Atmos. Chem. Phys. Discuss., 11, C11974–C11982, 2011
www.atmos-chem-phys-discuss.net/11/C11974/2011/

Atmospheric Chemistry and Physics 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.

E. Finessi et al.

e.finessi@isac.cnr.it

Received and published: 17 November 2011

The authors would like to thank Anonymous Referee #1 for his/her comments.

The referee comments followed by our replies are below.

Comment. I find that the AMS data really do not make the paper all that much stronger, aside for a general correspondence between the more highly oxygenated AMS factor and the HULIS factor from the NMR. In particular, the AMS factors - OOA1 and OOA2 - are a bit too "blunt" to be able to learn much from, when compared to the NMR factors.

Reply. It is well known that the results extractable by applying factorisation techniques

are strongly dependent on the dataset's variability. The authors agree with the referee in finding that the PMF-AMS results obtained here can appear somewhat less informative if taken in isolation. As stressed in the paper (pg 22625, line 19-22; pg 22626, line 3-5), this was due both to technical reasons as well as to the small time frame and the limited variability of the available dataset. It is agreed that the AMS results do not provide a detailed information in this case regarding the investigation of the composition of the particles, however we feel that the comparison of the aerosol NMR functional groups with the AMS-derived OA mass fragment measurements are significantly original and important. NMR-AMS comparisons on this level have not been published before and given the prolific use of the AMS (Jimenez et al., Science, 326, 1525-1529, 2009) it is important to understand how its framework fits with those provided by other methodologies. It must be stressed that this is a globally important aerosol type (biogenic SOA) and while AMS measurements have been made in these environments before, this does not provide any direct measurements of the chemical functionality, so comparisons with measurements such as HNMR must be performed if the chemical properties of this aerosol are to be understood. Nevertheless, following up the referee's suggestion, the importance of the AMS results has been reduced both by shortening the AMS sections and by changing the paper title in "Determination of the biogenic secondary organic aerosol fraction in the boreal forest by NMR spectroscopy.

Comment. P22625. What collection efficiency was used for the AMS data, and with what justification?

Reply. A collection efficiency of 0.5 was used, based on the comparison with DMPS data and on previous experience with the AMS ambient work. This is also consistent with previous laboratory work (Matthew et al., Aerosol Sci. Technol., 42, 884-898, 2008)

Comment. P22626, line 6. The AMS and DMPS data cannot "agree" with each other – they measure different quantities, mass and volume.

Reply. The comparison between the AMS and DMPS data is not certainly straight but burdened by a series of assumptions and complications including those stressed by the referee. Here, AMS mass concentration data were converted to volume concentrations using the densities reported by Cross et al. (Aerosol Sci. Technol., 41, 343-359, 2007). These were then compared with the volume concentrations derived from the DMPS data, assuming spherical particles. Given the complications associated with size cuts and refractory material, data have been compared just to verify the AMS collection efficiency, as commonly done in many other studies.

Comment. P22632, line 5. How much of this difference could be due to different size cuts on the inlets?

Reply. The difference between Q-AMS and filters OM concentrations can arise from a series of concurrent factors, including: a) different inlet size cuts; b) Q-AMS particle losses; c) filter positive artefacts and d) uncertainties associated with the use of OM/OC conversion factors. Since the inlet size cuts were quite similar (850 nm vs 1 μm) and there were not additional evidences for significant losses, the latter two factors are thought those mostly contributing to such difference.

Comment. P22635, line 13. For the NMR F1 factor, I am surprised that the authors appear to consider that this factor is contamination, given that they do not see it in their control blanks. Indeed, later, they do not include these data in their analyses (P22637, line 10 and afterwards). Without firm indications that these are contaminants, should not a full data analysis be also conducted with these data included? Also, are the spectra so specific that only n-butyl glycols are identified, or could other varieties be possible too? I guess the question I am asking is whether the authors have been too quick to rule out the possibility that this is a real atmospheric signal?

Reply. 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 Figures 11 and 13).

Comment- P22638, line 6. Better justification both here and earlier for why the factor of 1.8 is used to convert carbon to mass.

Reply. The constant conversion factor of 1.8 used here to estimate OA total mass from OC mass has been selected as the most appropriate value for non-urban water-soluble organic aerosol based on the results of various previous studies (Aiken et al., 2008; Decesari et al., 2007; Russel et al., 2003, Turpin et al., 2001). These studies used different approaches to investigate the OM/OC ratios of ambient aerosols, overall indicating a range between 1.2 and 2.4 for less and more oxygenated (aged) aerosols respectively. Based on H-NMR analysis (Decesari et al. 2007), an interval between 1.7 and 1.9 is recommended for water-soluble submicron aerosols. We have therefore applied an average constant value of 1.8 for our samples. The fact that other techniques, such as AMS, suggest OM/OC ratios slightly higher than 2 for the most oxidized fraction of the aerosol, and that some oxygenated functionalities may have eluded H-NMR characterization indicates that the NMR-reconstructed organic mass could be underestimated of ca. 10%. We acknowledge that the uncertainty associated with OM/OC conversion factors calculated for the filter samples can be significant, and can affect a quantitative comparison with the time-integrated AMS concentrations. However, the scope of this study was not to attempt an accurate closure of the organic mass budget using the NMR categories, being the recovery of NMR incomplete even for the water-soluble fraction. Our main target was to show the change in chemical

composition of particulate organic matter between air mass types making explicit links to the estimated biogenic and anthropogenic fractions, as provided by both NMR and AMS. The conversion of OC units to OM concentrations was motivated merely by the need of adopting the same metrics for the two techniques. We have refined Figures 11 and 13 to illustrate the comparison between AMS concentrations for OOAs and the reconstructed concentrations of the NMR factors for WSOC. Clearly, the incomplete recovery of NMR analysis, adsorption artefacts on the filters as well as some incidental mismatch between filter sampling time and the AMS observation time (such as on 30th March) cause AMS and total NMR mass concentrations to diverge. However, the WSOM mass speciated by NMR analysis is always a significant fraction of the total AMS concentration, hence the change in NMR compositions and factor distributions between the different periods of the campaign can be used to interpret the concurrent evolution of the AMS OOA composition (New Figure 13).

Comment. In general, can the AMS factors be compared to other AMS factors reported in the literature for biogenic SOA in mid-latitude forests (e.g. Slowik et al.)?

Reply. Given the similarity to the mass spectral profiles and the expected similarities in the atmospheric chemistry, yes. Not only with the results reported by Slowik et al., but also with those obtained at Hyytiälä by Allan et al. (Atmos. Chem. Phys., 2006), which was subsequently used in Jimenez et al. (2009), along with some other rural locations.

Comment. In general, there is implied in the paper that the HULIS NMR factor has some correspondence to the OOA1 factor from the AMS, in amount and time profile, i.e. highly oxygenated material. However, there is a claim made that this is not biogenic in origin, whereas the less oxygenated material is biogenic. I don't see the justification for this. In particular, while the more oxygenated material may be arriving with winds from the south, what is to say that the carbon is not of biogenic origin (at least in part) that has been highly oxidized by anthropogenic oxidants?

Reply. The NMR "HULIS-containing" factor shows spectral features, in terms of func-

tional group distribution, matching those characterizing samples collected in sites impacted by anthropogenic emissions (P22635, line 20). Also, it correlates positively with particle sulphate and nitrate ions and thus it is thought to be mainly representative for anthropogenically-originated organics. This factor shows a spectrum fitting those typical for HULIS standards (e.g. fulvic acid) which is expected to be the end-product of atmospheric transformation of both anthropogenic as well as biogenic organic aerosols (Jimenez et al., 2009). Unfortunately, the measurements performed during this experiment do not allow a more precise estimate of the contribution of fossil and modern carbon to the collected aerosol, and thus to the OOA1 or the HULIS-containing factors. We agree to provide a better clarification of this point in the revised work by adding the a text as follows: Contrary to the "terpene-SOA" factor for which we can compare with spectra obtained in controlled laboratory conditions, our interpretation of the "HULIS-containing" factor is based on the similarities with ambient samples collected in polluted areas, however we do not know how much these fingerprints are specific for the anthropogenic sources, which certainly contributed but we do not know the extent. The same polluted conditions may have led to the accumulation of more, and more oxidized biogenic SOA. Therefore the HULIS-containing factor should be considered a "maximum anthropogenic WSOC fraction", i.e., an upper limit, rather than exclusively anthropogenic.

Comment. Figure 8. When I compare F1-F3 in the two sets of solutions, they look remarkably similar, which makes we question the validity of F4 in the 4 factor solution. Indeed, earlier in the paper, it is stated that this factor is derived at close to the noise level. Although there is a nice correspondence between F4 and a lab terpene SOA, I nevertheless believe this caveat (that this is a pretty low signal-to-noise factor) needs to be more clearly stated in the Abstract and Conclusions.

Reply. F1 and F2 are pretty stable between the different solutions, while there is more variability between the algorithms in capturing the factors in the remaining fraction of NMR spectral resonances, but basically F3 in the three-factors solution accounts for the

amines plus some background signal, whereas the four-factor solution splits between the amine peaks (plus little background) (F3) and most of the background broad signal (F4). The fact that the time trend of amine concentrations is rather flat, whereas the background signal (not accounted for by F1 and F2) increases during the second period of continental air masses (15 – 16 April) is real (see Fig. 9), therefore we believe that F4 is not merely an artefact of factor analysis but points to an additional class of compounds.

Comment. Figures. I found many of the axis labels and figure line weights too small.

Reply. Figures have been modified accordingly in the revised text.

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

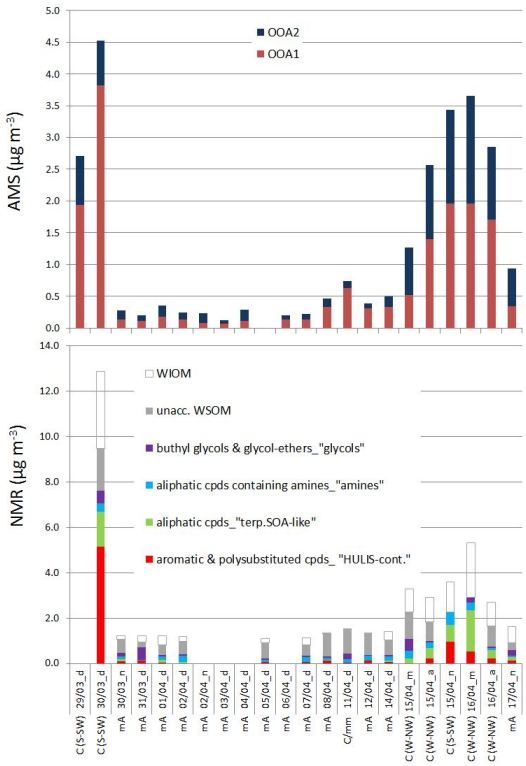

Fig. 1. New Fig. 11

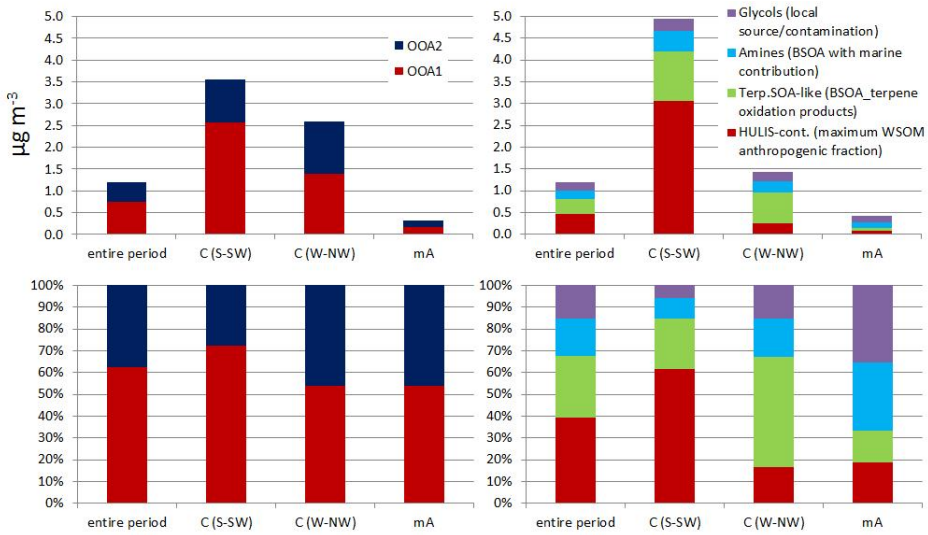

Fig. 2. New Fig. 13