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Discussions

Interactive comment on "Primary and secondary biomass burning aerosols determined by proton nuclear magnetic resonance (H-NMR) spectroscopy during the 2008 EUCAARI campaign in the Po Valley (Italy)" *by* M. Paglione et al.

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The authors would like to thank Anonymous Referee #3 for his/her through review.

The Referee's comments are copied below and followed by our replies

Detailed Comments:

P33348, L23: It says that investigating the correlations between high-resolution tracers and met data is the "main advantage" of PMF. It's not clear what high-resolution tracers

is. And what is it the main advantage compared too? The main purpose of using PMF on aerosol measurements is clearly to identify source contributions. Please reword to reflect exactly what is meant.

Authors Reply. Accepted. We reworded the sentence into the following: PMF is becoming common for organic source apportionment (Zhang et al., 2005; Lanz et al., 2007) and factor analysis of AMS data using PMF in its diverse implementations (including e.g. ME-2) has extracted biomass burning organic aerosol (BBOA) factors in multiple sites (Aiken et al., 2010; Elsasser et al., 2012; Crippa et al., 2013a etc.).

P33356, L24: "So called "OOA-a". Check other AMS-PMF records. I think this is typically called OOA-1 or LV-OOA. If so you should refer as that if using "so called" and then note that Saarikoski et al. calls it OOA-a

Authors Reply. True. We corrected the text.

P33357, L17-18: Why use conversion factors to calculate organic carbon loadings measured by the AMS? An HR-ToF-AMS was used for those measurements, for which high-resolution fitting calculates elemental concentrations directly? And Saarikoski et al. clearly did the HR analysis as it's presented throughout that paper.

Authors Reply. The so "conversion factors" were indeed the elemental ratios calculated by Saarikoski et al. We rephrased the sentence it in this way: In the following discussion, all concentrations of AMS factors for organic matter will be converted (using the OM/OC and H/C ratios reported by Saarikoski et al. (2012)) to μg/m3 of organic carbon (μgC m-3) for comparison with thermal analyses and of organic carbon and organic hydrogen for comparison with the NMR spectroscopic data.

P33359, L10: Is that necessarily true? Couldn't the higher hydrogen measurements in the AMS compared to the NMR be just as likely due to the AMS measuring the non-water-soluble fraction of aerosol? Both are probably contributing factors.

Authors Reply. This does not hold for the data shown in Figure 1d where the AMS

concentrations refer only to the sum of factors representative for the WSOC with two possible representations: a) OOAs + NOA, and b) OOAs + NOA + BBOA. The HOA was left out in this calculation.

P33360, L8-9: "H-C-O" is not a hydroxyl group. I'm assuming this is shown this way to indicate the carbon-attached H that NMR can actually measure. Perhaps this is standard notation in NMR, but it's chemically wrong as written. Please reword. It would probably be clearest if you note the functional group being quantified, the C-OH group in R-C(Hx)-OH, and then explain what NMR measures, the first H in "R-C(Hx)-OH". Otherwise, non-NMR people may be confused here.

Authors Reply. True. We changed it into "alkoxy groups" which is chemically correct..

P33361, L7: Whey is O3/NO2 used as a photochemical aging marker. Please provide references where this has been used or explain why it is being used rather than more commonly used indicators such as Ox=NO2+O3, NOx/NOy, or VOC ratios.

Authors Reply. The O3/NO2 ratio is not a universal tracer for photochemical age but it is a suitable one for this specific study. For most of the days, the diurnal cycles of NO2 and O3 resulted anticorrelated (Figure S9 in Saarikosky et al. 2012) because not only of the nighttime titration of ozone by NOx but also of the daytime development of a convective mixing layer. The morning increase of the mixing layer height was responsible for the dispersion of NOx which had accumulated overnight and for the entrainment of ozone from residual layers. Such entrained layers were characterized by aged organic aerosols and a relatively high sulfate content (Fig. 10 in Saarikosky et al. 2012). We used the O3/NO2 as a compact metric to trace both the photochemical and the atmospheric dynamic processes in this specific experiment.

P33361, L8-11: Confusing sentence. Reword.

Authors Reply. We omitted the sentence as unnecessary for the discussion.

P33362, L1-3 & P33362, L3-6: How can you estimate the amount of carboxylic acids

from the AMS? You cannot assume that for each CO2+ you have one carboxylic acid if this is what is being assumed here. Some ends up as CO+ while others can end up as part of a larger organic fragment. This fragmentation depends on the type of acid (see Fig 8 in Duplissy et al.: www.atmos-chem-phys.net/11/1155/2011/)

Authors Reply. The authors acknowledge that an exact relationship between C2H3O+ and CO2+ signals and carbonyl and carboxylic acid concentration has not yet been clearly established as the laboratory studies provided ambiguous results in this respect (Duplissy et al., 2011). However, it is possible that the fragmentation patterns of the specific carboxylic acids are less important in the ambient aerosol due to its greater molecular complexity. In fact, the CO2+ fragment has already been used as a proxy for total carboxylic acids in ambient samples (Takegawa et al., Aerosol Sci. Technol. 41, 418-437, 2007). We therefore partially accept the Referee's criticism and we delete the statement about the presumable degree of substitution based on AMS measurements and rephrased the sentence: "However the carboxylic acid concentrations determined by the NMR method are lower than those from AMS in most cases (Fig. 4) and their correlation is not good (R = 0.19). Such discrepancy could be explained by the unavoidable loss of volatile carboxylic acids during the chemical derivatization procedure, or by the formation of CO2+ fragments in the AMS vaporizer from groups other than carboxylic acids, like esters and peroxides".

P33365, L9-11: I think the authors are saying that ammonium nitrate was higher due to increased aerosol water content? This seems highly speculative. Couldn't higher ammonium nitrate be due to many other factors such as greater photochemical processing (HNO3 gas), cooler temperatures, higher NH3, different aerosol sources transported to site? Please clarify this connection, remove or provide stronger evidence.

Authors Reply. Those days (period III) were characterized by low Tmax and relative humidity frequently close to 100% (see Figure 1 in Saarikoski et al., 2012), therefore the ambient conditions were favorable for the formation of particulate nitrate. We made the statement less speculative: "Period III of the campaign was characterized by a sta-

bly stratified atmosphere, low maximum temperatures and high humidity (Saarikoski et al., 2012), with conditions favorable for the formation of particulate nitrate which indeed showed the highest concentrations of the campaign in those days. The correlation between F5 and aerosol nitrate suggests that the low-molecular weight amines occurred in the aerosol mainly as aminium nitrate and that its formation was regulated by gas/particle partitioning similarly than for ammonium nitrate".

Table 4: Why are Persons correlation coefficients (R) shown in Table 4 but R-squared values shown in the figures? Unless good reason, seems it should be consistent throughout.

Authors Reply. We converted all coefficients to R-values for sake of consistency through the text.

Figure 3a: It would be useful to show where the factors for this study lie on this plot. Consider adding these points.

Authors Reply. We accepted the suggestion of the Referee and added the functional group composition for the five factors to Figure 3a.

Figure 4: It looks like if one made correlation plots for the bottom two panels there may be no correlation. This lack of correlation seems to be skipped over and would seem important addressing the agreement of the methods and when/why they might be different. Can the authors add text discussing this.

Authors Reply. We did not discuss the lack of correlation between the AMS and the NMR concentrations in this dataset, because the database itself is very small and the coefficient of variation of the substitution degrees (amount of functional group over total WSOC) is also very small: between 17% and 21% (calculated for each concentration series as the ratio of the standard deviation to the mean), with the exception of the COOH groups (as fraction of WSOC) determined by NMR which vary to a greater extent (53%) because one sample showed a substitution degree double than the other

four. The fact that the NMR results for the COOH groups are not really in line with the AMS measurement is already highlighted in the text. In respect to the C=O, we believe that the small sample size and especially the small coefficients of variation do not allow to assess the correlation between the concentrations provided by the two methods. The results provided in this study are more oriented to compare the average functionalization degree measured by the NMR derivatizaion technique with that inferred by the AMS mass fragment concentrations.

Figure 8: Add R2 values to the figs or captions. On page 33367, lines 9-11, it says the correlations were very good but no statistical measure given.

Authors Reply. Corrected.

Interactive comment on Atmos. Chem. Phys. Discuss., 13, 33343, 2013.