Reply to Anonymous Referee #1

The manuscript shows simulations of black carbon (BC) and organic aerosols (OA) for the Paris metropolitan area for summer and winter periods during the MEGAPOLI field experiment. The main points are: 1) Primary organic aerosol BC are generally well modeled, 2) OA emissions from cooking are developed based on observed data and improve model performance, 3) Secondary OA in summer is well modeled, and 4) Secondary OA in winter is completely underestimated with the current SOA mechanism. The manuscript is well written, is of good quality and has good potential to be published after major changes. Please see my comments below.

General comments

(1) The explanation of why OOA in winter is underpredicted is not clear, too convoluted, and leaves more questions than answers. I think the authors should work more on it to make this article publishable. They should at least identify where these air masses come from when the extreme underestimation is found. Is this a problem with background concentrations? Maybe boundary conditions are to blame? Does it have to do with residence time over continental regions before reaching Paris? There are still some times where the model performs well, so the authors could also identify when and why this happens to provide better insight into the issue. They also propose a mechanism which could solve this problem, why not test it? This should be relatively simple given the expertise of the authors.
We have followed the suggestion of the reviewer and performed additional analysis of the observed and predicted wintertime OOA concentrations. This analysis shows that the OOA underprediction is persistent throughout the simulation period (new Figure S5). However, there are certain days (24 and 27 January and 4 and 7 February) during which the analysis of the AMS data suggests very high (more than 6 μg m^{-3}) OOA levels while PMCAMx predicts moderate levels (around 2 μg m^{-3}). Back-trajectory analysis (also added in the supplement as Figure S6) indicates that during these days the air masses arriving in Paris have all continental origin but are coming from a variety of areas (central France, Germany, Belgium, etc.). On the other hand, during the days with reasonable model performance the air masses were mostly clean coming from the Atlantic, the United Kingdom, Ireland, etc.). This further supports our hypothesis in the manuscript of rapid conversion of anthropogenic emissions to OOA during winter.

We have performed a number of sensitivity tests (including changes in boundary conditions) but we could not reproduce these high observed OOA levels in the Paris area without increasing dramatically at the same time the OOA over the rest of Europe. It should be noted that the same model did not show any serious underprediction of OOA over Europe in other sites (Fountoukis et al. 2014b). For example it did not show any bias in Cabauw in the Netherlands. Even more, the more than 5 μg m^{-3} of OOA observed during several days is a lot higher than the total OA measured in most sites in Europe. None of the known mechanisms that have been tested in previous applications of PMCAMx (Tsimpidi et al., 2010, Fountoukis et al., 2011, 2014b) explain these very high levels. So at this stage we think that it is important to report this significant discrepancy between observations and predictions thus encouraging future work in this direction. We have added discussion of these issues and two new figures in the supplementary information to address this important issue.

(2) The analysis performed is mainly for the model representation of diurnal cycles and average concentrations. I think what's missing is how well the model represents the day to day variability. Are the biases found persistent throughout the periods or occur only for exception events? If time series for the whole period are too saturated with data, the authors could plot the time series of daily means or daily distributions (with box and whisker plots). Try to include these plots as additional panels in figures already existent when possible. Please add this analysis for all species and seasons, especially for SOA (OOA) as it would be instructive to see the model representation of these regional events.
To address this point we have added new figure and revised existing ones in both the main paper and the supplementary information to show the corresponding day-to-day variability. During summer, the POA underprediction seems to be mostly systematic and persistent throughout the simulation period, while the performance for OOA is encouraging for almost all days (with the exception of 21 July). In winter OOA is underpredicted systematically during the majority of the days with some days showing much larger biases than others as discussed in our reply to Comment 1 above. The discrepancies for the POA concentrations during winter show up partly as scatter rather than bias as explained in the text due to discrepancies in the different POA components (i.e. BBOA, COA, HOA, etc.). The comparison for the daily mean concentrations of BC shows encouraging model performance during the summer and an overprediction during several days in winter. This is mostly due to an overprediction of the morning rush hour peak that is illustrated through the average diurnal profiles shown in Fig. 6. We would like to point out that the reproduction of the observed average diurnal variation is an important test of the ability of the model to reproduce observations for the right reasons and unfortunately few model evaluation exercises use this approach. We have also added discussion of the ability of the model to reproduce the day to day variation of the corresponding concentrations.

(3) The diurnal profile plots (Figs 6,7, S1) provide information only on the mean. The authors could redo these plots as box and whiskers plots, so besides the mean, it could show the spread of the distributions to see how well the model is able to capture it. This could be helpful when trying to explain observation and model discrepancies on the mean throughout the text.
We have revised these figures following the reviewer's suggestion. The revised figures now show the median as well as the spread (25th and 75th percentiles) of the distributions. We would rather exclude the whiskers (min and max values) as the figures are already busy with modeled and observed values on the same plots.

Comments by line. In the following I'm only including the last 2 digits of the page numbers

(4) Section 2,3. What did the authors used for boundary conditions for all species? If they used climatological profiles they could try to use boundary conditions from global models (e.g., MACC reanalysis) and making assumptions on the splitting of OA to see if this helps with the biases found later in the text.

Concentrations of species at the boundaries of the domain are based on measured average background concentrations in sites close to the boundaries of the domain (Zhang et al., 2007; Seinfeld and Pandis 2006). We have used the same boundary conditions as in Fountoukis et al. (2011). We have now added this information in the revised manuscript. Most global models have serious problems reproducing the regional OA concentration levels so it is not clear that their use in this study would be helpful or if it would further complicate the analysis by adding one more potential source of bias.

(5) Page 53, Line 27. What is the WRF configuration? Or reference where this is stated. What global meteorological conditions are used to force WRF?
WRF was driven by static geographical data and dynamic meteorological data (near real-time and historical data generated by the Global Forecast System (1×1 degrees)). 27 sigma-p layers up to 0.1 bars were used in the vertical dimension. Each layer of PMCAMx is aligned with the layers used in WRF. The WRF runs were periodically (every 3 days) reinitialized to ensure accuracy in the corresponding fields that are used as inputs in PMCAMx. We have added this information in the revised manuscript.

(6) Page 56, lines 20-26. This is confusing; maybe it would be better presented in a table with the components by site and season
This information is now included in the new Table 2.

(7) Page 57, lines 18-20. Did you conclude this just by looking at the emissions or by also looking at the modeled concentrations?
This is derived from both the emissions and the results of the source apportionment model (PSAT). This is now explained in the revised manuscript.

(8) Page 57, lines 23. Why there is a west to east gradient predicted during the summer? Identify source regions.
A west to east gradient is predicted during summer due to the regional source distribution and the corresponding evolution of photochemistry. We have added this explanation in the revised manuscript.

(9) Page 57, lines 24-25. By looking at Fig 2, it looks the other way around for winter, POA seems to dominate for this season.
We thank the reviewer for pointing this out. We have now corrected this into: *"OOA is predicted to account for approximately 90% of PM_1 OA at ground level over the Paris greater area (domain-average) during summer and 50% during winter."* The original sentence referred to the whole European domain.

(10) Page 58, Line 19. State that you will tackle this problem later in the text, as it reads like you found the problem but did nothing to correct it, which is not the case.
We added the corresponding statement.

(11) Page 58 Line 27-54. This paragraph could be improved by adding more analysis, not by just listing possible reasons for the discrepancy. For instance, you mention wind speed as a possible reason, so you could evaluate the model wind speed against observations specifically for the morning and for this site (only overall evaluation is done). Another reason could be that the diurnal cycle of traffic emissions is too sharp,

as you also see overestimation in morning BC concentrations. Also, could other sources of HOA that you are not considering in your model exist?
The evaluation of the WRF predictions (including the wind speed) along with the relevant discussion is in the following paragraph as well as in Section 5.4 (mixing height). As stated in the text, no systematic errors were found for the wind velocity. To avoid confusing the reader here we have deleted this sentence listing the wind speed as a possible source of error since the relevant analysis is presented in the next paragraph. Errors related to diurnal cycle of emissions or other sources of HOA, were meant to be inherent in the phrase "emission rate errors". However, to avoid misunderstandings we have expanded the text to include these as well.

(12) Fig S1. What about the 6 am peak in winter not represented by the model? Is this persistent throughout the days or episodic? What about the nocturnal biases?
Fig. S1 shows only summertime results. The time series analysis indicates that both the 6 am peak and the nocturnal bias in SIRTA during summer are episodic. There are two days (4 and 11 July) with a large vehicular-POA underprediction (by more than a factor of 5) at 10 pm and two other days (21 and 28 July) with a similar (a factor of 3-4) underprediction at 6 am. This shows up as an average bias in Figure S1 during these two times which, in fact, is not systematic. Furthermore in the revised Figure S1 (Fig. S2 now) which shows the median rather than the average, the 6 am peak is well represented by the model. We have added text in the revised paper discussing the above issues.

(13) Page 59, Line 8-13. Do you find any bias in POA or OOA for the days that the model fails to predict the temperature? You could include this discussion if you add time series of OA components.
For the specific times of the day and specific days during which WRF has the highest temperature errors we do not see any correlation with the POA or OOA bias. We have added this information in the revised text.

(14) Page 59, Line 28. Authors argue a problem in the spatial distribution of BB emissions. How were these emissions distributed? By population only? It is expected that sub-urban or rural homes use more wood-burning for heating than urban homes. Was this taken into account when distributing? If not, can you re-distribute the emissions using this criteria and see if you get an improvement?
In the MEGAPOLI emission inventory used in this work, BBOA emissions are distributed not only by population but also by taking into account the rural/urban areas as mentioned by the reviewer. In this paragraph, however, we argue that this approach might still include errors.

(15) Page 61, Lines 14-5. This paragraph is hard to follow. First you blame remote sources, but then you say that this shouldn't be the reason as you found in your previous study. But then at the end of the paragraph you go back to point to remote sources (BBOA). Please make it clearer.
We have added text and rephrased this paragraph to make it clearer to the reader. The main point here is that errors in remote sources (upwind of Paris) could only partly explain the OOA underprediction. There seems to be another reason as well.

(16) Page 62, Line 19. The minima of the average diurnal cycle are not the background values. Background values cannot be extracted from means as polluted

and background conditions are averaged. You can use box and whisker plots and compare the lower end of the modeled and observed distributions to get at how well the model represents background values
We have rephrased that part and also added the spread (25th and 75th percentiles) of the modeled and measured concentration distributions.

(17) Page 62, Lines 27-3. I think you should focus this analysis to the morning rise of the boundary layer rather than to the daily peaks, as is in the morning when you have the model misrepresentation. Compared to the observations, is the model able to capture the timing of the rise of the BL? If it's too slow then this would be a good explanation of what's happening. Maybe a plot of the derivative in time of the BL (maybe the diurnal cycle of it) could help. This is an important issue for primary aerosols representation which seems to be consistent across species, so you should dedicate a figure to it, at least in the supplement.
We thank the reviewer for pointing this out. We have added a figure in the supplement (Figure S7) with the diurnal cycle of the PBL height for both summer and winter campaigns. It seems that there is an underprediction of the morning rise of the boundary layer in SIRTA that could explain part of the BC underprediction. We have added this explanation in the revised manuscript.

(18) Page 63, Line 13. Why cooking emissions in summer are x2 in winter? Barbecues? Do you see variations between weekdays and weekends? Please elaborate.
This issue needs additional clarification. The primary OA emissions during winter were increased by a factor of 1.5 (compared to a factor of 3 in summer) because the original primary OA wintertime emissions were higher (in absolute values) than the summertime ones. As stated in the text, the total (absolute) OC emissions that were added to account for the missing cooking OA were 5.3 td^{-1} for the summer and 5.1 td^{-1} for the winter period. This rather small seasonal difference could indeed be due to summertime barbecues.
We did observe a variation of COA emissions during weekdays/weekends. Based on observed COA concentrations, the added weekend COA emissions were higher compared to the weekday emissions. Approximately 18.5% of total weekly COA was emitted during each weekend day and 12.5% on each weekday. We have added this in the revised text.

(19) Page 64, Line 2. Explain why this happens.
This is due to a well-mixed layer and strong vertical mixing during the day. We have added this in the text.

(20) Section 5.5. Show and discuss scatter-plot for POA in after adding cooking emissions for both seasons
We have added the scatter-plot for POA including now the COA emissions (new Figure 7) as well as a new table (Table 4) showing the statistics of this comparison for both seasons and for both POA and OOA. Text has been added to discuss this.

Technical Corrections

(21) Page 52, line 13. "fine" grid resolution.
Corrected.

(22) Page 53, line 21. Replace by advection and dispersion by transport.
Replaced.

(23) Page 62, Lines 6-7. This is statement cannot be deduced from Table 2. This probably should be Fig 5.
Corrected.

Reply to Anonymous Referee #2

The manuscript presents simulations of black carbon (BC) and organic aerosol (OA) components (e.g. POA, SOA, and cooking OA) from the PMCAMx model for Paris and compares these results against measurement taken at three ground sites during the MEGAPOLI summer and winter campaigns. It is found that the model provides reasonably good predictions of BC, with some discrepancies during the morning rush hour. In addition, model-measurement agreement is achieved for the summertime SOA concentrations. On the other hand, for the base case, there are significant differences between the model and the measurements for POA and for SOA during the wintertime.

The manuscript concludes that the substantial discrepancy in the POA concentrations is due to the lack of cooking emissions in the base case. When a cooking emissions inventory based on field observations is implemented in the model, much better model-measurement agreement is found, which supports the importance of including this source category in chemical transport models. For SOA during the wintertime, the reason for the discrepancy is unclear, although it is speculated that missing SOA formation pathways or inaccurate biomass burning emissions may be responsible.

Overall this is an interesting manuscript that is well within the scope of ACP, and the work certainly has the potential to be of high quality. However, there are a number of points in the manuscript where the inclusion of additional data, information, or sensitivity studies is needed and the current discussion lacks sufficient depth. This additional work will need to be included before final publication. The terminology used in the manuscript should be clarified as well, as discussed in the general comment below.

General comment

(1) If I understand correctly, the authors are using the term "anthropogenic SOA" to refer to SOA formed from anthropogenic VOCs. This makes the manuscript confusing, since one could have anthropogenic SOA formed from SVOCs and IVOCs as well. This confusion is particularly problematic in the discussion of aging in Section 2 as well as in the conclusions. In Section 2, does the rate constant of 1×10^{-11} cm^3 $molec^{-1}$ s^{-1} apply to anthropogenic SOA from only VOCs or to all anthropogenic SOA including SOA-iv and SOA-sv? In the conclusions, the authors state that 13 percent of summertime SOA "consists of anthropogenic SOA". This is a very dangerous statement as it gives the reader the impression that 87 percent of SOA is biogenic. I believe the correct conclusion is that 87 percent of summertime SOA comes from biogenic VOCs or primary SVOCs and IVOCs that are either biogenic or anthropogenic.
We agree that this terminology issue requires further clarification. When we refer to anthropogenic SOA (aSOA-v) we mean SOA from anthropogenic VOCs only. We use the notation SOA-iv for SOA formed during the oxidation of intermediate volatility organic compounds (IVOCs) and SOA-sv for the SOA from semi-volatile organic compounds (SVOCs). The aging rate coefficient of 1×10^{-11} cm^3 $molec^{-1}$ s^{-1} is applied to aSOA, and the 4×10^{-11} cm^3 $molec^{-1}$ s^{-1} coefficient is applied to SOA-sv and SOA-iv. We have made changes throughout the text to make this clearer. In the conclusions we have revised the above statement mentioned by the reviewer to avoid any misunderstandings.

(2) There is a similar problem with the alternating use of HOA and POA in the manuscript. Is there a difference between “predicted HOA” and “predicted POA”? This distinction is important because in older work HOA was used as a term to identify a product from component analysis of AMS data that was strongly associated with POA. However, with the improvement of AMS and PMF analysis, HOA has morphed into a quantity that is no longer equivalent to total POA, but instead it is more associated with only the vehicular component of POA. In the specific comments below some instances of this problem are noted. I recommend that the authors use terms such as “predicted total POA” and “predicted vehicular POA” rather than “predicted HOA” to avoid confusion.
We have made changes throughout the text following the reviewer’s suggestion. We now use the term “predicted total POA” instead of “predicted POA” and the term “predicted vehicular POA” instead of “predicted HOA” throughout the manuscript.

Specific Comments:

(3) Page 25551, Lines 3 - 6: I realize this sentence is not based on the authors’ own work, but it would be helpful if “larger geographic area” was better defined. Would this larger area be continental-scale versus local/city-scale or something else?
We have revised this sentence accordingly.

(4) Pages 25554 – 25555, Lines 23 – 7: This paragraph and the discussion of the percentages of OA and BC from various sources should be summarized in a table. Currently, the paragraph is difficult to read and it’s hard to compare the different percentages, which would be of interest.
We have added a table in the supplement summarizing these percentages and changed this part of text to make it easier to read.

(5) Page 25556, Lines: Lines 26 – 28: Additional information should be provided regarding the instruments used to measure black carbon. For example, what wavelengths were used for the absorption measurement, what are the instrument model numbers, what was the absorption coefficient used to determine the BC concentration, and were possible artifacts such as shadowing corrected? This information is critical for evaluating the model/measurement comparisons with respect to BC and needs to be included in the manuscript directly or via the appropriate references. Similarly, an uncertainty for the BC measurement should be reported in Figure 6.
We have added a reference (Freutel et al., 2013) that includes all the information regarding the instruments used and the corresponding analysis of their measurements. We also added information about the BC measurement uncertainty.

(6) Page 25557, Line 23: Is there an explanation for why a west to east gradient is predicted?
A west to east gradient is predicted during summer due to the regional source distribution and the corresponding evolution of photochemistry. We have added this explanation in the revised manuscript.

(7) Page 25557, Line 24: The terminology is confusing here. It seems like “OOA” is being used interchangeably with “SOA” in this paragraph. These aren’t exactly the

same thing – OOA is used to identify a component from factor analysis. Practically there is little difference, but only one name should be used, unless the authors are trying to distinguish between two different predicted quantities. This comment applies to the panel labels in Figure 2 as well.
This particular line includes a typo which we have now corrected. The revised text in now reads: *"OOA is predicted to account for approximately 90 percent of PM_1 OA at ground level over the Paris greater area (domain-average) during summer and 50 percent during winter."* The original calculation was actually for the whole European domain. To avoid any confusion we have now made changes throughout the manuscript and use only the term "OOA" instead of "SOA" when referring to the total oxygenated OA. As explained in Section 5.3, the modeled OOA is defined as the sum of SOA from anthropogenic VOCs (aSOA-v), SOA from biogenic VOCs (bSOA-v), SOA from IVOCs (SOA-iv) and SOA from SVOCs (SOA-sv).

(8) Page 25558, Line 20: Similar to the previous comment, the previous two paragraphs discuss POA concentration predictions by PMCAMx, and starting with this line PMCAMx predictions of HOA are described. Is this really a different quantity in the model? As the authors already mentioned, the baseline emissions inventory used in this work does not include cooking, so that means HOA and POA are the same quantity in the model. For the purpose of clarity, it is critical that the same name is used for the same quantity predicted by the model. Again, phrases such as "the model predicts low concentrations of HOA" are problematic since HOA is a term that is specific to factor analysis, whereas terms such as "vehicular POA" would be more accurate for describing model output.
We have revised this as mentioned in our reply to Comment 2 above and use the term "predicted vehicular POA" instead of "predicted HOA" throughout the manuscript as suggested.

(9) Page 25559, Lines 25 – 29: The authors should provide the prediction skill metrics of PMCAMx for BBOA in table format; similar to what has already been provided in the supporting information for HOA.
We have added a new table in the supplementary information (Table S3) with the corresponding BBOA skill metrics.

(9) Section 5.3: I agree with the first referee that the discussion of OOA in this section seems incomplete. An important shortcoming in the model predictions has been identified, but then there is no rigorous follow-up such as sensitivity studies. The article is not particularly long, so there seems to be a missed opportunity to explore the origin of this discrepancy. Since it is stated in the manuscript that there are large uncertainties in BBOA emissions, could the authors run a sensitivity study where the emissions of BBOA and the associated SVOCs and IVOCs are increased or modified in some other fashion? Alternatively, could a different parameterization be used for the formation of OBBOA?
To provide additional information about the characteristics of this underestimation we have now added a new figure in the supplement showing the time series analysis of observed and predicted concentrations of OOA in Paris during winter. This analysis shows that the OOA underprediction is persistent throughout the whole simulation period. However, there are certain days with extreme underestimation (24 and 27 January and 4 and 7 February) and a couple of other days during which the model performance is reasonable, at least during certain hours of the day (29 January and 3

February). A back-trajectory analysis (also added in the supplement) shows that during the days with the extreme underestimation, air masses originate from continental Europe, either within France or from the northeast (mostly Germany) while during the days with reasonable model performance the air masses were mostly clean coming from the Atlantic and western France. This further supports our hypothesis in the manuscript regarding the missing process forming SOA in the model.

We have performed a series of sensitivity tests but we could not reproduce these high OOA levels in the Paris area without increasing dramatically the OOA over the rest of Europe. It should be noted that the same model did not show any major underprediction of wintertime OOA over Europe in other sites (Fountoukis et al. 2014b). For example it did not show any bias in Cabauw, NL. A simple sensitivity test where the BBOA emissions (and the associated SVOCs and IVOCs) are modified would not add any value to the manuscript since the errors are not systematic and uniform throughout the domain and also seem to be related to a mechanism forming OOA during the periods of low photochemical activity. The sensitivity of the model's predictions to the uncertain IVOC emissions has been analyzed by Tsimpidi et al. (2010). Other possible sources of uncertainty that have been investigated in past applications of PMCAMx include uncertainties in the aging scheme, aqueous secondary OA formation and others. For example, in Murphy et al. (2011) we explored a two-bin reduction in volatility upon one oxidation step with a simultaneous decrease (by a factor of 2) in the aging rate constants. A slight underprediction of the OA mass was found in Finokalia during May 2008 compared to the base-case one-bin shift. Hodzic et al. (2010) and Grieshop et al. (2009) investigated a two-bin reduction (in addition to the one-bin base-case saturation concentration reduction) with a reduced OH reaction rate constant and found both to perform adequately. In Murphy et al. (2012) we added a detailed functionalization scheme to approximate the effect on volatility of adding relevant functional groups to the carbon backbone (Donahue et al., 2011). This approach alone resulted in a significant increase of the OA mass. Adding fragmentation to the detailed functionalization scenario decreased OA mass concentrations to the approximate magnitude predicted by the base case (which employs a simplified scheme that is currently used in PMCAMx) and brought the model into reasonable agreement with the OA mass concentration measurements. In our base case aging scheme we use this simplified scenario that tries to describe the net effect of the chemical aging reactions (both functionalization and fragmentation) without treating any of the two types explicitly. An additional SOA formation pathway that is not simulated here is the in-cloud SOA formation from glyoxal and methylglyoxal. In Murphy et al. (2012) we explored the contribution of this pathway to OOA concentrations at several European sites during both a summer and a winter period. Small enhancements to both average OA mass loadings (< 3 %) and O:C (< 10 %) at the surface were found. Their contribution to total SOA formed was low (0–4 %). We have added text in the revised manuscript summarizing the above issues.

(10) Supporting information, S3: All the figures showing model-measurements comparisons are diurnal averages except for this figure. In order to facilitate comparison the comparison of BBOA should be shown as a diurnal average as well.
We have made the recommended change.

(11) Page 25561, Lines 19 – 21: Wouldn't the SOA-iv concentrations also be underestimated and not just the SOA-sv concentrations? Based on the model description, it seems that there would be primary IVOCs emitted with the BBOA that has SOA forming potential.
True. We have now corrected this statement in the revised manuscript.

(12) Page 25562 – 25563, Line 27 – 9: The discussion in this paragraph of the possible reasons for the BC model-measurements discrepancy should be expanded; otherwise the conclusions are too weak. Firstly, the variability of the BC and mixing height measurements during the two campaigns needs to be presented in some fashion in the manuscript. (In fact, it seems that mixing height data is not shown anywhere in the manuscript.) For example, time series for the model and measurement results could be given in the supporting information, or the diurnal plots could use a box-and-whiskers format. Presenting only a diurnal average of the BC concentration and then mentioning only in the text the mixing layer heights for three specific days out of the entire campaign period is not sufficient for evaluating why the model has difficulty reproducing the BC concentration during the morning.
We have now expanded this part. Figure 6 now includes the variability (25th and 75th percentiles) of both the modeled and observed values for BC. We have also added a figure in the supplementary information showing the diurnal average plots of mixing height for both seasons and expanded the discussion related to that.

(13) In addition, it would be a simple sensitivity study to correct the predicted BC concentration for the underestimated mixing height using the LIDAR observations. I agree that there is a significant uncertainty in the observations, but such a comparison would still be interesting. If the corrected model prediction of BC still does not match the observation, despite a potential positive bias of the LIDAR, then that would strongly indicate that there are other reasons for the model-measurement discrepancy besides an inaccurate representation of the mixing layer height. (In other words a positive LIDAR bias would lead to an over correction of the model, which is currently overestimating the BC measurement.)
We thank the reviewer for pointing this out. We have added this correction of the predicted BC based on the mixing height underestimation and expanded this part of the discussion.

(14) Section 5.5: Given that the inclusion of cooking emissions substantially improves the model predictions, the authors should summarize the prediction skill metrics of PMCAMx for this sensitivity study in a table. In other words, create a third table that is analogous to Table 2, but for the results with cooking.
We have added the corresponding information to the revised paper with an additional figure and table.

(16) Page 25563, Lines 19 – 20: What was the temporal profile of the added cooking emissions during the winter period? Was it the same as during the summer period? If not, why is the temporal profile different?
The wintertime temporal profile of cooking emissions was slightly different than the summertime one because these are based on the observed diurnal pattern of COA concentrations during the two periods. We have now added this in the revised paper.

(17) Page 25563, Lines 24 – 26: The manuscript should also include a comparison of the modeled and measured COA for the SIRTA site. As described in Section 4, a COA factor was identified at the SIRTA site for both summertime and wintertime. So, it is not clear why this comparison is shown currently in the manuscript for only LHVP. This omission is conspicuous.
We focused our original analysis in the city center because its concentrations were relatively high. For completeness we have now added the comparison for SIRTA as suggested by the reviewer.

(18) Figure 7: Similar to a previous comment, showing only the diurnal average of the COA measurement does not give the reader sufficient information to interpret the results. A box-and-whisker plot would be strongly preferable or the corresponding time series should be included in the supporting information.
We have now added the variability (25th and 75th percentiles) of the reported averages with boxes. We would rather exclude the whiskers (min and max values) as the figures are already busy with modeled and observed values on the same plots.

(19) Page 25564, Lines 11 – 13: This sentence is confusing and its grammar/syntax should be verified. If the cooking OA can undergo aging in the model, does that mean cooking SOA is formed? Is the cooking OA assumed to be semi-volatile? Are IVOCs emitted with the cooking OA similar to other POA sources? More information is needed for a reader to evaluate this sensitivity test. While reading the previous paragraph, one is given the impression that the cooking OA is inert, but now that seems to not be the case.
We have checked and corrected this sentence. The VBS approach implemented in PMCAMx considers both primary and secondary OA as semi-volatile and photochemically reactive. This includes COA as well. As explained in the beginning of Section 5.5, COA was added in the sensitivity test by assuming an increase of the primary OA emissions. Since IVOCs are assumed proportional to the emitted primary OA mass, the addition of COA came with an increase of the IVOCs emissions. We have now clarified this point in the revised version of the paper.

(20) Pages 25565 – 25566, Lines 25 – 37: How much is the contribution of COA to the total OA during summertime? It seems like the importance of COA for the total OA would be much smaller than the 70 percent figure given for the fraction of POA contributed by cooking.
This is correct. The contribution of COA to the total OA during summertime is 20 percent. We have revised this sentence to make it clearer to the reader that this refers to the primary OA, not the total OA.

Technical Comments:

(21) Introduction: At several points in the text the term "Megacities" is capitalized, but it seems that lowercase should be used as this word is just an ordinary noun (e.g. Cities versus cities).
Corrected.

(22) Page 25551, Line 14: air massES
Corrected.

(23) Page 25553, Line 18: generation reactions
Corrected.

(24) Page 25556, Line 6: It appears that the acronym "GOLF" is not defined.
The definition has been added.

(25) Page 25560, Lines 5 – 6: The acronyms SOA-iv and SOA-sv have already been defined.
Corrected.

(26) Page 25560, Line 11: Should this be aSOA-v?
This is mostly transported OA from the boundaries and is considered to be part of bSOA-v.

Simulating the formation of carbonaceous aerosol in a European Megacity (Paris) during the MEGAPOLI summer and winter campaigns

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Abstract

We use a three dimensional regional chemical transport model (PMCAMx) with high grid resolution and high resolution emissions (4 × 4 km^2) over the Paris greater area to simulate the formation of carbonaceous aerosol during a summer (July 2009) and a winter (January/February 2010) period as part of the MEGAPOLI (Megacities: Emissions, urban, regional, and Global Atmospheric POLlution and climate effects, and Integrated tools for assessment and mitigation) campaigns. Model predictions of carbonaceous aerosol are compared against Aerodyne aerosol mass spectrometer and black carbon (BC) high time resolution measurements from three ground sites. PMCAMx predicts BC concentrations reasonably well reproducing the majority (70%) of the hourly data within a factor of two during both periods. The agreement for the summertime secondary organic aerosol (OA) concentrations is also encouraging (mean bias = 0.1 μg m^{-3}) during a photochemically intense period. The model tends to underpredict the summertime primary OA concentrations in the Paris greater area (by approximately 0.8 μg m^{-3}) mainly due to missing primary OA emissions from cooking activities. The total cooking emissions are estimated to be approximately 80 mg d^{-1} per capita and have a distinct diurnal profile in which 50% of the daily cooking OA is emitted during lunch time (12:00 – 14:00 LT) and 20% during dinner time (20:00-22:00 LT). Results also show a large underestimation of secondary OA in the Paris greater area during wintertime (mean bias = -2.3 μg m^{-3}) pointing towards a secondary OA formation process during low photochemical activity periods that is not simulated in the model.

1 Introduction

Megacities (cities with more than 10 million inhabitants) are major sources of gas and particulate pollutants affecting public health, regional ecosystems, and climate. Rapid urbanization requires efficient emission control strategies and cost-effective air quality management. One of the main challenges in the design of abatement strategies for large urban agglomerations is the quantification of the contributions of local and long-range pollutant transport as well as the identification of the emission areas affecting the receptor. Ambient fine particulate matter ($PM_{2.5}$) is one of the main targets of such pollution reduction strategies. Organic aerosol makes up a large part of $PM_{2.5}$ but despite its importance, it remains the least understood component of the atmospheric aerosol system. Understanding the formation and sources of organic aerosol in ~~M~~megacities is a critical step towards developing efficient mitigation strategies.

Intensive field measurement campaigns have been performed to characterize the chemical composition of particulate and gaseous pollutants in ~~M~~megacities such as New York (Sun et al., 2011), the Los Angeles basin (Hersey et al., 2011), Mexico City (Molina et al., 2010), London (Allan et al., 2010), Tokyo (Xing et al., 2011), and Beijing (Sun et al., 2010). In Europe comprehensive atmospheric measurements were recently conducted in the Paris metropolitan area as part of the MEGAPOLI project (Crippa et al., 2013a,b,c; Freutel et al., 2013; Freney et al., 2013). Freutel et al. (2013) analyzed aerosol mass spectrometer (AMS) measurements from 3 stationary sites in the Paris area during July 2009. They found that the origin of air masses had a large influence on secondary (oxygenated) organic aerosol (OOA) concentrations with elevated values (up to 7 µg m^{-3}) observed during periods when the site was affected by transport from continental Europe and lower concentrations (1 - 3 µg m^{-3}) when air masses were originating from the Atlantic. Crippa et al. (2013a) used positive matrix factorization (PMF) to perform organic source apportionment during winter 2010 in Paris. They identified three dominant primary sources (traffic: 11–15% of OA, biomass burning: 13–15% and cooking up to 35% during meal hours). Oxygenated OA was found to contribute more than 50% to the total OA and included a highly oxidized factor and a less oxidized factor related to aged wood burning emissions. Crippa et al. (2013b) focused on ~~S~~secondary OA (SOA) during both winter and summer in Paris and showed that OOA (local semi-volatile OOA (SV-OOA) and regional low-volatility OOA (LV-OOA)) was significant during both seasons (24–50% of total OA), while contributions from photochemistry-driven ~~S~~OOA (daytime SV-OOA) (9% of total OA) and aged marine OA (13% of total OA) were also observed during summertime. A semivolatile nighttime ~~S~~OOA factor correlating with nitrate was also identified representing 2% of total OA during summer and 18% in winter. Freney et al. (2014) analyzed airborne AMS measurements during summer and found that OA increased with photochemical aging demonstrating that it is necessary to take into account a ~~larger~~ continental-scale geographical area (compared to a local/city-scale area) when assessing the formation of SOA from urban emissions.

Organic aerosol has hundreds of sources, both anthropogenic and natural, in both the particulate and gas phases, while it can undergo complex atmospheric chemical and physical processing (Hallquist et al., 2009). The description of all these emissions and processes in Chemical Transport Models (CTMs) is not a trivial task. Earlier modeling efforts for the ~~M~~megacity of Paris (Sciare et al., 2010) have assumed that primary OA (POA) is non-volatile and used a single-step oxidation SOA scheme thus underestimating SOA concentrations by a factor of three. Even larger errors were encountered when aged air masses with high SOA levels arrived at the observation site. More recently, models taking into account the semivolatile nature of POA (Robinson et al., 2007) have been applied over Paris. Couvidat et al. (2013) applied the Polyphemus model, which incorporates a two-surrogate-species (hydrophilic/hydrophobic) SOA formation scheme taking into account POA volatility and chemical aging, during the MEGAPOLI July 2009 campaign. The model estimated a 30 - 38% local contribution to OA at the city center and overpredicted morning OC concentrations. Zhang et al. (2013) implemented the volatility basis set (VBS) approach into the chemistry transport model CHIMERE and applied it to the greater Paris region for the summer MEGAPOLI campaign. Simulation of organic aerosol with the VBS approach showed the best correlation with measurements compared to other modeling approaches. They also showed that advection of SOA from outside Paris was mostly responsible for the highest OA concentration levels. Fountoukis et al. (2013) examined the role of horizontal grid resolution on the performance of the regional 3-D CTM PMCAMx over the Paris greater area during both summer and winter and concluded that the major reasons for the discrepancies between the model predictions and observations in both seasons are not due to the grid scale used, but to other problems (e.g., emissions and/or process description). Skyllakou et al. (2014), using the Particulate Matter Source Apportionment Technology (PSAT) together with PMCAMx, showed that approximately 50% of the predicted fresh ~~primary organic aerosol (~~POA~~)~~ originated from local sources and another 45% from areas 100–500 km away from the receptor region during summer in Paris. Furthermore they found that more than 45% of ~~S~~OOA was due to the oxidation of volatile organic compounds (VOCs) that were emitted 100 - 500 km away from the center of Paris.

Although several uncertainties still exist in OA modeling (e.g. related to POA volatility, SOA yields, the aging parameterization), evaluation and improvement of emission inventories from ~~M~~megacities as well as from surrounding areas is of fundamental importance. Furthermore, the description of the subsequent aging of the emitted organic material and the formation of OOA is critical in OA modeling. In this work we use the 3-D regional CTM PMCAMx with ~~high~~ fine grid resolution to evaluate the OA and BC emission inventory in the megacity of Paris. We use an extensive set of factor analysis AMS data which allow a more in-depth evaluation of the formation and evolution of OA. We identify and quantify missing sources of OA during both seasons, explore possible emission and meteorological errors affecting the predicted BC concentrations and discuss missing or inadequate processes forming OA in the model.

2 Model description

PMCAMx (Tsimpidi et al., 2010; Fountoukis et al., 2011, 2014b) describes the processes of horizontal and vertical transport~~advection, horizontal and vertical dispersion~~, gas-and aqueous-phase chemistry, aerosol dynamics and chemistry, and wet and dry deposition. It is based on the framework of the CAMx air quality model (Environ, 2003). An extended SAPRC99 mechanism (Environ, 2003) is used in the gas-phase chemistry module. The OA treatment in PMCAMx is based on the Volatility Basis Set (VBS) approach (Donahue et al., 2006; 2009) for both primary and secondary organic species. Primary OA ~~(POA)~~ is assumed to be semivolatile with nine surrogate POA species used, corresponding to nine effective saturation concentrations ranging from 10^{-2} to 10^{6} μg m^{-3} (at 298 K) in logarithmically spaced bins (Shrivastava et al., 2008). POA is simulated in the model as fresh (unoxidized) POA and oxidized POA from i) intermediate volatility organic compounds (IVOCs) and ii) semi-volatile organic compounds (SVOCs) (SOA-iv and SOA-sv, respectively). The IVOCs emissions are assumed to be proportional (by a factor of 1.5) to the emitted primary OA mass (Tsimpidi et al., 2010; Shrivastava et al., 2008). The SOA volatility basis-set approach (Lane et al., 2008) of the model includes four SOA species for each VOC with four volatility bins (1, 10, 100, 1000 μg m^{-3}). Chemical aging is modeled through gas-phase oxidation of OA vapors using a gas-phase OH reaction with a rate constant of 1×10^{-11} cm^{3} molec^{-1} s^{-1} for ~~anthropogenic~~ SOA from anthropogenic VOCs (aSOA-v) and 4×10^{-11} cm^{3} molec^{-1} s^{-1} for ~~the primary OA~~SOA-sv and SOA-iv (Atkinson and Arey, 2003). Each reaction is assumed to decrease the volatility of the vapor material by one order of magnitude. More details about this version of the model can be found in Fountoukis et al. (2011; 2014b).

The parameterization of the biogenic SOA chemical aging in the VBS scheme in this work differs from that used by Zhang et al. (2013) in CHIMERE. In CHIMERE the biogenic SOA ages the same way as the anthropogenic SOA, while in our work these later generation reactions are assumed to lead to a zero net increase of the corresponding SOA because of a balance between the functionalization and fragmentation processes.

3 Model application

We simulate two periods (1 – 30 July 2009 and 10 January – 9 February 2010) during which intensive measurement campaigns were performed as part of MEGAPOLI. PMCAMx is used with a two-way nested grid structure which allows the model to run with coarse grid spacing over the regional domain of Europe, while within the same simulation, applying a fine grid nest over the Paris greater area (Fig. 1). The necessary meteorological inputs to the model were generated from the WRF (Weather Research and Forecasting) model (Skamarock et al., 2008) and include horizontal wind components, vertical diffusivity, temperature, pressure, water vapor, clouds and rainfall. WRF was driven by static geographical ~~data~~ and dynamic meteorological data (near real-time and historical data generated by the Global Forecast System (1×1°)). 27 sigma-p layers up to 0.1 bars were used in the vertical dimension. Each layer of PMCAMx was~~is~~ aligned with the layers used in WRF. PMCAMx was set to perform simulations on a polar stereographic map projection with 36 × 36 km^2 grid spacing over the European domain and a 4 × 4 km^2 resolution over Paris. The European modeling domain covers a 5400 × 5832 km^2 region while the Paris subdomain covers a total area of 216 × 180 km^2 with the Metropolitan area of Paris located centrally in the subdomain. Fourteen vertical layers are used extending up to 6 km in height with a surface layer depth of 55 m. The dimensions of the modeling domain are the same for both the summer and winter simulations. The model interpolates the meteorological input from the parent to the nested grid while high resolution emissions are used in the Paris subdomain. Concentrations of species at the boundaries of the domain are based on measured average background concentrations in sites close to the boundaries of the domain (e.g. Zhang et al., 2007; Seinfeld and Pandis 2006). We have used the same boundary conditions as in Fountoukis et al. (2011).

Inventories of both biogenic and anthropogenic emissions were developed and consist of hourly gridded emissions of gases as well as primary particulate matter. A description of the European emission data can be found in Pouliot et al. (2012). These emissions were modified by nesting high resolution emissions with emission inventories for four ~~M~~megacities in the European coarser grid of 36×36 km^2. More specifically, the base case emission data originate from the Netherlands Organization for Applied Scientific Research (TNO) and were compiled as part of the MEGAPOLI project. They were spatially distributed at a resolution of 1/8° × 1/16° (longitude × latitude). Furthermore, based on the TNO inventory, bottom-up emission data were used for four European megacities (Paris, London, Rhine-Ruhr and Po Valley). A description of the procedure for the nesting, comparison and origin of the different emission inventories is given in Kuenen et al. (2010) and Denier van der Gon et al. (2011).

The Paris emissions that form the core of the high resolution inventory for the domain used in this study originate from local authorities responsible for city emissions inventories and air quality (Airparif, 2010). A summary of total mass emission rates for the Paris greater area is given in Table 1. The largest source of primary OA in the wintertime emission inventory in Paris is residential (wood and fossil fuel) combustion, contributing 80% to the total anthropogenic OA emissions while during summer the traffic-related sector dominates with 35% contribution (Table S1). ~~More than 70% of the Parisian summertime BC emissions are originating from traffic sources.~~ During winter the traffic sector contributes approximately 40% to the total BC emissions in the Paris subdomain. This is more than a factor of two higher than the European average contribution and is due to the dense population in this area. The residential combustion sector contributes approximately 45% to the wintertime BC emissions in the Paris area which is about the same as the European average indicating low emissions per inhabitant in the Paris greater area for this specific source sector.

The chemical speciation of the volatile organic compounds is based on the speciation approach proposed by Visschedijk et al. (2007). Biogenic emissions were estimated using three distinct inventories. Plant canopy gridded emissions were estimated by utilizing the MEGAN (Model of Emissions of Gases and Aerosols from Nature) model (Guenther et al., 2006). MEGAN inputs are meteorological parameters estimated by the WRF model, the leaf area index and a set of emission factors for various chemical species at standard conditions. Since a large portion of the domain is covered by sea, marine aerosol emissions are also included. These are based on a marine aerosol model (O’Dowd et al., 2008) that estimates mass fluxes for both accumulation and coarse mode including an organic fine mode aerosol fraction. Inputs of the specific marine model are the wind speed components calculated by

WRF and the chlorophyll-a concentrations acquired using the GES-DISC Interactive Online Visualization ANd aNalysis Infrastructure (GIOVANNI) as part of the NASA's Goddard Earth Sciences (GES) Data and Information Services Center (DISC). Finally wildfire emissions are also included (Sofiev et al., 2009).

4 Measurements

Two intensive field campaigns were performed as part of the MEGAPOLI project (megapoli.dmi.dk/index.html) during summer (July 2009) and winter (January/February 2010) in the Paris area including AMS measurements of fine particulate matter from three ground sites (Beekmann et al., 2014). The Laboratoire d'Hygiène de la Ville de Paris (LHVP; Paris, 13th district; 48.827 N, 2.358 E) monitoring station is in the center of the city and is representative of Paris urban background air pollution (Sciare et al., 2010; Favez et al., 2007). SIRTA (Site Instrumental de Recherche par Télédétection Atmosphérique) is located in Palaiseau (48.714 N, 2.203 E), 20 km south-west of the city center and is characteristic of a suburban environment (Haeffelin et al., 2005). The GOLF (GOLF Poudrière) site (48.934 N, 2.547 E) is located approximately 20 km to the north east of the city center and is also suburban influenced by local (medium) traffic. High-resolution time-of-flight aerosol mass spectrometers (HR-ToF-AMS) (DeCarlo et al., 2006) were used at both the SIRTA and LHVP sites, while a compact ToF-AMS (C-ToF-AMS) (Drewnick et al., 2005) was deployed at GOLF. AMS OA measurements were analyzed by factor analysis (Crippa et al., 2013b) using the multi-linear engine (ME-2) algorithm (Paatero, 1999; Canonaco et al., 2013), the PMF2 algorithm (Freutel et al., 2013) and the PET toolkit of Ulbrich et al. (2009) (Crippa et al., 2013a,c). The factor analysis data used in this work are taken from Crippa et al. (2013b) for LHVP, from Crippa et al. (2013c) for SIRTA and from Freutel et al. (2013) for the GOLF site during the summer period while during winter all the data are taken from Crippa et al. (2013a). Table 2 shows the various OA components identified by the PMF analysis in each site and season. During the winter campaign factor analysis identified two primary OA components (hydrocarbon-like organic aerosol (HOA) and biomass burning OA (BBOA)) in GOLF with the addition of cooking-related organic aerosol (COA) component in LHVP and SIRTA. Two secondary components (low-volatility OOA related to wood burning emissions and a highly oxidized OOA factor) were identified in LHVP and GOLF and one OOA component in SIRTA. During summertime two primary OA components (COA and HOA) were identified in LHVP and SIRTA and one component (HOA) at GOLF. Finally, one OOA component was identified in GOLF, while three (marine-related OA, (MOA), low-volatility oxygenated OA (LV-OOA) and semi-volatile oxygenated OA (SV-OOA)) were identified at SIRTA and LHVP. BC was measured using a multi-angle absorption photometer (MAAP) in LHVP and GOLF and an Aethalometer in SIRTA (Freutel et al., 2013). The measurement uncertainty for the a~~A~~ethalometer and MAAP was 30% and 10%, respectively (Freutel et al., 2013).

5 Results and discussion

5.1 Model predictions over the Paris greater area

Figure 2 shows the predicted average ground-level concentrations of fine fresh primary OA, secondary OA and BC in the greater Paris area during July 2009 and January/February 2010. Overall, carbonaceous aerosol is predicted to account for 36% of total dry PM_1 mass concentration at ground level averaged over the Paris greater area domain during summer, followed by nitrate (20%), sulfate (16%) and ammonium (12%) with the remaining 16% comprised of crustal material, sea-salt and metal oxides. During the winter period the model predicts a higher contribution of carbonaceous aerosol (41%) and lower contributions for the secondary species: sulfate (12%), nitrate (12%) and ammonium (11%). Primary OA and BC are predicted to have higher levels in the city center while their concentrations decrease in the Parisian suburbs. The use of high resolution in both the emissions and grid simulation results in larger spatial concentration gradients compared to the resolution of 36 × 36 km^2 used by Fountoukis et al. (2013). During the winter period the model predicts much higher concentrations for both POA and BC compared to summer. Based on the PSAT results, t~~T~~he two largest sources of primary carbonaceous aerosol are the traffic-related sector and the residential (fuel and wood) combustion processes. The traffic source sector dominates in the contribution of the OA and BC emissions during summer while during wintertime the residential combustion is the largest contributor.

Secondary OA concentrations show a regional character in their geographical distribution during both seasons with higher concentrations predicted during summer due to stronger photochemical activity. A west to east gradient is predicted during summer following the evolution of photochemistry. OOA is predicted to account for approximately 90% of PM_1 OA at ground level over the Paris greater area (domain-average) during summer and 50% during winter.~~OOA is predicted to account for a little more than 90% of PM_1 OA at ground level over the Paris greater area during both seasons~~.

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5.2 Primary organic aerosol levels and sources

The prediction skill metrics of PMCAMx against factor-analysis AMS data for total POA concentrations from all three stations in the Paris greater area are summarized in Table 3~~2~~. Figure 3 shows an overall comparison of modeled versus observed values for both seasons. Primary OA in the model is the OA that is emitted in the particulate phase and has not undergone any chemical processing. The AMS total POA component in this comparison is the sum of HOA and COA during summer with the addition of BBOA during wintertime. During the summer period the model underpredicts total POA concentrations at all sites by, on average, 0.8 μg m^{-3}. Overall, only 15% of the hourly data from all sites (1700 data points in total) are predicted within a factor of two. At LHVP the agreement is slightly better but still poor, with 30% of the data predicted within a factor of two and a fractional error of 0.9. The day-to-day variability of modeled and observed concentrations in Paris center is shown in Fig. S1~~provided~~ in the supplement~~ (Fig. S1)~~. The daily-average~~d~~ total POA concentration is systematically underpredicted throughout most of the simulated days.

Factor analysis of the AMS data from downtown Paris showed that a major part (more than 70%) of observed total POA concentrations originated from cooking activities (0.5 μg m^{-3} on average) while only another 0.2 μg m^{-3} was attributed to HOA from traffic-related sources (Crippa et al., 2013b). Emissions from cooking sources are not included in the baseline emission inventories that are used in this work (Denier van der Gon et al., 2011). Therefore any POA concentrations that the model predicts during the summer period are mainly ~~H~~ primary OA from traffic-related sources. This is further explored in S~~s~~ection 5.5.

During summer the model predicts low concentrations of ~~H~~vehicular POA in Paris, ranging on average between 0.2 and 0.3 μg m^{-3}, in agreement with the observations (Fig.~~ure~~ ~~S1~~S2). There is little bias (FBIAS=0.1) and the mean error is 0.2 μg m^{-3} (Table S2~~1~~). In SIRTA the predicted average diurnal profile compares well with the observations capturing the morning peak at 8 am. The nocturnal bias in SIRTA (at 10 pm) is rather episodic with two days (4 and 11 July) exhibiting a large vehicular-POA underprediction (by more than a factor of 5). Interestingly, observations show no clear morning peak at the city center. The model, however, predicts a distinct diurnal profile, overpredicting ~~H~~vehicular POA concentrations at

LHVP during the morning rush hours. This overprediction of ~~H~~POA-traffic concentrations could be related to emission~~ rate error~~s (e.g. emission rate errors, errors in the diurnal cycle of emissions, missing sources of total POA emissions, etc.), errors in the geographical distribution of emissions in the high resolution domain (Fountoukis et al., 2013) or could also be affected by errors in the meteorology. ~~For example, underestimated wind velocities would lead to lower dilution of primary species and thus higher concentrations during certain days.~~ The source apportionment method can also induce errors. As HOA concentrations are quite low, the HOA fraction estimated by the statistical model has large uncertainty (30-50%).

Meteorological parameters used as input to PMCAMx (temperature, relative humidity and wind velocity) were compared against measurements available at SIRTA (Fig. S3~~2~~). In general, the WRF calculated meteorological fields are consistent with the measurements. Temperature is well reproduced with a mean bias of -0.7 °C. There are a few days where WRF underpredicts the maximum daily observed temperature by 2-4 °C which could theoretically result in an underestimation of POA evaporation and thus a small overprediction of POA. However, ~~for the specific times of the day and certain days that the model shows somewhat large discrepancies compared to the observed temperature,~~ no correlation between the temperature errors and ~~with~~ the POA or OOA bias was~~is~~ found. No systematic error is found in the wind velocity or relative humidity comparison (mean bias of 0.2 m s^{-1} and -0.5%, respectively).

During winter the agreement for total POA is better than in summer, with errors mostly due to scatter (mean error = 1.4 μg m^{-3}) but also a tendency towards underprediction (mean bias = -0.4 μg m^{-3}) (Fig. S1). Factor analysis of the AMS data from the city center showed an average of 1 μg m^{-3} from cooking sources, 1 μg m^{-3} from biomass burning and 0.7 μg m^{-3} from traffic (Crippa et al., 2013a). The model predicts an average of 2.2 μg m^{-3} for total POA which includes both ~~H~~vehicular POA and BBOA but no COA concentrations. Source apportionment results from Paris (Skyllakou et al., 2014) showed that approximately 70% of the modeled (PMCAMx) total POA concentration in Paris center is predicted to originate from biomass burning and 15% from traffic-related sources. This shows that the model underpredicts the concentrations of ~~H~~POA-traffic components during winter (Table S~~1~~2) while the problem with the missing COA emissions still exists but is now a smaller fraction of the total POA. The comparison between the predicted BBOA concentrations from PSAT against the factor analysis BBOA (Fig. S4~~3~~, Table S3) shows an overprediction in LHVP (mean bias = 0.3 μg m^{-3}) and underprediction at SIRTA (mean bias = -0.3 μg m^{-3}) implying errors in the geographical distribution of residential wood burning emissions in the Paris greater area.

5.3 Oxygenated organic aerosol

Figure 4 shows the comparison of predicted OOA concentrations against the factor-analysis AMS data for both seasons with the statistics of the comparison summarized in Table 3~~2~~. The modeled OOA is defined as the sum of ~~anthropogenic SOA from VOCs (~~aSOA-v~~)~~, ~~biogenic SOA from VOCs (~~bSOA-v (SOA from biogenic VOCs), ~~SOA from IVOCs (~~SOA-iv~~)~~ and ~~SOA from SVOCs (~~SOA-sv~~)~~. Contrary to POA, the comparison for OOA during the summer period is encouraging (Fig. S1). The model predicts an average of 1.5 μg m^{-3} of OOA at the three measurement sites without any significant concentration gradients between the city center (LHVP) and the suburban sites (Table 3~~2~~) while a 1.4 μg m^{-3} average concentration was estimated by the factor analysis. A large fraction (54%) of the predicted OOA concentration in LHVP is bSOA-v followed by SOA-sv and SOA-iv (33%) and aSOA-v (13%). Most of the OOA hourly measurements are reproduced within a factor of two (80% in both LHVP and GOLF and 60% in SIRTA) highlighting the ability of the model to reproduce the major secondary OA transport and transformation processes during a photochemically intense period. This was also shown by Zhang et al. (2013) when using the VBS scheme as opposed to the single-step SOA formation mechanism in LHVP during summertime. However, in disagreement with this work, the VBS scheme assuming increasing biogenic SOA yields with chemical aging of Zhang et al. (2013) systematically overpredicts ~~S~~OOA concentrations in the city center (by up to a factor of two). PMCAMx reproduces the observed ~~S~~OOA concentrations in LHVP during summer with reasonable accuracy (1.7 µg m^{-3} compared to 1.6 µg m^{-3} predicted by the model with a -0.05 fractional bias).

During the winter period however, the model performance is very different than in July. PMCAMx largely underpredicts OOA concentrations at all three sites with an overall mean bias of -2.3 µg m^{-3} (Table 3~~2~~). It is noteworthy though that the OOA levels estimated by the PMF analysis during the winter period are more than a factor of two higher than that of the summer period. PMCAMx on the other hand predicts that OOA during winter is 30-50% lower than during summer. Only 25% of the hourly data (2230 in total) are predicted within a factor of two. The model predicts less than 1 µg m^{-3} of OOA in the Paris greater area while the factor-analysis estimated a concentration of more than 3 µg m^{-3}. ~~A timeseries analysis (Fig. S5) shows that~~ T~~t~~he OOA underprediction is~~s~~ persistent throughout the ~~ whole~~ simulation period (Fig. S5)~~also seen in Fig. S1)~~. However, there are certain days with large (a factor of 3-5) underestimation (24 and 27 January and 4 and 7 February) and a couple of other days during which the model performance is somewhat reasonable at least during certain hours of the day (29 January and 3 February). A back-trajectory analysis (Fig. S6) shows that during the days with the larger underestimation, air masses originated from continental Europe, either within France or from the northeast (mostly Germany). while during the days with reasonable model performance the air masses were mostly clean coming from the Atlantic.

Possible reasons for this underprediction include errors in meteorology, emission rate errors of SOA precursors and missing or inadequate processes forming ~~S~~OOA in the model. However, no significant errors in the wintertime meteorological input were found from the evaluation of the meteorological parameters (Fig. S3~~2~~). Furthermore, PMCAMx was found to perform reasonably well for other PM components (e.g. BC) indicating that the meteorology is probably not the main reason for the OOA underprediction. Simulations with PSAT together with PMCAMx showed that approximately 80% of the predicted OOA during winter in Paris originated from long range transport from areas more than 500 km away from Paris. Compared to summer (45%), the model simulates more contribution from long range secondary OA sources during winter, because the timescale for its production is longer due to the slower photochemical activity (Skyllakou et al., 2014). Therefore any emission rate errors in OOA precursors, if true, should be present not only in the Paris greater area but also in the greater region of Europe. In fact recent studies (Bergstrom et al., 2012; Kostenidou et al., 2013; Fountoukis et al., 2014; Denier van der Gon et al., 2014) have pointed towards large uncertainties in the biomass burning emission estimates in many European areas. This could partly explain the wintertime underprediction of OOA in Paris. If BBOA emissions are significantly underestimated in European regions upwind of Paris, then the Parisian SOA-sv and SOA-iv concentrations formed in the model from BBOA would also be underestimated. From the factor analysis of Crippa et al., (2013b), an average of 1.3 μg m^{-3} was estimated for the oxygenated BBOA (OBBOA) concentration in Paris, significantly higher compared to the OBBOA predictions of PSAT (0.2 μg m^{-3}). However, this can explain only part of the large underprediction of OOA (-2.3 μg m^{-3}). Some recent studies have supported the transformation of BBOA to OOA without the presence of sunlight (Bougiatioti et al., 2013; Crippa et al., 2013a,b). A process forming SOA (and involving high NO$_x$ levels from polluted sites) that is not simulated in the model could explain the OOA underprediction in Paris. Furthermore, Fountoukis et al. (2014b) ~~PMCAMx was recently~~ evaluated PMCAMx against OOA factor-analysis AMS measurements from several sites all over Europe (Fountoukis et al., 2014b) during a wintertime period (February/March 2009) and an autumn period (September/October 2008) and showed good agreement with observations from both periods (mean bias = 0.4 μg m^{-3} and -0.2 μg m^{-3} respectively). Contrary to the present study though, the measurement sites in Fountoukis et al. (2014b) study included only rural and remote areas, while the more than 3 μg m^{-3} of OOA observed in Paris is a lot higher than other wintertime measurements in Europe. ~~A process forming SOA (and involving high NO$_x$ levels from polluted sites) that is not simulated in the model could explain the OOA underprediction in Paris. Some recent studies have supported the transformation of BBOA to OOA without the presence of sunlight (Bougiatioti et al., 2013; Crippa et al., 2013a,b).~~

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Other possible sources of uncertainty that are not explored here but have been investigated in past applications of PMCAMx include uncertainties in the aging scheme, the magnitude of IVOC emissions, aqueous secondary OA formation and others (Murphy et al., 2011, 2012; Tsimpidi et al., 2010). These studies have shown so far that the base-case OA scheme used in PMCAMx ~~has shown to~~ represents reasonably well the average atmospheric chemistry of OA.

5.4 Black Carbon

More than 70% of the hourly summertime BC data are predicted within a factor of two from all three sites (Fig. 5~~Table 2~~). The model, in agreement with the measurements, predicts the largest BC concentrations in the city center and the lowest at the suburban site of SIRTA. The overall mean bias (0.05 μg m^{-3}) shows encouraging agreement without any systematic errors. During the winter period, with the exception of SIRTA where only 12-hour data were available, the model performs similarly to the summer period with 68% of the data predicted within a factor of two (Fig. 5). A slightly higher overprediction is seen in LHVP (mean bias = 0.5 μg m^{-3}) compared to the summer period (Fig. S1). Both the model and the observations show higher BC concentrations in GOLF than in the city center due to a strong influence of nearby traffic.

Figure 6 shows the average diurnal profile of predicted and observed BC concentrations. PMCAMx does a reasonable job in predicting the ~~background~~ low concentrations (minima of the curves) of BC during both periods and in both the city center and the suburbs reproducing even the low levels of BC in SIRTA (down to 0.3~~4~~ μg m^{-3} in the evening). The small overpredictions in LHVP during summer and in both LHVP and GOLF during winter are mostly during the morning peak and could be related to errors in the traffic emission inventory, errors in the geographical distribution of emissions in the high resolution inventory (Fountoukis et al., 2013) or to an underestimation of the mixing height by the model. Boundary layer height observations were only available in the SIRTA site.

A timeseries analysis of BC concentrations at SIRTA showed that the model overpredicted the morning peak BC concentrations by more than a factor of two on July 13, 21 and 29. On July 13 the model-simulated mixing height is within 10% of the observed values while on the other two days the model underestimated the mixing height (up to 1200 m for an observed mixing height of about 3000 m during the day). It is difficult to quantify the extent of the error this model underestimation would induce to BC concentrations since the mixing height observations are also uncertain. Hodzic et al. (2009) reported a positive bias of 300–1000 m in the mixing height diagnosed from LIDAR observations (used here), as compared to the one from radiosonde profiles. We corrected the BC concentrations in the Paris city center f~~F~~or the~~an~~ estimated 20% average underprediction of the mixing height during the summer~~ we corrected BC concentrations in Paris city center by the same magnitude~~. This slightly improved model performance (MB was reduced from 0.3 µg m^{-3} to -0.1 µg m^{-3}) showing that the mixing height underestimation could partly explain the BC discrepancy.~~,~~ H~~h~~owever this is a rather crude~~simplified~~ correction since a large part (40%) of the city's BC ~~concentration ~~is transported from outside the city (Skyllakou et al., 2014). T~~Furthermore, t~~he model underpredicts the morning rise of the boundary layer during both summer and winter so this~~at~~ could also explain part of the BC underprediction in the morning (Fig. S7). Overall, the model predicts, in agreement with the measurements, surprisingly low concentrations of BC for a megacity of 10.5 million inhabitants (Beekmann et al., 2015).

5.5 Estimation of cooking OA emissions

Based on the comparison with the factor-analysis AMS data for COA (Section 5.2) a sensitivity simulation was run in which emissions of primary OA were increased by a factor of 3 during summer and 1.5 during winter to roughly account for the missing cooking emissions. These emissions were geographically distributed in the Paris greater area following the pattern of the population density. It should be noted that since IVOC emissions~~s~~ are assumed to be proportional to the emitted primary OA mass, the addition of COA ~~came ~~was accompanied by~~with~~ an increase of the IVOC emissions~~ as well~~. The total OC emissions added were 5.3 tons d^{-1} for the summer and 5.1 tons d^{-1} for the winter period, or approximately 80 mg d^{-1} per capita during each period. A distinct diurnal emission profile was used taking into consideration that COA concentrations were characterized by a prominent diurnal pattern with peak values during meal times (Crippa et al., 2013b). A variation of day-to-day~~weekly~~ emissions was also considered with approximately 18.5% of total weekly COA emitted (per day) on weekend days and 12.5% on weekdays. Figure ~~S4~~ S8 shows the temporal profile of the added cooking emissions during the summer period. The wintertime temporal profile used slightly differs from the summertime one, since these are based on the observed diurnal patterns of COA concentrations. As expected, PMCAMx predictions for total POA concentrations are much closer to observations when COA emissions are included in the inventory (Fig. 7, Table 4). The average summertime predicted total POA is increased to 0.7 μg m^{-3} and the fractional bias drops from -0.7 to 0.05 while the number of data predicted within a factor of two increases from 30% to 60%. In the other two sites the addition of COA considerably improves model predictions although a systematic underprediction still exists (MB = -0.2 μg m^{-3} in SIRTA and -1 μg m^{-3} in GOLF) which could be due to the simplified approach of distributing the COA emissions by population density in the greater area of Paris. During the winter period the addition of COA results in a reduced model bias for total POA concentrations in Paris city center (FBIAS drops from -0.3 to -0.01). ~~but also an overprediction (MB=0.5 μg m^{-3}) that is mainly from the errors in BBOA discussed in section 5.2.~~ The model performance for OOA remains practically unchanged with the addition of COA during both seasons (Table 4). Figure ~~7~~ 8 shows the averaged diurnal profile of COA concentrations predicted and observed during both seasons in LHVP and SIRTA~~at the city center~~. In SIRTA the model predicts low concentrations (< 0.5 μg m^{-3}) throughout the day during b~~m~~oth seasons in agreement with observations. In the city center t~~T~~he two peaks observed during meal times are reproduced with reasonable accuracy. Interestingly, this agreement is achieved when 50% of the daily cooking emissions are emitted during lunch time (12:00 – 14:00 LT) and only 20% during dinner time (20:00-22:00

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LT), although the nighttime maximum COA concentration is higher than the midday maximum (by a factor of two in summer). This is due to a strong vertical mixing during the summer days. During the winter period the addition of cooking OA emissions in the city center decreases the fractional bias for total POA concentrations in LHVP from -0.3 to -0.01 and in general significantly improves model predictions.

In a sensitivity test, we added cooking OA emissions in the entire domain assuming the same emission rate per person as in Paris. This is clearly a crude zeroth order approximation. Addition of cooking OA emissions to the inventory, leads to an increase of the total OA emissions by as much as a factor of 2-3 in some highly populated areas (Fig. ~~ure~~ S~~5~~9). These additional European cooking OA emissions do affect OA levels in Paris. Assuming similar chemical aging parameters as for the transportation OA we estimated that these emissions could increase average OA in Paris by 0.1-0.2 μg m^{-3} on average; a small but non-negligible contribution.

6. Conclusions

PMCAMx, a 3-D chemical transport model, was applied using both regional and urban domains to simulate the formation of carbonaceous aerosol during the MEGAPOLI summer and winter campaigns. A high grid resolution over the Paris greater area along with high resolution emissions (4 × 4 km^2) was used to examine the role of sources and production mechanisms in the organic aerosol and BC concentrations.

PMCAMx predicts BC concentrations reasonably well during both periods and in both the city center and the suburbs (FBIAS = -0.1 in summer and 0.1 in winter) reproducing the majority (70%) of the hourly data within a factor of two. The largest source of summertime BC concentrations is traffic (70%) and of wintertime the residential combustion

(45%). Almost 60% of the BC is predicted to originate from local sources during both summer and winter.

The agreement for the summertime secondary OA concentrations is also encouraging (mean bias = 0.1 μg m^{-3}) highlighting the ability of the model to reproduce the major secondary OA transport and transformation processes during a photochemically intense period. The model predicts that during the summer a large fraction (54%) of the ~~S~~OOA concentration in the city center is comprised of ~~biogenic~~ SOA from biogenic VOCs followed by SOA from semi-volatile and intermediate-volatility ~~SOA~~VOCs (33%) while a smaller fraction (13%) consists of ~~anthropogenic~~ SOA from anthropogenic VOCs.

Wintertime simulations showed a surprisingly large underestimation of ~~S~~OOA in the Paris greater area (mean bias = -2.3 μg m^{-3}) that has not been reported in any of the previous applications of the model in either the European or the United States domain. A process forming secondary OA (in a polluted environment with high NO_x concentrations and in the absence of light) that is not simulated in the model could partly explain this underprediction.

The model evaluation for primary OA concentrations revealed a major deficiency of the emission inventory, namely the missing primary organic aerosol emissions from cooking activities during both summer and winter. Based on the comparison with the factor-analysis AMS data for cooking OA, more than 5 tons d^{-1} (or 80 mg d^{-1} per capita) should be added in the emission inventory with a distinct diurnal profile in which 50% of the daily cooking emissions are emitted during lunch time (12:00 – 2:00 pm) and 20% during the dinner time (8:00-10:00 pm). This addition improved significantly the model performance for both summer and winter. This work strongly supports that much more attention should be paid to the OA emission inventories of ~~M~~megacities and more specifically to the cooking source sector. However, the remarkable diurnal variation of these emissions shows that more research is also needed towards a better understanding of which activities contribute to these emissions (e.g. meat grilling is one known important source of COA).

Focusing on ambient primary OA concentrations, the cooking source seems to be an attractive target for pollution reduction strategies since COA contributes 70% to total primary OA concentrations during summer. During winter both cooking (40%) and biomass burning (40%) are the two major contributors. Focusing on reducing BC concentrations, however, the traffic sector deserves the most attention during summer with the addition of residential combustion in winter.

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Table 1. Emission mass totals (in tons/month) for the Paris greater area as shown in Fig. 1.

Species	CO	NO	SO_2	NH_3	VOCs			Nitrate	Sulfate	Ammonium	BC	OC	Sodium	Chloride
					Isoprene	MT[1]	Other[2]							
Summer 2009														
Anthropogenic	27307	10562	556	1877	-	-	12042	-	44	-	455	1058	12	-
Natural (land)	2247	204	-	-	2861	1435	2390	-	-	-	-	-	-	-
Natural (Fires)	340	10	2	5	-	-	5	3	7	1	7	23	-	-
Winter 2010														
Anthropogenic	54041	15440	5713	1999	-	-	17089	-	158	-	726	1892	32	-
Natural (land)	314	30	-	-	26	211	301	-	-	-	-	-	-	-

[1] MT: Monoterpene emissions

[2] Other: Other VOCs excluding methane and methanol

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Table 2. OA components identified by the PMF analysis in each site during the MEGAPOLI summer and winter campaigns

OA components	Summer	Winter
LHVP	HOA, COA LV-OOA, SV-OOA, MOA	HOA, BBOA, COA OOA1, OOA2
SIRTA	HOA, COA LV-OOA, SV-OOA, MOA	HOA, BBOA, COA OOA
GOLF	HOA OOA	HOA, BBOA OOA1, OOA2

Table 3~~2~~. Prediction skill metrics of PMCAMx against observed hourly data.

	Summer				Winter			
POA	LHVP	SIRTA	GOLF	Average	LHVP	SIRTA	GOLF	Average
Mean predicted (μg m^{-3})	0.3	0.15	0.2	0.2	2.2	1.4	1.7	1.8
Mean observed (μg m^{-3})	0.7	0.5	1.6	1	2.7	2.4	1.3	2.2
FERROR[1]	0.9	1	1.5	1.1	0.7	0.8	0.65	0.7
FBIAS[2]	-0.7	-0.9	-1.5	-1	-0.3	-0.6	0.2	-0.3
MAGE[3] (μg m^{-3})	0.4	0.4	1.4	0.8	1.7	1.5	1.1	1.4
MB[4] (μg m^{-3})	-0.3	-0.4	-1.4	-0.8	-0.5	-1	0.4	-0.4
OOA								
Mean predicted (μg m^{-3})	1.6	1.5	1.6	1.5	0.9	0.8	0.9	0.9
Mean observed (μg m^{-3})	1.7	1.2	1.5	1.4	3.2	3.3	3	3.2
FERROR	0.3	0.4	0.4	0.4	1.1	1.2	1.1	1.1
FBIAS	-0.05	0.2	0.02	0.05	-1.1	-1.1	-1	-1.1
MAGE (μg m^{-3})	0.4	0.5	0.5	0.5	2.3	2.5	2.1	2.3
MB (μg m^{-3})	-0.1	0.3	0.07	0.1	-2.3	-2.5	-2	-2.3
BC								
Mean predicted (μg m^{-3})	1.6	0.6	1	1	1.9	1.8	2.3	2.1
Mean observed (μg m^{-3})	1.3	0.65	1.1	1	1.4	0.9	2.1	1.8
FERROR	0.5	0.6	0.4	0.5	0.5	-	0.5	0.5
FBIAS	0.07	-0.2	-0.1	-0.1	0.2	-	0.02	0.1
MAGE (μg m^{-3})	0.9	0.4	0.5	0.6	1	-	1.2	1.1
MB (μg m^{-3})	0.3	-0.05	-0.05	0.05	0.5	-	0.2	0.3

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[1] $FERROR = \frac{2}{n}\sum_{i=1}^{n} \frac{|P_i - O_i|}{(P_i + O_i)}$, where P_i represents the model predicted value for data point i, O_i is the corresponding observed value and n is the total number of data points.

[2] $FBIAS = \frac{2}{n}\sum_{i=1}^{n} \frac{(P_i - O_i)}{(P_i + O_i)}$

[3] $MAGE = \frac{1}{n}\sum_{i=1}^{n} |P_i - O_i|$

[4] $MB = \frac{1}{n}\sum_{i=1}^{n} (P_i - O_i)$

Table 4. Prediction skill metrics of PMCAMx with the addition of COA against observed hourly data.

	Summer				Winter			
POA	LHVP	SIRTA	GOLF	Average	LHVP	SIRTA	GOLF	Average
Mean predicted (μg m^{-3})	0.7	0.3	0.6	0.6	3	1.7	2	2.3
Mean observed (μg m^{-3})	0.7	0.5	1.6	1	2.7	2.4	1.3	2.2
FERROR	0.6	0.8	0.9	0.7	0.6	0.7	0.7	0.7
FBIAS	0.05	-0.5	-0.8	-0.5	-0.01	-0.5	0.3	-0.1
MAGE (μg m^{-3})	0.4	0.3	1	0.6	2	1.5	1.3	1.6
MB (μg m^{-3})	0.05	-0.2	-1	-0.4	0.5	-0.8	0.8	0.1
OOA								
Mean predicted (μg m^{-3})	1.6	1.5	1.6	1.5	0.8	0.7	0.8	0.8
Mean observed (μg m^{-3})	1.7	1.2	1.5	1.4	3.2	3.3	3	3.2
FERROR	0.3	0.4	0.4	0.4	1.1	1.2	1.1	1.1
FBIAS	-0.05	0.1	0.02	0.05	-1.1	-1.1	-1	-1.1
MAGE (μg m^{-3})	0.5	0.5	0.5	0.5	2.3	2.6	2.1	2.3
MB (μg m^{-3})	-0.1	0.3	0.08	0.1	-2.3	-2.6	-2	-2.3

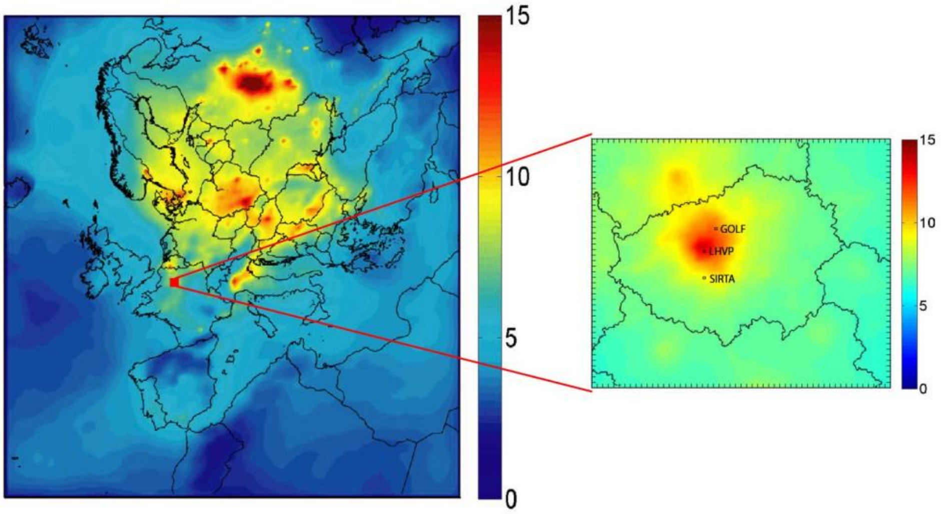


Figure 1. Modeling domain of PMCAMx for Europe. Also shown are the three measurement stations in the nested 4×4 km^2 subdomain of Paris. Color coding shows the predicted average ground concentrations (in μg m^{-3}) of PM_1 during winter 2010.

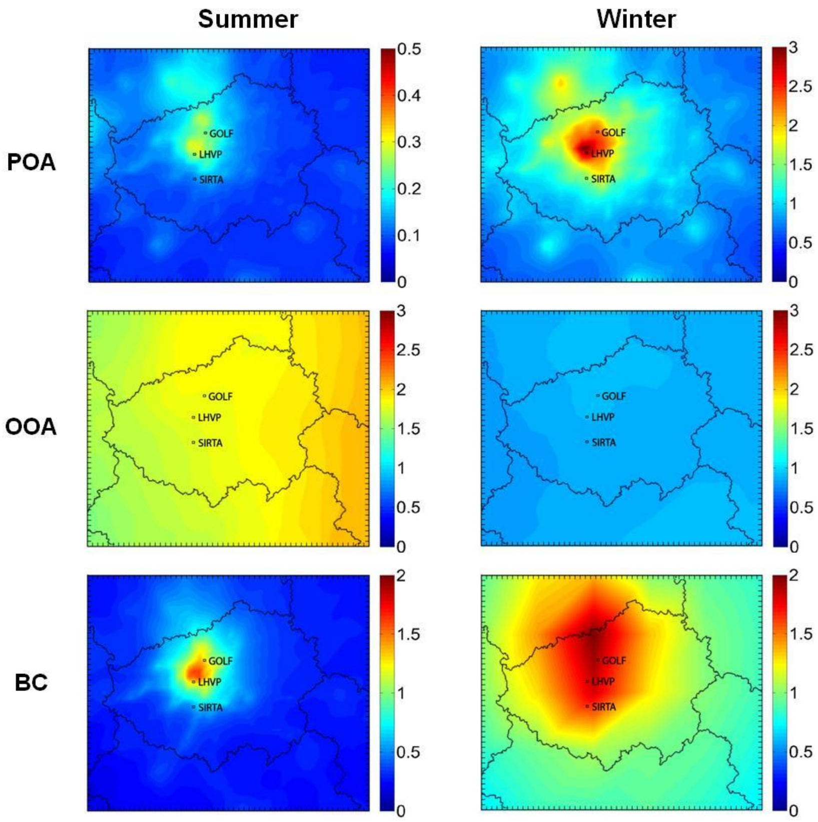
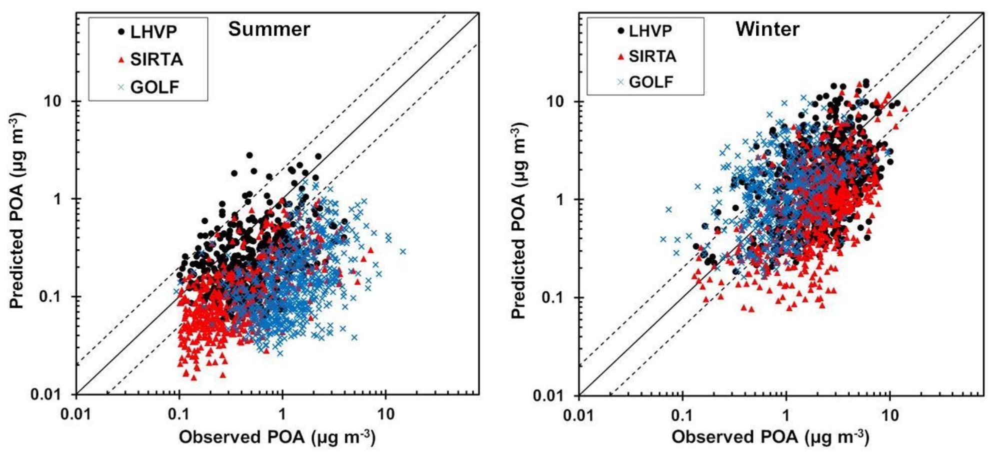


Figure 2. Predicted average ground concentrations (in μg m^{-3}) of fine fresh total POA, BC and OOA in the greater area of Paris during summer 2009 and winter 2010. Different scales are used.


LHVP
SIRTA
GOLF
Summer
Winter
Predicted POA (µg m^{-3})
Observed POA (µg m^{-3})
0.01
0.1
1
10

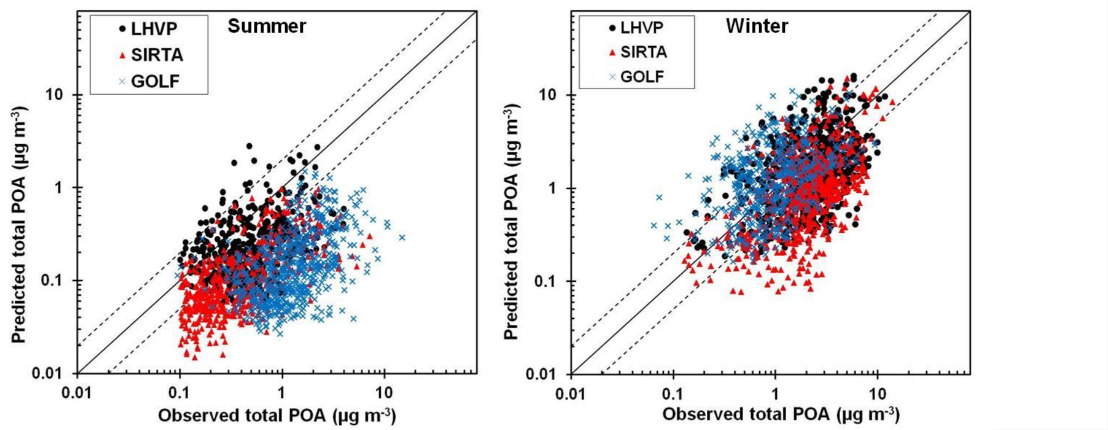

LHVP
SIRTA
GOLF
Summer
Winter
Predicted total POA (µg m^{-3})
Observed total POA (µg m^{-3})
0.01
0.1
1
10

Figure 3. Comparison of predicted vs. observed PM_1 total POA (μg m^{-3}) from the three measurement stations during the MEGAPOLI summer and winter campaigns. Each point is an hourly average value. Also shown are the 1:1, 2:1 and 1:2 lines. Observed data represent AMS factor-analysis results.

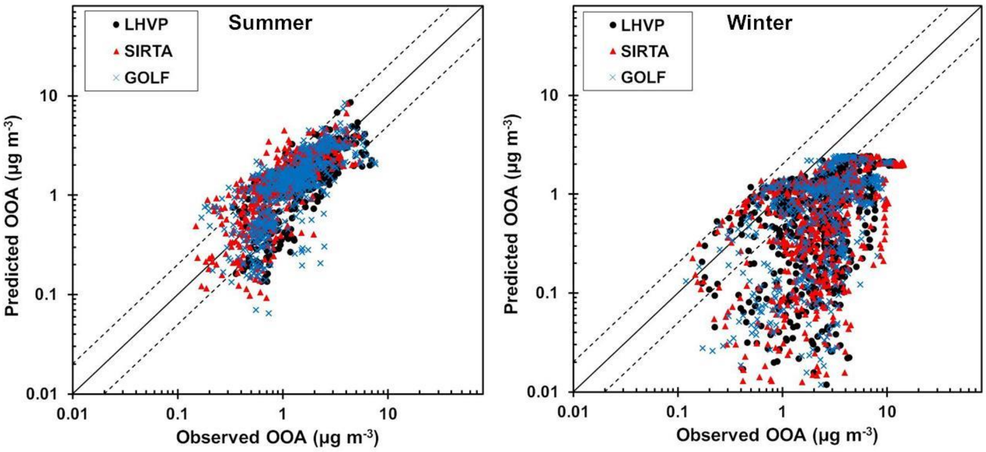


Figure 4. Comparison of predicted vs. observed PM_1 OOA (μg m^{-3}) from the three measurement stations during the MEGAPOLI summer and winter campaigns. Each point is an hourly average value. Also shown are the 1:1, 2:1 and 1:2 lines. Observed data represent AMS factor-analysis results.

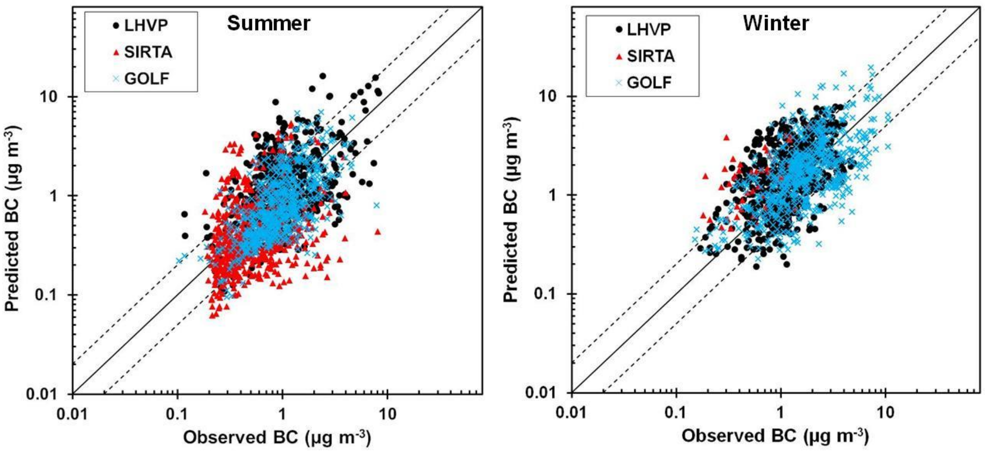
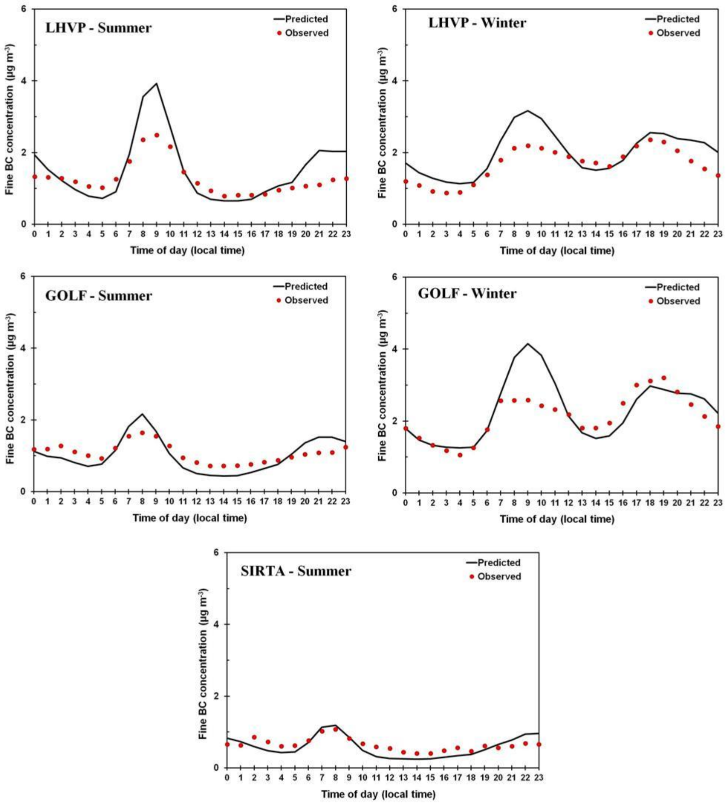


Figure 5. Comparison of predicted vs. observed fine BC (μg m^{-3}) from the three measurement stations during the MEGAPOLI summer and winter campaigns. Each point is an hourly average value with the exception of wintertime data at SIRTA where only 12-hour data were available. Also shown are the 1:1, 2:1 and 1:2 lines.


LHVP - Summer
LHVP - Winter
GOLF - Summer
GOLF - Winter
SIRTA - Summer
Predicted
Observed
Fine BC concentration (μg m^{-3})
Time of day (local time)
0
2
4
6
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23

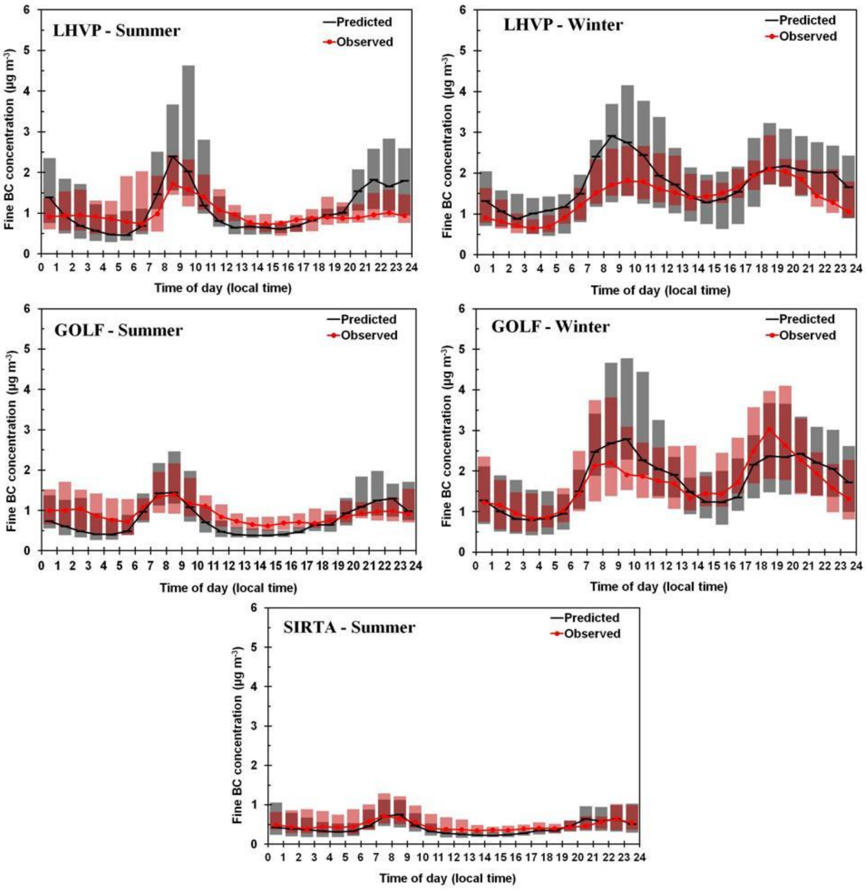


Figure 6. Average diurnal profiles of fine BC concentrations from the three measurement stations during the MEGAPOLI summer and winter campaigns. The shaded vertical bars indicate the 25th and 75th percentiles (gray color represents the predicted and pink the observed values).

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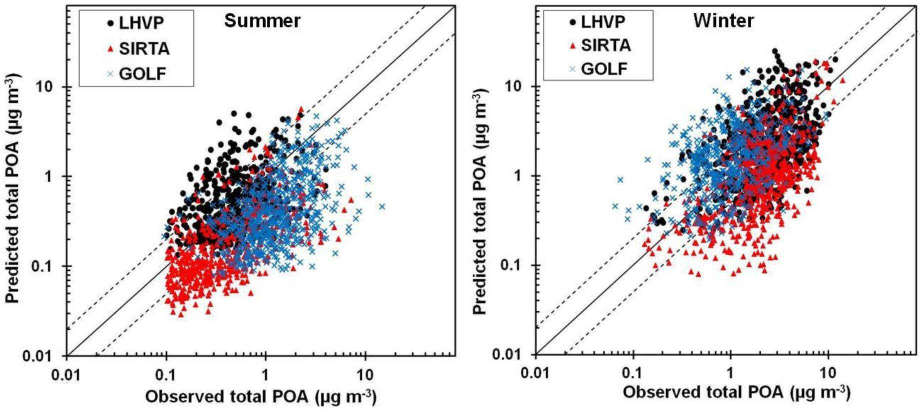

Figure 7. Comparison of predicted vs. observed PM_1 total POA (μg m^{-3}), including the added COA emissions, from the three measurement stations during the MEGAPOLI summer and winter campaigns. Each point is an hourly average value. Also shown are the 1:1, 2:1 and 1:2 lines. Observed data represent AMS factor-analysis results.

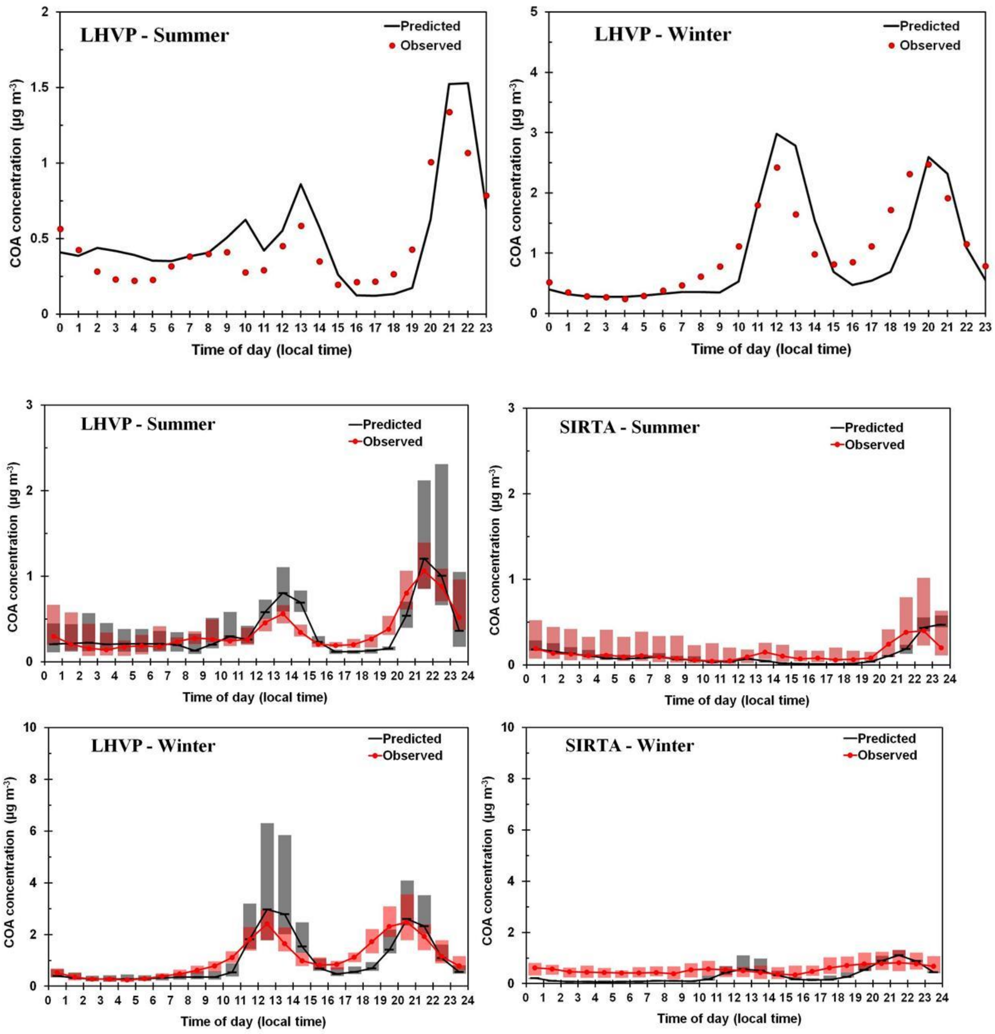

Figure 8~~7~~. Average diurnal profile of COA concentrations in LHVP and SIRTA during the MEGAPOLI summer and winter campaigns. The shaded vertical bars indicate the 25th and 75th percentiles (gray color represents the predicted and pink the observed values).