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Properties of dissolved and total organic matter in throughfall, stemflow and forest floor leachate of Central European forests

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Abstract

For the first time, we investigated the composition of dissolved organic matter (DOM) compared to total OM (TOM, consisting of DOM and particulate OM, POM) in throughfall, stemflow and forest floor leachate of beech and spruce forests using solid state ^{13}C nuclear magnetic resonance spectroscopy. We hypothesized that the composition and properties of OM in forest ecosystem water samples differed between DOM and TOM and between the two tree species. Under beech, a contribution of phyllosphere-derived fresh POM was echoed in structural differences. Compared with DOM, TOM exhibited higher relative intensities for the alkyl C region, representing aliphatic C from less decomposed organic material, and lower relative intensities for lignin-derived and aromatic C of the aryl C region, resulting in lower aromaticity indices and reduced humification intensities. Since differences in the structural composition of DOM and TOM were less pronounced under spruce than under beech, we suspect a tree species-related effect on the origin of OM composition and resulting properties (e.g. recalcitrance, allelopathic potential).

1 Introduction

Dissolved organic matter (DOM), often described as solutes passing filter $< 0.45\,\mu$m in pore size, contributes substantially to the biogeochemistry of carbon and nitrogen in forest ecosystems (Qualls et al., 1991; Michalzik and Matzner, 1999; Fröberg et al., 2006; Kindler et al., 2011). While many investigations addressed the nature and dynamics of DOM in terrestrial ecosystems (e.g., Qualls and Haines, 1991; Currie et al., 1996), only a few investigated the dynamics, but none the character of water-bound total OM (TOM) including the particulate OM fraction (POM; $0.45\,\mu\text{m} < \text{POM} < 500\,\mu\text{m}$). Since water-bound element and nutrient concentrations are conventionally measured after filtration (frequently to $< 0.45\,\mu$m pore size), the exclusion of the POM fraction potentially results in misleading inferences and budgeting gaps in studies of nutrient and energy fluxes in ecosystems (Michalzik and Stadler, 2005; Stadler et al., 2006). We are aware of only a handful of studies over the last 35 years which address POM or size equivalent in temperate broadleaved and coniferous ecosystems (e.g., Carlisle et al., 1966; Sollins et al., 1980; Likens et al., 1983; Lamersdorf and Blank, 1995; Levia et al., 2013). The majority of these studies highlighted the importance of OM $> 0.45\,\mu m$ to the overall budgets of C and N and other nutrients. Lamersdorf and Blank (1995) revealed a significant additional input of organic carbon and nitrogen to the soil with throughfall (TF) via the particulate fraction ($> 0.45\,\mu m$), amounting to 11–15 % for C and 14–21 % for N relative to the total annual input by litterfall and TF ($< 0.45\,\mu m$), respectively. The low C to N ratios of 12–14 for POM furthermore suggest that this material might be particularly relevant for microbial decomposition processes. These results are corroborated by recent findings for POM and DOM in TF of beech, spruce and pine forest stands (le Mellec and Michalzik, 2008; le Mellec et al., 2010). Though some knowledge of the amount and temporal dynamics of DOM and POM is available, the composition of OM in solution and its alteration by forest canopies, stem-surfaces and subsequently by the forest floor (FF) is largely unknown. The chemical nature of mobile OM is a prerequisite for advancing understanding of the C and nutrient cycling in forests. Alteration in the composition of OM with TF and stemflow (SF) routing through the canopy are driven by various abiotic and biotic processes. In this context, precipitation patterns (Mercier and Lindow, 2000), canopy architecture (Levia and Frost, 2006), atmospheric deposition (e.g. pollen, inorganic N deposition, Lamersdorf and Blank, 1995), increased nutrient leaching from damaged leaves and immobilization processes within the canopy mediated by phyllosphere microorganisms (Stadler and Müller, 2000) appear to be responsible for different release patterns and chemical qualities of OM from the forest canopy.

Work has demonstrated that tree species and spatial and temporal patterns of environmental conditions such as soil acidity influence cation cycling in temperate forests (Finzi et al., 1998; Levia et al., 2012). However, it is unclear how tree species influence chemical properties of DOM and POM in TF, SF and FF leachates and hence subsequently affect soil processes by varying chemical composition and associated functionality. For instance, in Germany spruce trees exhibit a denser foliage and higher leaf area index of 20.5 $m^2\,m^{-2}$ compared with 6.5 $m^2\,m^{-2}$ for beech, as well as higher needle surface roughness and higher leaf longevity (Rothe et al., 2002). Consequently, coniferous canopies provide a higher filtering capacity for airborne compounds and higher accumulation rate than broadleaved canopies. Additionally, spruce canopies exhibit higher rainfall interception rate values of 30–40 % compared with 17–20 % for beech canopies (Rothe et al., 2002). This might lead to longer periods of water availability, longer contact times for rainwater and needle surfaces and substrate availability and hence more stable environmental conditions within the phyllosphere, likely promoting the microbial decomposition of POM to DOM.

On the other hand, fresh beech leaves exhibit a high content of phenolic compounds that might also be relocated via raindrops and, to some extent, be converted to more complex substances at the soil surface (Coulson et al., 1960). In many studies, phenolic compounds released from living or dead plant material have been shown to be allelochemicals, affecting associated species (Wardle et al., 1998).

Solid state ^{13}C nuclear magnetic resonance spectroscopy with cross-polarization and magic angle spinning (CPMAS-NMR) is a nondestructive method that provides information on the chemical surroundings of C atoms forming the major component of OM. Consequently, solid state ^{13}C NMR spectroscopy is widely used for the characterization of a range of organic materials from various natural environments (Baldock et al., 2004). It has been applied to soil OM (Helfrich et al., 2006; Keeler et al., 2006), hot water extracts (Leinweber et al., 1995; Balaria et al., 2009) and DOM in aqueous solutions from aquatic (Schumacher et al., 2006) and terrestrial ecosystems (Guggenberger et al., 1994; Fröberg et al., 2003; Sanderman et al., 2008). Although the technique has been applied to POM from aquatic systems (McKnight et al., 1997; Lankes et al., 2008), to the best of our knowledge, it has never been applied to POM or TOM in aqueous samples from terrestrial ecosystems like TF, SF or FF leachates.

We have tested the hypotheses that the composition and resulting properties (i.e. chemical recalcitrance, allelopathic potential) of OM in filtered and unfiltered forest ecosystem water samples differ between (i) DOM and TOM and (ii) between the two tree species (beech vs. spruce).

2 Methods

2.1 Study sites

The sites are in three landscapes forming part of the German “Biodiversity Exploratories” (www.biodiversity-exploratories.de), which were established in 2006 as a scientific platform for biodiversity research funded by the German Research Foundation (DFG SPP 1374 "Exploratories for Large-scale and Long-term Functional Biodiversity Research“; see Fischer et al. (2010) for a detailed description). The three regions differ in environmental conditions (Table 1) and are representative of large areas of Central Europe. We selected three extensively managed “close to native” European beech forests (*Fagus sylvatica* L.; mature forest stands, protected for at least 60 years; see Fischer et al., 2010) in each of the three exploratories, since these forests are comparable with regard to tree age and tree species composition, stem density and forest management. In the Hainich–Dün exploratory we additionally collected samples from three Norway spruce (*Picea abies* (L.) H. Karst.) plantations.

2.2 Experimental set up

The experimental set up was identical for all the sites. At each exploratory, bulk precipitation (BP) was collected in five replicates from three open areas using 2 L polyethylene (PE) open funnel samplers (diameter 0.12 m). TF was sampled using rain collectors of the same type arranged in a cross-shaped grid with 20 replicates per forest site. The sampling bottles were wrapped with aluminum foil to minimize the impact of irradiation and algal growth and were equipped with a polyester net (mesh width

1.6 mm) to prevent sample contamination with coarse matter. SF was collected in three replicates per site using sliced polyurethane (PU) hoses (diameter 4 cm) as a collar installed at 1.60 m height, sealed with PU glue and connected with a polypropylene or PE barrel via a PE tube. To address the element input from the organic layer to the mineral soil, FF leachates were collected with three zero-tension lysimeters per site (280 cm^2 sampling area), installed in the vicinity of the TF samplers. They consisted of polyvinyl chloride plates covered with a PE net (mesh width 0.5 mm) connected with PE hoses to 2 L PE bottles stored in a box below ground.

2.3 Sampling procedure and analysis

BP, TF, SF and FF leachate samples were collected in September 2010 for ALB and the HAI beech sites and in August/September 2011 for SCH and the HAI spruce sites after a bi-weekly routine sample collection interval. The reasons to chose these sampling dates were threefold: beech canopies were fully developed, external inferring events such as pollen count by coniferous trees were terminated (mid May to mid June) and generally sufficient precipitation water occurs during this time of the year to perform the freeze-drying of large amounts of sample solutions for solid state ^{13}C NMR analysis. Individual samples of BP (3 × 5 = 15), TF (3 × 20 = 60), SF (3 × 3 = 9) and FF leachates (3 × 3 = 9), respectively, were pooled to one volume-weighted sample per sample type, sampling date and exploratory, respectively. The samples were stored in cooling boxes until further processing. At latest 24 h after collection, an aliquot of the BP, TF, SF and FF leachate samples was bottled unfiltered, whereas another was filtered with 0.45 µm cellulose acetate filters (Sartorius, Göttingen, Germany). Both the unfiltered and filtered aliquots were immediately frozen to prevent microbial alteration.

For solid state ^{13}C NMR analysis, between 400 and 800 mL of the filtered and unfiltered sample aliquots were freeze-dried (Christ Alpha 1–4, Osterode/Harz, Germany). Samples of BP contained insufficient amount (< 30 mg) of dry matter and could therefore not be analyzed with NMR spectroscopy. The same was true for three other ALB samples, encompassing the filtered TF sample and the filtered and unfiltered

SF samples. In total, 21 samples pooled from 9, 15 and 60 individual samples, respectively, were successfully analyzed by solid state ^{13}C NMR spectroscopy (Table 2).

Solid state ^{13}C NMR measurements were obtained with a Bruker DSX 200 NMR spectrometer (Bruker, Karlsruhe, Germany). CPMAS was applied with a ^{13}C resonance frequency of 50.32 MHz and a spinning speed of 6.8 kHz. A ramped ^{1}H pulse starting at 100 % and decreasing to 50 % of the initial power was used during a contact time of 1 ms in order to circumvent spin modulation during the Hartmann–Hahn contact. Pulse delays of 2 s were used for all spectra. Pre-experiments confirmed that the pulse delays were long enough to avoid saturation. Depending on the C content of the samples, 2070 to 130 939 scans were accumulated and a line broadening between 50 and 100 Hz was applied. The ^{13}C chemical shifts were calibrated relative to tetramethylsilane (0 ppm). Relative contributions from the various C groups were determined by integration of the signal intensity in the respective chemical shift regions according to Knicker et al. (2005). The region from 220 to 160 ppm was assigned to carbonyl (aldehyde and ketone) and carboxyl/amide C. Olefinic and aromatic C were detected between 160 and 110 ppm. O-alkyl and N-alkyl C signals were found from 110 to 60 ppm and from 60 to 45 ppm, respectively. Resonances of alkyl C were assigned to the region 45 to −10 ppm. We calculated the alkyl C/O-alkyl C (A/O-A) ratio for each fraction according to Baldock et al. (1997) as a sensitive index for the extent of decomposition. The relative aromaticity (in %) was estimated from the ratio aryl C/(aryl C + O-alkyl C + alkyl C) as proposed by Hatcher et al. (1981).

3 Results and discussion

3.1 ^{13}C NMR spectra

All spectra shown in Fig. 1 were dominated by the O-alkyl C region (110–45 ppm) and exhibited pronounced signals at ca. 72 ppm, corresponding to secondary carbinol C (i.e. C–2, C–3 and C–5 of pyranoside rings) in cellulose and hemicellulose (Almendros et al., 2000; Keeler et al., 2006; Lemma et al., 2007; Conte et al., 2010). Resonances at ca. 103 ppm were be assigned to anomeric C in carbohydrates (Rodríguez-Murillo et al., 2011), whereas N-substituted C of amino sugars contributed to the region between 58 and 51 ppm (Knicker and Kögel-Knabner, 1998). In all samples, a maximum peak in the carboxyl C region at ca. 172 ppm indicated the presence of carboxylic acids, amides and esters originating from compounds such as cutin, proteins and hydrolysable tannins (Lemma et al., 2007). However, unfiltered and filtered TF samples from the beech sites differed remarkably with regard to C composition. Unfiltered samples revealed clearly decreased signal intensities for the aryl C region (160–110 ppm) that mostly refers to lignin systems (ca. 135 ppm, unsubstituted; ca. 145 ppm, heterosubstituted; ca. 153 ppm, ether-linked; Conte et al., 2010; Rodríguez-Murillo et al., 2011) and increased intensities for the alkyl C region (45 to −10 ppm), corroborated with higher A/O-A ratio values and lower aromaticity indices for TOM vs. DOM (Tables 2 and 3).

This might likely point to aliphatic C from less decomposed organic material accompanied by reduced humification intensity compared with filtered TF samples, where the intensity of the aromatic C region (140–110 ppm) was amplified by 60 % on average. For the O-alkyl C (110–45 ppm) and carboxyl C (220 to 160 ppm) regions, the trends appeared inconsistent (Table 2, Fig. 1). In comparison with beech, the analysis of ^{13}C chemical shift regions of the unfiltered and filtered TF samples from the HAI spruce forests indicated only minor differences in C fraction composition (Table 2, Fig. 1). In this context, the C of the unfiltered TF samples exhibited slightly higher relative intensities for aliphatic C (45 to −10 ppm) and carbohydrate C (90–60 ppm) and lower relative intensities for aryl C (160–110 ppm) and carboxyl C (220–160 ppm) compared with filtered samples. This aspect was mirrored by the lower aromaticity index of the unfiltered samples (17.0) compared with the filtered samples (19.6) (Table 3). For the DOM in TF of a nearly 100 years old mixed Redwood and Douglas fir stand in California, Sanderman et al. (2008) found similar distributions in the relative intensities of chemical shift regions to the HAI spruce sites. In contrast, Fröberg et al. (2003) reported differing intensities for DOM in TF from a 35 yr old Norway spruce stand in southern Sweden, with lower carbonyl C and aryl C, but higher O-alkyl C contents, even resulting in lower A/O-A ratio (0.42) and aromaticity index (12.24 %). To our knowledge, there are no comparable studies of beech-derived TF samples as of SF samples in general.

As illustrated by difference spectra, unfiltered and filtered SF samples under beech as well as under spruce showed similar distributions and signal intensities (Fig. 1). However, the difference spectra from SCH samples exhibited pronounced peaks at ca. 30 ppm within the alkyl C region, which can be assigned to methylenes in fatty acyl chains (Lundberg et al., 2001). These peaks point to a local event at the SCH beech sites which might be derived from excretions of canopy insects such as the beech woolly aphid (*Phyllaphis fagi* L.) or other leaf-sucking insects. Herbivorous insect species are known to temporarily occur in mass infestations and then alter the input fluxes, especially of POM, by e.g. green leaf litter, wax wool excretion and cell tissue (Stadler et al., 2001; le Mellec and Michalzik, 2008). In this context, Greenway et al. (1974) reported on the composition of triglycerides found in cornicle secretions from a range of aphid families, including *P. fagi*. Additionally, Stanley-Samuelson et al. (1988) reviewed the formation of fatty acids in cuticular secretion components of other insect orders.

Regarding FF leachates under beech, unfiltered samples of two (HAI and SCH) out of the three exploratories exhibited higher intensities within the O-alkyl C region (110–45 ppm) and lower signals in the carboxyl C region (220–160 ppm) compared with the filtered samples (Fig. 1). While the aromaticity index among the FF leachate fractions were similar, with values around 22 and 24 %, the A/O-A ratio values were lower for the TOM than the DOM fractions (Table 3). This trend was observed for FF leachates from all the sites and for both tree species, except for the ALB beech sites. Here, the two fractions of FF leachate revealed only minor differences in C composition and A/O-A ratio. Again, no corresponding data for beech stands were available in

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the literature, but for a spruce forest site in southern Sweden, Fröberg et al. (2003) reported corroborating signal intensities from solid state ^{13}C NMR spectra of Oa layer solutions. In contrast, ^{13}C NMR data for FF leachates of a Californian mixed Redwood stand reported by Sanderman et al. (2008) exhibited lower intensities for alkyl C and remarkably higher intensities for the aromatic C region, resulting in an approximately halved A/O-A ratio compared with our spruce sites.

3.2 Differences in structural C composition along ecosystem compartments

At the beech sites, the compositional differences between DOM and TOM diminished from TF to SF and FF leachates. This might be related to longer stemflow–bark contact times due to the bark micro-relief, less changing environmental conditions and better substrate availability on the tree stem (Levia et al., 2012) and stagnant water on the litter surfaces of the forest floor favoring degradation of canopy-derived OM by the soil biota and epiphytic microorganisms that level out differences in the composition and quality between the two size fractions.

While DOM in spruce-derived TF samples comprised predominately a higher proportion of alkyl C (24.7 %), DOM in TF under beech was dominated by aryl C at the expense of alkyl C, resulting in remarkably higher aromaticity index values. A high proportion in aromatic C in DOM points to increased recalcitrance of DOM towards microbial degradability due to the inhibitory effect of these compounds on enzyme activity (Marschner and Kalbitz, 2003).

About 30 % of the aryl C was composed of phenolic C (Table 2), partly forming secondary metabolites which are known to inhibit both germination and growth of plants, thereby affecting the distribution patterns and composition of understory vegetation of forests (Rice, 1984; Muscolo et al., 2001; Hane et al., 2003). Furthermore, they affect the growth of mycorrhizal fungi (Lindeberg, 1985) and inhibit feeding by various fungi (Alfredsen et al., 2008) and potential herbivores (Dübeler et al., 1997; Petrakis et al., 2011). In their review, Wardle et al. (1998) concluded that the effect of plants with allelopathic potential on other organisms may ultimately result not only in net change at the population level (e.g. plant–plant interference), but in net change in ecosystem processes and functions (e.g. herbivory, decomposition and nutrient mineralization), which may be important in shaping plant community structure in the long term.

4 Conclusions

Structural data derived from solid state ^{13}C NMR analysis confirmed pronounced differences between filtered and unfiltered beech TF samples. The compositional differences between DOM and TOM diminished from TF to SF and FF leachates. This might be due to increased contact time and intensified microbial activity levelling out the compositional differences between the two OM fractions.

Since differences in the structural composition of DOM and TOM in TF and SF were less pronounced under spruce than under beech, we suspect a tree species-related effect on the origin of OM composition and resulting properties such as recalcitrance and allelopathic potential. To consolidate our findings on tree species-specific differences in the amount and functionality of OM in TF samples and ecological implications, research has to be extended spatially and to different tree species.

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Table 1. Environmental properties of the study regions (mainly given by Fischer et al., 2010; soil classification according to IUSS Working group WRB, 2006).

	Schorfheide-Chorin (SCH)	Hainich-Dün (HAI)	Schwäbische Alb (ALB)
Location	Northeast Germany (53° 2′ N, 13° 51′ E)	Central Germany (51° 10′ N, 10° 23′ E)	Southwest Germany (38° 24′ N, 9° 24′ E)
Altitude above see level	3–140 m	285–550 m	460–860 m
Mean annual temperature	8–8.5 °C	6.5–8 °C	6–7 °C
Mean annual precipitation	500–600 mm	500–800 mm	700–1000 mm
Geological substrate	Quarzitic glacial till	Triassic limestone with loess cover	Jurassic limestone
Main soil types	Cambisols Albeluvisols	Luvisols Stagnosols	Leptosols Cambisols
Main tree species	*Fagus sylvatica* L. *Pinus sylvestris* L. *Quercus* spp.	*Fagus sylvatica* L. *Picea abies* (L.) H. Karst. *Fraxinus excelsior* L.	*Fagus sylvatica* L. *Picea abies* (L.) H. Karst.

Table 2. Relative signal intensity (in %) of chemical shift regions revealed by solid-state ^{13}C NMR spectroscopy (filtered (f) and unfiltered (nf) samples of throughfall (TF), stemflow (SF) and forest floor (FF) leachates; n.a., not analyzed; ALB, Schwäbische Alb; HAI, Hainich-Dün; SCH, Schorfheide-Chorin).

	Integrated region		Chemical shift region		TF nf	TF f	SF nf	SF f	FF nf	FF f
	max.	min.								
HAI spruce	220	185	Carboxyl C	Carbonyl C	1.4	2.8	2.5	2.4	3.1	2.6
	185	160		Carboxyl C	9.2	9.7	10.2	10.2	12.8	12.7
	160	140	Aryl C	Phenolic C	4.9	5.7	5.6	5.5	6.0	5.8
	140	110		Aromatic C	10.3	11.5	11.5	11.1	12.8	12.2
	110	90	O-alkyl C	Di-O-alkyl C	9.0	8.6	9.7	9.6	8.7	8.2
	90	60		Carbohydrate C	29.3	27.4	29.9	30.4	25.3	24.8
	60	45		Methoxyl C	10.0	9.7	9.7	9.7	10.1	9.8
	45	–10	Alkyl C	Aliphatic C	25.8	24.7	20.9	21.1	21.3	23.9
HAI beech	220	185	Carboxyl C	Carbonyl C	3.9	1.5	2.4	2.1	2.4	4.4
	185	160		Carboxyl C	10.2	8.8	11.3	11.0	13.3	13.7
	160	140	Aryl C	Phenolic C	5.1	9.0	5.3	4.9	7.1	6.9
	140	110		Aromatic C	9.7	17.1	9.9	9.1	13.7	12.9
	110	90	O-alkyl C	Di-O-alkyl C	7.4	11.7	9.7	9.3	9.3	8.2
	90	60		Carbohydrate C	28.3	24.5	30.8	31.3	24.2	22.6
	60	45		Methoxyl C	8.5	8.6	9.5	9.8	10.4	9.9
	45	–10	Alkyl C	Aliphatic C	26.8	18.8	21.1	22.5	19.5	21.4
SCH beech	220	185	Carboxyl C	Carbonyl C	1.4	3.6	0.6	0.8	1.6	6.7
	185	160		Carboxyl C	9.3	10.2	9.5	10.7	9.6	11.9
	160	140	Aryl C	Phenolic C	7.0	10.2	3.9	5.3	6.5	6.2
	140	110		Aromatic C	13.3	19.0	8.2	9.7	13.4	12.0
	110	90	O-alkyl C	Di-O-alkyl C	10.2	11.9	8.2	8.8	9.9	8.1
	90	60		Carbohydrate C	27.0	23.5	30.6	29.4	27.5	24.0
	60	45		Methoxyl C	9.3	7.3	10.2	10.4	9.7	9.1
	45	–10	Alkyl C	Aliphatic C	22.5	14.3	28.8	24.9	21.7	22.0
ALB beech	220	185	Carboxyl C	Carbonyl C	1.9	n.a.	n.a.	n.a.	2.2	2.7
	185	160		Carboxyl C	10.1	n.a.	n.a.	n.a.	12.2	13.2
	160	140	Aryl C	Phenolic C	6.9	n.a.	n.a.	n.a.	6.1	6.3
	140	110		Aromatic C	12.7	n.a.	n.a.	n.a.	12.6	13.6
	110	90	O-alkyl C	Di-O-alkyl C	10.3	n.a.	n.a.	n.a.	8.9	9.4
	90	60		Carbohydrate C	28.6	n.a.	n.a.	n.a.	25.7	25.8
	60	45		Methoxyl C	8.7	n.a.	n.a.	n.a.	10.4	9.7
	45	–10	Alkyl C	Aliphatic C	20.9	n.a.	n.a.	n.a.	21.9	19.3

Table 3. Alkyl C/O-alkyl C (A/O-A) ratios and aromaticity (in %) calculated from chemical shift regions revealed by solid-state ^{13}C NMR spectroscopy of filtered (f) and unfiltered (nf) samples of throughfall (TF), stemflow (SF) and forest floor (FF) leachates; n.a., not analyzed; ALB, Schwäbische Alb; HAI, Hainich-Dün; SCH, Schorfheide-Chorin.

	Sample	A/O-A ratio	Aromaticity [%]
HAI spruce	TF nf	0.53	17.0
	TF f	0.54	19.6
	SF nf	0.42	19.7
	SF f	0.42	19.0
	FF nf	0.48	22.4
	FF f	0.56	21.2
HAI beech	TF nf	0.61	17.3
	TF f	0.42	29.1
	SF nf	0.42	17.7
	SF f	0.45	16.1
	FF nf	0.44	24.7
	FF f	0.53	24.2
SCH beech	TF nf	0.49	22.7
	TF f	0.33	33.9
	SF nf	0.59	13.5
	SF f	0.51	16.9
	FF nf	0.46	22.5
	FF f	0.53	22.4
ALB beech	TF nf	0.44	22.3
	TF f	n.a.	n.a.
	SF nf	n.a.	n.a.
	SF f	n.a.	n.a.
	FF nf	0.49	21.8
	FF f	0.43	23.7

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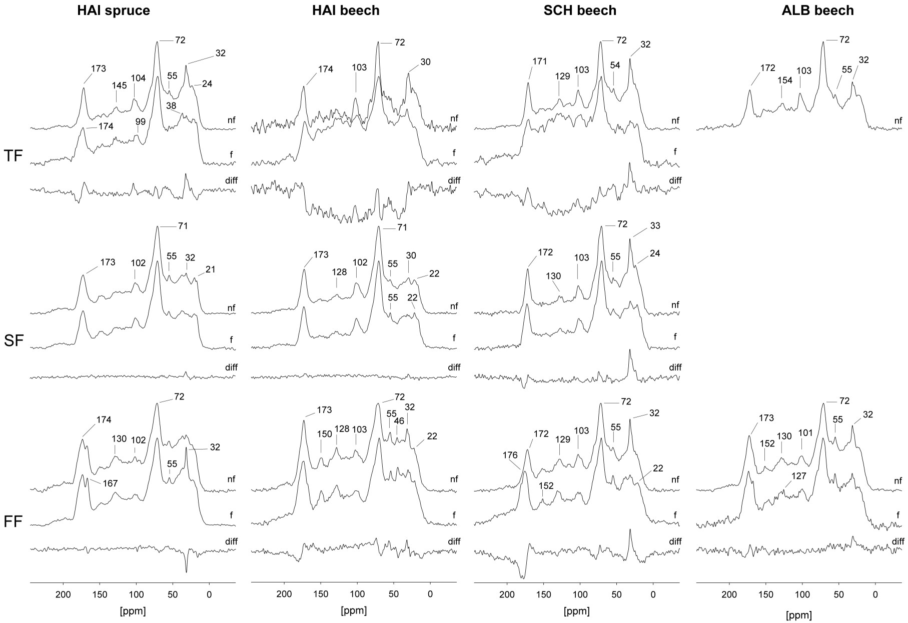

Figure 1. Solid-state CPMAS ^{13}C NMR spectra obtained from filtered (f) and unfiltered (nf) forest ecosystem water samples as well as calculated difference spectra (diff.) of both fractions; TF = throughfall, SF = stemflow, FF = forest floor leachate, ALB = Schwäbische Alb, HAI = Hainich-Dün, SCH = Schorfheide-Chorin.