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Atmospheric Chemistry and Physics 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.

Anonymous Referee #3

Received and published: 18 February 2014

Review of "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 Paglione et al.

This paper describes the comparison of two different techniques (NMR and AMS) for quantifying organic aerosol composition and sources at a rural location in the Po Valley, Italy. It discusses the different information that the two techniques provide about the sources and chemical composition of the aerosols sampled. Factorization methods are

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compared. Much of the focus is on characterizing biomass burning OA using these two techniques and they show two NMR factors with distinguishable fingerprints suggesting one is aged and one fresh. The AMS factors also showed two factors related to BB also with one primary and one aged. Importantly the two techniques split up the BB factors differently; however correlations are much improved by combining the two from each method together.

This is a well-written paper which clearly describes their measurements and analysis and provides a nice balance between stating strong conclusions a making a few speculative suggestions. Comparison of two independent methods is very valuable, especially between a widely used online method (AMS) and and offline one that is less often used for ambient aerosol measurements (however can draw on advanced methods/interpretations from other fields) and clearly contains both overlapping and complementary information which helps to better understand both methods. I can strongly recommend this paper for publication in ACP after a few minor to medium changes which are detailed below.

Detailed Comments:

P33346, L15: Should be “with respect to” (“with” was left out). This appears a few more times in the manuscript.

P33348, L15: Change “rich of” to “rich in”

P33348, L20: Reference De Carlo et al for HR-ToF-AMS

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.

P33349, L17: “compositions” should be singular

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P33350, L12: “an” ultrasonic

P33351, L29: labor “intensive”

P33356, L56: plurality mismatch: either “These. . .events” or “This . . ..event”

P33356, L14: Add other examples in Europe, for example in Spain “http://www.atmos-chem-phys.net/11/12067/2011/acp-11-12067-2011.html”

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

P33357, L5: “presented” not best word choice. Use “had”?

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.

P33357, L28: need “that” before “occurred”

P33358, L27: “semi-“ volatile, right? Volatile components would never be collected on the filters in the first place.

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.

P33360, L1: Need to add “and”.

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

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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.

P33360, L22: remove “faraway”

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.

P33361, L8-11: Confusing sentence. Reword.

P33361, L19: “diurnal” often refers to daily, not, “during the day”. Recommend “daytime” to avoid that confusion.

P33362, L1-3: quantify “in line with”

P3336X, 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/)

P33363, L15: change “were” to “was”

P33364, L12: change “worsen” to “hinders”

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.

P33367, L17: “can be” seems way too strong without providing evidence to support it. Consider “may be”

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P33368, L14: at “a” before “log-”

P33369, L3: change “between” to “of”

P33370, L15: “direct information” is vague. Please reword.

P33370, L19: change “one of such events” to “one such event”

P33371, L14: change “impoverished” to “depleted”

P33374, L9: need “The” before “Other”

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.

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

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.

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.

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

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