOM served as energy source for denitrification. In contrast, the utilisation of hydrophilic DOM by microorganisms in CE seemed to be limited by the low N availability. The results demonstrate that the transformation of Cerrado to pine plantations results in a reduction of the DOM fluxes to the deeper subsoil probably because of enhanced mineralisation associated with a more pronounced nitrification. The latter, however, needs further research that includes the direct measurement of gaseous N fluxes.

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