Response to reviewer and public comments on "Potential contribution of semi-volatile and intermediate volatility primary organic compounds to secondary organic aerosol in the Mexico City region" by Hodzic et al., ACPD-10 C28–C31 2010.

Responses to Reviewers

We thank the reviewers for their comments. Our responses follow below. The reviewer comments are given in regular font below while our responses are italicized and given in blue.

Response to Referee #1

R1.0) This paper summarises the results of a comparison exercise of a chemical transport model with atmospheric measurements of organic aerosol performed during MILAGRO in the Mexico City Metropolitan Area. The key theme of this paper is the use of the volatility basis set approach and the inclusion of schemes for the simulation of intermediate and semivolatile species (in the form of two published parameterisations and a reference run that does not include this). The authors find a general improvement in model accuracy when it is compared with AMS data, specifically the outputs from PMF analysis. However, various short falls remain, which are discussed.

This is a very topical paper and deals with an important subject, as there is currently a major effort into improving the general predictive capability when it comes to organic aerosols in the atmosphere. There are a variety of different approaches that can be taken and each will require careful and critical evaluation against real-world data in order for the science to advance. The MILAGRO study is an excellent opportunity for this, as it had many sampling platforms and a number of groups performing modelling exercises independently of one another. I would say this work is important and ultimately will probably deserve to be published in ACP, but regrettably, the paper in its current form suffers from a number of serious shortcomings (detailed below). Because some of these problems relate to the interpretive side of the paper, I feel it prudent that this paper should be published only after major revisions and subsequent re-review.

A1.0) We thank the reviewer for recognising the importance and merits of the present paper, and we will do our best to respond to reviewer's specific comments. Although the reviewer calls for "major revisions and subsequent re-review," the suggested changes are rather minor such as adding a table of acronyms, using the model evaluation metrics more consistently, discussing PMF rotationality, tweaking the title, and removing one figure. We are not sure which of these topics are so major that cannot be evaluated by the Editor and readers of ACPD based on a single round of review. Responses to each topic follow each reviewer comment below.

General comments:

R1.1) The most immediate problem with this paper is one of clarity. There is a general overuse of confusing acronyms and terms that a reader unfamiliar with this work would find rapidly overwhelming. For example, the first paragraph of page 661 required several reads before I could make sense of it. But even once the terms had

been established, the remainder of the paper became frequently abstract and often left me no wiser as to the scientific case being established. Given the number of important and very specific quantities being dealt with in this paper, many of which have already been defined in other works, it would be wrong to request that these be changed. Instead, I would recommend that the important quantities be summarised in a table or a series of bullet points in the introduction, defining the acronyms and also giving a concise description of their physiochemical properties that the reader can refer back to.

A1.1) Abbreviations are used to refer to the different fractions of organic compounds in the paper. Unfortunately there is a large underlying complexity and many types of precursors, OA, and SOA. Acronyms can be annoying to the reader but are necessary, i.e. the paper would not be any clearer if we had written "semivolatile and intermediate volatility organic species" instead of "S/IVOC" every time in the paper. As the reviewer states, we are using the same acronyms that are being established in this field. Thus the clarification that we can offer, as suggested by the reviewer, is to add a 'Terminology' table (Table 1) which defines the acronyms and describes their physiochemical properties. The following text was added to the paper:

- page 665, lines 20 (acpd online version):

"The terminology used for the various fractions and sources of organic compounds is given for reference in Table 1."

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

Gas-phase and semivolatile organic compounds

SVOC	**Semi-Volatile Organic Compounds**: primary species which have sufficiently low vapor pressure that are likely to dynamically partition between the gas and the aerosol phases (Robinson et al., 2007)
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)
S/IVOC	**SVOC + IVOC**
VOC	**Volatile Organic Compounds**: gas-phase organic species, in all cases of high volatility (e.g. toluene, isoprene, terpenes). Note that in order to clearly separate the families of SOA precursor gases, S/IVOC are not considered to be part of the VOC as defined here

Condensed-phase organic species

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.
POA	**Primary Organic Aerosol**: here treated as inert and non-volatile (REF run) or as semi-volatile (ROB and GRI runs)

SOA	**Secondary Organic Aerosol** (from all sources)
V-SOA	the fraction of SOA formed from oxidation of known VOC gaseous precursors; following the terminology of Tsimpidi et al., 2010
S-SOA	SOA formed from the oxidation of SVOC
I-SOA	SOA formed from the oxidation of IVOC
SI-SOA	S-SOA + I-SOA

Aerosol Mass Spectrometer specific terminology

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 oxygen content. It is generally understood as a surrogate for SOA.
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.

Also, to make the paper easier to follow we have shortened the abstract by eliminating the following sentences:

Abstract: "The predicted anthropogenic POA levels are found to agree within 20% with the observed HOA concentrations for both the ROB and GRI simulations, consistent with the interpretation of the emissions inventory by previous studies. The impact of biomass burning POA within the city is underestimated in comparison to the AMS BBOA, presumably due to insufficient nighttime smoldering emissions."

The following paragraph has also been clarified (P660-661):

"Recent studies (Lipsky and Robinson, 2006; Robinson et al. 2007; Huffman et al. 2008,2009ab; Sage et al., 2008; Grieshop et al., 2009) have shown that POA species should be treated as thermodynamically active compounds that can

evaporate from the particulate phase, react in the gas-phase, and repartition as SOA. In the conceptual model of Robinson et al. (2007), POA is co-emitted with two types of gases: (i) semi-volatile compounds (SVOC) which are characterized by a relatively low volatility and are in the substantial partitioning with POA, and (ii) intermediate volatility vapors (IVOC) which are highly volatile and remain preferentially in the gas-phase. S/IVOC species have traditionally been ignored in SOA modeling and are also typically neglected in VOC emission inventories. They are composed of species such as long-chain hydrocarbons with more than 18 C atoms, and can undergo multiple oxidation steps leading to a large amount of lower volatility precursors that are likely to partition to the aerosol phase downwind of source regions. Following Tsimpidi et al. (2010), we will refer to SOA formed from SVOC as "S-SOA, to SOA formed from IVOC as "I-SOA," and to the combination of S-SOA plus I-SOA as "SI-SOA.""

R1.2) The second major problem is a lack of focus in how the model treatments are being tested. The authors should be clear and consistent in what metrics they are using to test the models when comparing with observed data (for instance, was the % accuracy derived using linear regression, a ratio of means, or something more elaborate like orthogonal distance regression?). The authors do not pay nearly enough attention to the evaluation of how well temporal variability is captured, giving correlation statistics in only a handful of places. If this work is to present a thorough evaluation of different model treatments (i.e. REF, GRI and ROB), it should be consistent as to which tests it is performing and present all of the results for each test more systematically.

A1.2) To evaluate model skill in simulating organic aerosols the common statistical indicators are used in the original ACPD version, including the bias, root mean square and correlation coefficient. Table 2 presents the scores for OOA predicted by all 3 model simulations, while scores for POA, TOA, BBOA, OOA are also given in Figures 2-3, 7-9. As suggested by the reviewer the reference to these metrics has now been made more systematic in the text. The following sentences were added:

- Section 3.2.1: Primary organic aerosols:

"It is responsible for lowering the temporal agreement with observations and the correlation coefficients."

"A somewhat better agreement is reached in the late afternoon, although the temporal variability is not captured ($r^2 \sim 0$)."

- Section 3.2.2: Secondary organic aerosols

"Besides the bias reduction, the appreciable decrease of the RMS error (from ~ 7.0 to 5.3 µg/m^3) confirms the improved agreement with observations."

" This improvement can also be seen in terms of enhanced temporal agreement with the increase of the correlation coefficient from 0.24 to 0.28."

" The bias and RMS error exceed 3.4 and 5.7 µg/m3, respectively."

- Section 3.2.3: Total organic aerosols

" No substantial improvement is however seen in simulated TOA temporal variability, which correlates slightly better for ROB (R2=0.48) than for GRI (R2=0.46) and REF (R2=0.45) simulations. As suggested by diurnal profiles (Figure 2), this temporal mismatch is likely caused by the dominance of the nighttime errors featuring too high POA concentrations, due to a too low model mixing layer (Hodzic et al., 2009; Fast et al., 2009)."

- Conclusions:

"The diurnal variability characterized by the rapid SOA increase after sunrise is reproduced leading to higher temporal correlations for both simulations."

- Table 2 (acpd online version, Table 3 in the new manuscript):

We also agree that it is not indicated in the text what type of correlation coefficients are being used. The following sentence was added to explain that in Table 2:

" To measure the linear dependence between modeled and observed values, Pearson correlation coefficients are used throughout the paper.»

R1.3) This leads onto a more general conceptual issue as regards evaluating model performance. If REF gives a better result for an r2 test than GRI and ROB (as reported in section 3.2.3), then this would surely imply that it could give the best overall result if tuning was used. Granted, this wouldn't tell us anything about the underlying chemistry and may not lead to an overall skill improvement, but it does throw into question whether the GRI and ROB treatments are actually improving the model or whether they are getting the right answer for the wrong reasons. This issue must be discussed and discounted if the key conclusions of the paper are to be reached.

A1.3) We strongly disagree with the reviewer's interpretation of the results presented in section 3.2.3. This section compares the results of the predicted and observed total organic aerosol (TOA), which is composed of the primary and secondary organic fractions. We have shown in section 3.2.2 that the SOA production, therefore the chemistry, is better captured by the model when S/IVOC parameterizations are included, in terms of bias, RMS and correlations (i.e. increase in r2 from 0.37 for the traditional approach up to 0.56 for the GRI model). The model results for SOA suggest that S/IVOC chemistry (GRI and ROB treatments) is likely to be one of the important SOA formation pathways, although we agree that the details of the parameterization need further adjustments based on experimental work.

We do not doubt that higher SOA levels can also be obtained by tuning the traditional Odum-type mechanism (or any other mechanism, given enough tuning parameters). However, the amount of V-SOA precursors is well constrained (Fast et al., ACPD, 2009; Hodzic et al., ACP, 2009). Certainly one could unrealistically modify the vapor pressures to greatly increase the yields, however we do not consider such tuning in our paper as it does not have any experimental basis. Also, it has been shown (Madronich and Lee-Taylor, personal communication) that only a small fraction (<20%) of the observed SOA amount in Mexico City can be explained from the traditional aromatic precursors even when the chemistry is treated explicitly (i.e. master mechanism type simulation). Thus tuning up the V-SOA from traditional VOC

precursors by a large factor would almost certainly reduce the model-measurement discrepancies for the wrong reasons.

We have updated the model results for both ROB and GRI simulations as a small error was found in the initial treatment of SIVOC emissions. This update however does not change much our results (< 5%) and the conclusions of the paper. Concerning the TOA predictions, the recalculated correlation coefficients are r2(ROB)=0.48 and r2(GRI)=0.46. Therefore we agree with the reviewer's comment that r2 is quite similar for SIVOC and traditional (REF) runs, which is now explained in the paper (Section 3.2.3):

" No substantial improvement is however seen in simulated TOA temporal variability, which correlates slightly better for ROB (R2=0.48) than for GRI (R2=0.46) and REF (R2=0.45) simulations."

We believe that this limited improvement in r2 coefficients is related to the dominance of strong nighttime errors. This is now more clearly explained in the paper:

" As suggested by diurnal profiles (Figure 2), this temporal mismatch is likely caused by the dominance of the nighttime errors featuring too high POA concentrations."

R1.4) A major ambiguity when it comes to comparing outputs with AMS data is the issue of rotationality within PMF. It is possible that different solutions within the PMF analysis could lead to radically different assessments of both accuracy and temporal variations, but this topic gets little more than lip service in the current manuscript. As it stands, this is very inadequate. No information is given as to the reasons behind the choice of the number of factors or whether rotations were explored (e.g. by using the 'fpeak' parameter) and this should be documented. References to other papers or supplementary material would suffice, but this issue must be specifically summarised either way. Ideally, model outputs should be tested against alternative solutions to test how robust the comparisons are to this ambiguity.

A1.4) This manuscript uses the results of two PMF-AMS analysis (for T0 and the C-130) which have been extensively documented in other papers, which have already been published separately (Aiken et al., ACP 2009, and DeCarlo et al., ACPD 2010). Most of the content of both of those papers deals with the interpretation of the PMF solutions and its uncertainties. The Dzepina et al. (2009) paper focusing on the MCMA-2003 study (also in Mexico City) also presents some information on PMF results and correlation with tracers. Aiken et al. (ACPD 2010) then explores in greater detail the interpretation of the BBOA component and finds it generally consistent with other measurements. The Jimenez group has also published multiple previous papers on PMF analysis, most notably Ulbrich et al. (2009), where such uncertainties are investigated in great detail, as have other groups (e.g. Lanz et al., ACP 2007; ES&T 2008). Given that so much information is already in the literature, it would not be appropriate to repeat it here. The PMF results for the T1 site were already used by Hodzic et al. (ACP, 2009) while those for the G1 aircraft were discussed by Fast et al. (ACP, 2009). Those results have not been published separately, in part because their results were very similar to those already published by Aiken et al. and DeCarlo et al. Overall, while there are some uncertainties in the

PMF results due to rotations, they are nowhere nearly as large as the differences between the REF, ROB, and GRI simulations. The paper has been modified to more explicitly discuss the uncertainties and to add references to the previously published studies where these issues have been discussed in detail:

P670, L17: «Uncertainties associated with rotationality within sets of potential solutions of PMF analysis for the present dataset are documented in Aiken et al. (2009) and (DeCarlo et al. 2010). The implications of those uncertainties are much smaller than differences between the REF, ROB and GRI simulations.»

Specific comments:

R1.5) Please consider changing the title. The casual reader, who would probably not be aware of the terminology would be instantly turned off before they even got as far as the abstract. I would recommend changing it to something along the lines of 'An evaluation of atmospheric aerosol models incorporating treatments of intermediate and semivolatile organic components' or something, as this is far more descriptive of the work being presented.

A1.5) As suggested by the reviewer the title has been modified to read:

"Modeling organic aerosols in a megacity: potential contribution of semi-volatile and intermediate volatility primary organic compounds to secondary organic aerosol formation."

The reader is now aware that the paper presents a modeling case study.

The short title was also changed to "Modeling organic aerosols in a megacity" instead of "S/IVOC contribution to SOA formation" used previously and found to be too technical.

R1.6) I found the conclusions section a bit rambling and it left me slightly baffled as to what the core thesis of the paper is. If the authors are to make the case that the GRI or ROB treatments offer a genuine improvement in model performance or scientific understanding, they should state how the evidence shows this more clearly and concisely. If the authors are making specific recommendations for future model development, these and the evidence supporting them should also be made clearer.

A1.6) As suggested by the reviewer we stated more strongly the main hypothesis of the paper as well as the major results. The updated parts of the conclusion reads:

"In this study a meso-scale chemistry-transport model has been applied to investigate whether or not semi-volatile and intermediate volatility primary organic vapors contribute to the formation of SOA in the vicinity of Mexico City. The model has been updated to account for the dynamic treatment of POA emissions which includes both the gas/particle partitioning of primary species and the photochemical processing of associated vapors. Two approaches based on Robinson et al. (2007) and Grieshop et al. (2009) have been applied and inter-compared. The following are the principal findings of this study:"

"iv) The dynamic treatment of POA does not have major effects on its surface concentrations in the source region, and the model results remain close to ones obtained with the non-volatile POA assumption. However, both non-traditional treatments show a deficiency in regard to POA ageing with a tendency to over-evaporate POA upon dilution of the urban plume during the regional transport. Comparisons with measurements suggest that atmospheric HOA may be less volatile than assumed in these parameterizations and the sensitivity of SOA production to this parameter should be investigated in future studies.

v) This study also highlights the need for improvements in current parameterizations. Experimentally constrained amounts and partitioning/ageing parameterizations of S/IVOC are urgently needed for further progress in this area. In particular, the effect of fragmentation of oxygenated species leading to higher volatility species (Kroll et al., 2009) needs to be taken into account. Parameterizations which explicitly track both volatility and oxidation state (e.g. Jimenez et al., 2010) may also allow improved predictions of OA evolution and aging. Opportunities for improvement also lie in the better constrained dry deposition velocities of the S/IVOC species. Their values are likely higher than the ones considered in this study (based on NO2, Hodzic et al., 2009) and should be experimentally and/or theoretically constrained. Finally, we also note that the modeling of SOA is still underconstrained. The improved agreement with observations achieved here does not prove that S/IVOC are the major missing SOA source in megacity environments, and other possible pathways such as formation from very volatile species like glyoxal need to be explored in future studies."

R1.7) I consider figure 12 to be potentially misleading and of questionable merit. The plot it recreates, figure 2 in Volkamer et al. (2006), was designed to highlight the gap in fundamental mechanistic understanding when it comes to SOA formation. In presenting the graph as an updated version of this figure, this could give a reader the false impression that the gap in understanding has been shown to have been closed by this work. However, the volatility basis set approach effectively makes up for the short fall in the inventory of precursors and reaction routes by using semi-empirical parameterisations, so the lack of explicit understanding of the fundamental processes remains. It should also be pointed out that Johnson et al. (2006) were effectively able to achieve an observed/modelled ratio of unity through tuning, so using the runs featured in the Volkamer et al. (2006) plot as a basis for comparison with 'traditional' approaches is very unfair. The authors should by all means show that their approach delivers realistic mass concentrations (this, after all, is a key theme of the paper), but I would be strongly against the inclusion of figure 12 as it is currently presented.

A1.7) We strongly disagree with the reviewer comment and have decided to keep figure 12 in the revised paper. The reason for disagreement is that unlike suggested by the reviewer, this figure does not imply that the problem of SOA formation has been solved by accounting for S/IVOC chemistry. The figure simply summarizes the results of the current study and compares them with previous ones shown by Volkamer et al., 2006 and a few other studies. Although the agreement with the observations is improved when S/IVOC are included, we never said that this was a conclusive proof for the importance of this mechanism. We agree that the uncertainties regarding fundamental SOA formation processes remain as already mentioned and highlighted in the text. Indeed, we already wrote in the abstract "We note that our simulations did not include other proposed pathways of SOA formation

such as formation from very volatile species like glyoxal, which can also contribute SOA mass and especially increase the O/C ratio".

To make this clearer, we have modified the last sentence of the abstract to read:

"The agreement observed in this study is not sufficient evidence to conclude that S/IVOC are the major missing SOA source in megacity environments. The model is still very underconstrained, and other possible pathways such as formation from very volatile species like glyoxal may explain some of the mass and especially increase the O/C ratio".

And added the following sentence to the Conclusion:

"We note that the modeling of SOA is still very underconstrained. The improved agreement with observations achieved here does not prove that S/IVOC are the major missing SOA source in megacity environments, and other possible pathways such as formation from very volatile species like glyoxal need to be explored in future studies."

We agree that higher SOA levels can also be obtained by tuning of the traditional SOA model, as done by Johnson et al., 2006 and by Hodzic et al., 2009. However such "tuning" is just a modeling exercise that is disconnected from experimental reality. Neither of these two approaches is realistic as they lowered the volatility vapor pressures by 500 and 100 times in order to condense a much larger fraction of the semivolatile vapors into the aerosol. This is fine as a model sensitivity exercise, but we are baffled by the suggestion that it should be taken seriously as an independent model! It is unfair to compare the present work to these "tuning" experiments because the results shown here quantify the impact on SOA formation of two proposed parameterizations which are based on chamber experiments. These parameterizations were not tuned in order to explain the ambient observations.

References (in addition to the ones included in the ACPD paper)::

DeCarlo, P.F., I. M. Ulbrich, J. Crounse, B. de Foy, E. J. Dunlea, A. C. Aiken, D. Knapp, A. J. Weinheimer, T. Campos, P. O. Wennberg, and J. L. Jimenez, Investigation of the sources and processing of organic aerosol over the Central Mexican Plateau from aircraft measurements during MILAGRO, Atmos. Chem. Phys. Discuss., 10, 2445-2502, 2010.

Fast J.D., A. C. Aiken, J. Allan, L. Alexander, T. Campos et al., Evaluating simulated primary anthropogenic and biomass burning organic aerosols during MILAGRO: implications for assessing treatments of secondary organic aerosols, Atmos. Chem. Phys. Discuss., 9, 4805-4871, 2009.

Lanz, V. A., Alfarra, M. R., Baltensperger, et al.: Source apportionment of submicron organic aerosols at an urban site by factor analytical modelling of aerosol mass spectra, Atmos. Chem. Phys., 7, 1503–1522, 2007.

Lanz, V. A., Alfarra, M. R., Baltensperger, U., et al.: Source Attribution of Submicron Organic Aerosols during Wintertime Inversions by Advanced Factor Analysis of

Aerosol Mass Spectra, Environ. Sci. Technol., 42, 214–220, doi:10.1021/es0707207, 2008.

Tsimpidi, A. P., Karydis, V. A., Zavala, M., Lei, W., Molina, L., Ulbrich, I. M., Jimenez, J. L., and Pandis, S. N.: Evaluation of the volatility basis-set approach for the simulation of organic aerosol formation in the Mexico City metropolitan area, Atmos. Chem. Phys., 10, 525-546, 2010.

Responses to Referee #2

R2.0) The publication presents contribution of semi-volatile and intermediate volatile organic compounds emitted by combustion processes to secondary organic aerosol (SOA) formation, its transport and further transformation in the atmosphere for the Mexico City region. Two different state of the art SOA formation mechanisms were validated in the modeling study. In addition to comparing organic particle concentrations between the model and the observations, the authors involved another constrain – O:C ratios to validate the SOA parameterizations. This approach is quite innovative and deserves attention. I recommend the paper for publication. I would like to state below my comments:

A2.0) The authors would like to thank Dr. Ravan Ahmadov for his thoughtful comments and inputs to the revision process.

General comments:

R2.1) Introduction, lines 698-690: Here you talk about the strong underestimation of SOA from the "traditional" precursors, but as other authors have shown, using the more updated SOA yields and aging of anthropogenic condensable vapors can produce quite a bit of SOA (V-SOA) in the models apart from treating semivolatile POA and I-VOCs. Since the "REF" study (Hodzic, Jimenez et al. 2009) does not use such an approach, I think the authors should not strongly underestimate the role of V-SOA in predicting organic PM for the Mexico City region. A treatment of V-SOA with aging can remarkably affect O:C ratios as well, which are compared against the measurements in the paper.

A2.1) We agree that additional V-SOA can be formed from "traditional" VOC precursors (e.g. aromatics) if the most recent yields from chamber experiments are used. Such an approach was used by Dzepina et al. (2009), who compared the V-SOA formation for a case study in Mexico City when using yields similar to those in the present paper, and those from the updated chamber experiments of Ng et al. (2007). However as concluded on that paper "Traditional SOA precursors (mainly aromatics) by themselves still fail to produce enough SOA to match the observations by a factor of 7" when using the updated yields from Ng et al. (2007). Thus the recently updated yields cannot close the gap between measured and predicted SOA.

We are also aware of the recently proposed "aging of condensible organic vapors" formed from traditional VOCs. Such mechanism has been implemented by Tsimpidi et al. (ACP, 2010) for Mexico City, resulting in up to 10ug/m3 of additional V-SOA during daytime hours. However, we are not aware of ANY experimental support for the extremely high yields of this parameterization. Jimenez et al., (AGU Fall 2009, Talk A14D-06, "SOA Measurements vs. Models: A Status Report", and the basis of a paper in preparation of the same title) have shown that applying the mechanism described in Tsimpidi et al. in a simple back-of-the-envelope calculation leads to

extremely high yields (~100% under high NOx and ~130% under low NOx) of SOA for aromatic precursors in ~3.5 hrs at [OH] = 2e6 molec cm^{-3}, i.e. at an OH exposure of ~7e6 molec cm^{-3} hr. This is illustrated in the figure below.
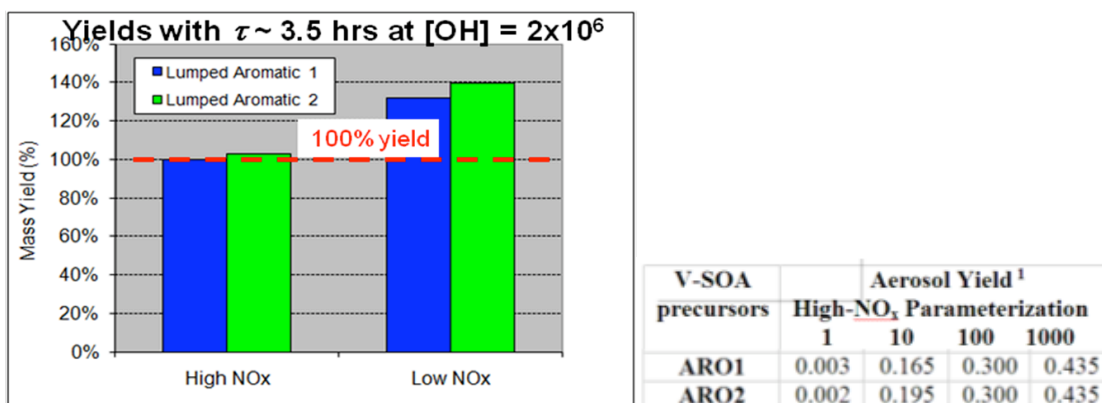
Figure 1: V-SOA yields from aromatic precursors estimated from the parameters of the Tsimpidi et al. (2010) V-SOA "aging" parameterization.

Typical chamber experiments with aromatics reach OH exposures in the range 5-70x10^6 molec cm^{-3} hr (see Fig. 10 of Ng et al., ACPD 2009, http://www.atmos-chem-phys-discuss.net/9/27745/2009/acpd-9-27745-2009.pdf, and also Ng, personal communication, for the high-NOx experiments). At that range of OH exposures and the OA concentrations in Mexico City, the aromatic SOA yields reported by Ng et al. (2007) are in the range of 5-10% under high NOx which is the most relevant condition here (per Dzepina et al., 2010). Even under low-NOx conditions, which are much less relevant to Mexico City, the aromatic yields are ~30-35%. Thus the "aging" parameterization used by Tsimpidi et al. (2010) is effectively producing yields which are about an order-of-magnitude (x4-20 times) too high, compared those in the most recent chamber experiments for the same degree of aging. Although chamber experiments have uncertainties such as correction for losses to the chamber walls, those uncertainties are much smaller than one order-of-magnitude. Thus we are not aware of any experimental basis for the extraordinarily high yields of the Tsimpidi et al. parameterization, and thus this parameterization has not been included in the present paper. We remain skeptical of the "aging" parameterization unless the parameterization is modified to be consistent with the results of Ng et al. (2007) for comparable OH exposures, or unless any evidence surfaces which is consistent with the Tsimpidi et al. version of the parameterization. The use of this parameterization should be avoided even if it improves the agreement with observations, as most likely the improved agreements would result from the wrong reasons. Any SOA parameterization that approximately reproduces the amount and timescale of urban SOA formation in the atmospheric observations (as e.g. in Fig. 2 of DeCarlo et al., 2010) will produce improved agreement with the observations. However only parameterizations with a physical basis should be implemented in models, and unsupported parameterizations can only be labeled "model tuning exercises."

R2.2) The paper refers to the "REF" simulation presented in Hodzic et al. (2009) stressing that the difference in the new runs is only the treatment of the organic species. However, since the implemented "ROB" and "GRI" parameterizations involve several OH reactions, it would be interesting to state whether these reactions change somewhat OH concentrations and consequently other reactive gases.

A2.2) It is true that "ROB" and "GRI" treatments involve several OH reactions and are likely to consume some OH in addition to the traditional SOA mechanism. OH concentrations for the traditional V-SOA formation have been evaluated against measurements in our previous study

(Hodzic et al., 2009). We have reported that the traditional SOA model has the tendency to underpredict the nighttime OH and overpredict the mid-day peak values by 20-30%. As suggested by the reviewer we have also carried out this comparison for the ROB and GRI simulations. The OH mid-day average levels were found to decrease from 0.42 ppt (REF) down to 0.30 ppt (GRI) and 0.25 ppt (ROB), and to agree better with the observed values of ~0.30 ppt. Also OH is the only reactive gas that is susceptible to be modified by the addition of SIVOC gas-phase reactions, since these species are assumed to not react with O3, NO3, etc. This is now explained in the new manuscript (Section 3.2.2):

"It should also be noted that ROB and GRI treatments involve several additional OH reactions and are likely to consume some OH in comparison to the REF simulation (Hodzic et al., 2009). The OH mid-day average levels were found to decrease from 0.42 ppt (REF) down to 0.30 ppt (GRI) and 0.25 ppt (ROB), which led to a better agreement with the observed mid-day values of ~0.30 ppt. Nighttime levels were still underpredicted. OH is the only reactive gas that is susceptible to be modified by the addition of SIVOC gas-phase reactions, since these species are assumed to not react with O3 or NO3."

R2.3) Lines 421-423: Certainly as stated the larger nighttime errors in the model may be caused by the improper simulation of the nighttime boundary layers. But, another source of the error is the comparison of the aerosol species taken from the lowest model layer against the surface measurements, which usually are carried out at 2m above the ground. I suggest this should be mentioned in the paper, since when the boundary layer is stable (especially during nighttime), this may lead to large uncertainties in the model-data comparisons.

A2.3) We disagree with the reviewer on this point. We are not aware of any AMS measurements that have been carried out at only 2m above ground. That may perhaps be true for aerosol sampling into filters, which is not relevant to our paper. When sampling from ground containers, an inlet is set up which reaches ~2 m above the top of the container, or about 5-6m above ground. Often longer inlets are set up, or sampling occurs from elevated structures. At T0 the measurements were carried out on top of a 5-story building at 28 m above ground, while the model results are reported at about 25m (average height of the model first layer). In addition, in previous projects we have tried to measure vertical gradients of submicron aerosol mass concentrations with the hope of deriving deposition fluxes from such gradients. These measurements have turned out to be extremely difficult because the gradients are so small that they are often smaller than the precision and uncertainty of the measurements, because aerosol dry deposition is so slow.

In summary, although vertical differences during nighttime can be very important for very reactive or sticky gases such as HNO3, they should be only minor for aerosols at the sampling heights used in this study. Thus this issue is expected to contribute a small fraction of the uncertainty to our model-measurement comparisons.

R2.4) Lines 495-497: Since the "worse" model skill in the prediction of the nighttime aerosol concentrations is emphasized, I suggest adding correlation coefficients only for daytime comparisons to the text as well.

A2.4) We agree that predicting the organic aerosols in our case study is more challenging during nighttime, especially for primary OA. As suggested by the reviewer, we have added the correlation coefficients for daytime TOA comparisons in the text (Section 3.2.3):

"Model predictions correlate somewhat better with daytime (6-18LT) observations of TOA for all three simulations i.e. ROB (R2=0.63), GRI (R2=0.52) and REF (R2=0.58)."

R2.5) Lines 735-738: As stated CO and SOA get diluted in the air in the same way, however the deposition (for the simulation time period, perhaps mainly dry deposition plays a role) will also change the concentrations of SOA. Hence, not only chemistry of SOA will change the SOA/dCO ratios. Please add information how the deposition processes are handled in the model.

Also, do you use dry deposition for the organic vapors? Depending on the deposition parameters for the vapors, the SOA production downwind may vary significantly.

A2.5) We agree that dry deposition is the more relevant mechanism for our study. Dry deposition of aerosols and gases is treated with a standard parameterization as discussed in Hodzic et al. (ACP 2009): "Dry and wet deposition for all gaseous and aerosols species are computed as a function of the friction velocities and stability of the lowest model layer (Wesely, 1989), and as a function of grid averaged precipitation rates and cloud water content (Tsyro, 2002; Loosmore and Cederwall, 2004), respectively." and "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., 2010)."

Bessagnet et al. (2010) have suggested that neglecting the dry deposition of organic vapors could result in an overprediction of V-SOA concentrations by up to 40% over some parts of Europe. As the dry deposition was determined based on water solubility of the partitioning organic vapors, this overestimation was reported to be larger during nighttime due to higher relative humidity.

A back-of-the-envelope calculation for the conditions in urban Mexico City is also presented by Dzepina et al. (2009), and we have added a brief citation of this paper for this point. The relevant text of the Dzepina paper reads: "The dry deposition of submicron particles is much slower than for gases. For example, Nemitz et al. (2008) recently reported measurements of the dry deposition velocity of submicron aerosols for an urban area at low wind speeds to be of the order of 1 mm s−1, which for a well-mixed PBL depth of 1000m will remove only 2% of the aerosol mass in 6 h. The dry deposition of oxidized gas phase species can be significantly faster. The range of deposition velocities estimated by current regional model parameterizations (Wesely et al., 1989) for HNO3 in Mexico City during MILAGRO is 7–60 mm s−1 (J. Fast, personal communication, 2008). This is likely an upper limit for the deposition velocity of oxygenated SVOC, since HNO3 is known to deposit very quickly compared to most other gas-phase molecules and most oxygenated SVOC should be less polar than HNO3. If that range of deposition velocities was applicable to oxygenated SVOC over a well-mixed PBL of 1000 m, 14–73% of the SVOC initially present would be removed in 6 h, which would reduce the predicted SOA by all models. "

In the present study, dry deposition for the organic vapors is considered. As this process is not well constrained from observations, we have used deposition velocities similar to NO2 assuming that organic vapors are not very water soluble species. For this reason the contribution of dry deposition remains low in our study. This following text was added to the manuscript to describe how the deposition was handled in the model (Section 2.1):

"Similar to Hodzic et al. (2009), in this work dry deposition for the organic vapors is considered (Wesely, 1989). As the deposition velocities for these species have not yet been experimentally determined, deposition velocities have been calculated similar to that of 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 to the amount of organic vapors.

As already explained in the response to Referee #1, in the Conclusion section we also added the following sentences highlighting the uncertainties in the dry deposition of S/IVOC:

"Opportunities for improvement also lie in the better constrained deposition velocities of the S/IVOC species. Their values are likely higher than the ones considered in this study (based on NO2, Hodzic et al., 2009) and should be experimentally and/or theoretically constrained."

R2.6) Specific comments: It would be useful to say little about the model settings – horizontal resolution etc. in the paper.

A2.6) A similar model configuration to Hodzic et al., 2009 is used in this paper. For more clarity we have given the horizontal resolution of the model in Section 2:

"For this study, the CHIMERE model is run from 11 to 31 March 2006 over the Mexico City region at both regional (35x35km2) and urban (5x5km2) scales using the same configuration and the same forcing (i.e. meteorology, emissions, boundary and initial conditions) as for our previous study presented by Hodzic et al. (2009)."

R2.7) Line 547: Correct "which are have . . ." 637: Correct "is increased . . ."

A2.7) This has been corrected.

Additional References

Bessagnet, B., et al., Impact of dry deposition of semi-volatile organic compounds on secondary organic aerosols, Atmospheric Environment (2010), doi:10.1016/j.atmosenv.2010.01.027.

Nemitz, E., Jimenez, J.L., et al.: An Eddy-Covariance System for the Measurement of Surface/Atmosphere Exchange Fluxes of Submicron Aerosol Chemical Species—First Application Above an Urban Area, Aerosol Science and Technology, 42: 8, 636 — 657, 2008.

Responses to Short Comments from Dr. Prakash Bhave

SC0) Overall, I find the content of this manuscript quite interesting. It builds upon the very thorough study conducted previously by the same authors (Hodzic et al., 2009). However, I agree with Anonymous Referee #1 that the paper "suffers from a number of serious shortcomings" and requires "major revisions and subsequent re-review." My reasons are complementary to those of Anonymous Referee #1 and R. Ahmadov, as described below. Before going further, I should come clean and acknowledge that I haven't paid enough attention to Mexico City modeling studies in the past because: (*1) I assumed the emissions inventory to be highly uncertain and to have very different characteristics than the inventories of more developed countries. (2) I did not expect the findings from intensive field campaigns in Mexico City to be generally transferable when modeling other less-polluted regions of the world.*

However, the surging number of organic aerosol (OA) modeling studies in Mexico City published in just the past year (e.g., Dzepina et al., 2009; Fast et al., 2009; Hodzic et al., 2009; Tsimpidi et al., 2009; Hodzic et al., 2010) has led me to question these pre-judgements. Given my relative ignorance of the Mexico City pollution studies, my comments here are restricted to the Abstract, Introduction, and Modeling Methods.

A0) We thank Dr. Bhave for these mostly excellent suggestions, and particularly welcome his new interest in the data and modeling from Mexico City. The comment reinforces our notion that the data from the 2006 campaign provide the observational basis for important advances in understanding of SOA formation and testing of the community models. We note that although "overstated conclusion" was mentioned in the summary line of the comment, the actual text of the comment does not identify any such overstated conclusions, but instead provides some useful suggestions for clarifying our manuscript. We have addressed each of these suggestions in detail below, and revised the paper accordingly.

SC1) Relaxed use of terminology:

In general, newcomers to any field of research are likely to be influenced by the most recent papers on the subject. Given the large number of recent studies on Mexico City coupled with the growing popularity of the VBS approach for modeling OA, the present study could potentially have a large influence on the future of OA modeling. For example, I expect that many scientists will soon begin translating the findings from these Mexico City studies into model applications over other domains (e.g., TexAQS2, CALNEX). To avoid the propagation of some erroneous concepts, I urge Hodzic et al. to exercise more caution and restraint when describing their findings as suggested in the following examples.

A1) The authors thank Dr. Bhave for acknowledging the relevance of this work to the SOA modeling community and its potential impact. We have tried to do our best to clarify the wording of the manuscript following his suggestions.

SC1-1) The authors state in their Abstract (P658 L5-7), "CHIMERE is applied to quantify the contribution to SOA formation of recently identified S/IVOC" There are several problems with this statement. First, SVOC have been known to exist for several decades and have even been quantitatively measured for more than a decade (e.g., Fraser et al., 1998) so they are by no means "recently identified." Second, most of the published information on IVOC has been deduced from anecdotal evidence and, to my knowledge, none of the IVOC have been chemically identified. Third, the emissions of S/IVOC from Mexico City are extremely uncertain (Tsimpidi et al., 2010) and their contribution to SOA are totally unknown, so it is very misleading to state that the S/IVOC contribution to SOA has been quantified in this study. Replacement of the word "quantify" with "obtain a rough estimate" would be more accurate. I find the authors' wording selection later in the Abstract (P658 L11-12) to be more appropriate: "This study highlights the important potential role of S/IVOC chemistry in the SOA budget"

Likewise in the Introduction (P663 L4-5), the authors appropriately state that "The overall objective of the present study is to assess the potential importance of SI-SOA in the highly polluted environment of Mexico City." I urge the authors to be even more conservative with this wording (e.g., change "assess" to "estimate").

Similarly on P663 L8, I would change "assessed by" to "attempted by" On P666 L11, the authors ought to change "determine" to "roughly approximate" or some other word that better conveys the enormous uncertainty in estimating S/IVOC emissions from Mexico City.

A1-1) We have added the following text to the paper to clarify some of the points raised by Dr. Bhave (P660-661):

"Although IVOC and SVOC species have been known to be present in urban atmospheres for at least a decade (Fraser et al., 1997), their role as potentially important SOA precursors was only identified in the recent work of Robinson et al. (2007) and related publications. SOA formation from some IVOCs has been established experimentally, e.g. naphthalene and heptadecane are two IVOCs whose SOA formation has been investigated in some detail in the Caltech and Carnegie Mellon chambers (Chan et al., 2009; Presto et al., 2009). Unfortunately many IVOCs and SVOCs are not separable by GC-MS and appear in the "unresolved complex mixture" (UCM), which led to the need to parameterize their amounts and SOA formation (Robinson et al., 2007)."

Some confusion appears to stem from the fact that in the past the term "SVOC" has been used more broadly to include all species sampled in diffusion denuders, while in the work of Robinson et al. (2007), SVOC was defined as those species partitioning appreciable into the particle phase, and IVOC are species of higher volatility than SVOCs but lower than that of the traditional VOCs (see Fig. 1 in Robinson et al., 2007). With this definition, the presence of IVOCs in the atmosphere has also been established by more than a decade (Fraser et al., 1997).

In any case, and as clearly said by Dr. Bhave, the goal of this paper is to provide an estimate of the potential contribution of S/IVOCs to the SOA formation in Mexico City based on available emission data and the published scientific literature. We already tried to use very conservative wording to reflect the uncertainties that exist in the POA emissions and parameterizations of SI-SOA, and are happy to make the suggested changes.

In the sentence: "..the 3D regional air quality model CHIMERE is applied to quantify the contribution to SOA formation of recently identified semi-volatile and intermediate volatility organic vapors (S/IVOC) in and around Mexico City..", the "recently identified" refers to their recently identified role as SOA precursors (Robinson et al. 2007). We also agree that in this same sentence word "quantify the contribution" could be too strong given the uncertainties, and we updated it to "estimate the potential contribution". Therefore we have changed the sentence to read: "In this study, the 3D regional air quality model CHIMERE is applied to estimate the potential contribution to SOA formation of recently identified semi-volatile and intermediate volatility organic precursors (S/IVOC) in and around Mexico City for the MILAGRO field experiment during March 2006."

We have changed "assess" to "provide an estimate of" P663 L4-5: "The overall objective of the present study is to provide and estimate of the potential importance of SI-SOA in the highly polluted environment of Mexico City."

We have updated "assessed by" to "attempted by" P663 L8: "1) quantifying the contribution of SI-SOA both within and downwind from Mexico City on much larger temporal and spatial scales than attempted by Dzepina et al. (2009) and Tsimpidi et al. (2009)"

We have changed "determine" by "estimate" P666 L11: "The first step of this approach was to estimate the amount of semi-volatile and intermediate volatility vapors that are co-emitted with the modeled particulate POA."

References:

Chan, A. W. H.; Kautzman, K. E.; Chhabra, P. S.; Surratt, J. D.; Chan, M. N.; Crounse, J. D.; Kuerten, A.; Wennberg, P. O.; Flagan, R. C.; Seinfeld, J. H. Secondary organic aerosol formation

from photooxidation of naphthalene and alkylnaphthalenes: Implications for oxidation of intermediate volatility organic compounds (IVOCs). Atmos. Chem. Phys., 9, 3049-3060, 2009.

Fraser, M. P., Cass, G. R., Simoneit, B. R. T., and Rasmussen, R. A. (1997). Air quality model evaluation data for organics. 4. C2-C36 non-aromatic hydrocarbons. Environ. Sci. Technol., 31(8):2356–2367.

Presto AA, Miracolo MA, Kroll JH, Worsnop DR, Robinson AL, Donahue NM. Intermediate-volatility organic compounds: a potential source of ambient oxidized organic aerosol. Environ Sci Technol. 2009 Jul 1;43(13):4744-9.

SC1-2) In the Abstract (P658 L26-28), the authors also state that "The predicted production from anthropogenic and biomass burning S/IVOC represents 40–60% of the total SOA at the surface during the day and is somewhat larger than that from aromatics" A reader might easily interpret this statement as a presumption that the S/IVOC from anthropogenic emissions and biomass burning are non-aromatic compounds, but I suspect this was not the authors' intent.

A1-2) We changed "aromatics" to "commonly measured aromatic VOCs " to refer to species such as toluene and xylene. The corresponding sentence was modified to read:

"The predicted production from anthropogenic and biomass burning S/IVOC represents 40-60% of the total SOA at the surface during the day and is somewhat larger than that from commonly measured aromatic VOCs."

SC1-3) In the Introduction (P660 L1-2), the authors state "many studies have reported that observed levels of SOA in polluted regions at both local and regional scales cannot be explained by current modeling assumptions". Statements such as this cast the false impression that SOA can be directly observed and that model output can be evaluated against such observations in some straightforward manner. A similarly misleading phrase is found on P664 L17. In both of these cases, the authors should be clear about the quantities being compared (e.g., observed OOA vs. modeled SOA).

On P663 L18, the authors make reference to "surrogate SOA concentrations." This seems to validate my concern about the earlier phrase "observed levels of SOA" but it is still unclear to new readers what is meant by the word "surrogate" in this sentence.

Are the authors referring to OOA? If so, that should be stated explicitly.

Also in the Introduction (P664 L7-8), the authors make reference to "The fair agreement between modeled and observed POA concentrations (Fast et al., 2009)". As in the case of SOA, this leaves readers with the false impression that POA can be directly observed and that model output can be evaluated against such observations in some straightforward manner. As the authors are well aware, there is no direct measure of ambient POA. Fast et al. (2009) are quite explicit in their Abstract, stating that modeled POA was compared with "primary anthropogenic" components derived from PMF. I urge the authors of this paper to sharpen their language in a similar manner. Another example of a misleading statement about observed POA is found on P663 L25.

A1-3) This comment appears to not be completely aware of recent developments in the OA measurement field. Although it is true that SOA and POA cannot be directly measured with 100% certainty, many recent studies have shown that HOA and OOA are very good surrogates of urban POA and of SOA from all sources, respectively, as shown by correlations with primary and secondary particle and gas-phase tracers, diurnal cycles, similarity of mass spectral profiles to those of primary emissions and chamber SOA, observed emission and deposition fluxes over urban areas, SOA formation in the laboratory from biogenic, biomass burning, and anthropogenic

precursors, etc. (e.g. Canagaratna et al., AS&T, 2004; Zhang et al., ACP 2005, GRL 2007; Volkamer et al., GRL 2006; Lanz et al., ACP 2007, ES&T 2008; Nemitz et al., AS&T 2008; Jimenez et al., Science 2009; Ulbrich et al., ACP 2009; Aiken et al., ACP 2009; Ng et al., ACP 2010). A particularly good example is the Mexico City case study described by Volkamer et al. (2006) and Dzepina et al. (2009), and shown most clearly in Fig. 1 of Dzepina et al. (2009). That case study follows a "Norte" event that brought clean airmass into Mexico City. During this period the wind speed is low and the growth of the boundary layer is limited, leading to accumulation of urban pollutants over the city. HOA is correlated with gas and PM primary species, while OOA shows no increase at all during the rush hour, and is instead correlated with gas and PM secondary species. Together with similar results published for Mexico City by e.g. Aiken et al. (2009), we believe that the use of HOA and OOA as surrogates for urban POA and SOA is justified. The measured OOA will include the SOA formed from anthropogenic, biogenic, and biomass burning sources (Jimenez et al., 2009), and as long as it is interpreted this way (as it is in our paper), the uncertainties in its quantification/interpretation are much smaller than the very large discrepancies between the REF simulation of SOA and the OOA measurements.

In the Abstract we clearly state that modeled organic aerosol concentrations are compared with organic aerosol components derived from PMF analysis of AMS spectra, with the following text: "The 3D model results are assessed by comparing with the concentrations of OA components from Positive Matrix Factorization of Aerosol Mass Spectrometer (AMS) data". And following the suggestions of Referee #1, we have added an additional table explaining the terminology used in the paper (see response to R1). The relationship between SOA and OOA, as well as POA and HOA is now clearly explained:

*"**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).*
***Oxygenated Organic Aerosols**: an OA component identified with PMF which is characterized by its high oxygen content. It is generally understood as a surrogate for SOA from all sources."*

The term SOA is commonly used to refer to secondary organic species from both measurements and modeling. So, we believe that in the introduction it is not very important to overemphasize the distinction between SOA and OOA, which is largely discussed in the rest of the paper. However as suggested by Dr. Bhave the following text was modified:

- In the Introduction, P660 L1-2: "many studies have reported that observed levels of secondary organic species in polluted regions at both local and regional scales cannot be explained by current modeling assumptions"

- In the Introduction, P664 L17: "V-SOA showed once again its limitations in the context of Mexico City (Hodzic et al., 2009), where consistent with previous studies (Volkamer et al. 2006; Dzepina et al. 2009) it failed to reproduce the observed amounts of OOA"

-On P663 L18, "surrogate SOA concentrations" was replaced by "OA component concentrations"

-In the Introduction, P664 L7-8: "The fair agreement between observed HOA and predicted POA concentrations (Fast et al., 2009)"

SC2) Methodology for estimating emissions:

Emissions of S/IVOC are among the largest uncertainties in this study, so the procedure for estimating them must be described clearly and thoroughly.

A2) We agree that the emissions of S/IVOCs are among the largest uncertainties in this type of study, given the current state of knowledge in this field. To estimate these emissions for Mexico City, we have used the same methodology as described by Dzepina et al. (2009) and Tsimpidi et al. (2010). We are glad to clarify the points that may still have been confusing.

SC2-1) The authors state (P666 L11-13) that the S/IVOC co-emitted with the modeled particulate POA is determined by "assigning a volatility distribution of POA concentrations." They go on to state (P666 L22-23) that "evaporated mass was added to the model in order to achieve equilibrium with the emitted POA." In lieu of these vague statements and the loosely-related equation that follows at the bottom of P666, the authors should articulate exactly how they derive S/IVOC from the inventoried POA values. In my opinion, the recent publication by Tsimpidi et al. (2010) does a fine job of this and may serve the authors as an example to emulate.

A2-1) These sentences taken out of context might seem unclear. However we already cited Tsimpidi et al. in P666 L19, as one of two references for the procedure to estimate the emissions of S/IVOCs. The major breakthrough of the Robinson et al., 2007 approach is that POA is no longer considered inert, but it is "assigned a volatility distribution" as explained in the paper (P666 L11-13) and is in equilibrium with its vapors ("evaporated mass was added to the model in order to achieve equilibrium with the emitted POA") that are omitted from the Mexico-City inventory. This concept is explained in P666. As stated in the paper, we have adapted the estimates of Robinson et al. (2007) without modification, so a reader can also refer to that work for further detail.

SC2-2) After arguing that only one third of the POA emissions reside in the particle phase at ambient conditions, the authors proceed to state (P667 L9-10) that "total SVOC emissions were determined by multiplying the POA emission fluxes by a factor of 3." As written, this implies that the authors have supplemented each ton of inventoried POA emissions with an extra 3 tons of SVOC. If so, that would result in only one fourth of the total emissions residing in the particle phase.

A2-2) Total aerosol and gas-phase organic carbon emissions (SVOC+POA) were assumed to be 3 times the initial POA emissions. We agree that this explanation could be confusing, and have changed it to: "Based on this assumption, total semivolatile plus aerosol phase emissions of organic species (POA+SVOC) were determined by multiplying the POA emission fluxes by a factor of 3."

SC2-3) In the next sentence (P667 L11), the authors state that "additional mass has been added to IVOC7, IVOC8, and IVOC9 ." Did the original inventory contain some emissions of these 3 species? If so, where did those emissions come from? If not, the sentence ought to be clarified accordingly (i.e., remove the words "additional" and "added").

A2-3) "Additional mass" refers here to "In addition to SVOC emissions (P667 L11)". The original inventory does not contain any S/IVOC emissions as explained throughout the paper, and this sentence was modified to avoid any confusion:

"In addition to SVOC, additional mass (also not present in the emissions inventory) has been added to account for emissions of higher-volatility vapors i.e. $IVOC_7$, $IVOC_8$ and $IVOC_9$."

SC2-4) In the next sentence (P667 L12-13), the authors state that the additional IVOC mass was "assumed to be 1.5 times the mass reported in POA emissions." This too is unclear. Is the 1.5 factor applied before or after the POA emissions were tripled?

A2-4) This sentence was clarified to read: "Following Robinson et al. (2007) this mass was assumed to be 1.5 times the mass of total gas and aerosol organic carbon emissions (POA+SVOC)."

SC2-5) The authors then argue that the factor of 1.5 is a conservative estimate, stating (P667 L13-14) that the "ratio of total IVOC to POA was experimentally determined, and it ranges from 1.5 to 3.0." As in my preceding comment, it is unclear whether or not the POA referred to in this ratio is inclusive of the SVOC that the authors have added.

Moreover, a careful search of the f values in Table 1 reveals no factor of 1.5 (aside from text in the caption). Summation of f values in the 3 IVOC bins (based on the definition provided on P666 L15) yields 170% or a factor of 1.7.

A2-5) With the change under A2-4, it is now clear that 1.5 applies to POA+SVOC emissions (IVOC=1.5*(POA+SVOC)=4.5*POA)

Table 1 does not state that the 3 last bins contain only IVOCs. The note of the Table 1 explains that:

"The majority of intermediate volatile species (IVOC) is not accounted for in the traditional POA emission inventories. This additional contribution has been added here to $SVOC_7$, $SVOC_8$ and $SVOC_9$ and represent 1.5 times the mass reported in POA emissions as in Robinson et al. (2007)."

The 7th bin contains both SVOC7 and IVOC1 species. To make this more obvious we added an additional column to Table 1 that gives the respective names of each species.

SC2-6) On P667 L16-19, the authors provide some ambient concentrations as an illustrative example of their calculations and refer to a previously published table (SI-3 by Dzepina et al., 2009). But even the example is misstated and adds confusion. The aforementioned table provides a gas/particle ratio of 6.7 for conditions in which the total particle-phase organic concentration (cOA) is 10 µg/m3. It is not referring to POA in isolation. However by this point, it is unclear what exactly the authors mean by the term "POA." I can only guess that POA is intended to mean the portion of SVOC that was initially emitted in the particle phase (i.e., one third or one fourth? of the material regarded as SVOC at the point of emission).

To complete this example, it would be helpful if the authors added a pair of parenthetical notes after each instance of the word "material" on L19 in which rough estimates of the extra material concentration (e.g. ~70 µg/m3) and total material concentration can be provided.

POA stands for the primary-emitted organic aerosols, which are in equilibrium with their primary vapors (S/IVOCs). This gas/particle partitioning of the emitted organic material (POA+S/IVOC) depends on the ambient mass of OA that is available for the partitioning. In presence of 10ug/m3 of OA, which is a typical level for Mexico City during the morning (Aiken et al., 2009), one can calculate using equilibrium partitioning theory and the volatility distribution of Robinson et al. (2007) that 87% of the emitted organic material (POA+S/IVOC) is in the gas phase. According to partitioning theory, the particle-phase fraction decreases (increases) as the OA available for partitioning decreases (increases). E.g. in presence of 1 ug/m3 of OA, the gas-phase fraction is 93%. This is described in more detail in Dzepina et al., (2009, SI-Table3).

Similar to Tsimpidi et al. (2010), we use a constant emission ratio to the POA emission inventory that is consistent with the average OA levels found in Mexico City. For example if the ambient concentrations of the emitted POA are 10 ug/m3 (and SOA close to zero), the total emitted

organic material (POA+S/IVOC) is 7.5*10=75 ug/m3 for the Robinson parameterization, of which 65 ug/m3 are in the gas phase (S/IVOC) and 10 ug/m3 are in the aerosol phase (POA). Thus the particle-phase fraction is 65/75 = 87%.

To avoid confusion, the corresponding text (P667-L16-19) has been changed to read: "Note that in presence of 10 µg/m3 of ambient POA and very low SOA concentrations, the total amount of primary organic material (POA+SVOC+IVOC) derived from the Robinson parameters is about 75 µg/m3 at 20C, of which 87% remains in the gas-phase (SVOC + IVOC = 65 µg/m3) (Table SI-3 of Dzepina et al., 2009)."

In the sentence P667 L20, the "extra amount of material" refers to the amount of introduced organic material (gas and particle) in this study according to the Robinson et al., parameterization. To avoid any confusion, this sentence was changed to read: "The extra amount of organic material introduced here (as S/IVOC) is small compared to the total observed organic gas + particle material in Mexico City "

SC2-7) On P667 L23-26, we learn that certain minor sources of POA "were not considered as semi-volatile in this study." This seems like a rather cryptic way of stating that those emissions are treated as non-volatile, unless I've misinterpreted this altogether. Are these emissions scaled up by a factor of 3 like the other sources? The authors rationalize this special treatment by stating that "their volatility distribution was not available." This phrase will give readers the false impression that the volatility distributions of all other organic aerosol sources have been measured. The rationale requires revision.

At the end of this paragraph (P668 L1), I believe the words "from the Tula complex" should be inserted before "were occasionally"

Given the critical importance of S/IVOC emissions to the conclusions of this study, the authors need to be crystal clear with their terminology and emissions treatment in the revised manuscript.

A2-7) The volatility distribution for primary organic material has been determined from experimental measurements by Robinson et al. (2007) for diesel exhaust. A similar distribution was reported for wood burning by the same authors. Vehicles and biomass burning are the major POA sources in Mexico City during MILAGRO according to all published estimates (e.g. Stone et al., 2008; Aiken et al., 2009, 2010), therefore it is appropriate to use the Robinson et al. distributions for the majority of the POA sources in this study. In the paper, we assume that all POA emitted from surface anthropogenic and biomass burning emissions follow the same S/IVOC distribution for the Robinson mechanism. The minor sources that have been treated separately are non-combustion industrial emissions, which are thought to be minor for POA according to all results from MILAGRO, and for which no information on the volatility distribution is available. For the GRI simulation we use the revised volatility distribution for wood burning emissions provided by Grieshop et al. (2009).

The paper was modified to read:

"All POA surface anthropogenic sources (e.g. traffic) as well as biomass burning emissions were considered as semi-volatile following the S/IVOC distribution determined by Robinson et al. (2007) for diesel exhaust and wood burning. POA emissions associated with elevated industrial sources (i.e. point sources) were not treated as semi-volatile (i.e. they were considered non-volatile with the same emission flux as in the inventory) in this study because their volatility distribution has not been reported."

SC3) Miscellaneous technical comments:

SC3-1) Some findings reported in the Abstract (P658) appear to be inconsistent with each other. On L17-19, the authors state that the addition of S/IVOCs enhances the modeled SOA concentrations by a factor of 3-6. Then on L26-28, they state that anthropogenic and biomass burning S/IVOCs represent only 40-60% of the total SOA. Can this apparent contradiction be resolved in the revised abstract?

A3-1) We agree that these findings were not clearly explained in the paper. The factor 3-6 refers to the increase in modeled concentrations, while 40-60% refers to the measurements. Also, we calculated the average increase in SOA predictions based on Table 2, and the increase due to the addition of S/IVOC chemistry ranges from a factor of 2 to 4. This has now been corrected in the manuscript: "

" The results show a substantial enhancement in predicted SOA concentrations (2-4 times) with respect to the previously published base case without S/IVOCs (Hodzic et al., 2009),.."

"The predicted production from anthropogenic and biomass burning S/IVOC represents 40-60% of the total measured SOA at the surface during the day"

SC3-2) In the Introduction (P660 L13-14), the authors state "Although activity coefficients are included in this formulation, they are typically set to 1 due to lack of constraints on their values."

A casual reader may interpret this as a shortcoming of traditional OA models, but the authors make this same assumption in their study (see P666 L17). Perhaps this entire sentence should be omitted from the Introduction, since it does not add valuable content to the paragraph.

A3-2) Done.

SC3-3) Grieshop parameterization. When describing this parameterization (P668 L21), the authors state that "No biomass burning emissions of IVOC are considered." This is contradictory to Table 1 (f7 = 10%) according to the definition of IVOC provided by the authors (P666 L15). The authors also imply (P669 L1-2) that revised OH reaction rate constants are provided in Table 1, but they are not.

A3-3) As explained in the paper, no BB emissions of IVOC are considered for GRI. The f7=10% belong to SVOC7 emissions. This has been made clear now in the paper by adding the corresponding names (SVOC and IVOC) to Table1.

Also, the value of the OH reaction rate constants for GRI has been added to the footnote of Table 1: "[(c)] The gas-phase oxidation by OH of all of the nine S/IVOC is assigned a rate constant of 4 $x10^{-11}$ cm^3 $molec^{-1}$ s^{-1} (ROB simulation), and of 2 $x10^{-11}$ cm^3 $molec^{-1}$ s^{-1} (GRI simulation)."

SC3-4) On P669 L6, the authors indicate that V-SOA forms from biomass burning. Which volatile organic compound(s) is this formation attributed to? Why isn't V-SOA formed from biomass burning in the traditional simulation (as implied from the lack of mention on P669 L11-13)?

A3-4) V-SOA stands for SOA formed from VOCs in the "traditional SOA model (REF)" in which SOA is formed from anthropogenic, biomass burning and biogenic precursors such as toluene, xylene, isoprene, monoterpenes, etc. In the sentence P669 L11-13 biomass burning was omitted by error, we have corrected for that as follows: "In this traditional simulation (referred as "REF" here, and as "BIO-T" by Hodzic et al. (2009)) SOA is formed from anthropogenic, biomass burning and biogenic VOC precursors."

SC3-5) Computational requirements. In a supplemental table, it would be very helpful of the authors to tabulate the full set of OA species that were added to CHIMERE for the present investigation. I gather from Hodzic et al. (2009) that 8 hydrophobic and 2 hydrophilic organic aerosol species were needed to simulate V-SOA in the REF simulation of the present study (presumably all 10 of these species were added in the gas phase as well as to each of the 8 particle size sections, yielding a total of 90 extra model species). How many more species were required to simulate the volatility distribution and O/C ratio of the modeled organic aerosol in this study? What was the computational expense of adding all these species?

A3-5) Accounting for S/IVOC emissions and chemistry is indeed computationally demanding. In addition to V-SOA species, we have added about 200 species to account for (1) the gas-phase and aerosol primary organics (partitioning of S/IVOCs before oxidation) from anthropogenic and biomass burning sources, (2) the gas-phase and aerosol secondary organics (partition into SI-SOA), (3) the amount of O and C in each volatility bin. This has roughly increased the computational cost of the model by a factor of two. We do not think that putting an additional table listing all the species is of great interest for the paper, as it depends on the type of the studies (anthropogenic only emissions, biomass burning, etc.) and the amount of information needed for a particular study (values of O, C, only mass, etc). The following sentence has been added to the manuscript in Section 2.2:

"Accounting for S/IVOC emissions and chemistry increased the computational cost of the model by about a factor of two compared to the REF simulation."

Responses to Short Comments from Dr. Heather Simon

SC0) As someone who is interested in model performance of OM/OC ratios using traditional SOA modeling, I was pleased to see this article in which O/C ratios are explicitly evaluated in the VBS framework. The model inter-comparison provided a good perspective on the differences in these model scenarios while making use of a rich dataset of ambient measurements for model evaluation. However, after reading the discussion paper I am left with some concerns.

A0) We are pleased that this work has arisen interest in the community and glad to account for improvements suggested by Dr. Heather Simon.

SC1) Comparisons between different model formulations show that each scenario outperforms the others in regards to at least one metric:

(1)REF: underpredicts SOA mass but has the best correlation for temporal variability of TOA. O/C was not evaluated.

(2)ROB: has reasonable agreement on SOA mass (within a factor of 2 according to section 3.2.2), low correlation for temporal variability at T0 and T1, poor agreement for O/C.

(3)GRI – over-predicts SOA mass (factor of 2 too high at T1 site every day), low correlation for temporal variability in TOA (at T1 and at T0 if you consider compensating errors mentioned in section 3.2.3), very good agreement for O/C.

Based on these results, the authors might critically evaluate whether VBS offers an improvement in model performance over traditional OA treatments? In section 4, it is mentioned that REF

produces SOA concentrations that are too low by a factor of 5-10. However, the authors should be clear that the REF scenario does not represent the most up-to-date traditional modeling. Evaluations of other traditional SOA models have found much better agreements with ambient estimates (Yu et al, 2007).

A1) We agree that the current S/IVOC parameterizations do not bring the final response to the model/observation gap for SOA in polluted regions. However the fundamental reason to include these parameterizations in our SOA model is that they represent species which are known to be present in the atmosphere and produce SOA, and which are missing from current models. It is not appropriate to decide whether to include them or not based on model performance parameters. They need to be included because they are present in the atmosphere. The purpose of the present paper is to evaluate the first parameterizations that have been proposed, in the context of the MILAGRO study which offers some of the best comparison data available to date.

Of course the detailed amounts, reaction rates etc. of the S/IVOC parameterizations will need to be refined as additional constraints on these values emerge from laboratory and source studies. This is already explained in the conclusion: "This study also highlights the need for improvements in current parameterizations. Experimentally constrained amounts and partitioning/ageing parameterizations of S/IVOC are urgently needed for further progress in this area. In particular, the effect of fragmentation of oxygenated species leading to higher volatility species (Kroll et al., 2009) needs to be taken into account. Parameterizations which explicitly track both volatility and oxidation state (e.g. Jimenez et al., 2009) may also allow improved predictions of OA evolution and aging."

In addition, as already explained in the Response to R2 (A2.1) we agree that additional V-SOA can be formed from "traditional" VOC precursors (e.g. aromatics) if the most recent yields from chamber experiments are used. Such an approach was used by Dzepina et al. (2009), who compared the V-SOA formation for a case study in Mexico City when using yields similar to those in the present paper, and those from the updated chamber experiments of Ng et al. (2007). However as concluded on that paper "Traditional SOA precursors (mainly aromatics) by themselves still fail to produce enough SOA to match the observations by a factor of 7" when using the updated yields from Ng et al. (2007). Thus the recently updated yields cannot close the gap between measured and predicted SOA in polluted regions.

The fact that a large discrepancy is observed between traditional V-SOA models and measurements in polluted regions has been conclusively demonstrated in many studies, as already discussed in the P660 of our ACPD paper. This is especially obvious in studies using highly time-resolved measurements in polluted regions. As already stated in our ACPD paper (P659 L25-27) "Biogenic SOA levels formed in clean regions appear to be well represented overall by "traditional" SOA models (e.g., Tunved et al., 2006; Hodzic et al., 2009; Chen et al., 2009; Slowik et al., 2009)." The study of Yu et al. (2007) focuses on rural areas where the importance of biogenic SOA should be larger, and thus the better agreement is not surprising compared to more polluted areas. That study also uses very slow OC measurements which are less useful for model evaluation than highly time-resolved measurements, as the possibility of compensating errors increases greatly over long model averaging periods. Finally, a recent update of the SOA mechanisms used in the same CMAQ model used by Yu et al. results in a larger underestimation of SOA across the US (Carlton et al., ES&T 2010).

SC2) I have additional concerns about the treatment of O/C in the GRI and ROB scenarios:

(1) A description of how O and C are modeled for each OA category (V-SOA, S/I-SOA, POA) should be added to the model formulation section. It is not clear from the current paper how these are being treated.

A2) The way O and C were modeled in this study was already explained in Section 3.3 of the ACPD paper (P678-679 of the ACPD version):

"Model O/C ratios were estimated using measured chamber values for V-SOA (Ant V-SOA=0.37; Bio V-SOA=0.40), hydrocarbon-like organic aerosol (Ant POA=0.06), and biomass burning organic aerosol (BB POA=0.30) reported by Aiken et al., (2008) and Shilling et al., (2009). The organic carbon content in the secondary organic matter formed from the S/IVOC vapors was directly determined from modeled species as both carbon and oxygen fractions are explicitly modeled."

a) Section 3.4.1 mentions that O and C are modeled explicitly for S/IVOC and that the O/C ratio is calculated directly from modeled O and C. The addition of oxygen from OH reactions (9% per reaction in ROB and 40% per reaction in GRI) is discussed, but this approach also requires an assumption about the O and C contents of the initial S/IVOCs. What O/C ratio is assumed for emitted S/IVOCs ?

The O/C ratio of the emitted S/IVOC is assumed to be zero. Although oxygenated species are emitted in e.g. vehicle exhaust, they represent only a small fraction of the mass. E.g. Aiken et al. (2008) reported an O/C = 0.06 for HOA. A similar bulk characterization of the O/C of gas-phase species is not available to our knowledge, therefore we have extrapolated the particle-phase results to those species.

b) A single O/C ratio based on chamber measurements is used for each of V-SOA, Ant POA, and BB POA. Does this mean that O and C are not explicitly modeled for these other types of OA? This seems to introduce inconsistency in the model treatment of OA from different sources given that the VBS was intended to represent a unifying framework for treating OA so that OA from all sources (POA, SOA etc.) is modeled using the same processes.

This is correct. In this paper we are not developing or modifying the previously-published SOA models, rather we are implementing and evaluating those models in the context of the MILAGRO dataset. We could modify the previously-published models in various ways to better reproduce the observations or produce a more consistent model treatment, however this would introduce an enormous number of possible modifications which would be poorly constrained by the model-measurements comparisons. We prefer to leave such model improvements to researchers studying and parameterizing such processes from laboratory and source data.

c) If O and C are not explicitly modeled for V-SOA and POA, does that mean that aging (addition of 9 or 40% mass with OH reaction) is not included for these OA subcategories?

This is correct for V-SOA as explained in the previous response. It is incorrect for POA, which is treated dynamically through the parameterizations of Robinson et al. (2007) and Grieshop et al. (2009), and which can gain oxygen through gas-phase reactions.

SC3) The addition of 40% mass from a single oxidation step seems physically implausible. Although the authors acknowledge that no mechanism has been proposed to explain this parameterization (page 668, lines 26-27), this finding might be repeated in the conclusions section. The fact that such an assumption is necessary to achieve realistic O/C values suggests that this modeling framework might be missing some key physical/chemical processes (aging, condensed-phase reactions etc.). A more in-depth exploration of this problem is needed since it has the potential to undermine the approach being used.

A3) We agree that this is an important area for improvement, which was already emphasized in the conclusion of the ACPD version (P668, point 5):

"This study also highlights the need for improvements in current parameterizations. Experimentally constrained amounts and partitioning/ageing parameterizations of S/IVOC are urgently needed for further progress in this area. In particular, the effect of fragmentation of oxygenated species leading to higher volatility species (Kroll et al., 2009) needs to be taken into account. Parameterizations which explicitly track both volatility and oxidation state (e.g. Jimenez et al., 2010) may also allow improved predictions of OA evolution and aging."

It is important to remember that the SI-SOA parameterizations used in our work are the first proposals to account for these missing species in current models. The fact that they have some limitations should not be an obstacle to evaluate the amount and properties of the SOA produced when these parameterizations are included in a 3D model. Further improvement of the SI-SOA parameterizations is a very active area of research for multiple groups at present, and in particular the reasons for the rapid O/C increase have been the subject of much discussion at recent conferences etc. In the context of our study, all we can do is to call for more research on this work.

SC4) I have one final technical comment. The employed DHvap values in this work appear to be overestimated. Though the values are based on published work by Robinson et al., (2007), recent laboratory findings report DHvap values in the range of 11-44 kJ/mol for SOA formed from a variety of gas-phase precursors (Offenberg, et al., 2006). [Note that the highest value here is lower than the lowest value used in this work.] SOA model predictions are very sensitive to Hvap values (Tsigaridis and Kanakidou (2003) and Henze and Seinfeld (2006)), e.g., diurnal SOA profiles are opposite of observations when the applied Hvap is too high (Pun and Seigneur, 2008). If temperatures in Mexico City were high during the modeled period, an unrealistically high Hvap value could help to explain the overpredictions of POA evaporation at the T1 site.

A4) We believe that the DHvap values used in our work are appropriate. The difference between the DHvap values for actual molecules and those used in 1 or 2-product SOA models was resolved by Donahue et al. (ES&T 2006). The reason why the DHvap used in 1 or 2 product models are unphysically low is because they are compensating for the fact that the real broad volatility distribution of the OA is being replaced with only one or two species. To produce similar evaporation upon heating as the real mixture, those species need to be assumed to have unrealistically low DHvap. A volatility basis set is by definition a representation of a broad volatility distribution and does not suffer from the same problem, and thus realistic DHvap need to be used for these species.