Atmos. Chem. Phys. Discuss., 11, C11983–C11997, 2011
www.atmos-chem-phys-discuss.net/11/C11983/2011/

Atmospheric
Chemistry
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Discussions

Interactive comment on "Determination of the biogenic secondary organic aerosol fraction in the boreal forest by AMS and NMR measurements" *by* E. Finessi et al.

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Received and published: 17 November 2011

The authors would like to thank Anonymous Referee #2 for his/her through review. We agree on the fact that the ACPD manuscript was not completely clear in its scopes, e.g., the comparison with AMS, and in some of its conclusive statements. It certainly needs substantial revisions and clarifications about what evidence on carbonaceous aerosol sources can be gained based on this dataset, and what information instead rests unspecified. We believe that the main conclusion of this paper, i.e., the apportionment of substantial aerosol OC fractions to distinct sources of biogenic SOA in the boreal forest, in a more specific manner than the AMS measurements alone indicate, is robust. Nonetheless, the Referee's criticisms on many specific aspects concerning the methodology or the interpretation of the factors are all good points. We provide below detailed replies. Our intention is to incorporate all these changes in an improved version of the manuscript for submission to ACP.

Comment. The biggest issue with this paper is that the AMS data is very weak. It is only for a short time, much of which probably close to the detection limits during marine events. The following PMF analysis of the AMS data is also subject to considerable uncertainty and can only distinguish 2 factors, as there is likely not enough variability in the data to do better. I would be in favour of reducing or removing much of the AMS discussion as it does not in my opinion add very much to paper and may in fact create more problems. The NMR analysis is almost a "stand alone" point to the paper and doesn't really need the AMS data.

Reply. See responses to reviewer 1.

Comment. The authors also used a ToF-AMS which they say was malfunctioning at the time of the study. However, later the authors mention that the ToF-AMS was able to resolve 2 factors as well. This begs the question: was the instrument malfunctioning or not? If not, it would seem that the Tof-AMS could help to answer a lot of the questions in the paper or at least corroborate the NMR findings. If one can do PMF on the ToF-AMS data then presumably they should also be able to look at the high-resolution data for specific fragments that would assist in the NMR interpretation. PMF of the high-res data is not required, but some important fragments seem likely to be resolvable. A more detailed look at the high resolution AMS data, in a qualitative way, must be done if possible.

Reply. While certain data products were obtainable (such as the UMR data), the W mode data was not of sufficient quality to offer any useful benefits to the analysis. PMF was attempted on the high resolution data but was highly problematic and did not yield anything beyond what was possible with the UMR data. It should be noted that because the AMS uses electron ionisation without any chemical separation, it is not given that any specific peaks within the ensemble will provide any insight into the chemical functionality of the organic aerosol (It should be noted that the marker peak investigated by Robinson et al. (2011) was not significantly evident in this study). We have used the overall data to compile statistics on elemental ratios however, and these are included in the manuscript.

Comment. There are inconsistencies with the NMR and AMS data. The authors state that biomass burning is an appreciable fraction of the NMR resolved data. However no BBOA AMS factor is resolved. Why is that? Also, water insoluble species account for a large fraction of the organic mass. Are these WINC associated with anthropogenic emissions? Fresher emissions? If so how is there no HOA factor resolved? These things lead me to believe that the Q-ams factor analysis may not have been as well performed as the authors claim, or simply cannot be reliably done with the data they have. Is the WINC a major part of fresh biogenic SOA then? Is this what the authors are inferring? If so, then this must be discussed and evidence shown. All this goes to the point of removing the AMS factor analysis as it is potentially misleading.

Reply. We have used levoglucosan to identify a wood burning contribution during the period of continental southerly air masses and also for the interpretation of the “HULIS-containing” factor, but we were probably too qualitative on this point and we did not specify the amount of wood burning products to be expected, and the text turned to be misleading. Levoglucosan peaks were actually detectable and measurable in a couple of NMR spectra, and specifically in those of the 30/3_day, 15/4_night filter samples with the former showing the highest amount. Based on NMR integrals, the levoglucosan concentrations were 223 and 15 ng m-3 respectively for the two samples, accounting the levoglucosan-C for 1.9% and 0.7% of WSOC. These values can be compared to 3% to 5% ratios obtained in areas directly impacted by wood burning (Matta et al., ACP 2003, Tagliavini et al. ACP 2006). The estimated contributions of biomass smoke to OC obtained by multiplying the levoglucosan concentrations by 7.35 as recommended by Fine et al. (2002) were 1.64 and 0.11 μg m-3 for the Hyytiälä samples of 30/3 day and 15/4 night. Such concentrations are relevant in absolute terms (Puxbaum et al., 2007), but they accounted for about 30% and less than 10% of OM concentrations estimated for the two days of the experiment (Fig. 11). They were also lower than the WSOM fractions apportioned to anthropogenic combustion sources by NMR ("HULIS-containing" compounds). In summary, levoglucosan data show that biomass burning was a significant source of particulate organic matter in Hyytiälä during the periods characterized by continental air masses, but such products did not account for the total WSOC fraction which was put in relation to anthropogenic sources by the NMR analysis. The anthropogenically-influenced WSOC, or "HULIS-containing" factor, is rather a mix of long-range transported pollution and wood burning products (pg 22636, line 4). Unfortunately, the Q-AMS operated discontinuously at the beginning of the campaign because of power disruptions and this resulted in reduced sampling time coverage (less than 50% for the 30/3_day sample, Fig. 5, upper panel). It is likely that the Q-AMS did not capture enough BB products to further resolve a BBOA factor. As for the HOA factor, the inspection of the m/z=57 peak would suggest that this do not represent a significant fraction of the AMS-reported organic matter. On the other hand, the WINC was found to account for a large fraction of the organic mass. In our opinion, this is an important result of this study rather than an inconsistency. In fact the correlation between the HOA and water-insoluble carbon is far from being obvious and it has to be proved yet outside urban environments. On the contrary, it is expected that the actual overlap between these two categories will depend on the different aerosol types. For these reasons, and since we consider that the relative contributions of OOA1 and OOA2 reported here are reasonable estimates, we are strongly in favour of the inclusion of the AMS PMF analysis as this helps to interpret the HNMR and source sectors, and provides context for the interpretation of similar AMS data products in other field studies.

Comment. Although it is important to have other methods for aerosol functional group characterization, what are the advantages of NMR for this task over other methods? In

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particular I am referring to FTIR which has been used on several occasions to measure functional groups from biogenic environments. How do these functional groups from this biogenic setting compare to others? (ie: Shwartz et al., 2010, ACP). This is an important comparison and will highlight potential differences or similarities between locations and methods. My recollection is that NMR detection limits are higher than for the FTIR approach. Is this correct?

Reply. The Referee's suggestion is well taken, and it is certainly worthwhile to compare with existing data of OC functional group distributions gathered in other forest environments and obtained with different methodologies. At the same time, the differences in specificity and recovery between the analytical techniques should always be kept in mind when comparing with literature data. Specifically, H-NMR analysis is probably one order of magnitude less sensitive than FTIR, it was developed only for WSOC analysis, and it provides only a rough speciation of oxygenated functionalities. On the other hand, H-NMR analysis provides a closer look to the C-H bonds, including the aromatic rings which are often difficult to observed directly using FTIR or AMS techniques. H-NMR spectroscopy exhibits probably a better resolution then FTIR in speciating the C-H bonds according to their "chemical environment" (i.e., their substituents) and it is able to retain the fine spectral structure of individual compounds (low-molecular weight amines, MSA, levoglucosan, mannitol, and some others). That is why in this paper we have integrated the traditional functional group analysis with a factor analysis for pattern recognition and spectral deconvolution: It is a way to exploit better the full resolution of NMR datasets. The comparison with the studies of Shwartz et al in the British Columbia is indeed interesting and worth to be mentioned because the picture of the main OM components arising from PMF - FTIR analysis is strikingly similar to that emerging from the present study in the Finnish boreal forest. Shwartz and coauthors identify one anthropogenic component ("combustion") and three probable biogenic factors, including a) alcohols, b) amines and 3) carbonylic compounds similar to terpene SOA, providing more or less the same speciation shown in Figure 9b of our paper. The functional group distributions of the American samples are somewhat

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different from ours, with a more aliphatic (C-H) content in the combustion factor compared to the carbonyl-rich biogenic SOA factor, whereas according to the NMR analysis of the Finnish samples it is the other way around (Fig. 10). We do not believe these differences are real: they probably fall in the uncertainty associated with the fact that water-insoluble species are not accounted for by the H-NMR analysis. In absence of collocated measurements, the comparison between different organic functional group speciation methods has to be kept to a qualitative level. The above information and detailed detection limits for the NMR analysis in the present study can be incorporated in an improved version of the manuscript.

Comment. The concept of evaporation of semi volatiles seems somewhat counter intuitive. The authors claim that the majority of the semi-volatile material was found in the marine air (70% of the WSOC, pg 22632). However, their own trajectories show that the marine trajectories probably contained the most aged air masses. One could argue (and it has been shown with AMS data on numerous occasions) that the most aged aerosols should contain the most oxygen and be the least volatile rather than the most. Why is this case different? The PMF of AMS data seems to be about 50% OOA2 most of the time and the largest OOA2 is found from the biogenic continental sector. Therefore it is unclear to me why there should be more evaporation during the marine periods. Also, the levels of everything during the marine times are very low. What confidence do the authors have in NMR and AMS measurements during these times? The authors state that "few" laboratory tests were done to confirm this evaporation effect. This should be expanded, to describe how they were done. It sees that they simply did the WSOC analysis prior to and after an evaporation step. If this is the case, then why not do the entire analysis without an evaporating step to avoid this issue all together?

Reply. The Referee's comment can be split into three independent questions: 1) Why a larger contribution of volatile material was observed during the period of most aged air masses? 2) What evidence have the authors about the amount and nature of volatile material in the filter samples? 3) Why the analytical protocol requires an evaporation step? Below our specific rebuttals and clarification: 1) Concerning the occurrence of volatile organic compounds during the background period. This is only an apparent contradiction, since Hyytiälä is not merely a receptor site but also right in the middle of a big photochemical reactor: the boreal forest. Therefore, very aged compounds originating from marine source faraway may coexist with very fresh gas-to-particle conversion products and other volatile that can be trapped in the filter matrix as adsorption artefacts. Indeed, new-particle formation proceeded unceasingly during the background period (Figure 4), witnessing the formation of condensable products from local sources. Our interpretation is that such sources were probably responsible for the small but constant supply of OOA2 and of "terpene-like SOA" (and possibly some of the amines) determined during the background regime and that overlap with the more aged components carried by marine particles. We also hypothesise that volatile organic compounds of local origin and collected on the quartz-fiber filter as positive artefacts are responsible for the 0.5 μg m-3 of OC which account for the evaporative losses of WSOC during sample preparation as well as for the mismatch between AMS and filter-based OC measurements during the background period (Figure 5). 2) Concerning nature and amount of the evaporated WSOC compounds. This topic was treated shortly in the manuscript and needs certainly to be explained in more details. WSOC concentrations were measured both in the extracts as well as in the concentrated solutions in order to obtain estimates of possible losses due to evaporation. The carbon fraction lost by evaporation estimated in this way was in average 30%. In overall this value was inversely correlated to the amount of WSOC per cm2, which is in agreement with our hypothesis pointing to positive sampling artefacts. Indeed, adsorption artefacts are typically more significant at low carbon loadings (e.g., Cheng et al., ACPD 9, 13739–13773, 2009). Additional tests by using standard water-soluble semi-volatile compounds were also performed to establish their recovery after evaporation, and specifically with maleic acid, pinic acid, cis-pinonic acid and vanillin. As expected more significant losses were observed for the aldehyde with respect to the acids, showing the former a recovery of 84% compared to values above 95% obtained for the acids. The high recovery found for the SVOC standards indicates that more volatile (VOC or “IVOC”) compounds were responsible for the observed evaporative losses. Such compounds were not likely partitioned on ambient aerosol particles, but became rather adsorbed on the filter matrix. 3) Concerning the necessity of drying the aqueous extracts. Given the NMR detection limit ($\sim$50 μgC), the inclusion in the procedure of an evaporation step (i.e. a concentration step) depends basically on the available amount of water-soluble organic carbon per cm2 of filter sample. Since a minimum volume of 0.5 mL per cm2 is required to get appropriate filter wetting and extraction, at least 25 μgC cm-2 are needed to avoid concentrating the extract solution for the NMR analysis. Unfortunately, this step could not be avoided for these filter samples because their WSOC loadings ranged from 0.5 to 3 μg C cm-2.

Comment. The authors point to potential particle losses as an explanation of the poor agreement between AMS and filter data. (pg 22632). There are any number of reasons for this disagreement that do not invoke particle losses. Some simple calculations of their particle losses can be done if the sampling tube dimensions are known. It is likely that particle losses are minor for the sizes that are transmitted into the AMS. Having said this, the evaluation of CE for the AMS must be examined further. How was this done?

Reply. The authors totally agree with the referee’s comment. Such difference may rely for example just on the conversion of OC into OM or be due to filter sampling artefacts, both issues which could actually be more relevant than particle losses. As for the collection efficiency, a value of 0.5 was used in this study based on previous experience with the AMS ambient work and on the comparison with DMPS. This is also consistent with previous laboratory work (Matthew et al., Aerosol Sci. Technol., 42, 884-898, 2008)

Comment. Pg 2263, line 25. the signal at m/z being less than 1% of the total is not surprising. The AMS is very destructive, and very few peaks have a fraction greater

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than this most of the time anyways. Therefore, this line is not very informative.

Reply. The sentence has been reformulated accordingly in the revised test as: "On average, the m/z 57 peak, which is often related to HOA (e.g. Lanz et al., 2007) and also BBOA (Aiken et al., 2009), is less than 1% of the total organic signal when that for m/z 44 peak is 11 %."

Comment. Pg 22636: The NMR factors seem to show that there is an “amine” factor from the marine sector (Pg 22636). However, there is also a significant amine fraction during the continental times. Does this imply that amines are part of biogenic SOA? If so, there must be some high resolution fragments from the ToF-AMS which will vary in time in a similar way to the amine NMR factor. This should be looked at. Many C-N containing fragments are resolvable with the ToF-AMS, especially if there is such a large amount of amine mass as they suggest during the time it operated. An amine contribution to continental BSOA is an important finding that must not be glossed over. A more detailed analysis might be able to discern traditional BSOA from amine BSOA.

Reply. Unfortunately, in this instance, the W mode data was not deemed to be of sufficient quality to reliably quantify any nitrogen-containing organic peaks. While the relative mass defects of oxygen-containing peaks and non-oxygen-containing peaks was large enough such that C:O ratios could be derived, no nitrogen-containing organic peaks were unambiguously detected.

Comment. Pg 22637: The authors note that the “glycol” factor is excluded from their analysis as a contamination. However, several pages prior, they say that they cannot rule it out but that there is no evidence one way or the other. Alcohol functional groups or ethers are not uncommon in aerosols, so I am somewhat confused as to why they dismiss this possibility outright. Some more careful analysis may reveal that it is a true factor, and unless they have direct evidence that it is an artifact, then it should be included in the analysis.

Reply. We copy here the reply to Referee #1 on the same topic. We agree to provide clarifications on this point in the manuscript. The observed signals show a good fit with the H-NMR spectra of ethylene glycol butyl ether and of 2-butoxyethyl acetate (Sigma-Aldrich online NMR library). Glycol ethers are chemicals commonly used in paints. Ethylene glycol butyl ether (butoxy ethanol) was identified among other VOCs of toxicological interest in urban areas (Gallego et al., J. Environ. Sci., 21, 333-339). If not laboratory contaminants, they may have originated from a local source at the sampling site or nearby. Their volatility is high (> 10-1 Torr), being in the VOC regime, hence if they were atmospheric constituents in Hyytiälä, they were most probably sampled as adsorption artefacts on the quartz-fiber filters. Nevertheless, since more firm indications are lacking we agree to include these data in the analysis as suggested by the referee (see new Fig. 11 and 13).

Comment. The basis for NMR names is a bit strange to me. Calling a factor "HULIS" to me implies a natural source. However, the authors state that it is anthropogenic instead. Perhaps a better name could be devised.

Reply. The names assigned to the NMR factors rely strictly on the similarity of their spectral features with standards. Accordingly to this, the second NMR factor has been named "HULIS-containing" based on its similarity with spectra obtained for HULIS standards (e.g. fulvic acid) which does not necessary imply natural sources only. In fact there is a general consensus on that highly processed organics, both anthropogenic as well as biogenic, tend in the atmosphere towards a common state referred often as HULIS (Jimenez et al., Science, 326, 1525-1529, 2009). The term "containing" has been further included in the name to highlight that this factor cannot be exclusively associated with the profile of fulvic acid since also signals of levoglucosan are visible. The authors prefer to keep this name since they could not find any other term suited for such factor better than this and also to avoid introducing additional exotic names in the literature.

Technical comments

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Abstract, line 6: the term “air mass concentrations” should be changed Changed in “concentrations”

Abstract, line 21: this line is poorly written and confusing. Line reformulated as: “The less oxidized component was enhanced in concomitance with air masses originating from the North-to-West sector, in agreement with previous investigations conducted at this site”

Abstract, line 24: “: : :associated with: : :.” Changed accordingly.

Pg 22622, line 6: remove one “be” Removed.

Pg 22623, line 10: do the authors mean thousands or hundreds of thousands? Thousands.

Pg 22624, line 17: remove “here” Removed.

Pg 22626, line 4: what type of noise are they referring to? We are referring to statistical or random noise, i.e. everything that would be averaged to zero.

Pg 22626: how many filter samples were analysed in the end? Detection limits for NMR? 22 filter samples; 50 μg WSOC.

Pg 22627, line 25: remove “the” from “positive: : :” Removed.

Pg 22628, line 1: change “turned out: : :.” to “was” Changed accordingly.

Pg 22628, line 21: grammar: : :not clear. Line reformulated as: “Given that f44 values are not expected, the solution having OOA2 f44=0.04 and FPEAK=$-$0.12 was finally selected as the best one”

Pg 22630, line 13: should be “: : :.in two other: : :.” Changed accordingly.

Pg 22632, line 4: should be “: : :.correlated: : :” Changed accordingly.

Pg 22634, line 4: do the authors mean m/z 44 /total org ? Yes. The text has been changed in "m/z 44 / OM"

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Pg 22634, lines 15-20: looking at one fragment (82) tells you very little especially if it is from the Q-AMS. m/z 82 can be from any number of species or breakdown products: : :therefore these lines are not very useful. Text deleted.

Pg 22635, line 26: either it is “low” or “appreciable” but I don’t see how it can be both. Text changed in “close to the limit of quantification”

Pg 22638, lines 5-11: what is the difference between WINC and WIOM? WIOM is the water-insoluble fraction not including EC, estimated as WIOM= (WINC-10%TC)*1.4 ; WINC=TC-WSOC.

Figure 1: put legends inside the plot not on the outside. Make text bigger overall. Figures modified accordingly.

Figure 5: Expand the scales as it is difficult to see the data in the middle section. Scales expanded.

Figure 6: there seems to be very little difference between OOA1 and OOA2. Such differences need to be highlighted. Additional m/z values have been added to guide eyes.

Figure 7: again expand scale and make text bigger and move legend inside. Figure modified accordingly.

Figure 8: just by looking one cannot see much difference between these factors. The different chemical shifts for each plot need to be pointed out in the figure so the reader can see the differences between factors easily. Figure improved accordingly.

Figure 10: seems like a repeat of figure 8. Could figs 8 and 10 not be combined into 1 figure? We would prefer to keep the two separated figures because the combining of the two results too difficult to read.

Figure 11: again expand scale and make font bigger: : :. Figure modified accordingly (see new Fig 11 in the replies to Ref.1).

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Figure 12: Another repeated figure. Most of the info in this figure can be extracted from the others. Remove it or combine with another. Figure removed.

Interactive comment on Atmos. Chem. Phys. Discuss., 11, 22619, 2011.

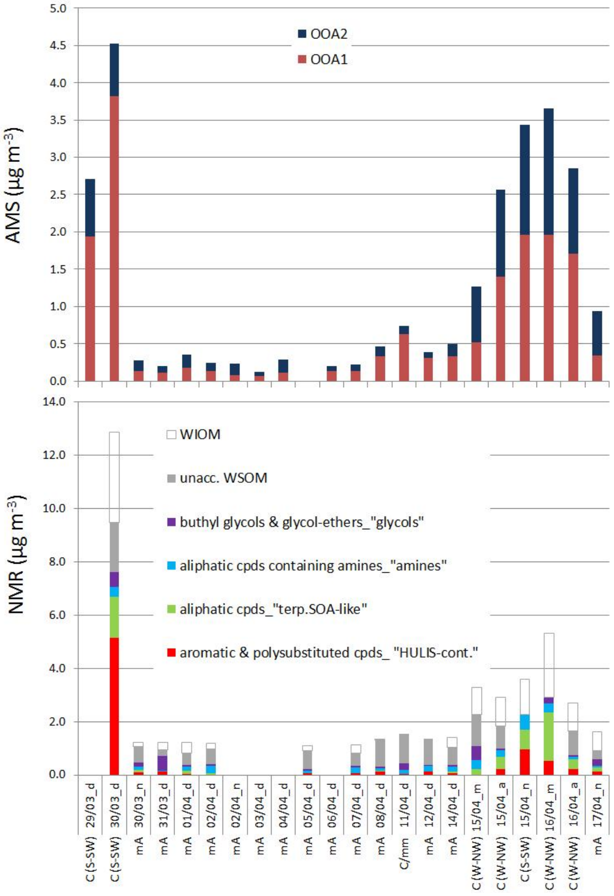

Fig. 1. New Fig. 11

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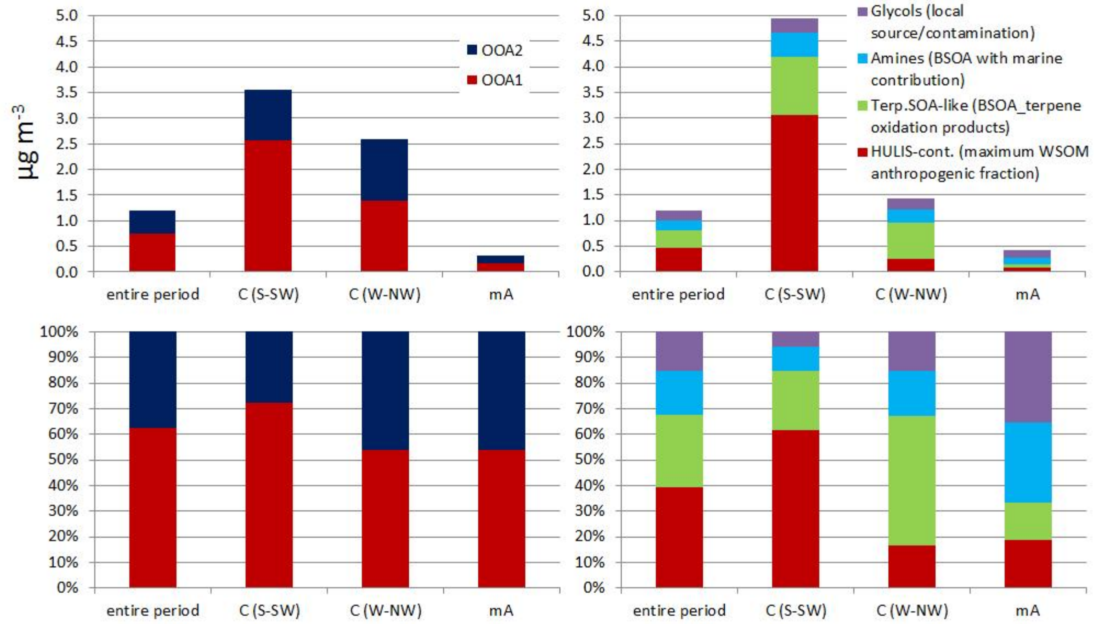

Fig. 2. New Fig. 13