

Interactive comment on “Investigating the two-component model of solid fuel organic aerosol in London: processes, PM₁ contributions, and seasonality” by D. E. Young et al.

Anonymous Referee #4

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Young et al. (ACPD 14, 20845–20882, 2014) investigate the composition and atmospheric significance of Solid Fuel Organic Aerosol (SFOA) relative to other organic aerosol components in the winter in London. The authors discuss the temporal trends of SFOA, the contribution of SFOA to total OA, and the potential sources of SFOA. The discussion is placed in the context of other atmospheric studies of biomass-burning OA, and efforts are made to address the physical meaning of the SFOA factor in terms of burn conditions, burn fuel, and atmospheric processing. The manuscript essentially represents a case study of a winter period during the long-term ClearLo measurements in London. In contrast to the more general companion paper (Young et al.,

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ACPD 14, 18739–18784, 2014), this paper focusses on high-resolution AMS (HR-AMS) measurements instead of unit-mass resolution (UMR) data.

The data presented are valuable and contain new and relevant information, highlighting the significant impacts of space-heating on London's air quality during winter. The authors have clearly invested a great deal of effort into the analysis of the entire data set, and this case study presents new information that will be relevant to future field studies and urban planning.

In my opinion, the manuscript should be accepted if the major comments listed below are addressed. In general, these comments reflect an impression that the paper includes very detailed analyses that do not provide more information than a brief description of the data would, and at some points appears to overinterpret the data. In addition, the paper could be much more concise if restructured so that background information could be introduced only once. For example, separate results and discussion sections may allow this.

Major comments:

1. The authors use the term "SFOA" to describe solid-fuel OA, emphasizing that other fuels such as coal contribute significantly (31% in the case of coal) to PM₁ in the UK. However, both of the SFOA mass spectra presented contain significant signals at m/z 60. This ion is a tracer for anhydrosugars such as levoglucosan, which are not expected to be abundant in coal-combustion smoke (Oros and Simoneit, 2000; Wang et al., 2014). So, is (a) the OA contribution of coal combustion being apportioned by PMF into the other factors, (b) is coal-combustion OA negligible, or (c) is the coal used in London generating a surprisingly high amount of anhydrosugars (or some other confounding molecule)? If (a) is true, the factors presented here are not SFOA factors. If (b) is true, there is no need to call these factors SFOA rather than BBOA (biomass burning OA). If (c) is true,

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then more data would be needed to demonstrate it.

2. The fact that the SFOA/BBOA generated by an entire city may not be adequately represented by a single mass spectrum, or even by two mass spectra, is undoubtedly a major challenge for an atmospheric study such as this one. The authors make a number of clear statements to this effect, but there are still some points at which the discussion might be reworded to reflect this fact.

First, since SFOA/BBOA is not a single chemical component nor a single source, statements such as "the mass spectral profile of SFOA is highly variable, the findings from this study may have implications for improving future source apportionment and factor analyses" (Abstract, line 18 p 20847) would be much more accurate if they were reworded along the lines of "the SFOA profiles reported in this study may provide a basis for the identification of SFOA in other environments". This also applies to the conclusion (p 20865, lines 4-11).

Second, the discussion on page 20859 lines 19-29 and page 20860 lines 5-7 does not make sense to me. The language of page 20859 lines 19-29 suggests that mass-spectral differences between the two PMF factors were not expected (probably unintentionally). The discussion of page 20860 lines 5-7 suggests that the two factors represent the endpoints of a continuum, by analogy to OOA (presumably referring to the continuum of volatilities or oxygenation observed for OOA). But this analogy breaks down because SFOA/BBOA composition may change with burn conditions, fuel type, age, and dilution. Over which dimension should SFOA1 and SFOA2 represent endpoints? And what evidence is there that they are endpoints, rather than simply two of the most-variable contributors to London OA during this particular period?

Third, PMF factors are occasionally discussed as though they are real entities, existing independently of the analysis itself. On page 20854, line 14, the statement "it is not always possible to separate OOA in to its two subtypes if ambient temperature and photochemistry are not sufficiently variable such as in the win-

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ter" is strange, because if ambient temperature is constant and photochemistry is negligible, then there is no meaning to the concept of two OOA subtypes anyway.

3. The reasoning behind the correlations of SFOA with NO_x and CO appears to be circular. First, it is noted that multiple NO_x and CO sources exist, including solid fuel burning and vehicle engines. Then, it is noted that the sum of SFOA1 and SFOA2 correlates better with NO_x and CO than the separate factors. Why is this noteworthy? One would also expect that summing *all* NO_x/CO sources would improve the correlation even more (neglecting differences in atmospheric lifetime).

The multiple linear regression fit also reads as though it follows circular reasoning. First, the fit is performed so that the regression coefficients explain as much of the variability in NO_x or CO as possible. Then, the fitted function is correlated with NO_x or CO. Since the goal of the fit was to explain more of the NO_x or CO variability in the first place, then the fitted function will necessarily be better correlated with those parameters.

Also, it is not clear exactly how the fit was performed. Here, the fit is described as a "multi-linear regression fit", citing Allan et al. (2010), who described the same analysis as a "bilinear fit". The written function indicates that multiple linear regression was performed with HOA and SFOA as predictors, but does not explicitly show how CO or NO_x were used. I presume that either CO or NO_x were used as the response variables? If this is the case, please use more standard regression language (multiple linear regression, predictor variables, response variable). Finally, the term "arbitrary" must be removed when describing the fit coefficients A and B; these coefficients are not arbitrary if their values were determined by least-squares. Perhaps it was the choice of a linear regression function that was arbitrary.

In my opinion, this entire section would be made clearer by simply stating the correlations between SFOA1 and SFOA2 with the gas tracers, and moving on to

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the final paragraph (Section 3.1), which states that both solutions could be valid (as expected, for such a PMF analysis) and states that the 5-factor solution was chosen based on physical meaning. The only value added by the regression seems to be that the assumed sources of SFOA1 and SFOA2 were allowed to have different OA/CO emission ratios.

4. "SFOA1 and SFOA2 differ by degree of oxygenation and therefore age" on line 10, page 20860 is not a sound argument as different fuels are known to produce BBOA of different degrees of oxygenation (e.g. Schneider et al., 2006, and the introduction of Section 4.3.2). Also, the estimated O:C ratios should include a citation of the method used, and should note the limitation that the AMS fragmentation table may not be valid for these POA samples.
5. p 20863, line 1: Why should the higher temperatures of flaming combustion produce more-functionalized OA? Why should lower temperatures give more alkanes? A citation would help here.
6. p 20864, lines 1-7: If the sources of SFOA were drastically different in the summer, then the diurnal trends should be considerably different to those of the winter. Including more information on the summer SFOA might significantly strengthen the arguments and interpretation of the winter data. (Would enhanced summer photochemistry be a plausible reason why HR-ToF-AMS SFOA was not identifiable?)

Minor comments:

- In general, ions are discussed in terms of their integer m/z (m/z 44, 60, 73, etc) rather than their actual identity, the identification of which is presumably the reason that the HR-ToF-AMS data are presented in a separate paper to the UMR AMS data. The actual ion being referred to should be named at least once in these cases.

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- The authors frequently switch between the past and present tense. For example, the paragraph on line 15, page 20856 is in the present tense while the remainder of that section is usually in the past. Line 6 on that page begins "the ... concentration was" and continues "this event is the result of...".
- The abstract (line 15-16 of page 20847) argues that the SFOA1/SFOA2 split is due to differences in wind direction, then also argues that the split may be due to differences in burn phase. How can burn phase be related to wind direction? Is the implication that poorer stove technologies are used in a poorer region of London, so that less flaming combustion occurs? I find it hard to make sense of this combination of statements.
- The abstract (line 21-23 of page 20847) claims that 20% of the OA mass is more than 18%. I find this hard to believe given the uncertainties inherent in PMF.
- Page 20849 paragraph 2, please define all categories and not just solid fuel and biofuel. Also, it is stated that distinguishing sources in this manner is important without explaining why.
- page 20849, paragraph 3, please spell out UK.
- p 20850, paragraph 3: the wording implies that POAs are only important to climate and health when associated with BC.
- p 20850, last paragraph: This would be clearer if you spelt out that the citations are from the same field study discussed here.
- p 20852, first paragraph: I think the true time resolution is the opposite: 30 minutes, obtained over 5 minutes; and not 5 minutes obtained only once per 30 minutes.
- p 20853, 2nd paragraph: This is not "potassium ion" but rather water-soluble potassium.

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- p 20853, the first paragraph of Section 3.1 reads as though the PMF analysis was highly subjective, as it only includes partial statements of the analysis. In contrast, the actual cited description makes it clear that the analysis was objective and thorough. The discussion also may fit better in a Methods section.
- p 20854, line 7: please cite Ulbrich et al. (2009) regarding factor splitting.
- p 20854, line 9: what is "divergence" in this context? Splitting?
- p 20854, line 22: this argument seems incomplete. Was it meant that all 3 (NO_x, CO and HOA) are emitted from vehicle engines?
- Section 3.2, p 20856: Why are averages and standard deviations presented, if the data are not scattered about their mean? The interquartile range would be more meaningful than the standard deviations.
- p 20856, line 19: Does "commercial cooking activities" mean restaurants, or something more?
- p 20857, line 18: "Imported" is a strange word for pollution.
- p 20857, line 21: black carbon is not always produced by combustion. Also, please add "In their study" to the following sentence to be clearer.
- p 20858, line 6: it would be more meaningful to state that the composition of these OA are not constant, rather than the mass spectra.
- Section 3.2: The diurnal trend plot would be improved by information on the variability of the data, such as shading the interquartile ranges. At the moment, there appear to be three peaks in the OOA which are not discussed.
- Section 4.2 discusses the variability of AMS mass spectra from different combustion sources. It seems to me that the point is about the actual variability in
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composition of the material produced. The section could benefit from some non-AMS citations and discussion.

- At p 20858, line 24, and p 20859, line 14-15: the SFOA factors are discussed in terms of other studies' BBOA factors. That the SFOA factors are mass-spectrally similar to BBOA raises the problem of definition described above.
- p 20859, line 19-29: the statements "there are differences in the structure of the peaks above and below the line" (of the normalized difference spectra), and "this suggests that the chemical groups are affected differently by what is driving the split between the factors" seem to be circular, because without differences in the temporal trends of these ions, PMF would not have been able to report two SFOA/BBOA factors.
- p 20861, line 7: please specify "wood, peat and coal" with "combustion", if applicable.
- p 20861, line 17: please clarify if the stronger correlation is referring to Yin et al's data.
- p 20862, line 28: typo: the conversion of organic matter to CO₂(g), not CO₂+.
- p 20863, line 15: "integer" m/z, not nominal.
- p 20863, line 24: please state that REPARTEE took place in London.
- p 20864, line 18: how can SFOA1 contain more organic matter than SFOA2? Both are organic components.
- Please capitalize the letters making up acronyms when introducing them.

References

Oros, D. and B. Simoneit. Identification and emission rates of molecular tracers in coal smoke particulate matter. *Fuel*, 79, 515-536, 2000.

Schneider, J., S. Weimer, F. Drewnick, S. Borrmann, G. Helas, P. Gwaze, O. Schmid, M. O. Andreae, and U. Kirchner. Mass spectrometric analysis and aerodynamic properties of various types of combustion-related aerosol particles. *Int. J. Mass Spec.*, 258, 37-49, 2006.

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