We thank John Van Stan and the two anonymous referees for their comments and useful suggestions, which helped us to rework our manuscript.

Response to referees:

<u>John Van Stan</u>

General comments

We extended the conceptualisation of OM biogeochemical processes in tree canopies by additionally elucidating the importance of the cortisphere processes on OM transformation and quality. We also added additional site information on forest structure metrics. With regard to the length of the sampling period, we added a reference addressing this issue.

Specific comments

0) The abstract is not detailed enough and most of the writing past line 7 is unclear. For example, is the TOM versus DOM comparison in lines 9-12 for all samples regardless of species?
→ For clarity, we reworked the abstract completely from line 7 onwards:

The ^{13}C NMR results, derived from 21 samples, point to pronounced differences in the composition of DOM and TOM in throughfall solution at the beech sites with TOM exhibiting higher relative intensities for the alkyl C region, representing aliphatic C from less decomposed organic material compared to DOM. Furthermore, TOM is composed of lower intensities for lignin-derived and aromatic C of the aryl C region resulting in lower aromaticity indices and a diminished degree of humification. Along the ecosystem compartments, differences in the structural composition of DOM and TOM under beech lessened in the order throughfall > stemflow ≈ forest floor leachate. In contrast to the broadleaved sites, differences between DOM vs. TOM in throughfall solution under spruce were only less pronounced and spectra were overall dominated by the alkyl C region, representing aliphatic C. Explanations to the reported results might be substantiated in differences in tree species-specific structural effects, leaching characteristics or differences in the microbial community of the tree species´ phyllosphere and cortisphere. However, the fact that throughfall DOM under beech showed the highest intensities of recalcitrant aromatic and phenolic C among all samples analysed, likely points to a high alleleopathic potential of beech trees negatively affecting other organisms and hence ecosystems processes and functions."

What is meant by "fresh" POM in line 8?
→ since this wording appeared too unspecific, we left that out while rewording the abstract from line 7 onwards (s. above)

What is meant by a "tree species-related effect on the origin of OM composition [and] properties" – tree structural effect, tree-specific leaching characteristics, tree phyllosphere and cortisphere microbial community differences?
→ We reworked the abstract and some parts of the introduction, hoping to clarify the results/ explanations (s. above and below).

More information is needed in the abstract, like:
(a) what is the list of OM characteristics and metrics derived from the 13C NMR spec (see Table 1 and Table 2)?
→ We added more information on those characteristic spectroscopic measures.

1

(b) How many total samples were analyzed?

→ This information is given P15093L1 of the Discussion paper. However, we changed the sentence to: "In total, 21 samples were analyzed by solid state ^{13}C NMR spectroscopy. Table 3 provides an overview over the sample consortium." We also added this information in the abstract.

(c) Which results indicated species-specific throughfall, stemflow, or litter leachates may differ in allelopathic potential (see discussion P15096L27-&)?

→ Among all samples analysed, throughfall DOM under beech showed the highest intensities of aromatic and phenolic C (Table 4). Compared to throughfall DOM under spruce, the values for phenolic C were nearly twice as high and the ones for aromatic C by a factor of 1.5 to 1.7 times higher. Phenolic C forms part of polyphenols, secondary metabolites, being known for their alleleopathical potential (Rice, 1984, Muscolo et al., 2001 and Hane et al., 2003). However, the striking high phenolic C signal in beech throughfall is just one suggestion to partly explain why for example the spreading of beech in Europe after the last glacial era was competitively that effective and persistent (Petrakis et al., 2011). Nevertheless, up to date, we are lacking of comparable measurements to assess the allelopathic potential of throughfall DOM composition of different tree species to prove our suggestion.
We reworked the entire "Results and discussion section" addressing that issue.

1) An overarching hypothesis formed regarding differences in TOM and TOM structural transformations between the two species (P15090L8-11) has two issues in its current form:
(a) it focuses solely on how leaf structural differences for F. sylvatica versus P. abies can alter OM vis-à-vis microbial communities and substrate interaction in the phyllosphere: this neglects the fact that these species also have quite different bark structures and branching architectures hosting microbial communities and substrates capable of interacting during the throughfall or stemflow process to alter OM.
(b) it neglects to mention that interspecific differences in phyllosphere and cortisphere microbial community structure/function may also play a critical role in altering TOM travelling through the canopy along hydrologic flow paths.

→ Thank you for these suggestions. We added a new section on the effects of differences in bark traits on OM composition:
"Interspecific differences in bark traits and cortisphere properties, e.g. bark texture and colour, influence the microclimate and arthropod fauna (Nicolai, 1986) the plant epiphyte (Wyse and Burns, 2011) and microbial community (Andrews and Harris, 2000) consequently affecting the amount and composition of OM as well. For example, enhanced bark microrelief increases the contact time of stemflow solutions with bark surfaces leading to an enrichment of aromatic hydrocarbons (Levia et al., 2012) likely due to the enhanced degradation and release of soluble lignin compounds (Guggenberger et al. 1994)."

2) A key introductory component supporting the need for this research is that POM might be particularly relevant to other nutrient cycles (specifically through microbial decomposition processes [P15089L11]). But, the authors don't cite any studies in support of this statement, nor do they provide explicit explanation of how POM's C:N ratios (or myriad other microbially-attractive qualities) support this statement. Please make this connection more explicit and substantiated by citations as it is a piece of the foundation supporting "why" your work is necessary.

→ To support the "why" for our work we included additional facts on the amount of extra incoming OM by the POM fraction and the impact of the C-to-N ratio of organic matter on degradation processes. Therefore, we changed the introduction part as follows:
"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 µm), amounting to 11–15% for C and 14–21% for N relative to the total annual input by litterfall and TF (< 0.45 µm), respectively. 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., 2009, 2010), where the additional input of C and N by particulate organic matter represented between 20–30% of the total organic C and 10–20% of the total N fluxes with throughfall. The low C-to-N ratios of 12–14 for POM as reported by Lamersdorf and Blank (1995) furthermore suggest that this material might be particularly relevant to promote microbial decomposition processes (Fontaine et al., 2004), while wider C-to-N ratios of > 30 tend to decelerate decomposition rates (Pérez-Harguindeguy et al. 2000).”

3) Citation issues in introduction:
P15088L22: the statement “only a few have investigated the dynamics” is lacking necessary citations – please cite which few studies have done so.
→ We added the lacking citations (Carlisle et al., 1966; Sollins et al., 1980; le Mellec et al., 2009, 2010).

P15089L16-18: the statement “The chemical nature of mobile OM is: : :” currently lacks citation. Please provide.
→ We added Guggenberger and Zech (1994) and the fundamental work on humic substances by Schnitzer and Khan (1972) and Wardle et al. (1998), addressing other ecosystem processes induced by altered DOM composition.

P15089L28: The citation Levia et al., 2012 is incorrectly cited, as the authors’ statement discusses cation cycling and the citation does not investigate cation cycling – only DOM. If the authors wish to stick to that research group’s work for a citation, a more appropriate reference would be Van Stan et al. (2012, The effects of phenoseason and storm characteristics on throughfall solute wash-off: : :, Sci. Tot. Environ., 430: 48-58) for throughfall ion work, or Levia et al. (2011, Atmospheric deposition and corresponding variability of stemflow chemistry: : :, Atmos. Environ., 45: 3046-3054) for stemflow ion work.
→ Thanks a lot for this clarification. We decided to add both references on ion cycling as suggested by the reviewer as well as Gersper and Holowaychuk (1971) and Levia et al. (2012) addressing changes in DOM.

4) Study site description is lacking some details that are necessary, in my opinion, for contextualizing/interpreting results (even though a previous site description exists in Fischer et al. [2010]). Specifically, the authors lack a comparison of stand structure for the plots to substantiate that the interspecific structural differences described in **P15090L8-11** are present. Although a basic description of the F. sylvatica plots is supplied (P15091L13-17), the P. abies plantations are not described: : : are they also similarly-aged or -sized compared to the F. sylvatica plots? How do stand characteristics (density, basal area, height, dbh, etc) between P. abies and F. sylvatica compare?
→ In an additional Table 2, we compiled stand structure data presented by Schwarz et al. (2014) and reworked the paragraph from P15091 L 15 onwards:
“These forests are comparable with regard to tree age and tree species composition and are similar with regard to stand density, mean diameter at breast height, basal area and forest management (Table 2). In the Hainich-Dün exploratory we additionally collected samples from three Norway spruce (*Picea abies* (L.) H. Karst.) plantations (Table 2). We only choose spruce sites of the Hainich-Dün site, because the Schorfheide-Chorin exploratory only provides pine (*Pinus sylvestris* L.) stands and the spruce stands of the Schwäbische Alb differ in tree species composition (Schwarz et al., 2014).

Why were P. abies plots only chosen at one observatory when, according to Table 1, there were plots available in the Schwaebische Alb site? Doesn’t the sole selection of P. abies sites from Hainich-Duen diminish the authors’ aim for comparison of these species across different environmental conditions? I believe these questions could be answered (briefly) to the benefit of the manuscript while still leaving some details to be found in Fischer et al. (2010).
→ We add explanations to the text (see added text above).

5) Can the authors please provide some further details regarding their methods:

P15092L10-12: What were the sample collection procedures, more specifically? E.g., what type of bottles were used to collect/store the water? How long were samples permitted to remain in the field after a storm (this has a big impact on what DOM character will be observed)? Were bottles acid washed and triple-rinsed with sample prior to collection?

→ For the synchronisation of the field sampling campaigns in all three study regions performed by three different working groups, we stick to a fixed routine sampling interval of 14 days.
Concerning the impact of the time on sample composition, a field incubation study by Michalzik et al. (1997) reporting on the chemical composition of bulk and throughfall solutions, exhibited, that the throughfall composition (concentrations of N species and DOC) exposed during August was rather stable over the first two weeks of field incubation before DOC concentrations started to drop. However, since we are not aware of any study testing temporal changes of the structural character of DOM and especially TOM during field exposure, it is speculative and therefore difficult to comment. The bottles were acid washed and triple-rinsed with sample prior to collection.

P15092L19: Are the "cooling boxes" simply refrigerators? Regardless, at what temperature were the samples stored?

→ The samples were stored on ice in a cool box until further processing in the laboratory.

6) Results: Figure 1 was absent: : : Not sure if it is something I did during the download or if Figure 1 is really just not there: : : So, I took the authors at their word during descriptions of the 13C NMR spectra.

→ Figure 1 was not absent (Please compare with the downloaded pdf file of the Discussion paper, Fig. 1 is found on the last page P15107)

7) Discussion:
(a) The introduction links TOM structure in canopy-derived hydrologic fluxes to canopy-based microbial communities, yet the discussion generally avoids this topic. Is this because no bulk precipitation samples could be analyzed via 13C NMR spec?

→ Your suggestion is partly true, since we were technically not capable to perform ^{13}C NMR analysis to the bulk precipitation, we therefore do not know the DOM/TOM composition of atmospherically deposited onto the canopy and what is "internally" within the canopy produced or transformed. However, we restructured the Results and Discussions section partly addressing this issue.

(b) Depending on how long samples were allowed to sit in the field, could the authors please provide a discussion of how this would affect the character of their DOM and POM measurements?

→ Please compare with our answer given under 5)

(c) P15096L3-6: Please discuss why the aromatic C-region intensities for FF leachates of Sanderman et al. (2008)'s mixed redwood stand were so much higher than observed for your Spruce sites.

→ In the paper by Sandermann et al. (2008) it is not clearly stated when the solutions for solid state ^{13}C NMR spectroscopy were sampled. We assume that it is a composite sample collected throughout the rainy season (representing most of the annual rainfall of 1,450 mm) covering a period from Dec 2005-May 06 (see p. 185, Soil water sampling and Fig. 4), while our samples were collected over 14 days in August/September. According to the results of Kaiser et al. (2001) on "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", diverting sampling period and season might partly explain the differences in DOM composition in concert with differences in soil properties and tree species composition (Redwood/Douglas fir), and especially with differences in climate and hydrology (Mediterranean vs. Temperate). In this context, enhanced hydrological flux generation (e.g. throughout rainy seasons)

was shown to increase the aromaticity of DOM by the intensified degradation of soluble lignin compounds as observed by Guggenberger et al. (1994) and Levia at al. (2012).
Given that background information we shortly addressed that question in the reworked results and discussion part.

Editorial comments:

Abstract, P15088L7-8: The phrase "echoed in structural differences" is unclear, please revise. The verb "echo" literally means "repeated" or "reverberated", but can more symbolically mean "shared characteristics with". How does F. sylvatica leaf surface-derived POM "repeat" or "have shared characteristics with" total organic matter (TOM) structure differences? The abstract was completely reworded leaving this irritating phrase out.

Moreover, TOM differences in what (species? landscape? source?)? The reworked abstract is hopefully more specific answering that question.

Introduction, P15088L22: Please replace "but" in the statement "but none the character of water-bound TOM: : :" with "and". We replaced "but" by "and" (see also below).
Also, please insert a verb into the statement between "none" and "the". Perhaps the statement could read "and none investigated the character of water-bound TOM: : :"? We changed the sentence as follows: [ ] …., only a few investigated the dynamics of particulate OM (Carlisle et al., 1966; Sollins et al., 1980; Le Mellec et al., 2010) and none the dynamics of water-bound total OM (TOM) including the particulate OM fraction (POM; 0.45 µm<POM<500 µm).

Introduction, P15090L12: In the statement "fresh beech leaves exhibit" – do you mean to say "fresh beech leaves leach"?
→ We reworked the whole section:
"In this context, beech trees potentially exhibit the highest amounts of phenolics in leaves (Bussotti et al., 1998), bark (Dübeler et al., 1997), wood (Mämmelä, 2001) and roots (Weissen and Praag, 1991) compared to co-occurring species. Phenolic compounds released from living or dead plant material have been shown to function as allelochemicals, affecting associated species (Rice, 1984; Wardle et al., 1998). An interspecific allelopathic potential on other organisms may result in net changes in ecosystem processes and functions (e.g. herbivory, decomposition and nutrient mineralization) (Wardle et al., 1998). However, the release of phenolic or other allelopathic compounds from living plant material via throughfall and stemflow and the effects on ecosystem processes and function is still insufficiently understood."

Methods, P15092L134:
Two issues: The verb tense "were" should be "was". And, the terms "count" and "terminated" could be replaced with clearer terms, like "release" and "over" respectively.
→ We rephrased the sentence: "…. developed, external inferring events such as the release of pollen by coniferous trees was over (mid May to mid June) and…."

Results, P15095L5-6: The statement "as of SF samples in general" is unclear. Do you mean that there are no studies reporting on stemflow 13C NMR spec-derived TOM characteristics and metrics? Please clarify.
→ Your interpretation is right and for clarification we reworked the statement:
"The discussion generally lacks of comparable data on TOM composition. To the best of our knowledge, there are no studies available reporting on solid state ^{13}C NMR spectroscopy-derived TOM characteristics in TF, SF and FF leachate samples under beech or other tree species."

Anonymous referee # 2

General comments
GC 1 I would have appreciated a list of abbreviations to help navigating the text, such as BP, FF; ALB, TF, HAI etc.
→ We're now providing a list of abbreviations.

GC 2 P 15090/L07-16 contain interesting hypotheses and I implicitly assumed they would be re-visited in the discussion or conclusion, but there they are not addressed explicitly. Can you extend on these?
→ We followed your suggestions.

GC 3 In Fig. 1 - Please add a line, marking zero, to the graph of the differences between filtered and unfiltered samples. It is difficult to make out where the difference is positive or negative.
→ We added the lines in Fig. 1.

GC 4 Fig 1, Table 2: The first lines in Section 3.2 say that differences in DOM and TOM diminished from TF to SF and FF. I understood this as implying an order, that is TF>SF>FF, and refers again to the differences in filtered and unfiltered samples shown in Fig. 1 and Table 2? The following sentences and also the first paragraph in the conclusions seem to further develop this suggestion. But in Fig 1 and also Table 2 the (absolute) differences between filtered and unfiltered samples seem to go in a different order order: TF>FF>SF. This needs to be clarified.
→ That is a tricky question and the order between SF and FF varies with the chemical shift regions being of interest and with the ratios (of aromaticity or of alkyl C/0-alkyl C) derived from them. If we only look at the chemical shift regions (now Table 3) then your impression is right. If we look at the aromaticity % or the alkyl C/0-alkylC ratio for SF and FF at the Schorfheide site (now Table 4), then differences appear more pronounced for the SF composition. However, since the order between compositional differences between SF and FF is less definite, we changed the order to TF > SF ≈ FF.

GC 5 Results vs. discussion: Much of section 3.1 reads like a results section, while 3.2 reads like a discussion section. In 3.1 some literature is cited for comparison, i.e. whether the observed differences were to the same direction in other studies, but there is no discussion of the potential mechanisms. Only one paragraph includes discussion on mechanisms, but only for a particular item (P 15095 L7-20), that is the possibly influence of insect infestation on the results.
I propose transforming section 3.1 into a results section (while I think it is ok to keep the references to the literature for comparing the measurements) and section 3.2 into an interpretation section (or simply "discussion"). For this, move the paragraph P 15095 L7-20 into (now) section 3.2. If you go with this suggestion, mechanisms would only be discussed in section 3.2 and the heading could be adjusted accordingly to help orientation for the reader. The current name of section 3.2 is misleading as "differences in structural C composition" are also a topic in section 3.1.
→ We understand your concerns and therefore we merged section 3.1 with 3.2, add subtitles for each ecosystem compartment, and insert discussions on mechanisms potentially driving the results and differences we observed. However, for the sake of clarity while presenting numerous NMR data, cited literature for comparison and potential mechanisms, we stick to a combined "Results and discussion" section.

Detailed comments
DC 1 P15089-L13: Sentence should start better with "Although"
→ We changed it to "although".

DC 2 P15089-L26: Better "Previous work" or "Previous studies"
→ We changed it to "Previous work".

DC 3 P15089-L26-28: I find this sentence far fetched to motivate the need to study the influence of tree species on properties of DOM. In fact it would read better if the sentence was erased.

→ According to reviewer #1 we reworded this sentence adding some references as well:
"Previous work has demonstrated that tree species and spatial and temporal patterns of environmental conditions such as chemical soil properties influence the input and cycling of cations (Gersper and Holowaychuk, 1971; Finzi et al., 1998; Levia et al., 2011; Van Stan et al., 2012) and DOM in temperate forests (Levia et al., 2012).

DC 4 P 15094-L3: I believe it is meant "were being" instead of "were be" or simply erase "be".

→ We corrected it to "were assigned".

Anonymous referee # 3

General comments

The authors have submitted a potentially interesting ms about water-transported organic compounds in, among others, throughfall, stemflow, and forest floor leachates.
To this purpose they have used three sites across Germany, each having stands with two tree species, namely common beech and Norway spruce.
→ That is not correct. There are no Norway spruce stands in the Schorfheide-Chorin exploratory. However, we address this issue in the last paragraph of the Introduction as well as in the Methods section 2.1 Study sites.

The authors have not given any clearly stated aim but mention in the Introduction that this is the first study to evaluate the relative sizes and the chemical composition of the main flows of dissolved organic matter and organic matter in suspension.
→ This is not correct. In the original Introduction we did not mention that this "is the first study to evaluate the relative sizes and the chemical composition…". In the revised version we reworked the Introduction as suggested by the other two reviewers, now clearly stating our aims: "Therefore, we present the first study investigating the composition of DOM compared to TOM by solid state ^{13}C NMR spectroscopy.
We tested the hypotheses that (i) the structural composition of DOM in filtered and TOM in unfiltered forest ecosystem water samples differ along ecosystem compartments and (ii) between tree species, exemplarily tested between beech and spruce at one of our study regions."

Thus, in the Introduction they give a very good motive for the study.
They also present two hypotheses namely that the chemical composition differ between total organic matter and dissolved organic matter as well as between the two tree species common beech and Norway spruce. In conclusion, the study is potentially valuable and can give new information.

When it comes to presenting their study in a manuscript the authors have not done a very good job (see also below). The main lines they sketch in the Introduction dissolve in the first section in Results. In fact, the present ms gives me the idea of a project report. I would recommend that the paper is

restructured (please see below). The aim(s) need to be clearly stated and a linguistic revision is needed. I would recommend that the authors should be encouraged to resubmit their paper.

→ To sharpen our aims, we restructured the Introduction and the Results and Discussion section. The paper was already revised by native speakers.

My advice would be to present an ms that gives focus onto one site and a comparison between spruce and beech, alternatively to use just the beech data for three sites. Either of these alternatives may give the impression of a finished study.

Specific comments

The authors describe their sites and the measurements carried out at them. Still, when studying tables 2 and 3, figure 1, and the para beginning on line 24 on page 15092 it appears that the authors have not enough data to make a good comparison of the two tree species. With spruce missing from two out of three sites there is no good possibility to develop thoughts about hypothesis (ii).

→ We like to emphasize that every throughfall (TF) sample analysed by ^{13}C NMR consists of a pooled sample made up of 60 individual TF solutions collected by 60 throughfall samplers at each exploratory (see P5 L139 in the Methods section). Even though we included only the three spruce sites at the Hainich-Dün exploratory, tree-specific properties are spatially well represented and the comparison of beech vs. spruce provides a good first insight into the interspecific differences in DOM and TOM composition.

"Individual samples of BP (3 sites x 5 replicates = 15), TF (3 sites x 20 replicates = 60), SF (3 sites x 3 replicates= 9) and FF leachates (3 sites x 3 replicates = 9), were pooled to one volume-weighted sample per sample type, sampling date and exploratory."

→ In the Methods section 2.1 Study sites, we give reasons why we were only able to sample the spruce sites at Hainich-Dün exploratory. "In the Hainich-Dün (HAI) exploratory we additionally collected samples from three Norway spruce (*Picea abies* (L.) H. Karst.) plantations (Table 2). We only choose spruce sites of the Hainich-Dün exploratory, because the Schorfheide-Chorin exploratory (SCH) only provides pine (*Pinus sylvestris* L.) stands and the spruce stands of the Schwäbische Alb exploratory (ALB) differ in tree species composition (Schwarz et al., 2014)."

→ Additionally, we clarified our hypothesis with regard to the tree species comparison (see above).

With the background presented in the Introduction I would expect that Results and Discussion starts with the main lines, for example amounts of bulk precipitation, amounts of stemflow as well as of DOM and POM plus forest floor leachates in both types of stands, thus data giving an overview. What I see is a detailed description of C-NMR spectra, which per se is all right as a subsection but which would fit in a bit later in the paper.

→ It was not the objective of this study to present flux data of DOM and TOM, but data on the chemical structure and properties of DOM compared to TOM. This was clearly stated in the title of the ms, in the first line of the abstract as well as in the introduction (P 15091 L 1). Since it was not possible to analyse bulk precipitation by solid state ^{13}C NMR spectroscopy (please see P 15092 L26), we focussed on throughfall, stemflow and forest floor leachate. However, based on the comments and useful suggestions of the other two reviewers we reworked the Abstract and Introduction to further clarify the aims and motivation of our study.

Further, this section (3.1) is intended to give the properties of the compounds identified but in part it is not clear to me what is data for spruce and what is beech. The text is not clearer as regards what refers to TOM and to DOM (hypothesis i) as the authors use the terminology 'filtered' and 'unfiltered'. Earlier, in Methods and Introduction they define the fractions by particle size (less than and bigger than 45 μm). It would be better and clearer to the reader to keep to the once defined terminology.

→ Although the first paragraph of the Introduction provides an overview over the terminology, we changed the wording of hypothesis i):
We tested the hypotheses that (i) the structural composition of DOM in filtered and TOM in unfiltered forest ecosystem water samples differ along ecosystem compartments and (ii) between tree species, exemplarily tested between beech and spruce at one of our study regions."

The authors write in the hypothesis para (last para in te Introduction) that they have an hypothesis about chemical recalcitrance and allelopathic potential. That hypothesis is not even approached in the text, except for some comments to references.
→ We understand your concerns and therefore we present additional information in the Introduction as well as in the Results and Discussion part.

The number of abbreviations and acronyms is a bit high and some terms are introduced which are not really necessary. Please remove such ones as PE for polyethylene and PU for polyurethane – they are not really used. In line 24 (last line) on p 15089 the list of 'DOM and POM in TF, SF and FF' is a bit hard on the reader.
→ Since "PE" for polyethylene is used five times within this paragraph we like to stick to the abbreviations.
Additionally, we will provide a list of abbreviations as suggested by Reviewer #2.

Page 15090 lines 4 thru 6. The authors mention two species and draw a conclusion about 'coniferous' vs 'broadleaved' ?
→ This part is shifted to the Results and Discussion section. There we clarified the terms by exchanging 'coniferous' by spruce and 'broadleaved' by beech.

Details

Key words are missing.
→ We're now providing key words.

Abstract. Use the full names of the two species ideally with the Latin name after. E.g. common beech (Fagus sylvatica). Further, often chemical compounds are introduced. Thus '….carbon (C).
→ We followed your suggestion.

Line 2. Define each term separately – thus total OM (TOM), consisting of DOM and particulate OM (POM)….
→ We reworked the abstract and defined each term separately.

Introduction.
Line 18. Introduce carbon (C) and nitrogen (N) before you use the chemical denominations.
→ We followed your suggestion.

Page 15089, line 10. Normally written C-to-N ratios
→ We changed to C-to-N ratios.

Same page line 15. What is OM in solution(?) – it seems to be in some kind of contrats to DOM in the line above? Or do you simply mean OM suspended in water?
→ For clarification we changed it to "TOM in solutions".

Page 15089 lines 19 thru 25. Split up that long sentence
→ We reworded the sentence to:

9

"In this context, precipitation patterns (Mercier and Lindow, 2000) and canopy architecture (Levia and Frost, 2006; Levia et al., 2012) basically alter the release of OM with throughfall. Atmospheric deposition (e.g. pollen, inorganic N deposition, Lamersdorf and Blank, 1995) and increased nutrient leaching from damaged leaves and immobilization processes within the canopy mediated by phyllosphere microorganisms (Guggenberger and Zech, 1994; Stadler and Mueller, 2000) appear to influence the chemical qualities of OM from the forest canopy."

Page 15090, line 7 the percentages 30-40% and 17-20%. Percent of what?
→ Percent of "rainfall interception rate values"
"Additionally, spruce canopies exhibit higher rainfall interception rate values of 30-40 % compared with 17-20 % for beech canopies (Rothe et al., 2002)."

Same page line 9 'time'
→ We corrected it to "time".

Methods

Section 2.1 The sentence staring with 'The three regions.....' Fits better at the end of the para
→ We reworked this paragraph (see above), ending with the reasons why we were only able to sample the spruce sites at Hainich-Dün exploratory.

Section 2.2.
First line; 'exploratory'? That word is an adjective in English. If the authors mean 'site' please write that.
→ It is more than a "site". It is a region/ landscape in which several forest sites are located. The concept of the "Biodiversity Exploratories" as a scientific platform for biodiversity research is elucidated in the paper by Fischer et al. (2010) and received international recognition. Overall, we are instructed by the steering committee of the "Biodiversity Exploratories" to use the term "exploratory" in a general sense, like e.g. "observatory". We therefore like to keep this word.

Set up should be setup.
→ We corrected it.

Line 2. Five replicates from each of the three open areas?
→ That is correct.
Line 4 '...collectors of the 'same type'... same type as what?
→ We used the same open funnel samplers (diameter 0.12 m) for collecting throughfall (TF) as well as bulk precipitation (BP). We collected BP in 5 replicates and TF in 20 replicates.
"… 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…"

Section 2.3
First para, first lines. Introduce the abbreviations ALB, HAI and SCH in he text. The same para, line 18 (3x3=9), respectively… why respectively?
→ We left the word "respectively" out.

Line 21. 'bottled'? Does that mean that you took an unfiltered sample? Third para (p 15093) line 20.

→ That is correct. We took an unfiltered solution to analyse TOM by solid state ^{13}C NMR spectroscopy.

Sensitive? Do you mean 'sensitivity'
→ We mean the adjective "sensitive" and not the noun.

Results and Discussion
First para (p 15094) line 3 delete 'be'
→ We corrected it to "were assigned".

Line 9 'differed remarkably' - from what?
→ "Unfiltered and filtered TF samples from the beech sites differed remarkably with regard to C composition."

Section 3.2, 2nd para, line 19 and 20. 'Enzyme activity' ?? It is importatnt for such a discussion to make clear what enzymes that were inhibited.
→ We followed your suggestion.

Conclusions
Last line '….research has to be extended spatially and to different tree species.' That phrasing is a bit surprising for a conclusion in this paper. Having read the Introduction and Methods I would expect that to be what this paper deals with. Three regions across Germany and two tree species.
→ Beech and spruce forests are the most common forest types in Germany and they are also representative for large regions in Central Europe. They provide important ecosystem services (e.g. nutrient and carbon cycling, biodiversity), which are worth to study. Since information on the structural composition of DOM and TOM in forest ecosystem water samples is generally scarce, we conducted this first orientating study including the three regions (or Exploratories) across Germany. That is why we also state that "…research has to be extended spatially and to different tree species."

Table 3 and in other places, e.g. Fig 1. 'unfiltered' is abbreviated nf? Why not uf?
→ We changed the abbreviations to "fil." for filtered and "unf." for unfiltered.

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

S. Bischoff[1]**, M. T. Schwarz**[2]**, J. Siemens**[3]**, L. Thieme**[3]**, W. Wilcke**[2,*]**, and B. Michalzik**[1]

[1]Institute of Geography, Friedrich Schiller University Jena, Löbdergraben 32, 07743 Jena, Germany
[2]Institute of Geography, University of Berne, Hallerstrasse 12, 3012 Berne, Switzerland
[3]Institute for Crop Science and Resource Conservation, Rheinische Friedrich Willhelms University Bonn, Nussallee 13, 53115 Bonn, Germany
[*]now at: Institute of Geography and Geoecology, Karlsruhe Institute of Technology, Reinhard-Baumeister-Platz 1, 76131 Karlsruhe, Germany

Correspondence to: S. Bischoff (sebastian.bischoff@uni-jena.de)

Abstract

For the first time, we investigated the composition of dissolved organic matter (DOM) compared to total OM (TOM, consisting of DOM, $< 0.45\,\mu m$ and particulate OM, POM $0.45\,\mu m < POM < 500\,\mu m$) in throughfall, stemflow and forest floor leachate of beech and spruce common beech (*Fagus sylvatica* L.) and Norway spruce (*Picea abies* (L.) H. Karst.) forests using solid state ^{13}C nuclear magnetic resonance (NMR) spectroscopy. We hypothesized that the composition and properties of OM in forest ecosystem water samples differed differ 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

The ^{13}C NMR results, derived from 21 samples, point to pronounced differences in the composition of DOM and TOM in throughfall solution at the beech sites with TOM exhibiting higher relative intensities for the alkyl C region, representing aliphatic C from less decomposed organic material , and lower relative compared to DOM. Furthermore, TOM shows lower intensities for lignin-derived and aromatic C of the aryl C region , resulting in lower aromaticity indices and reduced humificationintensities. Since a diminished degree of humification. Along the ecosystem compartments, 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)under beech lessened in the order throughfall > stemflow ≈ forest floor leachate.

In contrast to the broadleaved sites, differences between DOM vs. TOM in throughfall solution under spruce were only less pronounced and spectra were overall dominated by the alkyl C region, representing aliphatic C. Explanations to the reported results might be substantiated in differences in tree species-specific structural effects, leaching characteristics or differences in the microbial community of the tree species´ phyllosphere and cortisphere. However, the fact that throughfall DOM under beech showed the highest intensities of recalcitrant aromatic and phenolic C among all samples analyzed, likely

points to a high alleleopathic potential of beech trees negatively affecting other organisms and hence ecosystem processes and functions.

Abbreviations.

^{13}C CPMAS NMR	Carbon-13 cross-polarization and magic angle spinning nuclear magnetic resonance
ALB	Schwäbische Alb exploratory
A/O-A	Alkyl C to O-alkyl C ratio
BP	Bulk precipitation
DOM	Dissolved organic matter
FF	Forest floor
HAI	Hainich–Dün exploratory
OM	Organic matter
PE	Polyethylene
POM	Particulate organic matter
SCH	Schorfheide–Chorin exploratory
SF	Stemflow
TF	Throughfall
TOM	Total organic matter

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~~ (C) and nitrogen (N) 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~~ few investigated the dynamics ~~, but~~ (Carlisle et al., 1966; Sollins et al., 1980; le Mellec, Habermann; le Mellec et al., 2010) and

3

none the character of water-bound total OM (TOM) including the particulate OM fraction (POM; 0.45 μm < POM < 500 μm). Since water-bound element and nutrient concentrations are conventionally measured after filtration (frequently to ≤ 0.45 μm 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 μm to the overall budgets of C, 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 μm). 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, Habermann; le Mellec et al., 2010), where the additional input of C and N by particulate organic matter represented between 20–30% of the total organic C and 10–20% of the total N fluxes with throughfall. The low C-to-N ratios of 12–14 for POM as reported by Lamersdorf and Blank (1995) furthermore suggest that this material might be particularly relevant to promote microbial decomposition processes (Fontaine et al., 2004), while wider C-to-N ratios of > 30 tend to decelerate decomposition rates (Pérez-Harguindeguy et al., 2000).

Although some knowledge of the amount and temporal dynamics of DOM and POM is available, the composition especially of TOM in solutions and its alteration traversing forest canopies, stem surfaces and subsequently 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~~ as well as other ecosystem processes in forests (Schnitzer and Khan, 1972; Guggenberger and Zech , 1994; Wardle et al., 1998) . Alteration in the composition of OM ~~with TF and~~ in throughfall, stemflow (SF) ~~routing through the canopy are~~ and FF solutions are assumed to be driven by various abiotic and biotic processes. In this context, precipitation patterns (Mercier and Lindow, 2000) ~~, canopy architecture (Levia and Frost, 2006) , atmospheric~~ and canopy architecture (Levia and Frost, 2006; Levia et al., 2012) basically alter the release of OM with throughfall. Atmospheric deposition (e.g. pollen, inorganic N deposition, ~~Lamersdorf and Blank, 1995)~~ ~~,~~ Lamersdorf and Blank (1995)) and 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~~ (Guggenberger and Zech , 1994; Stadler and Müller, 2000) appear to influence the chemical qualities of OM from the forest canopy. Interspecific differences in bark traits and cortisphere properties, e.g. bark texture and colour, influence the microclimate and arthropod fauna (Nicolai, 1986) , the plant epiphyte (Wyse and Burns, 2011) and microbial community (Andrews and Harris, 2000) consequently affecting the amount and composition of OM as well. For example, enhanced bark microrelief increases the contact time of stemflow solutions with bark surfaces leading to an enrichment of aromatic hydrocarbons (Levia et al., 2012) likely due to the enhanced degradation and release of soluble lignin compounds (Guggenberger et al., 1994) .

~~Work~~ Previous work has demonstrated that tree species and spatial and temporal patterns of environmental conditions such as ~~soil acidity influence cation cycling~~ chemical soil properties influence the input and cycling of cations (Gersper and Holowaychuk, 1971; Finzi et al., 1998; Levia et al., 2011; Van Stan et al., 2012) and DOM in temperate forests ~~(Finzi et al., 1998; Levia et al., 2012)~~ (Levia et al., 2012) . However, it is unclear how tree species influence chemical properties of DOM and especially of POM in TF, SF and FF leachates and hence subsequently affect soil processes by varying chemical composition and associated functionality. ~~For instance, in~~

5

Germany spruce trees exhibit a denser foliage and higher leaf area index of 20.5compared with 6.5for 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 30–40compared with 17–20for 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 In this context, beech trees potentially exhibit the highest amounts of phenolics in leaves (Bussotti et al., 1998) , bark (Dübeler et al., 1997) , wood (Mämmelä, 2001) and roots (Weissen and Van Praag, 1991) compared to co-occurring species. Phenolic compounds released from living or dead plant material have been shown to be function as allelochemicals, affecting associated species (Wardle et al., 1998) . (Rice, 1984; Wardle et al., 1998) . An interspecific allelopathic potential on other organisms may result in net changes in ecosystem processes and functions (e.g. herbivory, decomposition and nutrient mineralization) (Wardle et al., 1998) . However, the release of phenolic or other allelopathic compounds from living plant material via throughfall and stemflow and the effects on ecosystem processes and function is still insufficiently understood.

Solid To elucidate the composition of DOM and TOM in terrestrial ecosystem water samples we applied solid state ^{13}C nuclear magnetic resonance spectroscopy with cross-polarization and magic angle spinning (CPMAS-NMR)is a , which 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. Therefore, we present the first study investigating the composition of DOM compared to TOM by solid state ^{13}C NMR spectroscopy.

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

2   Methods

2.1   Study sites

The sites are in three landscapes forming part of the German ~~"Biodiversity Exploratories"~~ "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"~~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~~.

These forests are comparable with regard to tree age and tree species composition, ~~stem density~~ and are similar to stand density, mean tree diameter at breast hight, basal area and forest management (Table 2). In the Hainich–Dün exploratory (HAI) we additionally collected samples from three Norway spruce (*Picea abies* (L.) H. Karst.) plantations ~~.~~ (Table 2). We only choose the HAI spruce sites, because the Schorfheide–Chorin (SCH) exploratory only provides pine (*Pinus sylvestris* L.) stands and the spruce stands of the Schwäbische Alb exploratory (ALB) differ in tree species composition (Schwarz et al., 2014) .

2.2 Experimental ~~set up~~setup

The experimental ~~set up~~ setup 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~~ Stemflow 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~~ polyurethane 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

Samples of 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~~ choose these

sampling dates were threefold: beech canopies were fully developed, external inferring events such as ~~pollen count~~ the release of pollen by coniferous trees ~~were terminated~~ was over (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 ($\cancel{3 \times 5 = 15}$ 3 sites $\times$ 5 replicates $= 15$), TF ($\cancel{3 \times 20 = 60}$ 3 sites $\times$ 20 replicates $= 60$), SF ($\cancel{3 \times 3 = 9}$ 3 sites $\times$ 3 replicates $= 9$) and FF leachates ($\cancel{3 \times 3 = 9)\ ,\ respectively,}$ 3 sites $\times$ 3 replicates $= 9$) were pooled to one volume-weighted sample per sample type, sampling date and exploratory, respectively. The samples were stored ~~in cooling~~ on ice in cool boxes until further processing in the laboratory. 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~~ < 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~~ 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 ($\cancel{< 30}$ < 30 mg) of dry matter and could therefore not be analyzed with NMR spectroscopy. The same ~~was~~ held 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~~ were analyzed by solid state ^{13}C NMR spectroscopy ~~(Table 2)~~. Table 3 provides an overview over the sample consortium.

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~~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~~

Throughfall
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~~160–110 ppm) that mostly refers to lignin systems ~~(ca.~~ [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~~), corroborated~~ ppm), corroborating with higher A/O-A ratio values and lower aromaticity indices for TOM vs. DOM (Tables ~~2 and~~ 3 and 4).

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~~140–110 ppm) was amplified by 60 % on average. For the O-alkyl C (~~110–45~~110–45 ppm) and carboxyl C (220 ~~to~~ −160 ppm) regions, the trends appeared inconsistent (Table ~~2~~3, Fig. 1). In essence, 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 effects of these compounds on enzyme activity (e.g. α-amylase, trypsin, lysozyme) (Rohn et al., 2002; Marschner and Kalbitz, 2003).

About 30 % of the aryl C was composed of phenolic C (Table 3), 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.

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~~3, 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~~90–60 ppm) and lower relative intensities for aryl C (~~160–110~~160–110 ppm) and carboxyl C (~~220–160~~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~~4).

The less pronounced differences in DOM and TOM composition under spruce compared to beech appear to be substantiated in differing interspecific canopy metrics. Spruce trees in Germany exhibit a denser foliage and higher leaf area index of 20.5 ~~old mixed Redwood and Douglas fir stand in California,~~ 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, spruce canopies provide a higher filtering capacity for airborne compounds and higher accumulation rate than beech 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 time for rainwater and needle surfaces and substrate availability and hence more stable environmental conditions within the phyllosphere, likely promoting the microbial decomposition of TOM to DOM and hence diminishing structural differences.

Compared to the HAI spruce sites, Sanderman et al. (2008) found similar distributions in the relative intensities of chemical shift regions ~~to the HAI spruce sites~~for DOM in TF of a nearly 100 years old mixed Redwood and Douglas-fir stand in California. In contrast, Fröberg et al. (2003) reported differing intensities for DOM in TF from a ~~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.

The diverting results from Sweden are likely due to the younger stand age or differences in stand structure and climate.

Stemflow

As illustrated by difference spectra, unfiltered and filtered SF samples under beech as well as under spruce showed similar distributions and signal intensities (Fig. 1.1). 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 (110–45110–45 ppm) and lower signals in the carboxyl C region (220–160220–160 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 34). 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 the literature, but for a spruce forest site in southern Sweden, Fröberg et al. (2003) reported corroborating similar 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.

3.1 ~~Differences in structural C composition along ecosystem compartments~~

~~At the beech sites, the~~ We assume that the diverting sampling period and season along with different climatic and hydrological conditions (Mediterranean vs. Temperate) are responsible for the differences in DOM composition. In this context, enhanced hydrological flux generation (e.g. throughout rainy seasons) was shown to increase the aromaticity of DOM by the intensified degradation of soluble lignin compounds as observed by Guggenberger et al. (1994) and Levia et al. (2012) .

In summary, the compositional differences between DOM and TOM at the beech sites diminished from TF ~~to SF and~~ $>$ SF $\approx$ FF leachates. This might be related to longer stemflow–bark contact ~~times~~ time due to the bark micro-relief, less changing environmental conditions and better substrate availability on the tree stem ~~(Levia et al., 2012)~~ (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)~~ Differing composition of DOM under beech vs. spruce might be substantiated in differences in tree species-specific structural effects, leaching characteristics or differences in the microbial community of the tree species´ phyllosphere and cortisphere (Guggenberger and Zech , 1994; Stadler and Müller, 2000) .

14

~~About 30of 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.~~ <u>The discussion generally lacks of comparable data on TOM composition as, to the best of our knowledge, there are no studies available reporting on solid state ^{13}C NMR spectroscopy-derived TOM characteristics in TF, SF and FF leachate samples under beech or other tree species.</u>

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 ~~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~~ <u>further</u> tree species.

References

Alfredsen, G., Solheim, H., and Slimestad, R.: Antifungal effect of bark extracts from some European tree species, European J. Forest Res.-Jpn., 127, 387–393, 2008.

Almendros, G., Dorado, J., González-Vila, F. J., Blanco, M., and Lankes, U.: ^{13}C NMR assessment of decomposition patterns during composting of forest and shrub biomass, Soil Biol. Biochem., 32, 793–804, 2000.

Andrews, J. H. and Harris, R. F.: The ecology and biogeography of microorganisms on plant surfaces, Annu. Rev. Phytopathol., 38, 145–180, 2000.

Balaria, A., Johnson, C. E., and Xu, Z.: Molecular-scale characterization of hot-water-extractable organic matter in organic horizons of a forest soil, Soil Sci. Soc. Am. J., 73, 812–821, 2009.

Baldock, J., Oades, J., Nelson, P., Skene, T., Golchin, A., and Clarke, P.: Assessing the extent of decomposition of natural organic materials using solid-state ^{13}C NMR spectroscopy, Aust. J. Soil Res., 35, 1061–1084, 1997.

Baldock, J. A., Masiello, C., Gelinas, Y., and Hedges, J.: Cycling and composition of organic matter in terrestrial and marine ecosystems, Mar. Chem., 92, 39–64, 2004.

Bussotti, F., Gravano, E., Grossoni, P. and Tani, C.: Occurrence of tannins in leaves of beech trees (*Fagus sylvatica*) along an ecological gradient, detected by histochemical and ultrastructural analyses, New Phytol., 138, 469–479, 1998.

Carlisle, A., Brown, A., and White, E.: The organic matter and nutrient elements in the precipitation beneath a sessile oak (*Quercus petraea*) canopy, J. Ecol., 54, 87–98, 1966.

Conte, P., De Pasquale, C., Novotny, E. H., Caponetto, G., Laudicina, V. A., Ciofalo, M., Panno, M., Palazzolo, E., Badalucco, L., and Alonzo, G.: CPMAS ^{13}C NMR characterization of leaves and litters from the reafforestated area of Mustigarufi in Sicily (Italy), Open Magnetic Resonance Journal, 3, 89–95, 2010.

Coulson, C., Davies, R., and Lewis, D.: Polyphenols in plant, humus, and soil. 1. Polyphenols of leaves, litter, and superficial humus from mull and mor sites, J. Soil Sci., 11, 20–29, 1960.

Currie, W. S., Aber, J. D., McDowell, W. H., Boone, R. D., and Magill, A. H.: Vertical transport of dissolved organic C and N under long-term N amendments in pine and hardwood forests, Biogeochemistry, 35, 471–505, 1996.

Dübeler, A., Voltmer, G., Gora, V., Lunderstädt, J., and Zeeck, A.: Phenols from *Fagus sylvatica* and their role in defence against *Cryptococcus fagisuga*, Phytochemistry, 45, 51–57, 1997.

Finzi, A. C., Canham, C. D., and Van Breemen, N.: Canopy tree–soil interactions within temperate forests: species effects on pH and cations, Ecol. Appl., 8, 447–454, 1998.

Fischer, M., Bossdorf, O., Gockel, S., Hänsel, F., Hemp, A., Hessenmöller, D., Korte, G., Nieschulze, J., Pfeiffer, S., Prati, D., Renner, S., Schöning, I., Schumacher, U., Wells, K., Buscot, F., Kalko, E., Linsenmair, K., Schulze, E., and Weisser, W.: Implementing large-scale and long-term functional biodiversity research: the biodiversity exploratories, Basic Appl. Ecol., 11, 473–485, 2010.

Fontaine, S., Bardoux, G., Abbadie, L., and Mariotti, A.: Carbon input to soil may decrease soil carbon content, Ecol. Lett., 7, 314–320, 2004.

Fröberg, M., Berggren, D., Bergkvist, B., Bryant, C., and Knicker, H.: Contributions of Oi, Oe and Oa horizons to dissolved organic matter in forest floor leachates, Geoderma, 113, 311–322, 2003.

Fröberg, M., Berggren, D., Bergkvist, B., Bryant, C., and Mulder, J.: Concentration and fluxes of dissolved organic carbon (DOC) in three Norway spruce stands along a climatic gradient in Sweden, Biogeochemistry, 77, 1–23, 2006.

Gersper, P. L. and Holowaychuk, N.: Some effects of stem flow from forest canopy trees on chemical properties of soils, Ecology, 52, 691–702, 1971.

Greenway, A., Griffiths, D., Furk, C., and Prior, R.: Composition of triglycerides from aphids of six different families and from different seasonal forms of *Aphis evonymi*, J. Insect Physiol., 20, 2423–2431, 1974.

Guggenberger G. and Zech, W.: Composition and dynamics of dissolved carbohydrates and lignin-degradation products in two coniferous forests, NE Bavaria, Germany, Soil Biol. Biochem., 26, 19–27, 1994.

Guggenberger, G., Zech, W., and Schulten, H.-R.: Formation and mobilization pathways of dissolved organic matter: evidence from chemical structural studies of organic matter fractions in acid forest floor solutions, Org. Geochem., 21, 51–66, 1994.

Hane, E. N., Hamburg, S. P., Barber, A. L., and Plaut, J. A.: Phytotoxicity of American beech leaf leachate to sugar maple seedlings in a greenhouse experiment, Can. J. Forest Res., 33, 814–821, 2003.

Hatcher, P. G., Schnitzer, M., Dennis, L. W., and Maciel, G. E.: Aromaticity of humic substances in soils, Soil Sci. Soc. Am. J., 45, 1089–1094, 1981.

Helfrich, M., Ludwig, B., Buurman, P., and Flessa, H.: Effect of land use on the composition of soil organic matter in density and aggregate fractions as revealed by solid-state ^{13} C NMR spectroscopy, Geoderma, 136, 331–341, 2006.

IUSS Working group WRB: Guidelines for Soil Description, 4th edn., Food and Agricultural Organisation of the United Nations, Rome, Italy, 2006.

Keeler, C., Kelly, E. F., and Maciel, G. E.: Chemical-structural information from solid-state ^{13}C NMR studies of a suite of humic materials from a lower montane forest soil, Colorado, USA, Geoderma, 130, 124–140, 2006.

Kindler, R., Siemens, J., Kaiser, K., Walmsley, D., Bernhofer, C., Buchmann, N., Cellier, P., Eugster, W., Gleixner, G., Grünwald, T., Heim, A., Ibrom, A., Jones, S., Jones, M., Klumpp, K., Kutsch, W., Larsen, K., Lehuger, S., Loubet, B., McKenzie, R., Moors, E., Osborne, B., Pilegaard, K., Rebmann, C., Saunders, M., Schmidt, M., Schrumpf, M., Seyfferth, J., Skiba, U., Soussana, J.-F., Sutton, M., Tefs, C., Vowinckel, B., Zeeman, M., and Kaupenjohann, M.: Dissolved carbon leaching from soil is a crucial component of the net ecosystem carbon balance, Glob. Change Biol., 17, 1167–1185, 2011.

Knicker, H. and Kögel-Knabner, I.: Soil organic nitrogen formation examined by means of NMR spectroscopy, in: Nitrogen-Containing Macromolecules in the Bio- and Geosphere, edited by: Stankiewicz, B., and van Bergen, P., ACS Symposium Series, American Chemical Society, Washington DC, 339–356, 1998.

Knicker, H., González-Vila, F. J., Polvillo, O., González, J. A., and Almendros, G.: Fire-induced transformation of C- and N-forms in different organic soil fractions from a dystric cambisol under a Mediterranean pine forest *Pinus pinaster*, Soil Biol. Biochem., 37, 701–718, 2005.

Lamersdorf, N. and Blank, K.: Evaluation of fine material input with throughfall for a spruce forest in Solling, FRG, by means of a roof construction, in: Ecosystem Manipulation Experiments: Scientific Approaches, Experimental Design and Relevant Results, edited by Jenkings, A., Ferrier, R., and Kirby, C., no. 23 in Ecosystem Research Report, Commission of the European Communities, Office for Official Publications of the European Communities, Brussels, 168–170, 1995.

Lankes, U., Lüdemann, H.-D., and Frimmel, F. H.: Search for basic relationships between "molecular size" and "chemical structure" of aquatic natural organic matter – answers from ^{13}C and ^{15}N CPMAS NMR spectroscopy, Water Res., 42, 1051–1060, 2008.

le Mellec, A. and Michalzik, B.: Impact of a pine lappet (*Dendrolimus pini*) mass outbreak on C and N fluxes to the forest floor and soil microbial properties in a Scots pine forest in Germany, Can. J. Forest Res., 38, 1829–1841, 2008.

le Mellec, A., Habermann, M., and Michalzik, B.: Canopy herbivory altering C to N ratios and soil input patterns of different organic matter fractions in a Scots pine forest, Plant Soil, 325, 255–262, 2009.

le Mellec, A., Meesenburg, H., and Michalzik, B.: The importance of canopy-derived dissolved and particulate organic matter (DOM and POM) – comparing throughfall solution from broadleaved and coniferous forests, Ann. For. Sci., 67, p. 411, 2010.

Leinweber, P., Schulten, H.-R., and Körschens, M.: Hot water extracted organic matter: chemical composition and temporal variations in a long-term field experiment, Biol. Fert. Soils, 20, 17–23, 1995.

Lemma, B., Nilsson, I., Kleja, D. B., Olsson, M., and Knicker, H.: Decomposition and substrate quality of leaf litters and fine roots from three exotic plantations and a native forest in the southwestern highlands of Ethiopia, Soil Biol. Biochem., 39, 2317–2328, 2007.

Levia, D. F. and Frost, E. E.: Variability of throughfall volume and solute inputs in wooded ecosystems, Prog. Phys. Geog., 30, 605–632, 2006.

Levia, D. F., Van Stan, J. T., Siegert, C., M., Inamdar, S. P., Mitchell, M. J.,Mage, S. .M, and McHale, P. J.: Atmospheric deposition and corresponding variability of stemflow chemistry across temporal scales in a mid-Atlantic broadleaved deciduous forest, Atmos. Environ., 45, 3046–3054, 2011.

Levia, D. F., Van Stan, II, J. T., Inamdar, S. P., Jarvis, M. T., Mitchell, M. J., Mage, S. M., Scheick, C. E., and McHale, P. J.: Stemflow and dissolved organic carbon cycling: temporal variability in concentration, flux, and UV-Vis spectral metrics in a temperate broadleaved deciduous forest in the eastern United States, Can. J. Forest Res., 42, 207–216, 2012.

Levia, D. F., Michalzik, B., Bischoff, S., Näthe, K., Legates, D. R., Gruselle, M.-C., and Richter, S.: Measurement and modeling of diameter distributions of particulate matter in terrestrial solutions, Geophys. Res. Lett., 40, 1317–1321, 2013.

Likens, G. E., Edgerton, E. S., and Galloway, J. N.: The composition and deposition of organic carbon in precipitation, Tellus B, 35, 16–24, 1983.

Lindeberg, G.: Stimulation of some litter-decomposing basidiomycetes by shikimic acid, Physiol. Plantarum, 65, 9–14, 1985.

Lundberg, P., Ekblad, A., and Nilsson, M.: ^{13}C NMR spectroscopy studies of forest soil microbial activity: glucose uptake and fatty acid biosynthesis, Soil Biol. Biochem., 33, 621–632, 2001.

Mämmelä, P.: Phenolics in selected European hardwood species by liquid chromatography–electrospray ionisation mass spectrometry, Analyst, 126, 1535–1538, 2001.

Marschner, B. and Kalbitz, K.: Controls of bioavailability and biodegradability of dissolved organic matter in soils, Geoderma, 113, 211–235, 2003.

McKnight, D. M., Harnish, R., Wershaw, R. L., Baron, J. S., and Schiff, S.: Chemical characteristics of particulate, colloidal, and dissolved organic material in Loch Vale Watershed, Rocky Mountain National Park, Biogeochemistry, 36, 99–124, 1997.

Mercier, J. and Lindow, S.: Role of leaf surface sugars in colonization of plants by bacterial epiphytes, Appl. Environ. Microb., 66, 369–374, 2000.

Michalzik, B., Dorsch, T., and Matzner, E.: Stability of dissolved organic nitrogen (DON) and mineral nitrogen in bulk precipitation and throughfall, Z. Pflanz. Bodenkunde, 160, 433–434, 1997.

Michalzik, B. and Matzner, E.: Dynamics of dissolved organic nitrogen and carbon in a Central European Norway spruce ecosystem, Eur. J. Soil Sci., 50, 579–590, 1999.

Michalzik, B. and Stadler, B.: Importance of canopy herbivores to dissolved and particulate organic matter fluxes to the forest floor, Geoderma, 127, 227–236, 2005.

Muscolo, A., Panuccio, M., and Sidari, M.: The effect of phenols on respiratory enzymes in seed germination, Plant Growth Regul., 35, 31–35, 2001.

Nicolai, V.: The bark of trees: thermal properties, microclimate and fauna, Oecologia, 69, 148–160, 1986.

Pérez-Harguindeguy, N., Díaz, S., Cornelissen, J. H. C., Vendramini, F., Cabido, M., and Castellanos, A.: Chemistry and toughness predict leaf litter decomposition rates over a wide spectrum of functional types and taxa in central Argentina, Plant Soil, 218, 21–30, 2000.

Petrakis, P. V., Spanos, K., Feest, A., and Daskalakou, E.: Phenols in leaves and bark of Fagus sylvatica as determinants of insect occurrences, Int. J. Mol. Sci., 12, 2769–2782, 2011.

Qualls, R. G. and Haines, B. L.: Geochemistry of dissolved organic nutrients in water percolating through a forest ecosystem, Soil Sci. Soc. Am. J., 55, 1112–1123, 1991.

Qualls, R. G., Haines, B. L., and Swank, W. T.: Fluxes of dissolved organic nutrients and humic substances in a deciduous forest, Ecology, 72, 254–266, 1991.

Rice, E. L.: Allelopathy, Academic Press, New York, 1984.

Rodríguez-Murillo, J. C., Almendros, G., and Knicker, H.: Wetland soil organic matter composition in a Mediterranean semiarid wetland (Las Tablas de Daimiel, Central Spain): insight into different carbon sequestration pathways, Org. Geochem., 42, 762–773, 2011.

Rohn, S., Rawel, H. M., and Kroll, J.: Inhibitory effects of plant phenols on the activity of selected enzymes, J. Agr. Food Chem., 50, 3566–3571, 2002.

Rothe, A., Huber, C., Kreutzer, K., and Weis, W.: Deposition and soil leaching in stands of Norway spruce and European beech: results from the Höglwald research in comparison with other European case studies, Plant Soil, 240, 33–45, 2002.

Sanderman, J., Baldock, J. A., and Amundson, R.: Dissolved organic carbon chemistry and dynamics in contrasting forest and grassland soils, Biogeochemistry, 89, 181–198, 2008.

Schnitzer, M. and Khan, S. U.: Humic Substances in the Environment, Marcel Dekker, New York, 1972.

Schumacher, M., Christl, I., Vogt, R. D., Barmettler, K., Jacobsen, C., and Kretzschmar, R.: Chemical composition of aquatic dissolved organic matter in five boreal forest catchments sampled in spring and fall seasons, Biogeochemistry, 80, 263–275, 2006.

Schwarz, M. T., Bischoff, S., Blaser, S., Boch, S., Schmitt, B., Thieme, L., Fischer, M., Michalzik, B., Schulze, E. D., Siemens, J., Wilcke, W.: More efficient aboveground nitrogen use in more diverse Central European forest canopies, Forest Ecol. Manag., 313, 274–282, 2014.

Sollins, P., Grier, C., McCorison, F., Cromack Jr., K., Fogel, R., and Fredriksen, R.: The internal element cycles of an old-growth Douglas-fir ecosystem in western Oregon, Ecol. Monogr., 50, 261–285, 1980.

Stadler, B. and Müller, T.: Effects of aphids and moth caterpillars on epiphytic microorganisms in canopies of forest trees, Can. J. Forest Res., 30, 631–638, 2000.

Stadler, B., Solinger, S., and Michalzik, B.: Insect herbivores and the nutrient flow from the canopy to the soil in coniferous and deciduous forests, Oecologia, 126, 104–113, 2001.

Stadler, B., Müller, T., and Orwig, D.: The ecology of energy and nutrient fluxes in hemlock forests invaded by hemlock woolly adelgid, Ecology, 87, 1792–1804, 2006.

Stanley-Samuelson, D. W., Jurenka, R. A., Cripps, C., Blomquist, G. J., and de Renobales, M.: Fatty acids in insects: composition, metabolism, and biological significance, Arch. Insect Biochem., 9, 1–33, 1988.

Van Stan, J. T., Levia, D. F., Inamdar, S. P., Lepori-Bui, M., and Mitchell, M.: The effects of phenoseason and storm characteristics on throughfall solute washoff and leaching dynamics from a temperate deciduous forest canopy, Sci. Total Environ., 430, 48–58, 2012.

Wardle, D. A., Nilsson, M.-C., Gallet, C., and Zackrisson, O.: An ecosystem-level perspective of allelopathy, Biol. Rev., 73, 305–319, 1998.

Weissen, F. and Van Praag, H. J.: Root growth inhibition effects of holorganic moder humus layer under spruce (*Picea abies* Karst.) and beech (*Fagus sylvatica* L.), Plant Soil, 135, 167–174, 1991.

Wyse, S. V. and Burns, B. R.: Do host bark traits influence trunk epiphyte communities?, New Zeal. J. Ecol., 35, 296–301, 2011.

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)
Altidute 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)~~ Stand structural properties and ~~unfiltered (nf) samples~~ management type of ~~throughfall~~ the study plots (~~TF~~dbh = tree diameter at breast hight; data from Schwarz et al., 2014)~~,~~ ~~stemflow (SF~~.

Region	Plot ID	Main tree species	Management type	Stand density (n ha^{-1})~~and forest floor (FF~~	Mean dbh (cm)	Basal area (m^2 ha^{-1})~~leachates; n.a., not analyzed; ALB,~~
Schwä~~bische Alb; HAI,~~ bische Alb	AEW7	Beech	extensively managed	200	85.2	33.3
	AEW8	Beech	extensively managed	276	56.9	40.0
	AEW9	Beech	extensively managed	376	42.5	31.7
Hainich-Dün~~, SCH,~~	HEW1	Spruce	age-class forest	276	49.4	43.0
	HEW2	Spruce	age-class forest	660	35.9	41.3
	HEW3	Spruce	age-class forest	651	32.2	42.7
	HEW10	Beech	extensively managed	377	50.3	34.3
	HEW11	Beech	extensively managed	568	51.1	36.7
	HEW12	Beech	extensively managed	326	54.9	36.5
Schorfheide-Chorin~~,~~	SEW7	Beech	extensively managed	155	61.2	36.9
	SEW8	Beech	extensively managed	154	68.0	38.3
	SEW9	Beech	extensively managed	259	52.5	43.6

Table 3. Relative signal intensity (in %) of chemical shift regions revealed by solid-state ^{13}C NMR spectroscopy (filtered (fil.) and unfiltered (unf.) 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 max.	min.	Chemical shift region		TF unf.	TF fil.	SF unf.	SF fil.	FF unf.	FF fil.
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 4. 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 (~~n~~fil.) and unfiltered (~~n~~unf.) samples of throughfall (TF), stemflow (SF) and forest floor (FF) leachates; n.a., not analyzed; ALB, Schwäbische Alb; HAI, Hainich-Dün; SCH, Schorfheide-Chorin.

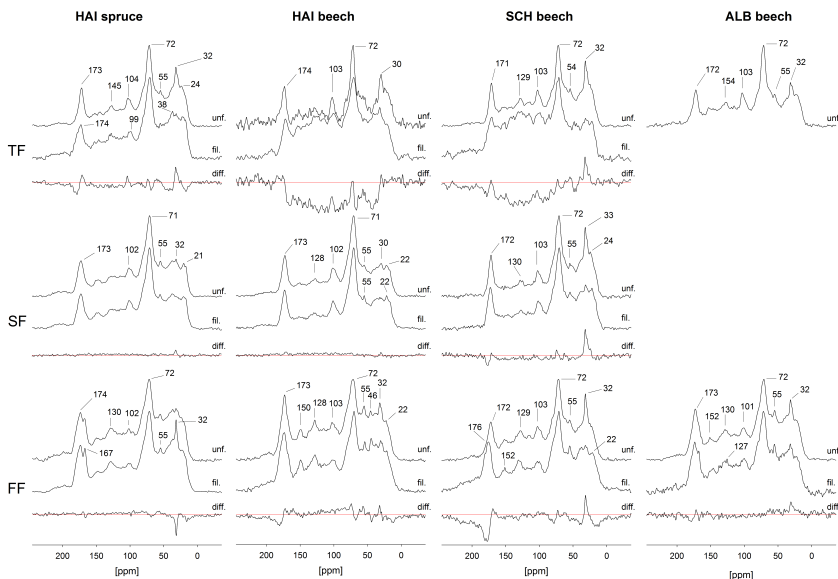|	Sample	A/O-A ratio	Aromaticity [%]
HAI spruce	TF ~~n~~unf.	0.53	17.0
	TF ~~n~~fil.	0.54	19.6
	SF ~~n~~unf.	0.42	19.7
	SF ~~n~~fil.	0.42	19.0
	FF ~~n~~unf.	0.48	22.4
	FF ~~n~~fil.	0.56	21.2
HAI beech	TF ~~n~~unf.	0.61	17.3
	TF ~~n~~fil.	0.42	29.1
	SF ~~n~~unf.	0.42	17.7
	SF ~~n~~fil.	0.45	16.1
	FF ~~n~~unf.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

Figure 1. Solid-state CPMAS ^{13}C NMR spectra obtained from filtered (~~f~~fil.) and unfiltered (~~nf~~unf.) 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; red lines indicate zero level within difference spectra.