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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.

Anonymous Referee #2

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The manuscript entitled “Determination of the biogenic secondary organic aerosol fraction in the boreal forest by AMS and NMR measurements” discusses the results from a field campaign in Finland. The location itself has been used to study biogenic SOA from forested environments on numerous occasions. The paper attempts to further constrain the molecular characterization of biogenic SOA by combining AMS measurements with NMR measurements from filter samples. The use of NMR is fairly novel and does lead to some potentially useful and interesting aspects with respect to biogenic SOA formation. However, there are several issues throughout the paper which detract from its importance, and make the conclusions at times somewhat weak. Some of these weaknesses are not the fault of the authors, as they are trying to make the

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most of a relatively limited data set. I do think that there is indeed some utility to publishing this work, but only after the significant issues described below are thoroughly addressed.

Specific comments:

One of the key points of this paper is that factor analysis of the NMR results seems to point to some interesting functionality to biogenic SOA, in that some BSOA may in fact be of marine origin. This is supported by the back trajectories to some degree. 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 favor 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.

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.

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

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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.

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 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: Schwartz 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?

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? Presumably one needs a lot of mass for NMR detection in the first place.

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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 seems 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?

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? Also, looking at the measured SMSP size distribution will be instructive, as will tell you if there were particles which could not be transmitted into the AMS (ie: too big).

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

Pg 22636: The NMR factors seem to show that there is an “amine” factor from the marine sector. 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.

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

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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.

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.

Technical issues:

There are a number of grammatical errors and poorly written sentences throughout. I have tried to note a few, but there are too many to explicitly state here and I have no doubt missed a few.

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

Abstract, line 21: this line is poorly written and confusing.

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

Pg 22622, line 6: remove one “be”

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

Pg 22624, line 17: remove “here”

Pg 22626, line 4: what type of noise are they referring to?

Pg 22626: how many filter samples were analyzed in the end? Detection limits for NMR?

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

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

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Pg 22628, line 21: grammar...not clear.

Pg 22630, line 13: should be "...in two other..."

Pg 22632, line 4: should be "...correlated..."

Pg 22634, line 4: do the authors mean m/z 44 /total org ?

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.

Pg 22635, line 26: either it is "low" or "appreciable" but I don't see how it can be both.

Pg 22638, lines 5-11: what is the difference between WINC and WIOM?

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

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

Figure 6: there seems to be very little difference between OOA1 and OOA2. Such differences need to be highlighted.

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

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 10: seems like a repeat of figure 8. Could figs 8 and 10 not be combined into 1 figure?

Figure 11: again expand scale and make font bigger...

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

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

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