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Atmospheric
Chemistry
and Physics
Discussions

Interactive comment on "Wintertime aerosol chemical composition and source apportionment of the organic fraction in the metropolitan area of Paris" *by* M. Crippa et al.

M. Crippa et al.

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This paper presents the AMS/PMF analysis from the winter MEGAPOLI campaign in Paris. This analysis has now become commonplace in urban intensive studies for the identification of primary sources in particular. The results are not particularly controversial, as they compare well with other datasets obtained in other studies in other cities. However, there is real novelty in how the authors have used the Aethalometer data and how they have compared the different measurement sites within the campaign. The end result is a largely well written paper that presents some useful, if not earthshattering, statistics regarding primary aerosols for Paris. I would recommend that this be

published in ACP subject to the following minor comments:

- There is some crossover between this paper and Freutel et al., which I was asked to review in tandem with this. I refer specifically to the technical details such as the scaling of the organics by a factor of 1.3. But curiously, the authors do not refer to this paper, which is unfortunate because it covers details regarding the intercomparison in more detail. This paper would benefit from referring to this directly.

The Freutel et al. paper is now referenced at page 22544 at line 20 and in the supplementary material section about the AMS intercomparisons.

"A scaling factor of 1.3 was applied to the organic concentrations measured at the stationary GOLF site after comparison with the mobile laboratory deployed at the same location (Freutel et al., 2012)."

"The low ion transmission efficiency of the C-ToF-AMS deployed at the GOLF stationary site has been taken into account with a scaling factor of 1.3 for the organic concentrations after the comparison with contemporary measurements performed with the HR-ToF-AMS deployed at the same location (Freutel et al., 2012)."

- As a matter of taste, I do not see it necessary that equations 2-4 need repeating, as these have already been presented numerous times in the papers cited by this work.

We prefer to keep the PMF equations in our manuscript.

- Page 22543, line 16: 'Lee et al.' should be outside the parentheses.

Modified in the manuscript.

- Page 22544, line 20: I don't particularly like the explanation for the scaling factor of 1.3 applied to the data. Is it not more likely that this could be caused by something to do with the vaporiser (e.g. different temperature) rather than the ion transmission function of the mass spectrometer?

Two different heater temperatures were used during the summer campaign for the C-

TOF-AMS (800°C during the first two weeks and 600°C during the last two weeks) and no difference was observed in the identified scaling factor (Freutel et al., 2012). So, the different ion transmission efficiency is probably the cause in the observed differences of the C-ToF-AMS and MoLa-AMS mass spectra.

- Page 22545, line 8: Rather than Weingartner et al. (2003), the authors should consider using the updated correction presented by Collaud Coen (2010, doi:10.5194/amt-3-457-2010).

In the Collaud Cohen et al. paper, the authors recommended that the new correction algorithm should be used only when nephelometer data was available; otherwise, they recommended that the Weingartner et al. (2003) algorithm should be adopted. In the present study, nephelometer data were not available and so the Weingartner et al. (2003) correction was applied.

- Page 22547, line 23: How many variables were downweighted as 'weak'?

Actually the number of weak variables was very low: zero for SIRTA and LHVP and 1 for GOLF (m/z 279).

- Page 22549, line 14: The use of a solution set with a nonzero fpeak for LHVP must be justified further. According to Paatero et al. (2002, doi:10.1016/S0169-7439(01)00200-3), while fpeak can be used to explore the amount of rotational freedom within a potential solution space, solutions associated with nonzero values can only be considered physically meaningful for certain systems. Unless there is a specific reason to prefer the fpeak=-0.1 solution, it would be safer to use the fpeak=0 version.

The following sentence was added to the manuscript

"The selection of the fpeak=-0.1 solution was motivated by the clearer separation obtained for several sources as discussed in section SI-6.3."

In section SI-6.3 the following clarification is reported:

"For the LHVP site, the fpeak=0 solution provided a BBOA MS with a very small contribution at m/z44 (which should instead contribute to biomass burning sources). Additionally, a clearer distinction between the OOA and OOA2-BBOA factor was retrieved (major differences both in the time series and mass spectra). For this reason we decided to discuss within this paper the fpeak=-0.1 solution."

- Page 22551, line 9: Replace 'pretty good' with something less informal.

This sentence has been removed accordingly with the suggestion of reviewer 1

- Page 22557, line 9: Another explanation for the org60 could be that it reflects a portion of the BBOA that is prevalent during a particular burn phase, hence the separation from the BBOA factor.

As clarified in the answers to Reviewer 1, from our analysis we were not able to determine if the OOA2-BBOA was a real secondary OA factor deriving from primary BBOA emissions, or if it was an atmospheric mixture of primary BBOA and secondary OOA or if it was a mathematical mixture of PMF due to the impossibility to clearly separate the OA sources peaking at night based on their temporal variation. Therefore we could not be too precise in the definition of this factor. However, an additional study was performed combining the UMR AMS data with contemporary PTRMS measurements performed at the LHVP site (Crippa et al., in preparation), where a clear separation of a BBOA factor and a nighttime SV-OOA was obtained. This means that our OOA2-BBOA factor was mainly a mathematical mixture of factors which were not completely separated by PMF. This represents one of the limits of PMF and therefore the publication of this additional work will help to compare results from different source apportionment techniques and their uncertainties.

The reference to Crippa et al. paper (in preparation) is now reported in the manuscript.

"Additional source apportionment analysis performed combining gas (PTRMS) and particle phase (AMS) measurements for the LHVP site allowed a clearer discrimination of a pure BBOA source and a secondary semi-volatile OOA (SV-OOA) (Crippa et al., in preparation)."

- SI-6.3: The authors did not explore a particularly wide range of fpeak values. It would have been informative to have seen at what point the algorithm failed to converge, produced unacceptable profiles or suffered a large increase in Q.

A new fpeak analysis was performed in order to explore a wider fpeak (-10,+10) and Q/Qexp range and results of these analyses are reported in section SI-6.3.

"Figure SI-6.3.1 shows the variation in the factor relative contribution in the fpeak range -10 to +10 for the LHVP site. Negative fpeaks reduce the split between the BBOA and OOA2-BBOA factors, while the HOA mass spectrum receives higher contributions from mass 44. This is especially the case for fpeak values below -3 (corresponding to a Q/Qexp variation around 10%). Similarly, positive fpeaks > 4 incorporated the OOA2-BBOA factor into the BBOA and OOA ones and a non-meaningful mass spectrum was obtained for highly positive fpeaks."

"Figure SI-6.3.2 shows the variation in the factor relative contribution in the fpeak range -10 to +10 for the SIRTA site. Negative fpeaks affect the separation of a cooking factor, in fact below fpeak=-4 the COA contribution disappears. Strongly positive fpeaks affect the separation of OOA and BBOA, providing a split of the BBOA factor and not a separation of two OOA components."

"Figure SI-6.3.3 shows the variation in the factor relative contribution in the fpeak range -10, +10 for the GOLF site. The separation of the OOA2-BBOA and OOA factors is fpeak dependent and affected by both negative and positive fpeaks. Negative fpeaks produced often unreasonable time series, while positive fpeaks influenced mainly the mass spectra."

- Figure SI-6.4.1: The scaling on the Q/Qexp graph is not much use, as it doesn't show how much variation there is in the red line. A new scale is now used for the left axis

of Fig. SI-6.4.1 in order to highlight the variation of Q/Qexp with seeds (which is very small).

Please also note the supplement to this comment:
http://www.atmos-chem-phys-discuss.net/12/C10538/2012/acpd-12-C10538-2012-supplement.pdf

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Interactive comment on Atmos. Chem. Phys. Discuss., 12, 22535, 2012.