

Review of ACPD-9-12207-12281-2009 by Hodzic et al., entitled: «Modeling organic aerosols during MILAGRO: application of the CHIMERE model and importance of biogenic secondary organic aerosols».

The authors would like to thank referee #2 for his thoughtful comments and additions to the review.

Responses to Referee #2

R2.0) This paper presents an interesting study which demonstrates the capabilities and weakness of an air quality model when applied to the extremely difficult problem of organic aerosol. The paper does have a number of weaknesses, as discussed by referee #1, and below. On the other hand, the paper is unusual in presenting comparisons for a number of pollutants and meteorological drivers, and for consideration of emissions uncertainties, and the authors are to be commended for doing a thorough job in this respect (too many papers discuss just OA, and one never knows if the model is capable of reproducing other pollutants, or if the emissions are just plain wrong).

A2.0) We thank the reviewer for the overall positive evaluation of our paper.

The more substantial problems are:

R2.1) The authors find that anthropogenic and biomass burning emissions are ‘reasonably captured’, since their modeled POA match the measured HOA reasonably well. It can be argued that this agreement is a bad sign, since Robinson et al. (2007) and others have suggested that the ‘emissions’ of POA will quickly evaporate on dilution. This problem is not mentioned at all in the text, and needs to be discussed.

A2.1) Unlike some emission inventories in the US, the emissions inventory for Mexico City appear to be consistent with the POA emissions AFTER initial dilution and evaporation of a substantial fraction of the initial POA. This has been discussed by Tsimpidi et al. (2009). Robinson et al. (2007) show that 3/4 to 4/5 of the undiluted POA from a diesel engine and woodsmoke evaporates upon dilution from levels of several 1000 $\mu\text{g m}^{-3}$ to ambient levels of 10 $\mu\text{g m}^{-3}$. However once that initial evaporation has taken place, additional evaporation and condensation in response to ambient temperature and concentration variations is smaller, see e.g. Huffman et al. (2009) who show that about 10% of the HOA evaporates in Mexico City when heated to 40C. Similar comparisons of modeled POA vs. measured HOA as those presented in this paper have been obtained with the same POA inventory by Fast et al. (2009) and Tsimpidi et al. (2009). If we allowed 3/4 to 4/5 of the POA in the MCMA inventory to evaporate, the POA concentrations would be underpredicted by a large factor.

We recognize the potential importance of semivolatile and intermediate volatility species, however examining their impact on the predictions of SOA for Mexico City is beyond the scope of the present (already very long) manuscript. We are preparing an additional paper where these emissions and their processing and impact on SOA are simulated.

We have added the following text to the paper to address this point (see page 12246, line 18): « Besides aromatic and biogenic precursors, there is reason to believe that semivolatile POA and intermediate volatility species (IVOCs) emitted along with it contribute greatly to the formation of SOA. A recent box-model study by Dzepina et al. (2009), suggested that these primary species could be responsible for about 50% of the observed SOA within Mexico-City for a local-SOA dominated case study during the MCMA-2003 field project. Tsimpidi et al. (2009) showed a contribution of these compounds of ~25% of the total SOA mass for a different time period during MCMA-2003, and partially due to using a more aggressive “aging” mechanism for traditional SOA which increased its relative fraction. The influence of this mechanism for the MILAGRO field project will be examined in a future publication. However, it should be mentioned that accounting for the volatility distribution of POA and its chemistry is not expected to significantly influence the predicted POA mass in Mexico City because the POA emissions inventory is consistent with the aerosol fraction that is left after the primary semivolatile organic vapors have evaporated (Tsimpidi et al., 2009). »

R2.2) The methodology introduced in section 5.5 to compare column integrated SOA seems flawed to me. The authors simply multiply observed ground-level SOA (OOA) by the PBL depth, assuming a uniform concentration. This makes no sense to me, since there will obviously be variations in the vertical concentration, and anyway there are large uncertainties with even the observed PBL depth. Indeed, p12216 says that these uncertainties amount to several 100m. I cannot understand how the proposed methodology is an improvement over the use of excess CO for example.

A2.2) We strongly disagree with the reviewer on this point. The boundary layer in Mexico City is strongly convective during the day and vertical mixing will reduce the gradients in pollutant concentrations. This is observed in vertical profiles of OA measured from the aircraft such as in DeCarlo et al. (2008). At night our approach will most likely overestimate the PBL-integrated concentration, but the point of this section is to show that the integrated concentrations are much larger in the middle of the day, so the night/day contrast if anything is underestimated by our approach. The point of this figure is to make clear the night/day contrast in total column mass, which is huge but is not apparent in the surface concentrations. Although admittedly there is some error introduced in this simple calculation, we can't think of any other way to illustrate this very important point.

Also, the point we are trying to make with these figures is different from the typical use of ratios of pollutants to excess CO. Those ratios are useful to normalize for dilution, but they do not help to illustrate the total mass of a pollutant in the atmospheric column, which is the point of our graph.

R2.3) The authors use a low-NO_x parameterization of isoprene. This seems like a bad choice for the Mexico plume. Surely the high-NO_x schemes for isoprene would have been more suitable?

A2.3) In the model isoprene SOA is formed over coastal areas where NO_x is low, and then advected over the MCMA as already explained in the paper (section 5.4). Isoprene SOA formed directly over the MCMA is dominated by the NO₃ mechanism, and the SOA formed by the low-NO_x mechanism over the city is very small. Therefore, a low-NO_x parameterization of isoprene is the appropriate choice for simulating biogenic SOA in Central Mexico region.

R2.4) The discussion of isoprene, with the back-of-the-envelope calculation given on p12240, confused me. Doesn't the coarser scale-run of the model cover the domain shown in Fig. 1, cover all the relevant distance scales? Why the discussion of 150km transport?

A2.4) Yes, the model does cover the appropriate processes and domain. The point of this simple calculation is to show in the simplest possible way that the amount of isoprene emitted in the vicinity of Mexico City is large and thus it can credibly produce enough SOA to affect concentrations in the city. We assume that SOA produced from isoprene within a 150km radius around Mexico City is likely to be advected into the city given the 5-7 days lifetime of the particle and the low wind meteorological conditions. This is explained in the paper p. 12240:

« Even though the lifetime of isoprene is relatively short (~1-2 hours), SOA formed from these precursors has a much longer lifetime (~5-7 days) and can be long-range transported to Mexico City from the Southwest and the Gulf of Mexico under the influence of the regional winds contributing therefore to the SOA regional background levels. An order-of-magnitude estimate of the regional contribution of isoprene to SOA background concentrations is presented here to evaluate the potential importance of this source. Given a relatively low wind speed during this period, we assume that isoprene emitted within a 150km radius around Mexico City can influence the regional SOA formation and reach the basin. »

R2.5) I agree with Ref #1 that when plots are given as an average over all stations, many difficulties (or good performances!) can be hidden. Given that the focus of this paper is on the OA results from just a few stations, I would have preferred to see comparisons of the modeled O₃, NO₂, etc. for these (T0, T1) stations. The "all-station" plots could be relegated to the supplementary material as background information on overall model performance.

A2.5) We have added the comparisons for gas-phase species at T0 and T1 to Supp Info. We prefer to retain the domain-wide analysis in the main paper figures because it provides a more valuable assessment of the model's ability to reproduce not only the temporal variability of concentrations (i.e. during the day, and day-to-day), but also the spatial distribution of pollutants within the basin. Anthropogenic emissions are

heterogeneously distributed within the city (e.g. different densities and traffic volumes of roads, industrial vs. residential areas, parks, etc) and meteorological dispersion plays a key role in determining the pollutant concentrations, and showing that the model with its coarse resolution (5x5km²) is capable of simulating the overall spatial features is very important. In addition, the RAMA routine monitoring network provides a much larger sample of measurements, with hourly reported and quality-checked data, that are more suitable to statistically evaluate the model. This evaluation will be less rigorous if we only used gas-phase data from T0 and T1. Finally, we disagree with the fact that the model 'good' or 'bad' performance is hidden in a statistical comparison with RAMA sites. Model performance is clearly reflected in statistical indicators such as the bias, root mean square, and the correlation coefficient. The following text has been added to reference the new figures in the paper: «The model evaluation for gaseous pollutants has also been performed separately for T0 and T1 intensive measurement sites, and the results can be found in SI-Figure 3 and SI-Figure 4. The model performance at these two sites is consistent with the results reported for the ensemble of the RAMA stations with e.g. the model bias for Ox below 5% and the correlation coefficient ranging from 0.66 and 0.73.»

R2.6) I would also have brought the Figures on OH and OOA into the main text - they are directly relevant for the discussions of the T0, T1 data-sets, and it is rather unusual to have the possibility of checking the OH from a model.

A2.6) We have moved the OH figure to the main text as Figure 9. We kept the OOA plot in the supplementary material.

R2.7) Finally, it would help the reader to have a table of emissions for both the fine and course domains, putting the various anthropogenic and biogenic sources in context.

A2.7) A table has been added to the Supplementary Information (see SI-Table 1).

Smaller comments:

R2.8) The discussion frequently mixes SOA and OOA terms for observations. Although the concepts are similar, the AMS measures OOA.

A2.8): We have revised the manuscript to use the term “OOA” when we are referring only to the measurements and “SOA” otherwise. When we are discussing the model-measurement comparisons it would be too confusing to keep referring to OOA and SOA, and the paper already noted that OOA is used as an SOA surrogate.

R2.9) p12209, line 17. The Dockery et al reference is now 15 years old - find something more recent if the evidence is indeed ‘growing’!

A2.9) We have replaced this classic reference with Pope and Dockery (2006).

Pope CA, Dockery DW, Health effects of fine particulate air pollution: Lines that connect. Journal of the Air and Waste Management Association, 56 (6), pages: 709-742, 2006.

R2.10) p12209, line 23. 'most of which' is water soluble - be more specific, is this 51% or 99%?

A2.10) This fraction varies depending on the study. Kondo et al. (2007) report that "Approximately $88 \pm 29\%$ of OOA was found to be water soluble on the basis of the comparison of the WSOC concentrations with those of oxygenated organic carbon (OOC) derived from the AMS data". The water soluble fraction of OOA for the Docherty et al. study is also in the range 80-90%. However other studies such as Favez et al. (GRL 2008) report larger fraction of insoluble SOA at certain locations and times. Due to the very few quantitative comparisons between OOC and WSOC, we prefer to retain the qualifier "most" here.

R2.11) p12210, line 14. Total OA mass can't be measured by AMS; only the fine fraction.

A2.11) The text has been corrected: «The latter technique has high time and size resolution and allows some characterization of the sources and types of species that make up the fine aerosol mass through factor analysis of the organic spectrum (Zhang et al., 2005ab). In particular surrogates of POA and SOA and several subtypes of each have been identified in multiple studies using this technique (e.g. Zhang et al. 2005ab, 2007; Lanz et al., 2007; Nemitz et al., 2008; Ulbrich et al., 2009).»

R2.12) p12211 and elsewhere. The Hallquist review article is 2009, not 2008 for ACPD. Also, this paper is now accepted for publication in ACP. This paper also contain some more recent references for aspects (e.g. aqueous processes) discussed from line 25 onwards.

A2.12) This reference has been updated. We also added a more recent reference for the aqueous processes.

R2.13) p12212, re Song et al. (2007). The authors remarks are correct as such, but the Song study only applies to very fresh POA. Any aging will quickly allow partitioning to POA.

A2.13) The statement from the reviewer is indeed a plausible hypothesis, but it is not backed up by any reference, and to our knowledge the details of SOA partitioning into realistic POA (activity coefficients) are still unknown. In any case the statement regarding the Song results is given as part of the introduction in which several recent developments about SOA formation are listed. In our study we have allowed the partitioning of SOA into a well-mixed POA+SOA phase as discussed on section 3.2.2 (p. 12219-12220 of the ACPD version). This is a conservative assumption which will

maximize the amount of SOA produced. To more clearly present these points in the manuscript we have modified that text to read:

“A recent chamber study by Song et al. (2007) suggests that SOA formation from biogenic compounds is insensitive to the presence of POA surrogates, although the applicability of those results to real POA is under investigation.”

R2.14) p12212, Lines 16. I would also say that OA measurements have suffered from the lack of chemical speciation, or of marker info (14C, etc.)

A2.14) We have modified the text to address this point as follows:

“Modeling of organic aerosols had suffered for a long time from the limited availability of ambient OA measurements (including speciation and tracers) due to the high cost, low sensitivity, and low time and size resolution of most OA measurement methods until recently (McMurry et al., 2000).”

R2.15) p12213. The Hildemann et al ref is missing from the reference list

A2.15) This reference has been added.

R2.16) p12213, lines 23 onwards. It would be good to put this small BSOA contribution in the context of results from other cities. Is Mexico city unique, or typical?

A2.16) Formation potential for secondary organic aerosol (BSOA) from biogenic sources is considerable worldwide given the dominance of BVOCs of the global budget of VOC emissions. That is in particularly the case in the tropics where biogenic emissions (Guenther et al., 1995, 2000) and concentrations of hydroxyl radicals are at their maximum (de Gouw and Jimenez, 2009). The small BSOA contribution in Mexico City reported in some previous studies (e.g. Volkamer et al., 2006; Dzepina et al., 2009) was due to the focus on periods dominated by SOA formation from urban emissions, while other studies (e.g. Tsimpidi et al., 2009) have used a small domain and thus have included regional SOA in their boundary conditions. We have shown in this paper that advected BSOA makes a non-negligible contribution to the background SOA of the Mexico City region, although its contribution to the SOA formed directly over Mexico City is very small in agreement with previous studies.

BSOA is commonly found through the world. 14C analysis have shown that 30–70% of organic carbon in aerosols in Europe (Szidat et al., 2004) and in the US (Lemire et al., 2002) is from modern carbon. Recent modeling studies (Tsikaridis and Kanakidou, 2007; Bessagnet et al. 2009) predict the dominance of the biogenic SOA fraction over continental Europe, although these conclusions may be affected by the underprediction of anthropogenic SOA which is not observed for biogenic SOA as discussed above.

We have updated the manuscript to read:

«However, substantial fractions (30–70%) of modern carbon have been reported in Europe (Szidat et al., 2004) and in the US (Hildemann et al., 1994; Lemire et al., 2002), which suggest an important biogenic contribution to the SOA production. However modern carbon also encompasses biomass burning POA and SOA (which may be strongly underestimated by models, e.g. Grieshop et al., 2009), some urban sources (Hildemann et al., 1994), as well as the possible influence of “hot” sources (Vay et al., 2009), so it is not possible to attribute all of the measured modern carbon in aerosols to biogenic SOA. Inside Mexico City city the formation of biogenic SOA is reported to be small, e.g. in a box-model framework Volkamer et al. (2006) report that isoprene and terpenes contribute less than 5% to the total VOC-OH reactivity while Dzepina et al. (2009) report that those species account for ~2% of the SOA predicted to form from these biogenic precursors inside the city. Their estimates were however of BSOA formed within the city (for a particular day characterized by very low regional background SOA) and do not preclude a potentially higher regional contribution to advected SOA during other periods. A more significant contribution of BSOA would be expected this tropical region where biogenic emissions (Guenther et al., 1995) and concentrations of hydroxyl radicals are at their maximum.»

R2.17) p12215. Give a brief indication (in % terms) of the level of agreement of AMS instruments and what "were consistent" means.

A2.17) This text has been revised as follows to address this point:

“Detailed analyses and intercomparisons of the AMS and related data are reported in separate publications (Aiken et al., 2008, 2009a, b; Herndon et al., 2008; Paredes-Miranda et al., 2008; Zheng et al., 2008; de Gouw et al., 2009; Huffman et al., 2009). The T0 AMS + refractory measurements (Aiken et al., 2009a) showed overall composition, diurnal cycles, and size distributions that were similar to those from previous data collected at another urban site during the MCMA-2003 campaign (Salcedo et al., 2006). Aiken et al. (2009a) and Paredes-Miranda et al. (2009) present intercomparisons which are consistent with the accuracy of +/-25%.”

R2.18) p12218, line 20, explain acronym ‘TBO’.

A.2.18) TPO is a surrogate used to design Octimene and Myrcene biogenic SOA precursors. This is explained in the paper on p12218:

«The gas-phase chemistry (oxidation by OH, O₃ and NO₃) of four biogenic SOA surrogates are considered in this study including α -pinene and sabinene (APIN); β -pinene and δ^3 -carene (BPIN); limonene (LIM); ocimene and myrcene (TPO).»

R2.19) p12219, line 16. Here the authors state that most SOA is not very hydrophilic. How is this consistent with the earlier statement that ‘most’ SOA is water soluble?

A2.19) Despite the appearances, the two statements are consistent as they refer to the partitioning of the organic species in water under levels of dilution that differ by about

six orders-of-magnitude. The statement on p12219 refers to the ability of the semivolatile SVOC species to dissolve in the aerosol water phase according to Henry's law. Given the limited amount of water in the aerosol phase (typically of the order of the aerosol concentrations of the other constituents) only a minor fraction of these SVOCs partitions to the water phase. In contrast, the statement about on p12209 about water solubility refers to the empirical definition of WSOC in which the OC is dissolved into a very large amount of water, reaching concentrations of the order of 100 parts-per-billion of the mass (R. Weber, pers. comm.). At such high dilution, many species that are only weakly soluble can still be fully dissolved. This topic has been discussed in some recent papers (e.g. Ervens et al., JGR, 2007; Clarke et al., JGR 2007; Cubison et al., ACP 2008). To reduce confusion about this topic we have modified the text on p12209 as follows:

“OA is composed of both primarily emitted compounds such as hydrocarbons and fatty acids, and also of chemically processed organic material (i.e. SOA) most of which is operationally-defined as water soluble under high-dilution (Kondo et al., 2007; Docherty et al., 2008) although it is generally not very hygroscopic (e.g. Ervens et al., 2007; Clarke et al., 2007; Cubison et al., 2008).”

R2.20) p12219, line 23. Why was NO₂ chosen as the model for OA deposition? Wesely's scheme has several organic species which would seem more similar in character.

R2.21) We used the same dry deposition parameters as in Bessagnet et al. (2009). Dry deposition for organic species is largely uncharacterized, and we have chosen a low deposition velocity similar to NO₂, in order to obtain a lower limit for the losses by deposition and thus an upper limit of SOA formation. We have clarified this in the paper text as follows:

“In this work we assume that all gaseous semi-volatile organic species undergo dry deposition based on Wesely (1989). As the deposition velocities for these species have not yet been determined, deposition velocities have been calculated similar to NO₂. The actual deposition velocities of the semivolatile and at least somewhat polar species that partition to SOA are likely to be larger than that of NO₂, however this assumption provides a conservative upper limit of the amount of SOA that the model can produce. Consideration of dry deposition with the NO₂ deposition velocity is expected to lower the predicted SOA concentrations by 10-20% with respect to a run in which dry deposition was ignored (Bessagnet et al., 2009).”

R2.21) p12221, The model setup described here suggests a nesting ratio of 7:1 was used. The normal recommended procedure for MM5 is 3:1. Why wasn't an intermediate nest used?

A2.21) The nested grids allow any integer spatial (DXcoarse / DXfine) refinement of the parent coarse grid in both MM5 and WRF models. But, the reviewer is right, often the ratio of 3:1 is being used for the MM5 nests. However, that is not mandatory. What seems to be more important is to have an odd (not even) ratio between the parent and nested domains, so 5:1 and 7:1 are perfectly reasonable nest ratios. The reason why an

odd ratio is preferred is because the model uses a grid staggering (Arakawa-B for MM5) meaning that horizontal wind components are normal to the facets of the grid cell, and that the other variables (i.e. mass, thermodynamic, chemistry) are calculated in the center of the cell. The choice of the nesting ratio will indeed define the way the fine grid will be overlapped on top of the coarse grid. For ALL odd ratios there is a spatial coincident point for each variable between the two grids: the middle fine-grid cell coincides with the coarse grid for all of the mass-staggered fields. Besides, (i) the MM5 model has already been used in this 7:1 ratio configuration for numerous studies that we have performed in the past, (ii) the MM5 model results reasonably well reproduce the meteorological parameters during this period, and finally (iii) our results are consistent with the WRF model meteorological results reported by Fast et al. (2009).

R2.22) p12222, I was amused to see a blog given as a reference, but the website did indeed contain proper data and descriptions. Still, I wonder how long-lived such a reference can be. Is there no other document which can be referred to?

A2.22) We agree that it would be more appropriate to have a more official web site or document, but to our knowledge those do not exist as of now.

R2.23) p12223. What about emissions of CO?

A2.23) CO emissions are provided by the 2002 Mexican emission inventory for the urban area and NEI emission inventory for the regional Mexico City area, as indicated on p12222. The contribution of the biogenic emissions to gas-phase CO is expected to be small in the Mexico City area.

R2.24) p12244 says that the comparison highlights the need for more complex parameterizations for air quality models. I don't see how adding complexity to a system where one doesn't know the basics can improve things?

A2.24) We agree that this sentence can be confusing, and we clarified it:

«This comparison once again highlights the limitations of the traditional SOA formation approach, and the need for more realistic SOA parameterizations for air quality models that can account for e.g. the multi-generational oxidation of gaseous precursors and chemical processing of SOA within the particle.»

R2.25) p12227. The model has some problems with the wind-field. This is likely inevitable, but I wonder how well MM5 captures surface features of the Mexico-city urban area - was any investigation made of the sensitivity to z0 for example?

A2.25) We have not made sensitivity tests to characterize the model sensitivity to the surface roughness. This might change the surface wind speed somewhat, but not the direction. This type of test is beyond the scope of the paper. Other groups are doing specific meteorological studies that incorporate urban canopy parameterizations.

R2.26) p12230, line 12. Don't say 'correctly simulated', use 'adequately simulated' or simulated reasonably well. I never expect to see a 'correct' simulation from a model!

A2.26) The text has been updated as suggested by the reviewer.

R2.27) p12247, line 4. I would remove the reference to the Hodzic et al. (2009) ACPD paper unless it really makes it to ACPD within the life-cycle of the current manuscript. Who knows what will be accepted for ACPD?

A2.27) We have removed the citation as suggested by the reviewer.

R2.28) p12248, Conclusions:

a) I didn't understand conclusion (1). How can a slight underestimate of PBL height give weaker dispersion?

a) We have replaced "dispersion" with "dilution" which hopefully clarifies this point.

b) Conclusion (II) is too vague - quantify.

b) This conclusion has been modified to read:

«The statistical comparison using the RAMA monitoring network (>20 stations) reveals an overall agreement between measured and simulated gas-species during the study period of March 2006. In particular, a small positive bias of 1.1 ppb and correlation coefficient of 0.78 between observed and predicted concentrations of oxidant Ox show the model ability to predict ozone chemistry.»

c) Conclusion (III) is also vague - avoid words like "reasonably reproduced", "no significant bias" ... give the numbers.

c) We have modified the text as follows:

« Observed concentrations of primary organic aerosols are reasonably reproduced by the model throughout the day (e.g. bias less than 15% at T0 and T1) indicating that there is no significant bias in aerosol primary emissions related to anthropogenic activities and biomass burning. POA peak values during the intense biomass burning periods (11, 18 and 21 March) are underpredicted by a factor of 2, most likely due to model coarse resolution (5x5km²). Our modeling results on POA are consistent with a previous study (Fast et al., 2009) that also simulated the MILAGRO period with the same emissions and also considered POA as non-volatile.»

d) Conclusion (V). The modeled BSOA is part of the base-model simulation, so what is that reduces the model overall bias?

d) Biogenic SOA are not part of the base-model simulation (ANT-T). Here we are referring to the reduction in the model bias between the ANT-T and BIO-T runs. We have modified this sentence as follows for clarification:

“Modeled SOA concentrations during nighttime are dominated by biogenics, with predicted BSOA levels close to 2 $\mu\text{g}/\text{m}^3$, reducing the model overall bias by 20% at all sites compared to the ANT-T case which does not include biogenic SOA.”

e) Conclusion (XI). Ref #1 has more to say on this, but when saying that "we have identified one of the important missing processes", then let the reader know which one. This is conclusion XI, so quite a few processes have been discussed already.

e) We have clarified this conclusion as follows:

«Obtaining perfect agreement with the observed SOA values is extremely challenging, and it is beyond the objectives of this paper, because of large uncertainties involved at every step of the SOA modeling. We have shown the importance of biogenic precursors in the formation of SOA in this region, but there are many more areas of uncertainty and directions for improvement to be considered, such as the formation of SOA from S/IVOCs (Robinson et al., 2007), in clouds (Lim et al., 2005), by reactions in the aerosol water phase (Volkamer et al., 2009), etc.»

R2.29) Table 2. very confusing.... why are so many different parameters given - they are all related. Use consistent parameters! Also, give references for the values used.

A2.29) In this table we were combining different data sources and had reported each on the original parameters. However we have simplified Table 2 to only provide the saturation concentration ($\mu\text{g m}^{-3}$).

R2.30) Table 4 is very small. Also, the equation for RMSE should have the $1/N$ outside the root sign.

A2.30) We will ask the production office to make this table bigger in the ACP paper. Also, we use the NCAR Command Language (NCL) function to calculate the root-mean-square difference between observations and the model, and $1/N$ is in the root sign as written in the paper.

R2.31) Fig. 1 - show where the small domain fits into the larger domain.

A2.31) We have chosen not to overlap the fine-size domain on Fig1b in order to keep this plot less cluttered. The location of the Mexico City is already indicated on this plot, as well as the topography, so we feel that adding a $2.8^\circ \times 2.5^\circ$ box around Mexico City will be too much information. However, we added the following sentence the caption of the Figure 1 to indicate the extent of the nested domain:

« The small-scale domain extends from 101.1°W to 98.3°W and 18.6°N to 21.1°N, and is embedded into the coarse-scale domain. »

R2.32) Figures - general. Why is the solid line used for the model results? This suggests an over-confidence in the model compared to the measurements.

A2.32): The solid line is being used for the model because generally the model provides continuous outputs for chemical variables while measurements usually provide discontinuous time series as it can be seen on the plot 6 of our paper. Therefore, having dots to represent measured quantities helps more clearly identify the temporal gaps in the measured time series. This is an arbitrary choice, commonly used in the modeling community that does not have anything to do with the overconfidence in the modeling results. If we were overconfident in the model, we wouldn't be comparing it with the observations. A full line is now being used for the new Figure 10 since this is an arbitrary choice.