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Atmospheric
Chemistry
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Discussions

Interactive comment on "Aerosol chemical and optical properties over the Paris area within ESQUIF project" *by* A. Hodzic et al.

A. Hodzic et al.

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The authors are thankful to both reviewers for their work. According to their rapports, both reviewers are in favor of publication of this paper in Atmospheric Chemistry and Physics although they raise a number of important questions addressed in this revised version of the manuscript.

1 SPECIFIC ANSWER TO REVIEWER 2

General Comment: *This study evaluates the performance of the urban-scale chemistry-transport model CHIMERE in simulating aerosol pollution episodes over the Paris region using aerosol measurements taken during the ESQUIF project. Specifi-*

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cally, measurements taken during two intensive observation periods during July 2000 were used as the basis for model evaluation. The ability of the model to simulate aerosol mass, chemical composition, three-dimensional distribution, and optical properties was examined. While the study is fairly comprehensive, some details and explanations are lacking. Even though detailed description of the measurements and data set is already provided in published papers, more details should be included in this paper to make the paper more self-contained and easier to read. More model description is also needed. Some questions that arise from the evaluation still need to be addressed.

The additional description of the data set and model formulation has been provided in order to strengthen our arguments and to answer to following reviewer's questions:

Comment 1 and 4: *There is no mention of what instruments were used to measure particulate organic matter and BC. How was the hydrophilicity (mentioned in section 5.4) of the aerosol determined? Are the AIRPARIF sites the same as the ground sites mentioned in section 2.2? If not, what instrumentations were used for the AIRPARIF network to measure ozone, NOy, and PM10?*

A map indicating the locations of the AIRPARIF stations and the Saclay ground site is needed. How many of the AIRPARIF stations are urban and how many are rural? Figure 3 indicates that ozone concentrations are very similar for urban and rural stations. What is the definition of an urban and a rural site?

Answer 1 and 4: Further description of the instrumental set and data has been provided in this new version of the manuscript. In particular the AIRPARIF measurement network has been described. An additional figure (Figure 2) representing the location of ground-based measurement sites has also been added in the manuscript as well as the following explanations (section 2.2):

The carbonaceous aerosol fraction was collected using glass fiber filters (Chazette and Liousse, 2001 and references in there). The thermal method was

applied for the separation and analysis of black (BC) and organic (OC) carbon aerosol components.

In addition to the ESQUIF campaign measurements, the routine ground observations of O3, PM10 and NOY from the AIRPARIF network have been considered in this study. The location of measurement sites are displayed on Figure 2. The typology of the AIRPARIF stations (urban, rural, etc.) is based on the site location and environmental criteria according to the national classification of air quality monitoring sites.

It should also be noted that ‘rural AIRPARIF stations’ are representative of urban background pollution levels and not of the remote clean atmospheric conditions, which explains the relatively small differences observed between urban and rural sites.

Moreover, the hydrophilicity (mentioned in section 5.4) of the aerosol was not measured directly. It was determined according to the shape of the lidar extinction profile. The fact that the lidar-derived extinction profile displays the sharp maximum at the top of the PBL which is linked to aerosol size growth with increasing RH (Hänel, 1976), is a strong indication that for 31 July the aerosols are essentially hydrophilic.

It is now explained in section 5.4: **On the other hand, the increase of the observed BSR layer is associated with an increase of the relative humidity from 55% at the surface to 80% at the top of the PBL (Figure 4) and could be explained by the aerosol growth caused by the uptake of water. This provides a strong indication that the observed aerosol is hydrophilic both in the clean air mass (upwind) and in the plume (downwind).**

Comment 2: *Similarly, more details must be provided about the aerosol model. How was secondary organic aerosol modeled? How were the aerosol dynamics and size distributions modeled? What gas-phase precursors relevant to aerosols are included? What is the model time step?*

Answer 2: A detailed description of the aerosol model has been provided in the corrected version of the manuscript:

Secondary organic aerosols (SOA) are formed by condensation of biogenic and anthropogenic hydrocarbon oxidation products and partitioned between the aerosol and gas phase through partition coefficients (Pankow, 1994). Heterogeneous chemical processes onto particles and fog droplets (nitrate production) and a simplified sulphur aqueous chemistry (sulfate production) are accounted for in the model. The thermodynamic equilibrium is computed using the ISORROPIA model (Nenes et al., 1998).

The aerosol population is represented using a sectional approach, considering 6 size bins geometrically spaced from 10 nm to 40 μm diameter in the standard configuration. Dynamical processes influencing aerosol population are also taken into account. New particles are formed by nucleation of H2SO4 (Kulmala et al., 1998) and grow as a result of the coagulation and condensation of semi-volatile species on preexisting particles followed by the coagulation processes.

The model calculations are performed with 2.5 minute chemical and 10 minute physical time steps for the small scale domain.

Comment 3: *Figure 1 is difficult to read and is not fully explained. For the flight tracks, what is the difference between the yellow and the gray lines? What are the blue lines? Consider using a three-dimensional figure to better represent the altitude and direction of the flight tracks. A brief description of the flight plan should be provided so that Figures 5, 7, and 8 are easier to understand. It would also be helpful to label the upwind and downwind portions in Figures 5, 7, and 8.*

Answer 3: We agree that the Figure 1 is difficult to understand; therefore the new version of the manuscript includes a more complete description of the figure. We apologize for not being able to make a new 3D plot including the flight patterns, the aerosol ground concentrations and the wind fields. The following text has been added in order to facilitate better comprehension:

Figure 1: Modeled PM10 concentrations (μg/m3) and wind fields (vector at bottom right is 5 m/s) at the surface on 19 (left) and 31 (right) July 2000 at 15:00 UTC. Flight patterns and flight hours are also indicated. The gray and yellow lines refer to the flight altitude of 900 m above mean sea level (MSL) and 4200 m MSL, respectively. The aircraft crossed the center of the plume twice on 19 July at 13 and 15UTC, and once on 31 July at 14UTC (see text for details). The city of Paris, crossed by the Seine river (blue color), is represented in the center of the map.

In-situ measurements of meteorological parameters and pollutant concentrations were performed within the mixed layer (PBL) at the flight altitude in the range 800-1300 m (900 hPa, indicated in gray color on Fig. 1), while lidar measurements of the aerosol vertical distribution were performed at 4200 m (600 hPa, indicated in yellow color on Fig. 1) above sea level.

Comment 5: *On page 12 the papers states "A very specific traffic pattern is expected during the last days of July when lots of people start their vacations." Is this "very specific traffic pattern" considered in the emissions used in the simulations? How is this pattern different from the "normal" pattern?*

Answer 5: The emission patterns of the Paris region are largely determined by traffic emissions. Therefore accounting for the day type (weekday or weekend) in the emission inventories is essential as it conditions the space/time variation of emissions and ozone production. Weekdays (Monday to Friday) exhibit similar emissions characteristics as rush hour traffic patterns with spike in NOX emissions occurring in the early morning and in the late afternoon, while on weekends the NOX emissions are reduced and spread throughout the day. While these patterns are fairly well accounted for in the emission inventories, the large uncertainties remain in the daily emissions distribution during the holidays. The holidays (e.g. 14 July) and the holiday weekends (end of July and beginning of August) are generally associated with increased travel by automobiles throughout the day, which are not currently accounted for in the model. These uncertainties in the space/time variations of emissions can result in modeling errors in the simulated ozone concentrations. According to the study of Beaver et al., 2006 conducted in the San Francisco region (Beaver et al, “Cluster analysis of meteorological states to understand the weekend-weekday ozone response in the San Francisco, CA Bay Area”) the holidays present higher ozone levels than the weekdays or weekends.

This is now explained in the section 5.1 **A very specific traffic pattern is expected during the last days of July when large numbers of people start their vacations. According to the recent study of Beaver et al. (2006), holiday emission patterns are characterized by higher emissions spread throughout the day, which can result in higher ozone levels than the weekdays or weekends.**

Comment 6: *The definition of total particulate matter (TPM; section 5.3) is confusing. The model simulates aerosols up to 40 μm in geometric diameter while the ground measurements include aerosols up to 10 μm in aerodynamic diameter. Does the simulated TPM in Figure 9 include mass of aerosols up to 40μm or 10μm? Is density correction applied for conversion of geometric diameter to aerodynamic diameter?*

Answer 6: The observed total particulate matter (TPM) concentrations include aerosol total mass up to 10 μm in aerodynamic diameter. This measured aerosol total mass is compared with the simulated aerosol total mass including particles smaller than 10 μm in aerodynamic diameter. Indeed, in the model R1 simulation the aerosol size distribution is represented using 11 size bins geometrically spaced from 10 nm to 20 μm in diameter. The aerosol particles are assumed spherical and each size section is characterized by its aerodynamic mean diameter. Therefore, the measured and observed aerosol concentrations used in this comparison are consistent as they are both given in aerodynamic diameters.

Comment 7: *Top of page 18 states that ignoring primary sulfate emissions is a possible* *reason for the negative bias, on the order of 30-60%, of the model in predicting aerosol sulfate mass. This is unlikely; 2% of the SO2 emissions is very small compared to secondary sulfate that is eventually formed downwind of emissions. Other factors are involved in the negative bias.*

Answer 7: We agree that the reasons for the model underestimation of sulfate concentrations are not clearly stated. The underestimation of sulfate concentrations by 30-60% by the end of July could be mainly attributed to the inefficient homogeneous sulfate production that prevails during dry anticyclonic conditions.

This is now explained in a more comprehensive way:

In the second period, from 21 to 26 July, the model tends to underestimate the observed sulfate concentrations by about 30-60% during both day and night time. This model negative bias is consistent with results obtained at different European sites (Bessagnet et al. 2004) and reveals that sulfate chemistry is difficult to simulate. The most likely reason is that the homogeneous sulfate production which prevails during dry anticyclonic conditions is too slow in the model. Moreover, an additional reason for the model negative bias could also be the absence of the primary sulfate emissions (Cousin et al., 2005 and references in there).

Comment 8: *The text in section 5.3.3 and the caption and labeling of Figure 12(b) are confusing. In Figure 12(b), are the plotted "Measurements" concentrations of POM or 85% of POM?*

Answer 8: We agree that the labeling of Figure 12 (b) is wrong. The plotted "Measurements" of organic matter account only for the secondary organic aerosol fraction (called SOA) in order to be directly comparable with model simulations. The 'observed SOA fraction' has been retrieved from the total aerosol organic matter POM based on the Lonati et al., (2005) results.

The caption of Figure 12 (b) is corrected as follow: **Figure 12: Daytime(D) and night-**

time(N) mean total (a) and secondary organic (b) aerosol concentrations (μg/m3) observed (black) and simulated (white) at Saclay site from 19 to 26 July. Bars indicate minimal and maximal values simulated over 9 grid cells surrounding Saclay station. The observed secondary organic fraction has been estimated from the total organic matter according to the SOA/POM=0.85 ratio reported by Lonati et al., 2005.

Comment 9: *How are the results (meteorological variables, ozone and NOy concentrations, and aerosol distributions) different between the R1 and R2 simulations? More specifically, does the vertical resolution of the model affect the results of meteorological variables and location of the plumes? How does aerosol bin resolution affect aerosol predictions?*

For this answer, please see the additional figure file.

Answer 9: In this study two simulations have been performed as described in section 3.2: the first simulation (R1), devoted to the assessment of the aerosol chemical composition at the ground, includes 8 vertical levels and 11 size bins, while the second simulation (R2), used for the comparison with airborne measurements, includes 20 vertical levels and 6 aerosol size bins. Thus, the R2 simulation is used to evaluate the model performances in simulating the meteorological and chemical variables along flight trajectories, as well as the plume transport and aerosol vertical distribution.

The impact of the vertical resolution on meteorological variables can be seen in Figures 1 (see additional figure file) and 2 which display vertical profiles of wind speed, relative humidity and potential temperature. The high resolution simulation gives more accurate results for model upper layers above 1.5 km of altitude, but the differences stay within 5-10%. Within the boundary layer and especially near the ground, the two simulations provide comparable results. This confirms that the low vertical resolution simulation (R1) is accurate enough to be used for the comparisons with ground observations. Along flight trajectories the comparison with the observations is not significantly affected by the model vertical resolution. The differences are low (<5% for ozone and NOx and 10% for RH, wind and pressure) and occurs mainly for high-altitude flight legs (4000m). Moreover, Figure 3 shows that the ozone plume position and intensity are not very sensitive to the model vertical resolution in our case study.

In addition, the comparison between R1 and R2 simulations shows that the aerosol bin resolution does not affect significantly the aerosol total mass and it composition. However, the mass size distribution of aerosol inorganic components (Figure 4) is changed, as the mean diameter of each size bin is modified. Since the results of this last comparison on the aerosol size distribution do not bring valuable information we have chosen not to discuss them in the manuscript.

The following comments have been included in the manuscript:

In section 3.2.Model simulations: **Therefore, the R1 simulation is evaluated against ground-based data, while the R2 simulation is used for the comparison with airborne observations as it is expected to be more accurate in higher altitudes.**

In section 5.2. Plume location and characteristics: **The comparison (not shown here) between the R1 and the R2 model runs indicates that the model results are not significantly affected by the model vertical resolution during the study period. The simulated meteorological variables and pollutant concentrations vary less than 5% within and 10% above the boundary layer.**

Comment 10: *What is the uncertainty in the lidar-derived AOT arising from assuming constant backscattering-to-extinction ratio and refractive index? How much variability is in the calculated refractive index using Mie theory and accounting for aerosol composition and relative humidity?*

Answer 10: The lidar-derived AOT was calculated from lidar backscattering profiles assuming constant backscattering-to-extinction ratio and refractive index. The lidar inversion procedure is described in Chazette et al., 2005. The aerosol refractive index was calculated to be (1.5 ± 0.05) - i (0.016 ± 0.0125) at 670 nm based on available AERONET data over the entire month of July 2000. The standard deviations, associated to the mean values of the refractive index, reflect the temporal variability of the aerosol properties and the error on the retrieved parameters. The backscattering-to-extinction ratio values retrieved through Mie theory give values between 0.013 and 0.018 sr-1 and are in good agreement with the Sun photometers observations. According to the results reported in Chazette et al., 2005, the mean relative error for the extinction coefficient is less than 10% when the inversion of lidar profiles is constrained using a Sun photometer and when the relative humidity stays lower than 75%, as is the case here. The different sources of uncertainty are well described by Chazette et al. (1995).

This is now better explained in the manuscript (section 5.5 Aerosol optical properties):

The lidar-derived aerosol optical thickness (AOT) and backscattering vertical profiles are compared with corresponding model-simulated optical parameters along flight legs. As described in Chazette et al. (2005), the lidar-derived AOT is calculated from lidar backscattering profiles at 532 nm using lidar inversion method and assuming constant backscattering-to-extinction ratio (0.014 sr-1), refractive index (m=1.5-0.016i) and Angstrom exponent (2.1). According to the results reported in Chazette et al., 2005, the mean relative error for the extinction coefficient is less than 10% when the inversion of lidar profiles is constrained using a Sun photometer and when the relative humidity stays lower than 75%, as is the case here.

In the model, the aerosol optical thickness is calculated using the Mie-theory extinction coefficients depending on the aerosol refractive indexes and their hygroscopic properties. For the comparison of AOT levels, the refractive index was fixed to m=1.5-0.016i to be coherent with observations, while for the comparison of the aerosol vertical distribution the refractive index depends on the aerosol composition and relative humidity (Hänel, 1976). The variability in the calculated refractive index using Mie theory and accounting for aerosol composition and relative humidity was calculated to be (1.49 ± 0.009) - i (0.06 ± 0.01) at 532 nm for 31 July over Paris region.

This is now better explained in the manuscript (section 5.5 Aerosol optical properties):

For the comparison of AOT levels, the refractive index is fixed to m=1.5-0.016i to be coherent with observations, as in Chazette et al. (2005), while for the comparison of the aerosol vertical distribution the refractive index depends on the aerosol composition and relative humidity (Hänel, 1976). The variability in the calculated refractive index using Mie theory and accounting for aerosol composition and relative humidity was calculated to be m=(1.49 ± 0.009) - i (0.06 ± 0.01) at 532 nm for 31 July over Paris region, which is in good agreement with the observations.

Comment 11: *In Figure 16(a), there is peak in aerosol backscattering ratio at altitude 1.5 km and latitude 48.7N. This location is upwind of urban Paris for this date and this peak is not simulated by the model (Figure 16(b)). To a lesser extend, this peak is also seen it the lidar-derived AOTs as shown in Figures 14 and 15. What is the reason for this peak in the lidar measurement and why is this peak not seen in the model?*

Answer 11: The two-dimensional lidar-derived aerosol backscatter ratio shown in Figure 16b and aerosol optical thickness shown in Figure 14 indicates an increase of the aerosol optical extinction between the southern and the northern parts of the Paris region: the optical thickness at 532 nm varies from 0.12 at 45 km south of Paris, over the countryside, to 0.16 over Orly, 15 km south of Paris, up to 0.26, 40 km north of Paris. The region mentioned by the referee (48.7N and 2.4E), located upwind of urban Paris, corresponds to the Orly airport. It displays higher aerosol optical thicknesses than the background area which are not reproduced by the model. The model underestimation of the aerosol optical extinction over the Orly airport on 31 July suggests that the aerosol load over this region is underestimated. The reason for this model discrepancy is the lack of specific holiday traffic patterns in the model emissions which occur during the last days of July when lots of people start their vacations. This results in an increase of the flight traffic that could be responsible for higher aerosol concentrations.

The following text has been added in the section 5.5. Aerosol optical properties: **Moreover, the higher AOT values (0.15-0.2) observed 15 km upwind of urban Paris over the Orly airport are also underestimated by the model. This model deficiency could be caused by the lack of specific holiday traffic patterns in the model emissions already mentioned in section 5.1.**

Comment 12: *Section 5.5 ("Other aerosol properties") should be moved to before section 5.4 ("Aerosol optical properties").*

Answer 12: Section 5.5 ("Other aerosol properties") has been moved to section 5.4 and renamed to "Aerosol size distribution and number concentrations"

Comment 13: *Clearly, the model does not predict aerosol size distribution well. The reason for this is not explained thoroughly in the paper. What are the initial and boundary conditions for aerosol size distributions? Are they unimodal, bimodal, or trimodal? Wrong initialization can easily lead to wrong results. A strong possibility, as mentioned in the paper, is that more and smaller size bins are needed to limit numerical diffusion. The model includes aerosols up to 20 μm in diameter. Given that there are negligible aerosol mass and number above 10 μm in diameter, more size bins should be used in the smaller diameter range.*

Answer 13: We agree that the model does not predict correctly the aerosol size distribution observed during the campaign. Simulated mass distributions are unimodal and much wider than the observed ones. Here, we present the most likely reasons for such model behavior. (i) As suggested by the referee one of the possible reasons can be the initial and boundary conditions for aerosol size distribution. However, we do not believe that this is the main reason that explains the model/observation discrepancies since aerosol boundary conditions are multimodal. Indeed, the species available from GOCART are: mineral dust, hydrophobic and hydrophilic organic carbon (OC), hydrophobic and hydrophilic black carbon (BC), and sulfates. For dust, GOCART provides a 7-bin representation from 0.2 to 12 um in diameter. For sulfate and carbonaceous species, we assume a classical distribution from Seinfeld and Pandis, (1998). These spectral distributions proper to GOCART are interpolated to the CHIMERE aerosol size distribution. Moreover, the primary aerosol emissions are lognormally distributed in 3 modes characterized by the mean diameter and the sigma dispersion parameter (D(1)=0.1 um, sigma(1)=1.6 ; D(2)=05 um, sigma(2)=1.4 ; D(3)=25 um, sigma(3)=1.4).

(ii) More likely reason for the model deficiency is the numerical diffusion in transsectional transport (absorption) already mentioned in the manuscript. It acts to smooth gradients in the mass distribution and could be responsible for the model's wide distribution. Higher resolution in the aerosol size distribution (more aerosol sections) limits the numerical diffusion, however it does not lead to a bimodal aerosol distribution. The lack of the coarse-mode aerosols in model simulations is mainly due to the missing aerosol heterogeneous formation processes. The presence of a significant amount of calcium in the observations confirms the possible heterogeneous formation of coarse nitrate as calcium nitrate which is not accounted for in the model. The investigation of the role of such a process is addressed in our recent work (Hodzic et al. 2006).

This is now explained in the new version of the manuscript:

Finally, other ions such as calcium and sodium are also observed in the coarse mode with respective mean diameters in the ranges 3-5 μm and 2-3 μm. The presence of a significant amount of calcium confirms the possible heterogeneous formation of coarse nitrate as calcium nitrate previously discussed. The results reported in our recent study (Hodzic et al., 2006) show that the introduction of the heterogeneous formation of coarse nitrate onto dust particles in the model increases considerably coarse nitrate concentrations of 0.5-2 μg/m3 during the ESQUIF study period (see Fig. 6 in Hodzic et al., 2006) and leads to a bimodal aerosol distribution.

Section 3.1.Model configuration:

The GOCART model provides a spectral size distribution for mineral dust, hydrophobic and hydrophilic organic carbon (OC), hydrophobic and hydrophilic black carbon (BC), and sulfate particles ranging from 0.2 to 12 μm in diameter which is interpolated to the CHIMERE aerosol size representation.

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