Atmos. Chem. Phys. Discuss.,
https://doi.org/10.5194/acp-2017-665-RC1, 2017

Atmospheric Chemistry and Physics
Open Access
Discussions

Interactive comment on "Formation of secondary organic aerosol coating on black carbon particles near vehicular emissions" *by* Alex K. Y. Lee et al.

Anonymous Referee #1

Received and published: 28 August 2017

General comments

This paper compares SP-AMS and AMS data at an urban location in the US to infer details concerning the behaviour of black carbon aerosols and SOA formation in this environment. This is partly facilitated by the dataset exhibiting a strong diurnal profile, meaning that traits can be reported with decent statistical power, in spite of the sampling period being relatively short. While the quantitative accuracy of the SP-AMS may be questionable (many of the RIEs and CEs are simply assumed rather than calibrated here), this does not form the major part of the science. This paper is well written and has the potential to provide some useful insight relevant to ACP, however I feel that the discussion side of the paper needs more work. Specifically, the authors appear to be making two unsafe assumptions often inappropriately made when analysing data

Printer-friendly version

Discussion paper

of this nature; firstly, they seem to be assuming that the patterns are governed by sources and in situ processes (neglecting advection), akin to a box model and second, they seem to be treating the PMF factors as discrete chemical entities. While I'm sure the authors are aware of the issues here, this is not currently reflected in the text and a few conclusions are made that I would regard as unsafe. I recommend that this be published subject to major corrections.

Specific comments

There an issue that I can see regarding the conclusions of the comparison of organic factors from the two AMSs in that the authors appear to be treating the PMF-derived SOA factors as discrete chemical types. While this could hypothetically be the case, it is far more likely that when applying the simple PMF data model to a chemically complex system such as this, the two SOA factors for each instrument represent the mathematical endpoints of a distribution of data, within the non-negativity constraint imposed. This being the case, a direct comparison of the two instruments' factors may be problematic; given that it is known their mass spectral responses to different organic materials are fundamentally different, their respective factorisations could end up being very different in character for the same aerosol simply through virtue of how the spectra are distributed in multivariate space and what endpoints are converged on by the solver. As a suggestion, a more objective comparison of the two datasets might be achieved if the primary factors (determined using PMF) are subtracted from the data matrices then metrics such as elemental ratios derived from what is left (assuming it is all secondary), e.g. as new points on figure 7. See https://www.atmos-chem-phys.net/15/6351/2015/.

An entire line of discussion – comparing the behaviour of organics to sulphate – I consider to be deeply flawed in the way it has been approached here. Outside of aqueous-phase processing (which is almost certainly not happening here, given the low humidities), the formation lifetime of sulphate from the gas phase oxidation of sulphur dioxide tends to occur on the timescale of weeks (far beyond the timescale where

Printer-friendly version

Discussion paper

NOy/NOx is a useful indicator of photochemistry), which means that a diurnal pattern observed here is extremely unlikely to be a manifestation of the chemistry. I would consider it far more likely that the relatively modest pattern that does exist (noting that the vertical axes in figure 5d are not scaled from zero) is caused by the transport of regional pollution or marine air into the area during the day and concentrations decreasing at night through dry deposition in the nocturnal inversion layer, consistent with the wind speeds. It may also be that an analogous process, driven by dynamical rather than chemical processes, may be occurring for the highly oxidised SOA.

The third paragraph on page 8 makes a lot of very speculative statements concerning mechanisms that I do not consider to be adequately supported by the evidence and in certain cases implicitly rely on assumptions I do not consider safe. Not least of which is the tendency, as described in the general comments, to implicitly treat the factors represent discrete chemical types. But beyond this, I find the following lines of discussion to be problematic:

1) By using sulphate as a point of comparison for OOA, there is an intrinsic assumption that the precursors have similar sources on a regional level. While this is often the case at many sites, there are locations around the world (e.g. London) that do not conform to this behaviour. More evidence should be presented here that this is the case before drawing inferences concerning the chemical behaviour of these.

2) OOA-1 is described as being bimodal, however to my eyes, the trace in figure 5g simply has one very broad mode in its diurnal profile. Regardless, I fail to see how this constitutes evidence that there are different mechanisms in play in the morning versus the afternoon, so additional evidence to support this must be presented. Also see the comment concerning the treatment of SOA factors as discrete.

3) While a factor may correlate with nitrate, I consider it too much of a jump to assume that they are mechanistically related. I consider it more likely that they are formed over similar timescales and/or have similar thermodynamic properties.

Printer-friendly version

Discussion paper

Figure 5g: What are the red dashed lines?

Page 10: I would propose a much simpler explanation for the trends in the more highly oxidised material. If this is being formed regionally on longer timescales (as with sulphate), then this would already exist within the accumulation mode (which does not necessarily have to contain black carbon) and simply be advected in during the day. The less oxidised SOA formed more locally on shorter timescales could preferentially condense onto the BC particles through simple virtue of these Aiken mode particles presenting a larger overall surface area to the condensing gases. While it is hypothetically possible that there may be a mechanistic preference for material to condense onto certain surfaces because of their chemical nature, this would be a contentious statement to make and I do not see the data here as supportive of this notion.

Technical corrections:

Page 3, line 15: Which 42i was fitted with the photolytic converter? I assume the NOx instrument, but this should be explicit

Page 5, line 5: If the particle beam was found to be wider than the laser beam, this means that some particles may undergo incomplete vaporisation at the edges of the laser, which would in turn bias the measurement towards the coatings rather than the cores (see http://cires.colorado.edu/jimenez-group/UsrMtgs/UsersMtg16/JDASPAMSfocusing.pdf). This should be added as a caveat.

Interactive comment on Atmos. Chem. Phys. Discuss., https://doi.org/10.5194/acp-2017-665, 2017.

Printer-friendly version

Discussion paper