

Dear Referee#1,

Thank you for your valuable comments that will help improving this paper. Please find below the response of the authors.

Comment #1: "Although the text is generally well written, there are quite some linguistic errors (often wrong prepositions). This is disturbing and it is worth to carefully go through the text and to revise the text accordingly."

Authors' answer: The text has been carefully read again by the authors and some linguistic errors have indeed been noticed and then corrected.

Comment #2: "The boundary layer height (BLH) is used as a factor that has an impact on PM2.5 concentrations. Quantitative values for BLH are used in this paper without description of how BLH was calculated. This should be explained in section 2 (Material and methods)."

Authors' answer: The following paragraph has been added in Sect. 2.6 accordingly:

"Boundary Layer Height (BHL) is taken from simulations with the PSU/NCAR mesoscale model (MM5; Dudhia, 1993; Grell et al., 1994). In the vertical, 23 sigma layers extend up to 100 hPa. MM5 is forced by the final analyses from the Global Forecast System (GFS/FNL) operated daily by the American National Centers for Environmental Prediction (NCEP), using the grid nudging (grid FDDA) option implemented within MM5. The Medium Range Forecast scheme (MRFPBL) has been used to parameterize turbulence in the boundary layer (Troën and Mahrt, 1986)."

Comment #3: "Pages 29414 and 29415: The rather homogenous spatial variability of OM is interpreted as resulting from mid- or long-range transport. This is hard to believe as the main explanation given that Paris is such a large urban environment. Can the spatial homogeneity be a consequence of secondary formation processes of precursor emissions in the Paris region (mentioned in the conclusions section but not in section4)? The time needed for gas-to-particle conversion could explain the observed spatial variability of OM, the high observed fOC-OM values support this. SOA formation as an important factor for low spatial variability should be discussed/considered. The same is true for the subsequent discussion of SIA, the general statement that SIA is mainly due to mid- or long-range transport appears not well justified and probably is too much of a simplification."

Authors' answer: As mentioned by the reviewer, it is legitimate to expect a rather significant impact of Paris itself on regional OM concentrations. However, based on the recent EU-MEGAPOLI summer and winter field campaigns, a number of evidences show that this influence is rather weak.

Quasi-Lagrangian measurements performed under connected flow conditions between three stationary sites - distributed over an area of 40 km in diameter in the greater Paris - were used by Freutel et al. (2013) to estimate the influence of the Paris emission plume onto its surroundings during the MEGAPOLI summer campaign. This influence was found to be rather small for primary pollutants (including Primary Organic Aerosols). Moreover, the authors state that: "The secondary aerosol particle phase species were found to be not significantly influenced by the Paris megacity, indicating their regional origin". Identical conclusions were obtained during the winter period by Crippa et al. (2013), concluding that OA was mainly secondary and mostly controlled by mid- or long-range transport. Simulations of organic aerosol were performed by Zhang et al. (2012) during the MEGAPOLI summer campaign, using the chemistry transport model CHIMERE. Long range transport of SOA to Paris was shown to be well reproduced by the model. These authors report that: "The advection of SOA from outside Paris is mostly responsible for the highest OA concentration levels. During advection of polluted air masses from north-east (Benelux and Central Europe), simulations indicate high levels of both anthropogenic and biogenic SOA fractions, while biogenic SOA dominates during days with advection from Southern France and Spain".

Last but not least, the location of our rural sites was chosen so that at least two stations were not affected by Paris plume. The rather homogeneous OM concentrations observed at our rural site

clearly shows that conclusions drawn during the MEGAPOLI summer/winter campaigns are valid for the rest of the year.

In conclusion, we agree with the reviewer that the time needed for gas-to-particle conversion could explain the observed spatial variability of OM, which would be supported by the high observed f_{OC-OM} values. We also agree with the reviewer that the homogeneity of OM is likely a consequence of the mainly secondary nature of OA. However, based on the aforementioned studies, Paris does not appear as the major contributor of OA at the regional scale. It is also worthwhile noting that regional contributions of fine PM have also been reported for US cities (Bari et al., 2003; Lall and Thurston, 2006; Pitchford et al., 2009; Qin et al., 2006; Raman and Hopke, 2007; Rizzo and Scheff, 2007).

As suggested by the reviewer, the section dealing with the regional homogeneity of OA (Sect. 4.2.3, first paragraph) has been further discussed; in particular the following paragraph has been added:

Page 29415, line 4: “It is worthwhile noting that given the large expected emissions associated with the Larger Urban Zone of Paris, it could reasonably be assumed that the OM spatial homogeneity observed in our study is the consequence of secondary formation processes of precursor emissions in the Paris region. The time needed for gas-to-particle conversion would explain the observed spatial variability of OM, which would be supported by the high observed f_{OC-OM} values. Nevertheless, modeling and experimental studies conducted during the EU-MEGAPOLI summer and winter field campaigns by Crippa et al. (2013), Freutel et al. (2013) and Zhang et al. (2012) do not support this assumption. Conversely, the aforementioned studies report that i) OA is mostly controlled by mid- or long-range transport (Crippa et al., 2013), ii) the influence of the Paris emission plume onto its surroundings is rather small for primary organic aerosols (Freutel et al., 2013) and iii) the highest OA levels are due to the advection of SOA from outside Paris (Zhang et al., 2012).”

Comment #4: “The conclusions section can be shortened and repetition of results that have already been presented in the Discussion section 4 should be avoided.”

Authors’ answer: The conclusion section has been shortened and repetition of results that have already been presented in the Discussion section 4 has been avoided accordingly. In particular:

+ Page 29417, from line 4 to line 5: “(11 September 2009–10 September 2010)” has been deleted.

+ Page 29417, from line 21 to line 26: “(higher than $15 \mu\text{g m}^{-3}$ on average from December to April)”, “(between 10 and $15 \mu\text{g m}^{-3}$ during 25 May, June, September, October, and November)” and “(below $10 \mu\text{g m}^{-3}$ during July and August)” have been deleted.

+ Page 29418, from line 6 to line 13: “Gravimetrically determined $\text{PM}_{2.5}$ annual mean concentrations are 15.2, 14.8, 12.6, 11.7 and $10.8 \mu\text{g m}^{-3}$ for SUB, URB, NER, NWR and SOR sites, respectively. The annual average chemical composition is also comparable at every site, showing high proportions of OM (38–47% 10 of $\text{PM}_{2.5}$ mass on average at the five sites), nitrate (17–22%), non-sea-salt sulfate (13–16 %), ammonium (10–12 %), EC (4–10 %), mineral dust (2–5 %) and sea salt (3–4 %), which is in agreement with fine aerosol chemical composition commonly reported in Europe.” has been deleted.

+ Page 29418, from line 13 to line 21: “(e.g. for NWR plotted against URB sites: slope=0.79, $r^2 = 0.72$, $n = 335$)”, “(e.g. for NWR plotted against URB sites: slope=0.91, $r^2 = 0.89$, $n = 335$)” and “(e.g. for SOR plotted against URB sites: slope=0.27; $r^2 = 0.03$; $n = 335$)” have been deleted.

If necessary, this conclusion could be further shortened, and could be limited to the following:

« This study allowed the construction of a one-year database describing the daily chemical composition of fine aerosol ($\text{PM}_{2.5}$) in the region of Paris. It comprises EC, OC, Cl^- , NO_3^- , SO_4^{2-} , Na^+ , NH_4^+ , K^+ , Mg^{2+} , and Ca^{2+} aerosol compositions at five sites being characteristic of urban, suburban and rural backgrounds.

The chemical mass closure methodology was applied for the determination of the OC to OM conversion factor (f_{OC-OM}). Comparable f_{OC-OM} values were determined for the URB and SUB sites (1.95) and for the rural sites (2.05), which is consistent with the strong homogeneity of OC concentrations observed in the region and its aged (i.e. oxidised) nature.

The temporal variability of $PM_{2.5}$ was investigated, showing a very strong daily variability at the five sites for PM mass and chemical compositions. The influence of specific meteorological parameters was highlighted: i) anticyclonic conditions, low temperatures, low BLH and mid- or long-range transport of air masses originating from the continental European sector lead to the highest pollution events of the year, whereas ii) precipitations or western (oceanic) air masses lead to the lowest PM levels.

The spatial variability of fine aerosol is very similar at the regional scale during most of the year, suggesting the substantial influence of mesoscale meteorological parameters and mid- or long-range transport. Nevertheless, emissions of local anthropogenic sources lead to higher levels at the URB and SUB sites.

The very large quality controlled aerosol database presented here within the LSCE-AIRPARIF "Particles" project will allow the identification of the major sources of PM as well as their geographical origins, which are prerequisites to implement effective abatement policies. In conjunction with the use of specific tracers, this aerosol database will also help in better documenting primary and secondary sources as well as atmospheric processing of carbonaceous aerosols. Furthermore, this chemical database should help modellers to better understand the transport and transformation of aerosols in the region, or toxicologists to better assess the toxicity of individual chemical compounds, to mention only a few. »

Additional corrections:

Page 29396, line 17: "UR" has been replaced by "URB".

Page 29397, line 11: "has been" has been replaced by "have been".

Section 2.3.3: the transmission method (TOT) was here applied. This information has been provided accordingly.

Page 29403, line 15: Yes indeed, this means that the reference signal of the TEOM-FDMS was used here only. This sentence has been modified as follow:

"TEOM-FDMS was running at 30°C and was not corrected for semi-volatile materials (i.e. only the reference signal of the TEOM-FDMS was used here, without taking into account the SVM mass provided by the FDMS), in order to be as close as possible to our laboratory conditions."

Page 29410, line 15: In this Sect. 4.1.2 we wanted to see if days exhibiting "high" PM levels were influenced by air mass origins; therefore, a PM level threshold had to be defined. Ideally, the threshold chosen would have been the $PM_{2.5}$ EU daily limit value; unfortunately, such $PM_{2.5}$ daily limit value has not been defined by the EU yet. Currently, the only limit value existing for the $PM_{2.5}$ fraction in the EU is the annual limit value of $25\mu\text{g}/\text{m}^3$. In our study, since the $PM_{2.5}$ annual value has been calculated as the average of $PM_{2.5}$ daily values, it appeared interesting to take as a threshold the $25\mu\text{g}/\text{m}^3$ level. In fact, mathematically speaking an exceedance of the $PM_{2.5}$ annual limit value of $25\mu\text{g}/\text{m}^3$ is in our case due to each day exhibiting concentrations higher than $25\mu\text{g}/\text{m}^3$.

The threshold value of $25\mu\text{g}/\text{m}^3$ has also been chosen in our study because it is the $PM_{2.5}$ 24h-mean World Health Organisation Air Quality Guideline value (see http://whqlibdoc.who.int/hq/2006/WHO_SDE_PHE_OEH_06.02_eng.pdf, page 9). Given your comment, this last explanation might appear less arbitrary to the reader; it has thus been mentioned in the manuscript as follow:

Page 29410, line 15: "We attempted to quantify this phenomenon by focusing on days showing PM_{grav} concentrations higher than $25\mu\text{g}/\text{m}^3$, which is the $PM_{2.5}$ 2015 EU annual limit value and the $PM_{2.5}$ 24h-mean World Health Organization Air Quality Guideline value. A total of 50 days fulfilled the aforementioned criterion on the whole duration of the campaign".

Page 29412, line 15: the sentence has been modified as follow:

« Interestingly, when focusing on individual days a very high temporal variability is generally observed at the same time at the five sites. For instance, PM_{grav} levels range from 49.4 to 62.0 $\mu g m^{-3}$ on 27 January 2010, and from 3.9 to 5.9 $\mu g m^{-3}$ on 29 January 2010 according to sites; therefore after only 2 days, PM levels have been reduced by a factor ranging from 10 to 14 according to sites. »

Page 29425, line 24: the following reference has been added:

Hamaoui-Laguel, L. : Ammonia emissions from agricultural activities: impact on air quality, Les émissions d'ammoniac par les activités agricoles: impact sur la qualité de l'air, PhD thesis, University of Paris Diderot, Paris 7, 2012.

Figure 2: the time-series of PM_{10grav} – PM_{10chem} has been added accordingly.

Legend of Figure 3 and scatter plots in supplementary materials: the error bars represent the uncertainties associated with the different type of measurements. For OC, PM_{grav} and $PM_{TEOM-FDMS}$ uncertainties have been calculated based on the information given by the constructor (e.g. 5% for OC measurement as mentioned in page 23399, line 2). For the “Missing mass” fraction, uncertainties have been calculated as the sum of the uncertainties associated with each chemical fraction taken into account for its calculation. The following information has been added: Figure 3: “Error bars represent the uncertainties associated with $PM_{TEOM-FDMS}$ and PM_{grav} measurements”. Figure S2: “Error bars represent the uncertainties associated with OC measurements and the Remaining mass calculation”.

Thank you again for your help.

Kind regards,

The authors

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