Reply to Anonymous Referee #2

We thank the reviewer for the careful reading of the manuscript and helpful comments. We have revised the manuscript following the suggestion, as described below.

(1) There have been some other recent papers in ACP (Hozdic et al. and Tsimpidi et al, both cited in the paper) that also apply this non-traditional SOA model to Mexico City. The paper needs to clearly state what it is doing differently than those previous papers (different episode, different component of model, etc). It also needs to more directly compare the conclusions of these different papers with its conclusions. My sense is that the predictions here are pretty similar to Hozdic, but not as similar to Tsimpidi which attributed less SOA to the non-traditional SVOC and IVOC precursors. Highlighting the similarities and differences between this and previous attempts to use these models to simulate OA in Mexico City would help the community start to focus in on the strengths and uncertainties of the new approach.

We have included a paragraph about the comparison of the present study with Hozdic et al. (2010) and Tsimpidi et al. (2010) as follows:
"*Hozdic et al. (2010) applied a CTM to estimate the contribution of SOA of POG and IVOC during MILAGRO 2006. In their SOA model, the condensable oxidation products from both anthropogenic and biogenic precursors are lumped into 9 groups of surrogate compounds according to their physico-chemical properties, and the mechanisms suggested by Robinson et al. (2007) and Grieshop et al. (2009) were used to simulate the SOA formation from POG and IVOC. Hozdic et al. (2010) found that the predicted production from anthropogenic and biomass burning POG and IVOC represents 40-60% of the total measured SOA at the surface in the one-month simulation from March 1 to 31, 2006 in and around Mexico City. In the present study, the predicted SOA from POG and IVOC by the mechanism of Robinson et al. (2007) represents about 22% of the observation in the urban area of Mexico City, less than those in Hozdic et al. (2010). Tsimpidi et al. (2010) performed about one-week OA simulation during April 2003 in the MCMA by using the volatility basis-set approach, in which both primary and secondary organic components are assumed to be semivolatile and photochemically reactive and are distributed in logarithmically spaced volatility bins. They have attributed less SOA to the non-traditional SVOC and IVOC precursors.*"

(2) Definitions – A challenge in this paper is that the NT-SOA model that blurs the traditional definitions of SOA and POA which can create confusion. At points my head was swimming with acronyms and terms, not sure what they mean (SVOC, IVOC, POA, POG, OPOG, etc) plus all the acronyms for the cases. Examples of problems include – "POA" appears to refer to the primary organic particles and to the combination of the primary SVOC vapors and particles. The also paper uses the term anthropogenic precursors to refer to both traditional anthropogenic precursors and the new SVOC and IVOC precursors. There are other examples of definitional problems (POG ,OPOG). A reader who is not intimately familiar with the approach is likely to be very confused. The paper needs to precisely define the different parameters and clearly describe how these concepts related to terms used in other papers (e.g. Hzodic, Tsimpidi, Shrivastava, etc). Getting the terms and definitions straightened out is a

key need in this area.

We have clearly defined the terms and acronyms we have used in the manuscript and also added a table in the Supplementary Information (SI) section about the detailed definitions (Table SI-1).

(3) Sections 2.2.1 and 2.2.2: A major different between the two model is that different yields are used for the traditional SOA precursors (e.g. pg 23957 says "updated based on laboratory results from recent smog-chamber" for NT-SOA model). That difference needs to be clearly stated. How different are those yields than those in the T2-SOA model. Please provide a table in the supplemental information with the stoichiometric yield coefficients and the rate constants for the different lumped species used in both models (NT-SOA and T2-SOA) for the traditional SOA precursors. For the NT-SOA what are yields for low and high NOx and how do you branch between. In addition, to providing the yield data (stoichiometric coefficients and rates) in a table, the authors need to provide a plot of yield curves in the supplemental material comparing the parameterizations for the traditional SOA would be very helpful. In addition, one could also simply say at a COA of 10 µg/m3 the yield of the NT-SOA model for some precursor is some multiple of the T2-SOA model in the main text to emphasize this issue here.

We have added the SI as suggested. In the SI, we have included the paragraph about the SOA yields on Pages 3-4:

"*In the present study, we have used two approaches to investigate the SOA formation based on the SAPRC 99 chemical mechanism. Nine SAPRC surrogate VOCs are considered as the SOA precursors. These lumped compounds are listed in the Table SI-2, with the reactions to form the SVOCs and the rate constants. The T2-SOA model employs a traditional 2-product method to predict the SOA production from VOCs. The mass-based stoichiometric yield coefficients, the effective saturation concentrations, and molecular weight of SVOCs at 298 K are listed in Table SI-3. In the NT-SOA model, the SOA formation from the oxidation of VOCs is predicted using four SOA species whose effective saturation concentrations at 298 K are 1, 10, 100, and 1000 µg* m^{-3}*, respectively, instead of the traditional 2-product parameterization. In addition, the SOA yield from VOCs is* NO_x*-dependent. The high-*NO_x *and low-*NO_x *yields are listed in the Table SI-4. For the SOA yield branching from high-*NO_x *and low-*NO_x *conditions, we first calculate the loss rate of RO2 radicals due to their reactions with NO and* NO_3 *(defined as* LR_N*), and the loss rate of RO2 radicals due to self reactions and their reactions with peroxy radicals (defined as* LR_O*). If the high-*NO_x *yield is* α_{high} *and the low-*NO_x *yield is* α_{low}*, the SOA yield* α *is calculated as:*

$$\alpha = \alpha_{high}\frac{LR_N}{LR_N + LR_O} + \alpha_{low}\frac{LR_O}{LR_N + LR_O} \qquad (4)$$

Figure SI-1 shows the variation of the SOA mass yield from toluene (major component of ARO1 in SAPRC 99) with the total organic aerosol concentration (C_{OA}*) in the T2-SOA and NT-SOA models under high* NO_x *conditions. The SOA mass yield used in the NT-SOA model is higher than that in the T2-SOA model and when COA is equal to 10 µg* m^{-3}*, the SOA mass* *yield used in the NT-SOA model is about 4 times of that in the T2-SOA model. Detailed discussions can be found in Hildebrandt et al. (2009).*"

(4) Page 29358: "The total amount of material (POA+SVOC+IVOC) introduced in the NTSOA model is 7.5 times of the particle phase POA emissions." This is presumably about modifying inventories. This needs to be greatly expanded. A factor of 7.5 is much larger than what was used in the original Robinson et al. (2007) Science paper. It is also much larger than the range of cases consider in Shrivastava et al. 2008. JGR paper. What is the basis for the 7.5. Are there any data that support using this or was it chosen because it made the POA calculations basically work. In addition what volatility distribution was used for the primary emissions? What is the particle phase POA emissions? This needs to be at least a paragraph, and presumably a short section since inventories are a key issue for the NT-SOA approach. Note that there is some description of the inventories for more traditional species in section 2.3. This should be pulled together. Have the earlier studies that have applied the NT-SOA model to Mexico City also used a factor of 7.5. It seems like this is a critical uncertainty. I was surprised that it was not considered in the sensitivity studies. The paper would be greatly improved if there was sensitivity runs done with this parameter.

We have added a paragraph in the SI on Pages 4-5 about the modification of the POA emission for the NT-SOA model.

"*The MCMA 2006 official emission inventory is used in the simulations and the POA emissions are modified and distributed by volatility based on dilution experiments for the non-traditional SOA model to account for the primary organic emissions (Tsimpidi et al., 2010). The primary organic emissions must include the emitted primary organic aerosols before their dilution in the atmosphere. However, the current POA emission inventory as described above is based on ambient measurements at an urban site; according to the volatility theory, part of the emitted POA has already evaporated and is excluded in the official emission fluxes. Laboratory experiments, in which diesel exhaust and wood smoke emissions were measured at different levels of dilution, have demonstrated that the measured primary organic aerosols in ambient conditions represent 15-40% of the primary organic aerosol actually emitted, depending on the ambient organic aerosol concentration and temperature (Lipsky and Robinson, 2006). Thermal denuder measurements in Mexico City during MILAGRO (Huffman et al., 2009a; Dzepina et al., 2009) have also shown that POA in Mexico City is semivolatile. The average concentration of the organic aerosols in Mexico City was in the range of 20* $\mu g/m^3$ *during the MCMA-2003 campaign (Salcedo et al., 2006). In this range of organic aerosol ambient concentrations, the measured organic particle material is approximately one third of the total emitted organic aerosols (Figure 1a of Robinson et al., 2007). Therefore, in order to estimate the total semivolatile organic emissions, the OA particulate inventory is multiplied by a factor of 3. Source test data for wood combustion, gasoline vehicles and diesel vehicles which used a sample train of quartz filters in combination with denuders and/or bents (Schauer et al., 1999, 2001, 2002) has shown that the mass of unmeasured IVOC vapors is between 0.25 to 2.8 times the existing primary OA emissions. In the present study, the OA emissions were distributed by volatility (Table 4) using the volatility distributions of Shrivastava et al. (2008). This distribution was* *derived by fitting gas particle partitioning data for diesel exhaust and wood smoke assuming that the mass of unmeasured IVOC emissions is equivalent to 1.5 times the primary organic aerosol emissions. The total amount of material (POA+SVOC+IVOC) introduced in the model is 7.5 times the particle-phase POA emissions, which is similar to the factor calculated from partitioning theory and ambient data by Dzepina et al. (2009). Several studies about OA simulations in Mexico City have been used the method to modify the POA emissions suitable for the non-traditional SOA model (Dzepina et al., 2009; Tsimpidi et al., 2010; Hodzic et al., 2010)*".

Tsimpidi et al. (2010) have evaluated the sensitivity of SOA simulations to the volatility distribution of the POA emissions. Please see (8) below about the discussions.

(5) Comments on Section 3.1.2 I was surprised the paper only compared predictions to the PMF factor. The paper should at least have some comparison (before comparing to the factors) about how well it does reproducing the overall OA. Note that total OA profile is shown in Figure 16, but is never really discussed in the paper. A lot of the discussion in section 3.1.2 related to diurnal profiles, which are eventually shown in Figure 11 (etc). It is very hard to see things like two peaks in long time series such as the ones shown in Figure 4. The paper should move Figure 11 up much sooner and discuss it in section 3.1.2 (one can wait on discussing he sensitivity results later in the paper). It would be good to get that figure earlier.

We have added the total OA comparisons and discussions in Section 3.1.2 and the following sections:
In Section 3.1.2: "*Figures 4a and 4b show the comparison of modeled and observed total organic aerosol (TOA) diurnal profiles at T0 and T1, respectively. In general, the T2-SOA model substantially underestimates the observed TOA at T0 during daytime, with the NMB of -31% and IOA of 0.62. The NT-SOA model improves the daytime TOA simulations at T0, particularly during rush hours and, compared to the T2-SOA model, the NMB and IOA are increased to -10% and 0.82, respectively. The underestimation of TOA in the T2-SOA and NT-SOA models are rather large at T1 compared to measurements, particularly during daytime and in the two models, the NMB and IOA are about -50% and 0.50, respectively. One of the possible reasons for the TOA underestimation at T1 is that the POA emissions in the present study do not include the contribution from biomass burning. Although the biomass burning is less important during the simulation period with convections, it still plays a role in the suburban area, such as trash burning, which is less impacted by the convective precipitation.* "

In Section 3.1.2: "*Figure 5 shows the diurnal cycles of observed and simulated TOA, POA, and SOA concentrations at T0 and T1 averaged over the simulation period. The T2-SOA and NT-SOA models both underestimates the observed TOA at T1, producing about only half of the observations. At T0, the T2-SOA model underestimates the observed TOA during daytime, and although the NT-SOA model improves the TOA simulations, the underestimation of TOA is still large between 10:00 and 16:00 LT.*"

In Section 3.2.3: "*As shown in Figure 9a and 9b, the NT2-SOA model improves the TOA simulations compared to the NT-SOA model at T0 and T1, but the underestimation at T1 is still large.*"

In Section 3.2.4: "*The NT2E-SOA model reproduces the observed TOA concentrations generally well at T0, with the IOA of 0.88. Although the NT2E-SOA model yields more TOA mass than the NTE-SOA model at T1, it still underestimates the observed TOA substantially.*"

In Section 4: "*The traditional SOA model generally significantly underestimates the TOA concentrations in the urban area during daytime and in the suburban area entirely. The IOAs in the urban and suburban area are 0.46 and 0.62, respectively. The non-traditional SOA model improves the TOA simulations, particularly in the urban area with the IOA of over 0.82, but still underestimates in the suburban area.*"

We have also moved Figure 11 (now Figure 5) in section 3.1.2 and discussions:
"*Figure 5 shows the diurnal cycles of observed and simulated TOA, POA, and SOA concentrations at T0 and T1 averaged over the simulation period. The T2-SOA and NT-SOA models both underestimates the observed TOA at T1, producing about only half of the observed value. At T0, the T2-SOA model underestimates the observed TOA during daytime, and although the NT-SOA model improves the TOA simulations, the underestimation of TOA is still large between 10:00 and 16:00 LT. At T1, the T2-SOA model substantially underestimates the observed POA concentrations during rush hours but overestimates in the rest of the day. The NT- SOA models predict less POA mass compared to the T2-SOA model during rush hours but successfully produce the observations in the remaining time. In addition, the T2-SOA model fails to yield the high level of the observed SOA mass during daytime. The NT-SOA models improve the SOA simulations in the afternoon, but still underestimate the observation, which is plausibly caused by missing background SOA transport and we plan to investigate further. At T0, the T2-SOA and NT-SOA models show good performance in simulating the POA diurnal cycles, but the modeled POA concentrations in the NT-SOA models are more consistent with the observations than those from the T2-SOA model during rush hours and daytime. The NT-SOA model still substantially underestimates the observed SOA concentrations between 08:00 and 16:00 LT, which is plausibly attributed to the conditions used in simulations, such as meteorological fields, boundary conditions, emissions, OH treatment, aging of SVOC and IVOC, etc. One of the most important factors dominating the performance of air quality models is the simulation of meteorological fields. However, according to the O_3 and CO simulations (Figures 2 and 3), the WRF-CHEM model generally performs well in simulating the plume formation and movement during daytime, indicating the reasonable simulations of meteorological fields. In the following sections, we will discuss the uncertainties except from meteorological fields in the SOA simulations.*"

(6) Page 29363 "Although an updated 2006 MCMA inventory has been utilized in this study, our POA simulations are comparable to those reported by Hodzic et al. (2009) and Fast et al. (2009) when the POA is considered as non-volatile." Presumably this is true because you

bumped up the POA emissions by a factor of 7.5 in this paper. I.e. if you didn't increase emissions a lot of POA would have evaporated and the comparisons with the non-volatile model would not look so good. These issues need to be discussed and they tie back closely to what you are doing with the inventory.

We have only modified and distributed the POA emissions by volatility based on dilution experiments for the non-traditional SOA model. For the traditional model with the assumption of non-volatile POA, the POA emissions used in the present study is similar to those in Fast et al. (2009) and Hodzic et al. (2009), but we have used an updated version for 2006. We have modified the sentence to avoid confusion as follows: "*Although an updated 2006 MCMA emissions inventory has been utilized in this study, our POA simulations **in the T2-SOA model** are comparable to those reported by Hodzic et al. (2009) and Fast et al. (2009) when the POA is considered as non-volatile.*"

(7) "The SOA production from anthropogenic precursors is increased by 33% in the NT- SOA model compared to the T2-SOA model, indicating the high formation of SOA from anthropogenic aromatics in the NT-SOA model" Presumably this is because you are using different (and higher) yields than in the T2-SOA model. This needs to be pointed out as the explanation for this change. Since you are using different yields than it is not necessarily a fair comparison. Presumably a second factor of partitioning, in that the NT-SOA forms more OA than the T2-SOA model so even if the yield curves were the same the amount of SVOC in the condensed phase would be higher in the NT model.

We have removed "indicating the high formation of SOA from anthropogenic aromatics in the NT-SOA model" and also added sentences as follows: "*The SOA production from the oxidation of anthropogenic VOCs is increased by 33% in the NT-SOA model compared to the T2-SOA model, and contributes 36% of the predicted SOA concentrations during the six-day simulation period. Compared to the T2-SOA model, the higher SOA mass yield from anthropogenic aromatics in the NT-SOA model is the main reason for the higher SOA formation. In Figure SI-1, the SOA mass yield from toluene used in the NT-SOA model is about 4 times of that in the T2-SOA model when the total mass concentration of OA is 10 μg* m^{-3}*. In addition, in terms of the gas-phase partitioning, the NT-SOA model produces more OA than the T2-SOA model, therefore even if the yield curves were the same, the amount of SVOC in the condensed phase would be higher in the NT-SOA model.*"

(8) Section 3.2.1 – Seems like a big uncertainty that is not considered is uncertainty in emissions of IVOC/SVOC.

We have added a brief discussion about the uncertainty in emissions of IVOC/SVOC from Timspidi et al. (2010): "*It is worthy to note that the distribution of POA emissions in the NT-SOA model might also constitute a critical uncertainty for the SOA simulations. Tsimpidi et al. (2010) have examined the sensitivity of SOA simulations to the volatility distribution of the POA emissions, which is the same as in the preset study (Table SI-5). In a low volatility case, where the emissions in the low volatility bins (*C^**:* 10^{-2}*–*10^{2} *μg* m^{-3}*) are doubled and the* *emissions in the high volatility bins are set to zero, they found that the predicted SOA is increased by 0.5 μg m*$^{-3}$ *compared with the base case. The doubled emissions of the IVOCs in the high volatility bins (*C^**: *10^4*–*10^6* μg m*$^{-3}$*) also result in 0.5 μg m*$^{-3}$ *SOA more than that in the base case.*"

(9) Page 23970 "NT2-SOA model generally produces less POA mass than the NT-SOA model at T0 and T1, especially during nighttime and rush hours, which is caused by the decrease of the enthalpy of vaporization of POG in the NT2-SOA model." I do not understand this. You are using Clausius Clapeyron to describe T dependence of C*? The Greishop formulation has lower delta hvaps so should have lower temperature sensitivity.

Yes, we have used the Clausius-Clapeyron equation to describe T dependence of C^* (Please see Equation (3) in SI). We have added the following explanation: "*When the temperature is the same, the lower enthalpy of vaporization of POG results in the higher effective saturation concentration of POG and further is not favorable for the condensation of POG to form POA in the NT2-SOA model, compared to the NT-SOA model.*"

(10) Page 29376 – "The underestimations of SOA concentrations are principally caused by the OH treatment, emissions, aging of the SOA from anthropogenic precursors, and boundary conditions." What about aging of SVOC and IVOC? That mechanism is very uncertain.

We have changed the sentence as suggested: "*The agreement of the simulated SOA with observations can be improved by changing the OH treatment, emissions, aging of SVOC and IVOC, and boundary conditions. Other factors, such as SOA formation pathways, or precursors which one simply has not accounted for, could cause the majority of the underestimation.*"

(11) Table 1 – Please also provide the same statistical measures for performance for O3 and CO so that the reader can directly compare how the model does at these sites against these pollutants in addition to SOA. Also adding statistics for total OA (in addition to those for POA and SOA).

We have added the statistical measures for performance for O_3, CO, and total OA in Table 1.

(12) This paper has 16 Figures. That seems like too many. For example, Figures 8 and 10 seem somewhat duplicative with Figure 4. Maybe just show figure 4 with total time series for the two base cases and then use the average diurnal patterns (e.g. Figure 11)? I thought Figure 11 was more useful in assessing model performance and should be discussed more prominently and earlier in the paper. Figures 11-16 are different version of average diurnal profiles. Many of these are only briefly discussed in the text. It seems like combining these all of the OA (POA and SOA) into one multi-panel figure would help the reader get a quick overall sense of how the model performs for different cases.

We have moved Figure 11 (now Figure 5) to Section 3.2.1. Figures 8 and 10 (now Figures 9 and 11) show the average diurnal patterns. We have also combined Figure 15 and 16 (now Figure 15).

Minor comments

(13) Example of definitional problem – page 29356 "the oxidation of six primary organic gases (POG)" these are traditional SOA precursors. However on at bottom of page 29357 POG refers to the IVOC and SVOC vapors associated with the POA. Maybe POG is used for all primary organic gases, but this should be clarified. The paper then starts to discuss OPOG … A reader not very familiar with this approach will likely be very confused.

We have changed "the oxidation of six primary organic gases (POG)" to "the oxidation of six lumped organic species". We have also provided the definition for OPOG: "*OPOG represents the oxidized POG*". In addition, we have added a table about the detailed definitions of the terms and acronyms used in the study in SI (Table SI-1).

(14) Page 23957 line 22 "In the base case, we assume that the organic condensable gases (OCG) produced from the oxidation of anthropogenic and biogenic VOCs do not react further with OH radicals to reduce the volatility. Tsimpidi et al. (2010) and Murphy and Pandis (2009) have assumed that these first generation products continue to react and age. The importance of this anthropogenic SOA aging process will be explored in a sensitivity test in a subsequent section." This is out of place and belongs in the description of the treatment of traditional SOA (previous paragraph) and not the SVOC/IVOC SOA.

We have moved the paragraph to the description of the treatment of traditional SOA (previous paragraph) as suggested.

(15) "The simulated organic aerosols in the WRF-CHEM model are compared with the AMS data analyzed using PMF at T0 and T1 (Aiken et al., 2009)." The paper should add one short paragraph summarizing what that analysis found for the period in question. OOA was X, HOA was Y, and BBOA was Z, etc.

We have added a short paragraph: "*During the simulation period at T0, the observed mean OOA concentration was 8.1 µg* m^{-3}*; the HOA concentration was 5.8 µg* m^{-3}*; and the BBOA concentrations was 0.60 µg* m^{-3}*. At T1, the observed mean OOA concentration was 0.90 µg* m^{-3}*; the HOA concentration was 4.8; and the BBOA concentration was 1.2 µg* m^{-3}*.*"

(16) Page 29362 –"The good agreement between the long-lived predicted CO and the corresponding measurements" there is only good agreement during the day? How well does the model reproduce the spatial variability of the CO?

We have included the CO distribution plots in Figure 2 and the following discussions: "*The spatial distributions of calculated and observed near-surface concentrations of CO at 14:00 and 17:00 are also shown in Figures 2c and 2d, respectively. The WRF-CHEM model* *performs well in simulating the CO distribution compared with the measurements at the RAMA monitoring sites.*"

(17) Page 29364 "the saturation of the POG due to evaporation of POA" I don't understand the word saturation?

We have changed "the saturation of the POG due to evaporation of POA" to "*the condensation of the POG due to evaporation of POA*".

(18) Page 29364 – "With the significant decrease of POA emissions at T1, the NT-SOA model produces less POA than the T2-SOA model because most of the emitted POA evaporates to keep the saturation of the POG in the NT-SOA model." Decrease in POA emissions? But you increased them by a factor of 7.5? There are also some definitional issues here. You are using POA to presumably refer to both the primary organic particles and the SVOC vapors? What is saturation of the POG?

We have rephrased the sentence as follows: "*With the significant decrease of the OA emissions at T1 compared to T0, the NT-SOA model produces less POA than the T2-SOA model because the emitted POA tends to evaporate to keep the gas-particle partitioning in the NT-SOA model.*"

(19) Page 29366 – "anthropogenic precursors" this is another example of problems with definitions. Are anthropogenic precursors the traditional VOC precursors (e.g. single ring aromatic) or do they also include IVOC and SVOCs in the NT model. My sense is that the term is used different ways in different places. This needs to be made consistent.

We have changed "the anthropogenic precursors" to "*the oxidation of anthropogenic VOCs*".

(20) Page 23957 line 1 – the "traditional" SOA formation … note that you have nontraditional SOA also formed in this model that is not represented using the four species basis set.

We have changed "the SOA formation" to "*the traditional SOA formation*".

(21) Typo "in the basin are contributed to the development of high O3."

We have corrected the typo.

(22) Is all of the OA assumed to form a pseudo ideal solution?

No, but all condensable organics are assumed to form a pseudo-ideal solution. See SI Page 2 for the detailed discussion.

(23) Caption for Figure 4 (and other figures). "Diurnal variations" This is really the time

series. Diurnal variations – or diurnal profile shown later.

We have changed “Diurnal variations” to “diurnal profile”.

(24) Figure 10. Brown hard to differentiate from black. Change brown to some other color.

We have changed the brown to yellow.

(25) Caption for Figure 13 – labels for panels (a) and (b) are switched.

We have switched the labels.

(26) “the WRF-CHEM model underestimates the glyoxal concentrations” please be quantitative. By how much. A factor of 2, 5 …?

We have added the quantitative estimation for the glyoxal simulations as follows: “*the WRF-CHEM model underestimates the glyoxal concentrations by a factor of 2.*”

(27) Page 29372 “At T1, the T2-SOA model significantly underestimates the observed POA concentrations but overestimates in the rest of the day.” I am not sure what this sentence is saying.

We have changed the sentence: “*At T1, the T2-SOA model significantly underestimates the observed POA concentrations during daytime but overestimates in the rest of the day.*”

(28) Page 29373 “One of the possible reasons for the daytime gap between the model and the observations is the underestimation of ARO2 during daytime,” This paragraph seems like it fits in the sensitivity study section. It is describing a new sensitivity study tweaking both inventories and glyoxal.

We have added a section: “***3.2.5.2 Impacts of Aromatic Emissions***”

(29) Page 29374 – “according to recent laboratory studies and model results” I am not aware of any laboratory studies that have looked at aging of anthropogenic SOA. All of the references given here are for modeling studies.

We have removed “laboratory” from the sentence.

(30) Page 29375 – “performs well in modeling the daytime O3 and CO,” How much better is the performance of the model for O3 and CO relative to POA and SOA. It seems like performs pretty well for POA?

The POA simulations in the suburban area are not good compared to the measurements. We have clarified as follows: “*The traditional SOA model performs reasonably well in simulating* *the POA concentrations* ***in the urban area*** *with the IOA of 0.81*" and "*the non-traditional model also considerably improves POA simulations during daytime* ***in the urban area***".

(31) Page 29377 – glyoxal contributing about 9.6% But in some formulations shown here it was much less. How about "at most 9.6%."

We have changed "glyoxal contributing about 9.6%" to "*glyoxal contributing at most 9.6%*".

(32) Table 2 – It seems like you are repeating some of the cases here from Table 1. For example, the NT2E-SOA model is in both? But the numbers are different.

Yes, in Table 2, we have included the results of the NT2E-SOA model as the base case to compare with the other sensitivity studies. We have checked Table 1 and Table 2 and corrected the inconsistency of the results of the NT2E-SOA model.

(33) Figure 2 – It is impossible to see where the data are. How does the model do predicting the spatial variation of CO?

We have re-plotted the plots and included the CO distribution plots in Figure 2.

Simulations of Organic Aerosol Concentrations in Mexico City Using the WRF-CHEM Model during the MCMA-2006/MILAGRO Campaign

Guohui Li(1,2)*, M. Zavala(1), W. Lei(1,2), A. P. Tsimpidi(3,4), V. A. Karydis(3,4), S. N. Pandis(3,5), M. R. Canagaratna(6), and L. T. Molina(1,2)

(1) Molina Center for the Energy and the Environment, La Jolla, CA, USA
(2) Massachusetts Institute of Technology, Cambridge, MA, USA
(3) Department of Chemical Engineering, University of Patras, Patras, Greece
(4) Institute of Chemical Engineering and High Temperature Chemical Processes, Foundation of Research and Technology Hellas, Patras, Greece
(5) Department of Chemical Engineering, Carnegie Mellon University, Pittsburgh, PA, USA
(6) Aerodyne Research Inc, Billerica, MA, USA

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* Correspondence to: G. Li (lgh@mce2.org) and L.T. Molina (ltmolina@mit.edu)

Supplementary Information Section

The supplementary information (SI) is mainly about the SOA modeling approach used in the study. The main references include Dzepina et al. (2009), Hodzic et al. (2009, 2010), Hildebrandt et al. (2009), and Tsimpidi et al. (2010). In addition, we have also provided a table (Table SI-1) defining the terms and acronyms used for organic compounds.

Section SI-1: Gas-particle Partitioning

In the present study, the gas-particle partitioning of any SVOC is calculated based on the assumption that the bulk gas and particle phases are in equilibrium and that all condensable organics form a pseudo-ideal solution (Odum et al., 1996), which is reasonable based on the time scales of gas-particle equilibrium for submicron particles (Seinfeld and Pandis, 1998). According to Donahue et al. (2006), considering a certain mass concentration of condensed-phase organic mass, C_{OA}, a partitioning coefficient $X_{p,i}$ can be defined for condensable compound i:

$$X_{p,i} = \left(1 + \frac{C_i^*}{C_{OA}}\right)^{-1} \tag{1}$$

where C_i^* (µg m^{-3}) is the effective saturation concentration of condensable compound i. It is worthy to note that Pankow (1994) defined the absorption partitioning coefficient $K_{om,i}$ as:

$$K_{om,i} = \frac{1}{\zeta_i C_i^*} \tag{2}$$

where ζ_i is the activity coefficient of condensable species i in the absorbing organic phase. Therefore, deviation from the above gas-particle partitioning theory may occur if the organic solution is not ideal, such as near sources in urban environments with a large amount of freshly emitted particles. Given the large uncertainties in the SOA models, the non-ideal effects are not expected to dominate the prediction uncertainties (Dzepina et al., 2009).

The temperature dependence of saturation concentrations is calculated by the Clausius-Clapeyron equation:

$$C_i^* = C_{i,o}^* \frac{T_0}{T} \exp\left[\frac{\Delta H_{vap}}{R}\left(\frac{1}{T_0} - \frac{1}{T}\right)\right] \tag{3}$$

where C_i^* (μg m^{-3}) and $C_{i,o}^*$ (μg m^{-3}) are the effective saturation concentrations of condensable compound i at temperature T (K) and at reference temperature T_0 (K), respectively, ΔH_{vap} (kJ mol^{-1}) is the enthalpy of vaporization and R is the ideal gas constant.

Section SI-2: SOA Models

In the present study, we have used two approaches to investigate the SOA formation based on the SAPRC 99 chemical mechanism. Nine SAPRC surrogate VOCs are considered as the SOA precursors. These lumped compounds are listed in Table SI-2, together with the reactions to form the SVOCs and the rate constants. The T2-SOA model employs a traditional 2-product method to predict the SOA production from VOCs. The mass-based stoichiometric yield coefficients, the effective saturation concentrations, and molecular weight of SVOCs at 298 K are listed in Table SI-3. In the NT-SOA model, the SOA formation from the oxidation of VOCs is predicted using four SOA species whose effective saturation concentrations at 298 K are 1, 10, 100, and 1000 μg m^{-3}, respectively, instead of the traditional 2-product parameterization. In addition, the SOA yield from VOCs is NO_x-dependent. The high-NO_x and low-NO_x yields are listed in the Table SI-4. For the SOA yield branching from high-NO_x and low-NO_x conditions, we first calculate the loss rate of RO_2 radicals due to their reactions with NO and NO_3 (defined as LR_N), and the loss rate of RO_2 radicals due to self reactions and their reactions with peroxy radicals (defined as LR_O). If the high-NO$_x$ yield is α_{high} and the low-NO$_x$ yield is α_{low}, the SOA yield α is calculated as:

$$\alpha = \alpha_{high} \frac{LR_N}{LR_N + LR_O} + \alpha_{low} \frac{LR_O}{LR_N + LR_O} \tag{4}$$

Figure SI-1 shows the variation of the SOA mass yield from toluene (major component of ARO1 in SAPRC 99) with the total organic aerosol concentration (C_{OA}) in the T2-SOA and NT-SOA models under high NO$_x$ conditions. The SOA mass yield used in the NT-SOA model is higher than that in the T2-SOA model and when COA is equal to 10 μg m^{-3}, the SOA mass yield used in the NT-SOA model is about 4 times of that in the T2-SOA model. Detailed discussions can be found in Hildebrandt et al. (2009).

Section SI-3: POA Emissions

The MCMA 2006 official emission inventory is used in the simulations and the POA emissions are modified and distributed by volatility based on dilution experiments for the non-traditional SOA model to account for the primary organic emissions (Tsimpidi et al., 2010). The primary organic emissions must include the emitted primary organic aerosols before their dilution in the atmosphere. However, the current POA emission inventory as described above is based on ambient measurements at an urban site; according to the volatility theory, part of the emitted POA has already evaporated and is excluded in the official emission fluxes. Laboratory experiments, in which diesel exhaust and wood smoke emissions wee measured at different levels of dilution, have demonstrated that the measured primary organic aerosols in ambient conditions represent 15-40% of the primary organic aerosol actually emitted, depending on the ambient organic aerosol concentration and temperature (Lipsky and Robinson, 2006). Thermal denuder measurements in Mexico City during MILAGRO (Huffman et al., 2009; Dzepina et al.,

2009) have also shown that POA in Mexico City is semivolatile. The average concentration of the organic aerosols in Mexico City was in the range of 20 μg m^{-3} during the MCMA-2003 campaign (Salcedo et al., 2006). In this range of organic aerosol ambient concentrations, the measured organic particle material is approximately one third of the total emitted organic aerosols (Fig. 1a of Robinson et al., 2007). Therefore, in order to estimate the total semivolatile organic emissions, the OA particulate inventory is multiplied by a factor of 3. Source test data for wood combustion, gasoline vehicles and diesel vehicles which used a sample train of quartz filters in combination with denuders and/or bents (Schauer et al., 1999, 2001, 2002) have shown that the mass of unmeasured IVOC vapors is between 0.25 to 2.8 times the existing primary OA emissions. In the present study, the OA emissions were distributed by volatility (Table SI-5) using the volatility distributions of Shrivastava et al. (2008). This distribution was derived by fitting gas particle partitioning data for diesel exhaust and wood smoke assuming that the mass of unmeasured IVOC emissions is equivalent to 1.5 times the primary organic aerosol emissions. The total amount of material (POA+SVOC+IVOC) introduced in the model is 7.5 times the particle-phase POA emissions, which is similar to the factor calculated from partitioning theory and ambient data by Dzepina et al. (2009). Several studies about OA simulations in Mexico City have been used the method to modify the POA emissions suitable for the non-traditional SOA model (Dzepina et al., 2009; Tsimpidi et al., 2010; Hodzic et al., 2010).

Supplementary Information Reference

Donahue, N. M., Robinson, A. L., Stanier, C. O., and Pandis, S. N.: Coupled partitioning, dilution, and chemical aging of semivolatile organics, Environ. Sci. Technol., 40, 2635–2643, 2006.

Dzepina, K., Volkamer, R. M., Madronich, S., Tulet, P., Ulbrich, I. M., Zhang, Q., Cappa, C. D., Ziemann, P. J., and Jimenez, J. L.: Evaluation of new secondary organic aerosol models for a case study in Mexico City, Atmos. Chem. Phys., 9, 5681–5709, 2009.

Hildebrandt, L., Donahue, N. M., and Pandis, S. N.: High formation of secondary organic aerosol from the photo-oxidation of toluene, Atmos. Chem. Phys., 9, 2973–2986, 2009.

Hodzic, A., Jimenez, J. L., Madronich, S., Aiken, A. C., Bessagnet, B., Curci, G. , Fast, J., Lamarque, J. F., Onasch, T. B., Roux, G., and Ulbrich, I. M.: Modeling organic aerosols during MILAGRO: application of the CHIMERE model and importance of biogenic secondary organic aerosols, Atmos. Chem. Phys., 9, 6949–6982, 2009.

Hodzic, A., Jimenez, J. L., Madronich, S., Canagaratna, M. R., DeCarlo, P. F., Kleinman, L., and Fast, J.: Modeling organic aerosols in a megacity: potential contribution of semi-volatile and intermediate volatility primary organic compounds to secondary organic aerosol formation, Atmos. Chem. Phys., 10, 5491–5514, 2010.

Grieshop, A. P., Logue, J. M., Donahue, N. M., and Robinson, A. L.: Laboratory investigation of photochemical oxidation of organic aerosol from wood fires 1: measurement and simulation of organic aerosol evolution, Atmos. Chem. Phys., 9, 1263–1277, 2009.

Huffman, J. A., Docherty, K. S., Mohr, C., Cubison, M. J., Ulbrich, I. M., Ziemann, P. J., Onasch, T. B., and Jimenez, J. L.: Chemically-resolved volatility measurements of organic aerosol from different sources, Environ. Sci. Technol., 43, 5351–5357, 2009.

Lipsky, E. M. and Robinson, A. L.: Effects of dilution on fine particle mass and partitioning of semivolatile organics in diesel exhaust and wood smoke, Environ. Sci. Technol., 40, 55–162, 2006.

Odum, J. R., Hoffman, T., Bowman, F., Collins, D., Flagan, R. C., and Seinfeld, J. H.: Gas/particle partitioning and secondary organic aerosol yields, Environ. Sci. Technol., 30, 2580–2585, 1996.

Pankow, J. F.: An absorption model of gas/particle partitioning involved in the formation of secondary organic aerosol, Atmos. Environ., 28, 189–193, 1994.

Robinson, A. L., Donahue, N.M., Shrivastava, M. K.,Weitkamp, E. A., Sage, A. M., Grieshop, A. P., Lane, T. E., Pandis, S. N., and Pierce, J. R.: Rethinking organic aerosols: semivolatile emissions and photochemical aging, Science, 315, 1259–1262, 2007.

Salcedo, D., Onasch, T. B., Dzepina, K., Canagaratna, M. R., Zhang, Q., Huffman, J. A., DeCarlo, P. F., Jayne, J. T., Mortimer, P., Worsnop, D. R., Kolb, C. E., Johnson, K. S., Zuberi, B., Marr, L. C., Volkamer, R., Molina, L. T., Molina, M. J., Cardenas, B., Bernab, R. M., Mrquez, C., Gaffney, J. S., Marley, N. A., Laskin, A., Shutthanandan, V., Xie, Y., Brune, W., Lesher, R., Shirley, T., and Jimenez, J. L.: Characterization of ambient aerosols in Mexico City during the MCMA-2003 campaign with Aerosol Mass Spectrometry: results from the CENICA Supersite, Atmos. Chem. Phys., 6, 925–946, 2006, http://www.atmos-chem-phys.net/6/925/2006/.

Schauer, J. J., Kleeman, M. J., Cass, G. R., and Simoneit, B. R.T.: Measurement of emissions from air pollution sources, 2. C-1 through C-30 organic compounds from medium duty diesel trucks, Environ. Sci. Technol., 33, 1578–1587, 1999.

Schauer, J. J., Kleeman, M. J., Cass, G. R., and Simoneit, B. R. T.: Measurement of emissions from air pollution sources, 3. C-1-C-29 organic compounds from fireplace combustion of wood, Environ. Sci. Technol., 35, 1716–1728, 2001.

Schauer, J. J., Kleeman, M. J., Cass, G. R., and Simoneit, B. R. T.: Measurement of emissions from air pollution sources, 5. C-1-C-32 organic compounds from gasoline-powered motor vehicles, Environ. Sci. Technol., 36, 1169–1180, 2002.

Seinfeld, J. H. and Pandis, S. N.: Atmospheric Chemistry and Physics: From air Pollution to Climate Change, Second Edition, Wiley-Interscience, New York, 2006.

Shrivastava, M. K., Lane, T. E., Donahue, N. M., Pandis, S. N., and Robinson, A. L.: Effects of gas-particle partitioning and aging of primary emissions on urban and regional organic aerosol concentrations, J. Geophys. Res., 113, D18301, doi:10.1029/2007JD009735, 2008.

Tsimpidi, A. P., Karydis, V. A., Pandis, S. N., Zavala, M., Lei, W., and Molina, L. T.: Evaluation of the Volatility Basis-Set Approach for Modeling Primary and Secondary Organic Aerosol in the Mexico City Metropolitan Area, Atmos. Chem. Phys., 10, 525–546, 2010.

Table SI-1. The terminology used for the various fractions and sources of organic compounds.

Gas-phase organic compounds (Same as Tsimpidi et al. (2010))	
VOC	Volatile Organic Compounds: gas-phase organic species, in all cases of high volatility (e.g. toluene, isoprene, terpenes).
SVOC	Semi-Volatile Organic Compounds: species which have sufficiently low vapor pressure and are likely to dynamically partition between the gas and the aerosol phases.
POG	SVOC, emitted or formed due to evaporation of POA in the atmosphere (Robison et al., 2007)
OPOG	Oxidized POG by OH
IVOC	Intermediate Volatility Organic Compounds: organic species which have high enough vapor pressure to reside almost completely in the gas phase, but which have lower vapor pressure than the traditional VOCs (Robinson et al., 2007)
Condensed-phase organic species (Same as Hodzic et al. (2010))	
OA	Organic Aerosol: includes both primary and secondary fractions. It includes carbon mass (OC) and also the oxygen, hydrogen, and nitrogen mass which is part of OA.
TOA	Total Organic Aerosol
POA	Primary Organic Aerosol
SOA	Secondary Organic Aerosol (from all sources)
Aerosol Mass Spectrometer specific terminology (Same as Hodzic et al. (2010))	
AMS	Aerodyne Aerosol Mass Spectrometer
PMF	Positive Matrix Factorization: a mathematical factorization method applied to AMS time-dependent spectra that allows determining the contribution of different OA components to total OA mass as a function of time (Ulbrich et al., 2009, and references therein).
HOA	Hydrocarbon-like Organic Aerosols: an OA component identified with PMF which is consistent with mass spectral signatures of reduced species such as those from motor vehicle emissions. It is generally understood as a surrogate for urban combustion-related POA (Aiken et al., 2009a, and references therein).
OOA	Oxygenated Organic Aerosols: an OA component identified with PMF which is characterized by its high oxygencontent. It is generally understood as a surrogate for SOA from all sources.
BBOA	Biomass Burning Organic Aerosols: an OA component identified with PMF which is characterized by spectral features typical of biomass smoke. It is thought to be dominated by biomass burning POA, while biomass burning SOA is mostly apportioned into the OOA component.

Table SI-2. Lumped compounds considered as SOA precursors, the reactions to form SVOCs and the rate constants.

Species	**Major Components**	**Reactions**	**Rate Constant (298 K) (cm^3 $molec^{-1}$ s^{-1})**
ALK4	C_5-C_6 Alkanes, Cyclopetane, Trimethyl Butane, Trimethyl Pentane, Isopropyl Alcohol, n-Propyl Alcohol	ALK4 + OH	4.39×10^{-12}
ALK5	C_7-C_{22} n-Alkanes, C_6-C_{16} Cycloalkanes, Branched/Unspeciated C8-C18 Alkanes	ALK5 + OH	9.34×10^{-12}
OLE1	Propene, C_4-C_{15} Terminal Alkenes	OLE1 + OH OLE1 + O_3 OLE1 + NO_3	3.23×10^{-11} 1.06×10^{-17} 1.26×10^{-14}
OLE2	Isobutene, C_4-C_{15} Internal Alkenes, C_6-C_{15} Cyclic or di-olefins, Styrenes	OLE2 + OH OLE2 + O_3 OLE2 + NO_3	6.33×10^{-11} 1.07×10^{-16} 7.27×10^{-13}
ARO1	Toluene, Benzene, Ethyl Benzene, C_9-C_{13} Monosubstituted Benzenes	ARO1 + OH	5.95×10^{-12}
ARO2	Xylenes, Ethyl Toluenes, Dimethyl and Trimethyl Benzenes, Ethylbenzenes, Naphthalene, C_8-C_{13} Di-, Tri-, Tetra-, Penta-, Hexa-substituted Benzenes, Unspeciated C_{10}-C_{12} Aromatics	ARO2 + OH	2.64×10^{-11}
CRES	Cresols	CRES + OH CRES + NO_3	4.20×10^{-11} 1.37×10^{-11}
ISOP	Isoprene	ISOP + OH ISOP + O_3	9.82×10^{-11} 1.28×10^{-17}
TERP	α-pinene, β -pinene, Limonenene, Carene, Sabinene, other monoterpenes	TERP + OH TERP + NO_3 TERP + O_3 TERP + $O(^3P)$	8.27×10^{-11} 6.57×10^{-12} 6.88×10^{-17} 3.27×10^{-11}

Table SI-3. Parameters used in the T2-SOA model.

SOA Precursors	**SVOC$_1$**		**SVOC$_2$**		**Molecular Weight** (g mol^{-1})
	α (µg m^{-3}/µg m^{-3})	C* (µg m^{-3})	α (µg m^{-3}/µg m^{-3})	C* (µg m^{-3})	
ALK4					
ALK5	0.0718	0.3103			150
OLE1					
OLE2	0.36	111.11	0.32	1000.0	150
ARO1	0.071	1.716	0.138	47.855	150
ARO2	0.038	2.165	0.167	64.946	150
CRES	0.05	0.2611			150
ISOP					
TERP	0.0864	0.865	0.3857	11.804	177

Table SI-4. SOA yield scenarios using a four-product basis set with saturation concentrations of 1, 10, 100, and 1000 $\mu g\ m^{-3}$ at 298 K.

SOA Precursors	Aerosol Yield[*] High-NOx Parameterization				Aerosol Yield High-NOx Parameterization				Molecular Weight ($g\ mol^{-1}$)
	1	10	100	1000	1	10	100	1000	
ALK4	0.000	0.038	0.000	0.000	0.000	0.075	0.000	0.000	120
ALK5	0.000	0.150	0.000	0.000	0.000	0.300	0.000	0.000	150
OLE1	0.001	0.005	0.038	0.150	0.005	0.009	0.060	0.225	120
OLE2	0.003	0.026	0.083	0.270	0.023	0.044	0.129	0.375	120
ARO1	0.003	0.165	0.300	0.435	0.075	0.225	0.375	0.525	150
ARO2	0.002	0.195	0.300	0.435	0.075	0.300	0.375	0.525	150
CRES									
ISOP	0.001	0.023	0.015	0.000	0.009	0.030	0.015	0.000	136
TERP	0.012	0.122	0.201	0.500	0.107	0.092	0.359	0.600	180

[*] The SOA yields are based on an assumed density of 1.5 $g\ cm^{-3}$.

Table SI-5 Parameters used to treat partitioning of POA emissions.

C^* at 298K (μg m^{-3})	0.01	0.1	1	10	10^2	10^3	10^4	10^5	10^6
Fraction of emissions	0.03	0.06	0.09	0.14	0.18	0.30	0.40	0.50	0.80
Emission Phase (Particle: P; Gas: G)	P	P	P	P	P	P	G	G	G
Molecular Weight (g mol^{-1})	250	250	250	250	250	250	250	250	250
ΔH (kJ mol^{-1}) (Robinson et al., 2007)	112	106	100	94	88	82	76	70	64
ΔH (kJ mol^{-1}) (Grieshop et al., 2009)	77	73	69	65	61	57	54	50	46

Supplementary Information Figure Captions

Figure SI-1: The SOA mass yield from toluene (y-axis) with the total organic aerosol concentration (x-axis) under high NO_x conditions. Blue line: used in the T2-SOA model; Red line: used in the NT-SOA model.

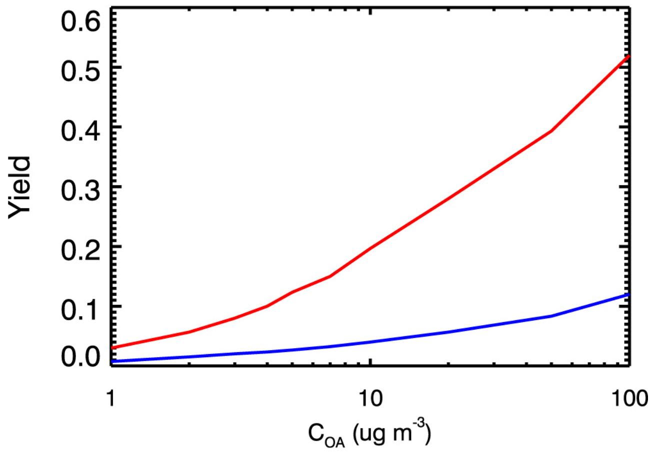

Figure SI-1