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Atmospheric
Chemistry
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Discussions

Interactive comment on "Contributions from transport, solid fuel burning and cooking to primary organic aerosols in two UK cities" *by* J. D. Allan et al.

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P19105, L17: ": : :greatest fraction: : :" – revise

Response: Changed to "majority"

P19105, L20: ": : :travel: : :" – revise

Response: Changed to "penetrate"

P19105, L26-L27: "At distances removed: : :" – revise

Response: Changed to "Further downwind"

P19106, L22: “applied to other sources of atmospheric aerosol data” – revise

Response: Changed to “other types”

P19106, L27: In this study, OA was separated into HOA, charbroiling, wood burning, and food cooking OA.

Response: Agreed, but this second cooking factor only appeared when 6 or more factors were invoked and it was labelled as ‘minor’. Rather than discuss the validity of the result, the text has been modified to say “factors that included HOA. . .”.

P19106, L27: With the MCA, more than two components can be resolved (Zhang et al., 2007): : : but it is certainly not restricted to three components. Revise.

Response: Corrected.

P19106, L29: Also mention that OOA, type 2, and OOA, type 1 could be associated with different volatilities (see e.g. Lanz et al., 2007).

Response: Added.

P19107, L4-5: “chemically younger” – revise

Response: Changed to “less chemically processed”

P19107, L25: “These are much larger cities compared to Zurich” – why is this important here?

Response: This was added to highlight the fundamental differences between this and the work of Lanz et al. This is referred to specifically in the revised version.

P19108, L14: “lightly-used” – revise

Response: Removed and the following is inserted at the beginning of the subsequent sentence: “Given that the park road is not used intensively by motor vehicles,”

P19109, L15: I do not understand why a newer instrument would measure more organics (but less chloride, as an example). Please explain.

Response: Two instruments may differ not necessarily because of newer technology, but due to subtleties in the tuning altering the effective relative ionisation efficiency of various species. This is stated in the revised version.

Are these intercepts significantly different from 0?

Response: They are nonzero, but not significantly so compared to the magnitude of the measurements. This is already stated in the text.

Please indicate the uncertainty associated with these numbers.

Response: Error estimates associated with fits have been added.

P19109, L10: “the instrument” - mention again the type of instrument (C-ToF-AMS)

Response: Corrected

P19109, L22: I suggest estimating the collection efficiency, CE, via total AMS aerosol + black carbon, BC (derived from the mentioned MAAP instrument), versus PM1.

Response: We have no collocated measurement of PM1, so cannot make this calculation.

P19111, L8: maybe "as provided by P. Paatero (University of Helsinki)"

Response: Changed.

P19111, L10: Why is PMF applied to high-resolution AMS data is still in its "relative infancy" (compared to PMF applied to unit-mass resolved data)? Please explain.

Response: The following text has been added: “Additional complications arise during the use of the high resolution data introduced by subtleties and variations in the peak shape and m/z calibration fitting. These, in turn, can introduce artefacts in the output of the PMF analysis and uncertainties not accounted for in the standard error model.”

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P19111, L17-18: 300 cumulative steps seem rather small given the large datasets.

Response: All the presented fits converged successfully before this number of steps, so this is a moot point.

P19111, L29: I do not understand this cut: are there no low signal-to-noise fragments at m/z < 200? In contrast, I expect some relevant PAHs to be found at m/z > 200.

Response: While PAH signals exist in this regime, they are typically small and of poor signal-to-noise due to ion counting statistics, instrument background and interference from other organic species present.

P19112, L4 sqq.: I agree that m/z 18 is depending on (scaled to) m/z 44, but there

are more such interdependencies in AMS mass spectral data. One could also argue that a strong weighting of m/z's 18 and 44 is justified, as they make up for such a large fraction of the organic mass.

Response: The other interdependencies are small compared to those that exist below m/z 20. Giving additional weight to m/z 44 was found to be detrimental to the fits and has already been covered by Ulbrich et al. (2009).

P19112, L12: In contrast, such plumes (e.g. wood burning plumes) may introduce the variability necessary to separate distinct sources (e.g. wood burning) by PMF: : : but I agree that singular emission events might also cause some positive artefacts for those sources: in such cases, I suggest relaxing the non-negativity constraints for the factor time series.

Response: As stated in the PMF manual, “Non-negativity is usually a necessary condition in order that the results might be interpreted as physical quantities.” Given that we are aiming to quantify all of the factors, relaxing this constraint is not desirable. We would see this as better fitting at the expense of quantitativity.

P19112, L24: maybe “non-refractory”?

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Response: Corrected.

P19112, L25: “: : :organics dominate with contributions from sulphate: : :” – revise

Response: Changed to “organics are the dominant fraction, with contributions from sulphate”

P19112, L26: “behaviour”?

Response: Changed to “fractionation”

P19113, L12: “where” or “when”?

Response: Corrected.

P19113, L27: I doubt if the AMS represents the appropriate instrument to detect organic sulphur. After vaporization and ionization, it may be measured as OM + SO42-

Response: Agreed. This point is echoed in the revised text.

P19114, L7: “oxidized” or “oxygenated”?

Response: Corrected.

P19114, L14: the “slight dip around midday“ in the OOA diurnal cycle is plausible. In the morning hours, aged OOA is down-mixed into the increasingly high boundary layer and the photochemical aging is not prominent before the after-noon hours.

Response: This line of discussion has been added to the text.

P19114, L15: Please expand on this question: was OOA, type 2, not present in these campaigns or was it always condensed in the aerosol-phase and has therefore no distinct temporal variability (i.e. it can not be separated by PMF)? Is the OOA-factor derived here a mixture between type 1 OOA and type 2 OOA (2:1, 3:1?)?

Response: Note that the two types represent do not represent specific chemical states but end points in a continuum of a highly complex mixture of organic species; their discrete nature is a feature of the modelling approach applied. The variance referred to is the variability within the OOA detected and as such, only one factor could be derived. Given that the chemical nature of types 1 and 2 OOA varies according to dataset, reporting a mixing ratio for this dataset is not possible. The following text has been added to the end of the paragraph: “That is not to say that ‘type 2’ OOA is not present, rather it is not possible to distinguish it from the ‘type 1’ material and so the fraction is reported as a single factor.”

P19116, L19: “consistent with combustion HOA” – revise

Response: Changed to “HOA from combustion”.

P19117, L9 and elsewhere: replace “4 factor solution” by “4-factor solution”

Response: Changed.

P19117, L19: “: : :giving alternative solutions that while typically not the most

optimal: : :” this sentence will not get your ideas across to the reader.

Response: Revised to, “This gives alternative solutions that while typically not the most optimal (in terms of Q) , still satisfy the convergence criteria.”

Furthermore, a Paatero-citation would be more appropriate at this instance.

Response: A reference to Paatero et al. (Chemometr Intell Lab, 60, 253-264, 2002), has been inserted.

P19117, L22: What is meant by “mass spectral space” and “time series space”?

Response: This refers to the increased angular separation (i.e. decreased dot products) of the factors either by comparing the mass spectra or time series. The revised text states this more explicitly.

P19118, L1: The high Q/Q.exp-values are rather surprising, also in the view of similar studies (Lanz et al., 2007, Ulbrich et al., 2009) that reported Q/Q.exp values close to

1. I wonder if A.) this difference is due to the instrumentation (ToF-AMS vs. Q-AMS with relatively low S/N) and B.) if this ratio can be reduced by specifying a model error > 0% in PMF2 v4.2.

Response: Agreed on both points and this is now mentioned in the text.

P19118, L8: As a matter of taste, I would put these mass spectra into the supplementary section.

Response: Figure moved.

P19118, L11: ": : :it was clear that some of the mass that would otherwise have been assigned to SFOA was being assigned to the other factors." – this sentence is not clear.

Response: Revised to, "In both situations, the fractional contribution of SFOA to the total organic mass decreased, indicating that the mass that would otherwise have been contained within these peaks was being assigned to different factors."

P19118, L : I agree that rotational ambiguity and other program settings (including the number of factors) determine the worst-case uncertainty of the PMF-AMS analysis. However, I disagree to call this uncertainty "confidence interval". This term should not be used in that context.

Response: Removed and replaced with "level of ambiguity"

P19119, L16: "other local combustion sources" – such as : : :?

Response: The following has been added: "such as space heating, which would also contribute to SFOA."

It should also be mentioned that no perfect agreement between PM from combustion and gaseous pollutants from combustion can be expected (different formation and removal processes).

Response: The following has been added: "While perfect correlation with gas phase markers would not be expected (due to variations in source functions and different removal processes),"

P19119, L15: ": : :also: : :also: : :" - revise

Response: Corrected.

P19119, L16-17: ": : :using: : :using: : :" - revise

Response: Corrected

P19119, Equation 1: What is meant by f(HOA, SFOA)? Primary combustion OA (=HOA+SFOA)? The equation reads as if you modelled HOA and SFOA from HOA and SFOA: : :. I am not sure if I got the authors' idea, but maybe one should include the terms CO and NOx in this equation?

Response: This is the fitting function that is matched to the combustion tracers during fitting, with A, B and C being the fitting parameters. Given the combustion tracers are treated as independent variables, their inclusion in the fitting function is not warranted. This is made clearer in the revised version.

P19119, L21: "gas phase concentration" maybe you mean mixing ratios of gaseous pollutants

Response: Changed.

P19119, L26 : ": : :improve the NOx values: : :" – usually, models are not used to improve measurement values.

Response: Changed to "did not improve the values of r corresponding to the NOx comparison"

P19120, L8: ": : :dwarfed: : :" – revise

Response: Changed to "insignificant compared to"

P19120, L24: why was there not enough "OOA variation" to separate OOA1 and

OOA2?

Response: Often, the variations within OOA are driven by changes in temperature changing the mass fraction of semivolatile component. A speculative reason for the lack of ability to separate these factors may be that these campaigns did not experience large enough variations in temperature.

P19120, L1: ": : :OOA, which assuming it is secondary in nature: : :" please note that Weimer et al., 2008 characterized primary wood combustion OA by an OOA-like mass spectrum (depending in burning conditions: : :).

Response: This is discussed later in the text but a cross-reference has been inserted.

P19122, L11: Please use a more descriptive title (4.2 Combustion factors) (disambiguation: "emission factors")

Response: Changed to "Primary combustion emissions"

P19122, L17: I am not sure if a measurement campaign can be called "experiment"

Response: Changed for the sake of consistency, but it is worth noting that in the atmospheric measurement community, the term 'experiment' (as used in the acronym 'REPARTEE', amongst several others) is routinely used to refer to intensive measurement campaigns.

P19123, L12-13: given the high m/z 44-to-m/z 57 ratio in the OOA by Weimer et al. (2008) it is rather likely that this primary OOA from wood burning (smouldering phase) would be classified as OOA by PMF and usually (but wrongly) interpreted as SOA.

Response: Not necessarily. One advantage of PMF2 is that because it fits in two dimensions, components that have similar mass spectral profiles can still be resolved if their temporal trends are different enough. The similarity of the AMS response to SOA and biomass burning HULIS means that there is some inherent ambiguity in trying to resolve these components, which is reflected in the range of fractionations found when

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exploring the rotations using the fpeak parameter. This is made clearer in the revised version.

P19123, L22: “raw AMS spectra” – do you mean: average organic MS?

Response: Changed in revised version

P19126, L6-7: “: : :using a quadrupole-based AMS, the PMF analysis failed to identify the COA component...” why? Do you have explanations for this behaviour?

Response: This is because of the signal-to-noise limitation on PMF analysis. This is stated in the revised version.

P19130: It could be added to this discussion that “charbroiling aerosol” comprises a broad mixture of all sorts of aerosols from char, oil, accelerant, meat, vegetable (wood), fat etc. burning, and that these latter contributions have variable importance and are difficult to separate. In any case, I think it is not very surprising that “charbroiling aerosols” as characterized by Mohr et al. (2008) had no (a minor) impact on ambient OA in UK cities, in wintertime.

Response: This is already touched on in the paper and given more emphasis in the revised version.

P19132, L19: “: : :not significant enough: : :” what are the “significance”-criteria? Either it’s significant or not.

Response: Changed to “not represent enough variance”

P19132, L25-27: What are the standard deviations of these emission ratios?

Response: The standard deviations derived from the fits are on the order of less than 1 μg m-3 ppm-1 and this is now reported in section 4.3. However, we consider this minor relative to the uncertainty imposed by the rotational ambiguity and these have now been reported in the conclusions.

P19133, L21: “a prioi” – revise

Response: Removed

P19144: Please indicate uncertainties associated with intercepts and slopes

Response: Addressed above.

P19148: Figure 1: the term “Volume concentration” (y-axis) does not apply to AMS data shown in figure.

Response: The volume concentration is estimated using assumed material densities applied to the AMS mass concentrations, so it does apply. This is stated in the revised version.

P19149: Figure 2: time-axes should be labelled “date” rather than “date and time” (this also applies to some other figures).

Response: Changed

The text in the caption could be more descriptive.

Response: Caption expanded.

P19152: Figure 4: I assume that the correlations OOA vs. AMS-sulphate etc. are not very sensitive to rotations. Is this correct?

Response: Yes, but we consider this to be more or less academic. A good correlation between sulphate and OOA is dependent on a consistent ratio of precursors within the source footprint. Given that VOC and SO2 source fields are known to be distributed differently within the UK, a perfect correlation should not be expected anyway.

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