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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Aerosol particle measurements at three stationary sites in the megacity of Paris during summer 2009: meteorology and air mass origin dominate aerosol particle composition and size distribution" *by* F. Freutel et al.

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This paper presents a very comprehensive interpretation of the combined measurements from multiple site during the MEGAPOLI campaign in Paris. On reading the paper's title, one might be forgiven for expecting this paper to be a hypothesis-driven analysis, however it is a very weighty piece of work that explores many aspects of the data collection and analysis, ranging from technical issues to reporting statistical analysis of the results. While certainly encompassing, it does seem to ramble in places. However, it isn't a bad paper as such and does present interesting and useful statistics regarding Paris that are compared well with other recent megacitiy campaigns. I would therefore recommend that this be published, subject to the following comments:

General comments

The running title "Air mass origin dominates aerosol characteristics in Paris" is perhaps a little bullish considering that this is only the results from one measurement campaign. To really make that statement, one would have to show it applies to long-term data. Suggest a reword.

Yes, the running title might be a bit misleading due to limited space. We suggest to use "Aerosol characteristics in Paris during summer 2009" for the final version.

While thorough, I would venture that the authors go a little overboard on the analysis in places. In particular, after reading sections 3.4 and 3.5, I was left wondering how these contributed to the main conclusions of the paper. While it would be difficult to change too much at this stage, the paper would benefit from being more succinct and to the point in places.

Here, we do not agree with the reviewer, as we think that the information provided in sections 3.4 and 3.5 are essential for our general conclusions of the manuscript. This is also supported by a comment by reviewer #1, who states that section 3.5 is the "most interesting contribution of the paper".

In section 3.4 we show that indeed sulfate, OOA and nitrate are homogeneously distributed over the greater region, not only Paris, and that furthermore also the upwind stations are likely influenced by local emissions, as can be seen in the much lower concentrations of HOA, NOx and BC at the background location far away from the city and any sources compared to the Sub SW site. All these conclusions could not have been drawn with the same confidence without this case study.

However, in response to this comment, to make more clear to the reader why we include this discussion, we have added an additional sentence in Section 3.4:

"This enables the differentiation between pollutants dominated by emissions within the urban agglomeration and pollutants which are transported from outside the city to Paris."

In section 3.5 we discuss one of the main key points of this manuscript: an estimate, even if rough, of the influence of the emission plume of Paris onto its suburbs.

Therefore we think removing these two sections would rather weaken the manuscript as a whole.

The 30% scaling applied to the Sub SW AMS is very worrysome and it is very disappointing that the authors were evidently unable to find the underlying reason why this was needed. It should be stated whether the common causes of 'bad' AMS calibrations have been individually ruled out, specifically that the calibration particles were dry, appeared to be of the correct size (using the PTOF data) and did not appear to contain any contamination (based on the mass spectrum). If the calibration was performed by comparison to a CPC (as opposed to using BFSP data), the authors must provide an estimate of the influence of multiply charged particles and technical details on the CPC and the plumbing configuration used to split the AMS and CPC flows (including whether mixing was used).

We would also have liked to find the exact reason for the need of this scaling, however, from our available data we have not found any clear indication where it could originate from. The calibrations were checked carefully including all tests suggested by the reviewer, but no indication could be found that these indeed could account for the

differences observed. BFSP data were used for the IE calibrations, as now is also stated in the manuscript (Section 2.2.2). Particles were dried using a silica gel diffusion dryer, and from PToF and MS data no indication was found that they were not of the correct size or contained any contamination, so to our best knowledge, IE calibrations were done properly. However, even though the reason for the need of the scaling is unclear, the scaling factor used can be obtained independently by comparison to both, the MoLa AMS or to the Sub SW SMPS system (see also Crippa et al., 2012), so we are confident that the scaling procedure yields correct results for the Sub SW AMS measurements.

The authors do not present sufficient evidence to suggest that new particle formation is taking place. While there is certainly an abundance of smaller particles during the day, there is nothing to even suggest that anything other than primary sources are responsible. There is certainly nothing resembling the typical 'banana' behaviour seen at other sites, or the order-of-magnitude increase in CPC concentrations that would indicate that a nucleation burst has taken place. Given the lack of strong SO2 sources and the large pre-existing particulate surface area, new particle formation would intuitively seem unlikely, so I would recommend that this very speculative line of discussion is taken out entirely unless the authors can present stronger evidence.

In response to this comment, we have reworded the section in order to avoid the implication that particle nucleation necessarily is taking place. However, if not particle nucleation, then particle growth certainly occurs, if not every day, then at least in some events, which may not be reflected adequately in the median diurnal cycle shown. We have therefore adjusted the colour scaling of Fig. 5b slightly to enhance contrast and make this easier to see. The section now reads:

“As mentioned above, the diurnal cycle of OOA shows an increase in OOA mass concentration around noon, when also indications for particle growth are observed in the diurnal cycle of the EAS size distributions. Sources of these growing particles may either be freshly nucleated particles (with unknown composition), or small particles originating from primary emissions (e.g., engine exhaust). This larger abundance of smaller particles is consistent with simultaneously increasing number concentration measured by the CPC, reaching its maximum around 16:00 - 17:00 (Fig. 5b, all measured at Sub NE). These events must be taking place over extended areas, as the probed air masses are not stagnant, but constantly moving over the stationary measurement site at wind speeds of about 2.6 m s-1 (average value)."

We have furthermore deleted the sentence "New particle formation was observed in the diurnal cycles of EAS and CPC, which will be described below." in the same section, where the OOA diurnal cycle is discussed.

Specific comments

Page 22208, line 15: Reword "well comparable"

Reworded to "showed good agreement"

Page 22211, line 5: The authors need to be specific whether the Allan et al. tables were used, or the subsequently modified version presented by Aiken et al. (this can be checked against the Colorado wiki).

To make this clearer this is now stated more specific in the final manuscript (Section 2.2.2):

"…applying the standard fragmentation table ((Allan et al., 2004), with modifications according to (Aiken et al., 2008), except for the Downtown site) with the respective individual corrections inferred from the measurements of particulate-free air."

Page 22211, line 13 (and elsewhere): The authors need to specify whether MS or BFSP data was used for the ammonium calibrations (MS is strongly recommended).

All RIE NH4 values were taken from MS data. The information was added in the respective paragraphs in the revised manuscript (Section 2.2.2).

Page 22211, line 27: The AMS vaporiser has a much stronger influence in the relative peak intensities of the organic spectra than the mass spectrometer ion transmission function. Considering this with the different sulphate RIEs, I would say it more likely that the discrepancies are due to different vaporiser function.

We would have thought this initially as well. However, during the campaign, two very different vaporizer temperatures were used for the C-ToF-AMS (2 weeks at 800°C, 2 weeks at 600°C, see page 22210, lines 7ff). No difference in the scaling factor between the two AMS at this sampling site was observed for these two periods; but there should be significant differences if the vaporizer temperature had that strong an influence. Both sulphate and organics m/z's show a smaller relative intensity at higher m/z for the C-ToF-AMS than for the MoLa AMS during intercomparison periods; therefore, ion transmission still seems the most likely explanation to us.

Page 22212, line 2: One way of interpreting the organic discrepancy between the two instruments is to surmise that the RIE of the organic fraction had drifted in the same manner as the sulphate. That being the case, it might make more sense to alter the RIE rather than apply a scaling to the data products.

Yes, indeed what is implied is that the RIE value for both organics and sulphate has changed for the same reason. However, only for sulphate the RIE was measured in laboratory measurements; for organics, no RIE measurement in the lab was performed due to the complicated mixture of many (unknown) organic compounds in atmospheric aerosol. Since we only inferred the scaling from the comparison to a different instrument, and not measured it directly in independent measurements, we did not want to "hide" this by simply inserting it into the organics RIE, but to state it clearly in the text.

However, to make the similar source of discrepancy for organics and sulphate more clear, we inserted in the final version of the paper the information that this scaling in fact can be understood as a different RIE (Section 2.2.2):

“Therefore, organics measured by the AMS at Sub NE were scaled with a factor of 1.5 (which would correspond to an effective RIE of organics of 0.93) to account for this effect.”

Page 22213, line 6: Rather than using an average density, why not calculate a timedependent density from the AMS measurements? This would give a more accurate volume estimation.

The comparisons were changed according to the reviewer’s comment in the final manuscript; the changes to using an average density are very minor though, because the density does not vary strongly throughout the campaign. The text was rewritten to:

“To convert mass concentrations into total particle volume concentrations, particles were assumed to be spherical and to exhibit a time-dependent density. The latter was inferred from the varying chemical composition and from densities of 1.72 g cm-3 for NH4NO3, 1.77 g cm-3 for (NH)2SO4, 1.5 g cm-3 for organics, and 2 g cm-3 for BC (the average density of the whole campaign would correspond to 1.65 g cm-3). The sum of calculated total particle volume from BC mass concentration and total mass concentrations measured with the AMS agrees reasonably well with the SMPS total particle volume concentration (m = 0.93, R2 = 0.54; before scaling: m = 0.74, R2 = 0.56) (Fig. S3).”

The corresponding Figure S3 was changed accordingly.

Page 22213, line 12: The SMPS cutoff of 500nm is based on mobility diameter, which translates to a vacuum aerodynamic diameter of 825nm, which is actually quite close

to the AMS cutoff.

The reviewer is absolutely right! This was mistakenly stated in the original manuscript. The sentence in the final manuscript was reworded accordingly:

“The upper size cut-off of the SMPS at about 500 nm (dmob) corresponds to a vacuum-aerodynamic diameter of about 800 nm, which is similar to the cut-off for the BC and AMS measurements.”

Page 22218, line 11: I would prefer uncentred R2 (normalised dot product) when comparing mass spectra.

We kept to Pearsons R2 for all correlations within the manuscript (time series and mass spectra) to avoid confusion.

Page 22218, line 12: The exact source of the reference spectra must be stated.

Changed, thank you! The references were accidentally only given in Table S7, not in the main text. It now reads (Section 3.1):

“The respective mass spectra correlate very well (Pearson’s R2 typically about 0.8) with reference mass spectra of HOA (hydrocarbon-like organic aerosol; (Ulbrich et al., 2009)) and cooking-related organic aerosol (Allan et al., 2010; He et al., 2010), which both are related to primary emissions. . . . , and the respective mass spectra correlate very well with low-volatile OOA (low-volatile oxygenated organic aerosol, R2 about 0.9) and to a lesser extent also with semi-volatile OOA (semi-volatile oxygenated organic aerosol, R2 about 0.6 to 0.7) (both from (Ulbrich et al., 2009)).”

Page 22222, line 3: A typical wind speed corresponding to ‘fast’ should be given.

In the final manuscript, we have added the information: “this corresponds to a travelling velocity of the air mass of approximately 1200 km per day, i.e. an average transport velocity of $\sim$14 m s-1"

Page 22225, Line 10: This period would be sufficient if cloud processing was important during this period (which, presumably, it wasn't).

We changed the sentence as follows to account for this:

"This lack of differences between the two types of "Atlantic" air masses in SO4 diurnal cycles and average mass concentrations indicates that the relatively short residence times over land for both of these air masses are (in the absence of cloud processing) not sufficiently long to generate SO4 from precursor gases that were picked up (Seinfeld and Pandis, 2006)."

Page 22227, line 1: Do the authors really mean 'SO3'?

We changed it to "SOx" to include all gaseous sulphur oxides.

Table 1: The table caption seems excessively long. Consider presenting this information differently.

We have now moved the information about model / manufacturer in a separate column in the table itself instead of in a footnote.

Figure 1: Could a map be overlaid on this?

We would have preferred this as well, however, in order to avoid copyright issues, we went for the more simplified version shown. However, it contains all information needed within the context of this analysis.

Figure 5: The exponent on the CPC units has been truncated.

Changed, thank you.

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