Atmos. Chem. Phys. Discuss., 14, C7119–C7125, 2014
www.atmos-chem-phys-discuss.net/14/C7119/2014/

Atmospheric Chemistry and Physics Discussions
Open Access

Interactive comment on "Megacity emission plume characteristics in summer and winter investigated by mobile aerosol and trace gas measurements: the Paris metropolitan area" *by* S.-L. von der Weiden-Reinmüller et al.

S.-L. von der Weiden-Reinmüller et al.

sl.vonderweiden@mpic.de

Received and published: 16 September 2014

The authors would like to thank the referee for the valuable comments. We have responded to all comments and revised the manuscript accordingly. Details of our responses to each comment are shown below.

Anonymous Referee #1

In their manuscript, von der Weiden-Reinmüller et al. compare mobile and stationary aerosol and gas-phase measurements of background air and the emission plume of the European megacity Paris. In particular, they use the mobile laboratory MoLa to measure the submicron aerosol chemical composition, aerosol number concentrations and size distributions, and atmospheric trace gases at various fixed stations, to measure cross sections of the emission plume, and to carry out quasi-Lagrangian experiments following the emission plume from the Paris center to the surroundings. The authors use fresh pollution markers such as black carbon and hydrocarbon-like organic aerosol (HOA) to identify and characterize the emission plume, then compare pollutant concentrations in the emission plume and background air, study the spatial distribution of pollutants in the emission plume, and finally investigate aging of the organic aerosol in the emission plume.

The manuscript is well structured and clearly written. The presented results are an important contribution to the MEGAPOLI project, and will help designing future field experiments investigating urban emission plumes and their interpretation. The authors show that the mobile laboratory MoLa is a valuable tool in studying urban emission plumes and their impact on air quality in surrounding areas. The supplementary material nicely complements the manuscript. I recommend publication of this manuscript in ACP after taking into account the following comments:

a) In section 2.2, please add some more information about the instrumentation, e.g. a table with the types of instruments used in this study.

Reply by the authors: A short table (now Table 1) summarizing the instruments and measured variables used for the measurements presented in this study was added to the manuscript. A table with more information on each of the instruments operated within MoLa was already presented in von der Weiden-Reinmüller et al., 2014 (AMT 7,p279-299). Instead of repeating all this information we reference this paper here.

b) p. 11259, l. 9/10: Please give an estimate or quantify the mass fraction typically contributed by m/z > 100.

Reply by the authors: Due to the strong fragmentation in the hard evaporation/ionization process in the aerosol mass spectrometer the majority of signal is found at small m/z. Typically in the order of < 1% of the total signal and about 5 % of the organics signal is found for m/z > 100. This information was added to the text (Page 11259, Line 10). Only when extremely large organic aerosol fractions of polyaromatic hydrocarbons are measured (which do not show such strong fragmentation in the AMS), the fraction of signal at m/z > 100 might be well above 10%. However, such a situation was not encountered during this work.

c) p. 11261: How would PMF results change if local pollution events were removed from the data before positive matrix factorization as compared to removing data when OC mass concentrations are larger than 50 ug m-3. Also, please discuss the uncertainties of the changes in the composition of the organic aerosol (p. 11272) taking into account a 30 % uncertainty in ambient AMS data for absolute mass concentrations of individual factors derived by PMF. How will this affect the significance of the plume contribution estimates shown in Fig. 3, the changes in the average organic mass spectra presented in Fig. S4 (supplementary material), and the correlation coefficients shown in Tab. 2?

Reply by the authors: Before performing the PMF calculations individual data points with extraordinarily large organics concentrations (outliers) should be removed from the dataset because otherwise the PMF results will be dominated by these few data points and biased results will be generated. There is no general rule where the threshold should be set. In order to remove the most “severe” peaks but not removing large fractions of the dataset we arbitrarily chose to set the threshold to 50 μg/m3 as described in the text. This threshold has nothing to do with local contamination events at the first place. As also described in the text all data identified to be contaminated by local sources have been removed from the data set after the PMF calculations have been finished. In order to make this clearer we slightly modified the text in the respective locations (section 2.4.3). In order to determine uncertainties of the PMF calculations

Full Screen / Esc
Printer-friendly Version
Interactive Discussion
Discussion Paper

several variations have been made to the input data set. For example PMF has been performed with and without removal of such outliers. PMF has been performed on the full data set collected during MEGAPOLI and on the mobile and stationary data sets separately. PMF has been performed with a large variety of “seed” and “fpeak” values. All these calculations have shown that “seed” variations resulted in only very small (∼5%) variations of the results while variations due to “fpeak” variations are in the order of ∼20%. For the more robust factors (HOA and aged OOA) the variations due to removal or not of the outliers are in the order of 5-15% while for the other PMF factors these variations can be up to 50%. All these efforts have shown that especially for less “robust” factors there can be significant uncertainty in the mass concentration of these factors due to the decisions made by the person who performs the analysis. However, this is not the point of the reviewer’s comment. The major question is whether or to which extent these uncertainties affect conclusions drawn from such data. Generally, the result of a PMF analysis is a rather subjective decision. Often several very different solutions are possible. It is the operator’s duty to base the decision of the selected solution on as many as possible external facts like comparison with time series of other variables, comparison of resulting mass spectra with spectra from data bases, etc. The mass concentrations of the various PMF factors resulting from such a process have uncertainties in the order of the values presented above. There is an additional uncertainty of AMS mass concentrations in the order of 20-30% mainly due to imperfect calibrations and assumptions needed to convert raw data into mass concentrations of individual species. In this work we mainly base our conclusions on the comparison of species or PMF factor mass concentrations measured at different locations. All these concentrations were calculated with the same calibration and correction factors and with the same PMF settings, i.e., only additional uncertainties from the PMF analysis itself remain. Due to this fact the uncertainty of the relative concentrations or the variation of the concentrations is much lower than the uncertainty of the absolute concentrations or the uncertainty of concentrations derived using different PMF settings. We estimate these remaining uncertainties to be in the order of 5-10%

and therefore we do not expect them to affect the significance of our conclusions. To avoid a long discussion of all the effects and consequences we added a short sentence stating that the relative uncertainties of the AMS mass concentrations are significantly lower than those of the absolute values and thus do not affect the significance of the results (section 2.4.3).

d) p. 11273: The mode in the aerosol number size distributions at a diameter of 10 nm (Fig. 4) may be an artifact as stated e.g. by Freutel et al. (2013; Atmos. Chem. Phys., 13, 933–959): Âż>The comparison shows a mode in the number distribution measured by the FMPS around 10 to 15 nm which is likely an artefact due to the inversion algorithm used for this instrument (A. Wiedensohler, personal communication, 2012).Âń< Please include this information and briefly discuss it.

Reply by the authors: We included this information in the manuscript and added after “The large error bars especially of the background distribution indicate that there was a large temporal and spatial variation in the occurrence of small aerosol particles.” (p11274 in the first version of the manuscript): “In addition the particle mode around 10 nm might be affected by artefacts due to the inversion algorithm used for this instrument (A. Wiedensohler, personal communication, 2012).”

e) p. 11275/76: I was distracted by the CO2 data in Fig. 5 (especially in Fig. 5b) when the discussion in the text focused primarily on the comparison of measured and modeled HOA concentrations. Therefore, I suggest removing the CO2 example from Fig. 5. You may add an additional figure showing the good agreement between the plume shape and spatial extent of other measured fresh pollution markers.

Reply by the authors: Here we do not agree with the statement that the discussion focuses primarily on the HOA concentrations. Indeed, the discussion starts with a comparison of modelled primary organic matter and measured HOA concentrations (p11276 in the first version of the manuscript). However, one page later (p11277) also the CO2 distribution across and along the emission plume is discussed in almost similar extent. Since, in addition, Figure 5 seems not to be overloaded to us we decided to keep the CO2 data in this figure.

Technical comments:

p. 11251, l. 17: Please clarify what "the second process" refers to.

Reply by the authors: To make this clearer we modified the sentence to: “The aerosol particle size distribution in plume air masses was influenced by nucleation and growth due to coagulation and condensation in summer, while in winter only the latter process (i.e. particle growth) seemed to be initiated by urban pollution.”

p. 11267, l. 10: Change "average O/C ratios are shown" to "average O/C ratios in organic aerosol are shown".

Reply by the authors: We changed the text according to the suggestion.

p. 11281, l.17: Replace "regression coefficient" by "correlation coefficient".

Reply by the authors: The reviewer is correct that “regression coefficient” is not the adequate term. We changed “regression coefficient” into “coefficient of determination”, which is the square of the correlation coefficient and which we used here.

p. 11283, l.14: Change "secondary pollutants as particulate sulfate" to "secondary pollutants such as particulate sulfate".

Reply by the authors: We changed the text according to the suggestion.

Fig. 1: In the figure caption, replace "squares" by "diamonds".

Reply by the authors: We replaced “squares” by “diamonds” as suggested.

Tab. 1: The columns showing the plume contributions in summer and winter are hard to read. Please split these two columns into four columns, showing the absolute concentrations and the relative contributions in separate columns, respectively.

Reply by the authors: We changed the table (now Table 2) according to the suggestion.

The second and third columns are now both split into two columns each.

Tab. 2: Replace "regression coefficient" by "correlation coefficient" in the caption of Tab. 2.

Reply by the authors: We changed “regression coefficient” into “coefficient of determination” as discussed above.

Interactive comment on Atmos. Chem. Phys. Discuss., 14, 11249, 2014.