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Atmospheric
Chemistry
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Discussions

Interactive comment on "Quantitative determination of carbonaceous particle mixing state in Paris using single particle mass spectrometer and aerosol mass spectrometer measurements" *by* R. M. Healy et al.

Anonymous Referee #2

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Title: Quantitative determination of carbonaceous particle mixing state in Paris using single particle mass spectrometer and aerosol mass spectrometer measurements Author(s): R.M. Healy et al. MS No.: acp-2013-150

The paper uses multiple instruments to quantify mass concentrations from a co-located single-particle mass spectrometer to understand trends in particle composition and apportion sources in Paris during the wintertime. These single-particle trends are compared to trends from other instruments. These trends in particle sources and mixing state were then used to quantify local versus transported sources of particulate mat-

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ter to Paris. The paper is overall well-written and provides a unique perspective on particulate matter by exploring trends in mixing-state and mass concentrations. My biggest concern is how the relative sensitivity factors were derived for scaling the particle types obtained from the ATOFMS. Specifically, I wonder if the method of obtaining relative sensitivity factors for the different particle types, presumably by comparison to co-located instrumentation, would inherently bias the ATOFMS data to agree with these same co-located instruments. I recommend that the authors address this comment possibly through a more in-depth discussion of procedures used to obtain mass concentrations. My specific comments can be found below:

Page 10350, Line 26: What diameter of tubing was used for sampling?

Page 10351, Line 7: Were all acquired spectra dual polarity? Particulate water can suppress negative ion formation [Neubauer et al., 1998]

Page 10351, Line 15: Were particles dried before being sampled by the ATOFMS as well?

Page 10354, Line 16-24: Please explain in more detail how you determined RSFs for the different chemical species. I'm assuming you compared the RPA to the mass concentration from the different instruments. Wouldn't this bias your correlations since you are scaling ATOFMS peak areas to the very same instruments that you are showing correlations for?

Page 10355, Line 12: What is the significance of the changing slopes? Might this suggest that in addition to hourly scaling factors, hourly average mass spectra with an appropriate slope be used to scale data to mass concentrations?

Page 10355, Lines 25-27: It is surprising that marine air masses dominated the meteorology for so long yet little sea salt was observed. Perhaps much of the sea salt was aged into sodium nitrate particles, could this be confirmed by PILS? You attempted to quantify NaCl, but I'm not convinced you are apportioning the nitrate properly since

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much of the nitrate mass might be associated with sea spray particles that have reacted with nitrogen oxides (see [Gard et al., 1998; Gaston et al., 2011])

Page 10357, Line 19: Why is the accumulation of ammonium nitrate assumed for the detection of the EC-OA-NOx particle type? Why not the accumulation of photochemically produced nitrate?

Page 10357, Line 21: Your finding that EC-OA-NOx particles are larger than EC-OA-SOx and EC-OA particles is consistent with [Moffet and Prather, 2009]. This should be noted.

Page 10357, Line 21: Please state the size modes for each soot type.

Page 10358, Line 5: These trends should be commented on more in each particle class section so the reader doesn't have to refer back to the figures each time.

Page 10358, Line 12: Your spectra for fresh biomass burning aerosol, including the large CN and NO2 peaks, agrees with spectra obtained from smoke plumes by [Pratt et al., 2011]. This paper also shows spectra indicative of aging plumes, please compare.

Page 10359, Line 20: Is there more diesel combustion in these regions that would contribution more sulfate?

Page 10359, Line 24: Suggest citing papers that show enhanced sulfate formation due to aqueous phase processing/during elevated RH conditions as this is a well-documented process.

Page 10360, Line 5-7: This particle type could also be K-OA-NOx particles with a thick organic coating that masks the K. How does the size mode compare to K-OA-NOx? if it is larger, then the additional coating would make sense as a source for this particle type.

Page 10360, Line 17: Do you see oxalic acid (m/z -89) and/or HMS (m/z -111)? This would suggest the prevalence of aqueous phase processing.

Page 10360, Line 24: Were any ions indicative of organosulfates present (see [Hatch et al., 2011])?

Page 10361, Line 17: What about the formation of iminium salts from TMA and either nitrate or sulfate (see [Pratt et al., 2009])?

Page 10362, Line 18: Consider making Figure S5 a main figure.

Page 10364, Line 7: Also the instrumentation was different for these ratios in the Crippa paper. How would this bias the ratio?

Section 3.3: It is interesting that your agreement with the AMS factors improves when fresh and aged particle types are combined. Could your study contribute to improvements in PMF analysis to help AMS data further distinguish particles based on their age?

Page 10365, Line 20: I thought most AMS's have a lower size limit than this. State in the experimental what the size limits are of the AMS.

Page 10366, Line 20: How did m/z 43 compare to OOA? See [Qin et al., 2012] who showed that SOA is well tracked by this ion marker.

Page 10367, Line 4: Is it be possible that the AMS cannot vaporize some of the OOA and is missing a portion of the organics?

Page 10367, Lines 7-9: I suggest showing a temporal of COA. Could you try searching for markers for nonanal (see [Silva and Prather, 2000]), a tracer for meat cooking? What about searching for m/z 57 vs 59, the same ion used by the AMS for meat cooking?

Minor Comments

Page 10348, Line 5: Change from “impact significantly upon” to “significantly impact”

Page 10348, Line 26: What is your distinction between EC and BC?

Page 10349, Lines 3-4: Change “predominant” to “dominant”

Page 10349, Lines 3-4: Any estimates for how much vehicular emissions contribute vs biomass burning?

Page 10350, Lines 5-7: How does the addition of a light scattering module help improve quantification?

Page 10350, Line 22: Add reference for the aerodynamic lens ATOFMS [Su et al., 2004]

References:

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Moffet, R.C., and K.A. Prather (2009), In-situ measurements of the mixing state and optical properties of soot with implications for radiative forcing estimates, PNAS, 106 (29), 11872-11877.

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Silva, P.J., and K.A. Prather (2000), Interpretation of mass spectra from organic compounds in aerosol time-of-flight mass spectrometry, Anal. Chem., 72 (15), 3553-3562.

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Interactive comment on Atmos. Chem. Phys. Discuss., 13, 10345, 2013.

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