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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 #1 for his/her comments as well as for the grammar corrections. The Referee's comments are copied below and followed by our replies.

General: Not enough information is presented regarding the factorisation of the HNMR data (the AMS PMF analysis is covered by the Saarikoski et al. paper). The authors state their reasons for not using the solution sets with 6+ factors in section 3.4, however these results are not shown graphically, which would be very useful to see. These could very easily be included as supplementary material. Additionally, the factorisation also presumably needed to employ an estimate of measurement precision but the authors give no explanation for how this data was generated. The fact the Q/Qexp values in figure 5 are very high (around 30) may suggest that these uncertainty estimates are too low and therefore potentially wrong.

Authors Reply. We accept the Referee's suggestions to improve the discussion about the NMR factor analysis methodology. We will treat these aspects in the revised sections 2.3 and 3.4 and in a new section of the supplementary material, which will report the diagnostics (the Q function) as well as alternative solutions with a greater number of factors. Most importantly, it should be noted that Figure 5 of the original manuscript reported the Q/Qexp for the MCR and NMF methods, not PMF. These algorithms do not account for the measurement uncertainty and the function (Q) to minimize is the sum of residual squares:

(See Fig.1 for the equation)

The fact that the above sum is not normalized by the measurement uncertainties means that Q is not adimensional, and its actual value depends on the units used in the sample concentration matrix. Therefore, in general the ratio Q/Qexp, where Qexp is defined here analogously than for PMF, will not converge to 1. We acknowledge the fact that the use of the ratio Q/Qexp as a diagnostic for methods other than PMF can be misleading. For this reason, we now simply report the variation of Q with the number of factors as a diagnostic for the factor analysis performed using the MCR and NMF techniques. Figure 5 of the original manuscript was moved in supplementary material and its new version now is Fig. S1.

P33354, L8: The use of an exclusively flaming fire presents an issue because real domestic fires produce emissions through a combination of flaming and smouldering. Were smouldering fires investigated? If not, why not?

Authors Reply. The exact procedure was the following: the fire was started and kept flaming for about 90 minutes by several add-ons of beech logs. At the end, the fire was smoldering. All phases were combined in one filter sample. We will add these specifics in the revised version of section 2.4.

P33362, L16: This concluding sentence seems to be a little pointless. The high degree of substitution in organic particulates is something that is already well established, so I do not see the need to view this as confirmation.

Authors Reply. Accepted. We removed the sentence.

P33372, L1: The Jimenez and Ng references are perhaps not the most appropriate because they do not deal with biomass burning specifically. Jolleys et al. (doi: 10.1021/Es302386v) and Cubison et al. (doi: 10.5194/acp-11-12049-2011) may be more appropriate.

Authors Reply. Accepted.

Figures 1, 3 and 8: The regressions presented presumably use standard least squares fits, however given that it is not apparent which of the two measurements is the most accurate, orthogonal distance regression would probably be more appropriate.

Authors Reply. We agree. We re-calculated the regression line equations with a total least squares (orthogonal) method in Fig. 1 and 8. With respect to the previous analysis, the new regression lines brought to slightly different conclusions about the relationship between WSOC and the OC concentrations accounted for by the AMS factors. The new slopes in Figure 1a are of about 1 (1.15 and 0.91 with and without BBOA, respectively), thus suggesting a substantial overlap between WSOC and the AMS factors for the oxygenated organics, leaving HOA the only plausible contributor to the water-insoluble organic carbon. We kept the regression lines calculated with the ordinary least squares (OLS) regression in Figure 3c, because the result was not significantly different and also because in that case our x data (O3/NO2) are affected by a much smaller instrumental uncertainty than the y quantities, and the use of OLS seemed more appropriate (Smith et al., American Journal of Physical Anthropology, 140:476–486, 2009).

Figure 5: This figure appears to be of a low quality. The final version should be in a vector format (e.g. eps)

Authors Reply. The quality was improved and the figure was moved into supplementary material.

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$$Q^2 = \sum_{i=1}^{m}\sum_{j=1}^{n}(x_{i,j} - g_{i,k} * f_{k,j})^2$$

Fig. 1. Object function Q representing the sum of squared residuals

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