Reply to Anonymous Referee #1

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) Pg 29350, line 9: define MCMA the first time you use it.

We have added the definition for MCMA: "*MCMA (Mexico City Metropolitan Area)*"

(2) Pg 29351, line 24-25: remove ".and probably play an important.......(Pope and Dockery, 2006)" since this essentially repeats what you said about aerosols in general.

We have removed the sentence as suggested.

(3) Pg 29352, line 10: Write out SVOC in full when you define it. Don't combine a word and an abbreviation.

We have added the definition for SVOC: "*SVOCs (Semi-Volatile Organic Compounds)*.

(4) Pg 29354, line 18: How is new particle formation parameterized in the model? This should be explained briefly (not just with a citation). New particle formation is a poorly understood process, but one which may have a substantial influence on the partitioning of SOA species, therefore the way in which the model determines the timing and magnitude of the events needs to be described.

We have added a brief description about the nucleation parameterization in the present study as follows: "*The new particle production rate is calculated due to binary nucleation of* H_2SO_4 *and* H_2O *vapor. The nucleation rate is a parameterized function of temperature, relative humidity, and the vapor-phase* H_2SO_4 *concentration, following the work of Kulmala et al. (1998), and the new particles are assumed to be 2.0 nm diameter. However, several recent studies have shown that organic vapor is involved in the nucleation process (Zhang et al., 2004; Paasonen et al., 2010), which may have a substantial influence on the partitioning of SOA species.*"

(5) Pg 29356, Model descriptions: Isoprene can make a significant contribution to SOA, probably even in urban areas. Is this species not included in either of the models?

We have clarified as follows: "*In addition to the biogenic emission, an anthropogenic emission source is added to isoprene equal to 0.014 time of the ethylene emissions (Borbon et al., 2001; Hodzic et al., 2009) to improve the isoprene simulation during rush hours.*"

(6) Pg 29356, line 23: The organics are assumed to form a pseudo-ideal solution – How valid is this assumption? Near sources in urban environments, probably not very. There should be some discussion of the effects of solution non-ideality.

We have added discussions on Page 2 of the Supplementary Information (SI):
"*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, 2006). 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:*

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

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:*

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

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).*"

(7) Pg 29356, line 25: I don't understand something here. You mention that nine surrogate compounds are used for the POA components. Which components are these assumed to represent? Do you have any non-aerosol emissions in this model version? Do you include VOC?, these don't seem to be specifically mentioned here.

We have added a table (Table SI-5) about the nine surrogate compounds used for the POA components on Page 12 of SI.

(8) Pg 29357, line 14: "Robinson et al 2007"

We changed "Robison et al., 2007" to "Robinson et al., 2007".

(9) Pg 29357, line 19: Discuss the suitability of applying this single reaction rate to all species. How is this justified?

We have added the following discussions: "*Based on the chamber studies of diesel exhaust, Robinson et al. (2007) have assumed that POG and IVOC react with OH with* $k_{OH} = 4\times10^{-11}$ cm^3 $molec^{-1}$ s^{-1} *(Atkinson and Arey, 2003). Each reaction is assumed to reduce the volatility of the vapor material by an order of magnitude (e.g., shifting material from a C* of 100 to 10*

μg m^{-3}), with a small net increase in mass (7.5%) to account for added oxygen. Although it is known that gas-phase organic reactions can lead to bond scission (Kroll and Seinfeld, 2008), this mechanism assumes that no VOC of higher volatility, CO, or CO2 are formed, which if taken into account would reduce the amount of SOA formed. Another structural uncertainty of the NT-SOA model is the lack of particle-phase accretion reactions (e.g., Barsanti and Pankow, 2005), which if included would increase the amount of model SOA produced. It is worthy to note that the aging process is still very uncertain. Grieshop et al. (2009) has proposed a variation of the mechanism based on the evolution of chamber SOA from wood smoke that has a similar distribution of semi-volatile species as diesel emissions. In the new mechanism, every generation of oxidation decreases the saturation concentration (C) of the products by two orders of magnitude per oxidation step and the mass increase per oxidation step is 40% but the oxidation rates with OH is decreased to 2×10^{-11} cm^3 molec^{-1} s^{-1}.*"

(10) Pg 29357, line 8: This can't be generally stated. Isoprene SOA yields for example do increase with increasing VOC/NOx ratio, but then they peak and decrease as a ratio of about 1 is exceeded. Likewise for monoterpenes although a higher VOC/NOx ratio is reached before the yield decreases again. Sesquiterpenes on the other hand, form higher SOA yields as NOx values increase. See Hoyle et al. ACP 11, 321–343, 2011 for a summary.

We have added the following discussions: "*However, the NO_x-dependent SOA yields from biogenic precursors are more complicated and variable. In the review paper of Hoyle et al. (2011), isoprene SOA yields increase with increasing VOC/NO_x ratio, but then they peak and decrease as the ratio of about 1 is exceeded. Likewise for monoterpenes although a higher VOC/NO_x ratio is reached before the yield decreases again. Sesquiterpenes, on the other hand, form higher SOA yields as NO_x values increase. In the present study, NO_x-dependent SOA yields from biogenic precursors are calculated as those from anthropogenic precursors.*"

(11) Pg 29357, line 21: On what is the 7.5% assumption, or the shift by one volatility bin based? Is there any published evidence that shows that an oxidation reaction with OH will reduce the volatility by an order of magnitude, or add 7.5% to the mass of a compound?

Please see response to (9) above.

(12) Pg 29358, line 11: Why is the sum of POA + SVOC+IVOC = 7.5POA? Is this some kind of emission scaling based on the mass of POA, or did the total just coincidently come to 7.5POA? If it is the latter, then you should re-phrase this sentence to clarify.

We have added a paragraph and a table (Table SI-5) about the POA emission in SI (Pages 4-5):
"*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) 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 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)."

(13) Section 2.3: Explain the terms "O_3-convection North" and "O_3-convection South". When you describe the model you must include at least a sentence describing each aspect you mention. Simply providing citations for the PBL scheme, the microphysics scheme etc. is not informative enough.

We have added the definitions for "O_3-convection North" and "O_3-convection South": "*O_3-convection South occurs when there is a weak northerly wind component aloft with rain in the southern part of the basin. O_3-convection North occurs when there is a weak southerly wind component aloft with a gap flow and rain in the northern part of the basin.*" We have also added brief descriptions for the physical parameterizations as follows: "*The modeling system employs the Lin microphysics scheme (Lin et al., 1983), a sophisticated one that includes ice, snow and graupel processes, suitable for real-data high-resolution simulations. The PBL scheme used is the Yonsei University (YSU) scheme (Noh et al., 2001), which includes non-local-K mixing in the dry convective boundary layer, vertical diffusion based on the Richardson number in the free atmosphere, entrainment explicitly determined, and PBL depth from the thermal profile. The Noah land-surface model (Chen and Dudhia, 2001) is used in simulations, in which vegetation effects are included and soil temperature and soil moisture in four layers are predicted. A longwave radiation parameterization (Mlawer et al., 1997) and a shortwave radiation parameterization (Dudhia, 1989) are used for the radiation* *process.*"

(14) Page 29359 line 12: so it seems that you do account for isoprene emissions. You really need to list the species which are accounted for in the model description, even if they are combined into a lumped species.

Yes, we have included the biogenic and anthropogenic emissions of isoprene. We have added a table in SI about the VOCs considered as SOA precursors (Table SI-2).

(15) Figure 2 is rather hard to inter pret. It should be made clearer by making the squares showing the measurement points larger, and removing the outlines of the different regions within the city area.

We have re-plotted the figure as suggested.

(16) Page 29361 line 18: "are contributed to the development" change to "contribute to the development".

We have changed "are contributed to the development" change to "contribute to the development" as suggested.

(17) Page 29362 line 16: You say that the night time O_3 deviates from the measurements except on the 26th. I think figure 3 shows that the deviation is rather especially large during the night of the 26th. Do you have any idea what causes the over estimation in the O_3 and the underestimation in CO on the night of the 26th?

We have clarified as follows: "*During the night of March 26, the overestimation of O_3 concentrations and underestimation of CO concentrations are rather large due to the dominance of the air mass transported outside of Mexico City with high O_3 and low CO concentrations.*"

(18) Page 29362 line 17: "the complexity of the night time chemistry" What aspects of the chemistry in particular does the model have difficulties with? Please be more specific.

We have removed "the complexity of the night time chemistry" because we find that the main reason for the nighttime deviation of O_3 and CO concentrations is "*such as difficulty of adequately representing nocturnal layers and their mixing (Li et al., 2007) and the evacuation efficiency of the pollutants in the city (Zhang et al., 2009).* Please see (17) above.

(19) Page 29362 line 26: The model simulates the emissions during the day time? Aren't the emissions prescribed? Figure 4,6,8,9,10 – There are times with no data. Please state if there is a reason for this, or if the values are so low that they do not show up on the plot.

We have not simulated the emissions during the daytime and the emissions are prescribed.

We have clarified as follows: "*The good agreement between the long-lived predicted CO and the corresponding measurements suggests that the model simulates reasonably well the meteorological fields and the CO emissions are also reasonable during daytime*."

In Figures 4, 6, 8, 9, and 10, the times with no data mean that the observation at that time is missing or no observation.

(20) Page 29363 line 12: "...based model) diurnal" – change to : "...based model) for the diurnal"

We have changed "...based model) diurnal" to "...based model) for the diurnal".

(21) Page 29363 line 7: "throughout the entire episode" – actually there is an overestimation until the 27th.

We have rephrased the sentence: "*However, the T2-SOA model significantly underestimates the observed POA during rush hours from March 27th to 29th at T1 and on 28th and 29th at T0*"

(22) Page 29363 line 8: If the inventory was really missing sources, then why do you have an overestimation early in the episode? You should also mention that the 25th and 26th are Saturday and Sunday, presumably this explains some of the different pattern of emissions. The 24th on the other hand is Friday, and also shows no sign of a rush hour in panel c of figure 4.

We have removed the statement about missing sources at T1 and also clarified below: "*During the period from March 24th to 26th, the T2-SOA model overestimates the observed POA during rush hours. In this time period, the early morning winds from the north of the basin transport the pollutants from the Tula industrial complex and cause the overestimation of POA at T1. March 25th and 26th are Saturday and Sunday, which also explain some of the different patterns of emissions.*"

(23) Page 29363 line 25-page 29364 line 4: How do you get higher values of POA in the NT-SOA model than in the T2 model for the morning rush hour? POA is non volatile in the T2 model, isn't it? So there should always be more in the T2 model than in the NT model.

In the T2-SOA model, the POA is assumed to be non volatile, but in the NT-SOA model, the POA is assumed to be semi-volatile and the partitioning between the POA and POG is influenced by the dilution. We have clarified as follows: "*As T0 is located near the urban center of Mexico City, it is directly influenced by the urban emissions. The POA is assumed to be semi-volatile in the NT-SOA model, thus a large part of the emitted POA evaporates to form the POG and is oxidized/aged to form SOA. In the early morning, large emissions of POA and low PBL height facilitate the condensation of the POG due to evaporation of POA and result in high levels of the POA. In addition, the low OH concentrations are not* *favorable for the efficient oxidation of the POG due to evaporation of POA.*"

(24) Page 29364 line 18 "reproduces the variability" – this is quite an over statement. The t2 model shows some squiggles which in some cases occur at the similar times to the peaks in the measurements, but just as often entirely fail to capture the changes in the measurements.

The T2-SOA model significantly underestimates the observed SOA concentrations, so compared with the measurements, the simulated variability is not so obvious. If the Figure 4f is plotted using a logarithmic mass axis, the simulated variability in the T2-SOA model becomes more evident. Please see Figure 10 in Li et al. (2010). We have also clarified as follows: "*In general, the T2-SOA model qualitatively reproduces the variability of SOA during daytime at T0 (Figures 4b and 4d).*"

(25) Page 29365 line 27 "two distinct peaks" I only see one peak. If there really is a second peak, it's certainly not distinct.

In general, the two peaks are distinctly observed, particularly from March 27 to 29. However, when the hourly averaged observation is plotted using filled circles in the figures, the second peak tends to merge with the first one. Please see Figure 11 about the two peaks of the observations at T0 and T1.

(26) Page 29366 line 14-16: It is true that many of those aspects mentioned could contribute to the underestimation, however we don't really gain anything from presenting a list of the usual reasons models may not match the observations. You need to convincingly identify those aspects with the largest influence, and not just speculate on the possible causes. A few lines later you mention that the based on the CO and O3 simulation, the met fields look ok. Good, so you can already remove the meteorological fields from your list. What about the others?

We have discussed other factors except the meteorological fields in the following sections.

(27) Page 29367 line 17: change "Monoterpene" to "Monoterpenes"

We have changed "Monoterpene" to "Monoterpenes" as suggested.

(28) Page 29371 line 15: change "considerably" to "slightly"

We have changed "considerably" to "slightly" as suggested.

(29) Page 29372 line 13-14: "missing background SOA transport" This statement stands a bit alone. You should mention that you look at it in more detail later.

We have rephrased the sentence: "*The non-traditional SOA models improve the SOA simulations in the afternoon, but still underestimate the observed SOA, which is plausibly* *caused by missing background SOA transport that we will investigate in more detail later.*"

(30) Page 29373 line 8: The NT2E version has fixed OH levels, as I understood it, so these are not going to change as you suggest here. For the other model versions, sure.

No, in the NT2E-SOA model, the OH levels are not fixed, but the aging process does not feedback to the gas-phase chemistry.

(31) Page 29374 line 17-18: Given the underestimation during the night and morning, I don't think aging of anthropogenic SOA is the only problem.

We also believe that aging of anthropogenic SOA is not the only problem resulting in the underestimation during the night and morning. We have changed the sentence as follows: "*However, there are still debates in the chemical aging of the SOA from anthropogenic VOCs (George and Abbatt, 2010)*"

(32) Page 29376 line 17-19: The agreement with observed SOA can be improved by changing these things, and some of them may contribute to the model underestimation, but you have not proved in this study that any of them were actually responsible for the model underestimation. There is a big difference in those two statements. There could well be, for example, SOA formation pathways, or precursors which one simply hasn't accounted for, which cause the majority of the underestimation.

We have changed the statement as suggested: "*The agreement of the simulated SOA with observations can be improved by changing the OH treatment, emissions, aging of SVOCs, 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.*"

(33) Page 29376 line 23: change "considerably" to "slightly".

We have changed "considerably" to "slightly" as suggested.

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

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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

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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 μg 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
$\triangle H$ (kJ mol^{-1}) (Robinson et al., 2007)	112	106	100	94	88	82	76	70	64
$\triangle H$ (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.

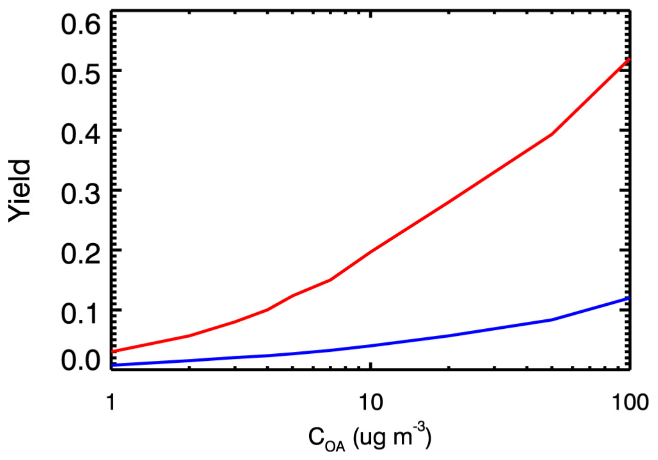

Figure SI-1