Atmos. Chem. Phys. Discuss., 12, C13084–C13099, 2013
www.atmos-chem-phys-discuss.net/12/C13084/2013/

Atmospheric
Chemistry
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Discussions

Interactive comment on “Formation of organic aerosol in the Paris region during the MEGAPOLI summer campaign: evaluation of the Volatility-Basis-Set approach within the CHIMERE model” *by* Q. J. Zhang et al.

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Received and published: 2 March 2013

Answer to referee 1: This paper applies the volatility basis set approach for representing organic aerosols, that is becoming more widely used in regional models, and evaluates the model with measurements collected during the MEGAPOLI campaign in the vicinity of Paris. Although the focus is on organic aerosol, the paper also presents the performance of trace gases, inorganic aerosols, and black carbon. The authors run the CHIMERE model with various configurations to examine how predictions of organic aerosol vary based on a previous treatment of SOA and two variations of the

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VBS approach. The paper is well written and organized, the discussion of the results is balanced in terms of the possible uncertainties that can contribute to model errors, and the figures are easy to read and interpret. However, there are a number issues described next that need additional clarification from the authors before the paper is suitable for publication.

Reply : We thank the referee for this general positive evaluation. His suggestions were taken into account, and certainly improved the paper.

General comments:

1. Introduction: The introduction provides a brief review of the volatility basis set approach and its use in models. This material is a bit dated and does not include more recent work in the past 2-3 years that have shown that VBS formulations have can also overpredict OA in some instances and have provided lab/field observations (e.g. Virtanen et al., 2010; Vaden et al., 2010, 2011) that question some of the underlying assumptions employed by the VBS. Many of the assumptions employed by VBS are largely unconstrained by data (e.g. assuming SVOC emissions are 3 times POA emissions, each oxidation reaction increases mass by 7.5%). So the work on VBS is a bit more complicated than what is presented in this paper. However, there have not yet been any alternative theories for the entire lifecycle of SOA that can now be used by models so the use of VBS in this paper is still appropriate.

Reply: These three useful references are added on p29478:

line 13: "…there is considerable uncertainty in their representation in 3-D models (Volkamer et al., 2006; Hallquist et al., 2009; Virtanen et al., 2010)"

line 20: "Semi-empirical formulas used for the estimation of vapor pressure and enthalpy of surrogate products may also induce additional uncertainty (Hallquist et al., 2009; Vaden et al., 2010, 2011; Valorso et al., 2011)"

References to be added:

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Vaden, T. D., Song, C., Zaveri, R. A., Imre, D., and Zelenyuk, A.: Morphology of mixed primary and secondary organic particles and the adsorption of spectator organic gases during aerosol formation, Proc. Natl. Acad. Sci. U. S. A., 107, 6658-6663, 10.1073/pnas.0911206107, 2010.

Vaden, T. D., Imre, D., Beranek, J., Shrivastava, M., and Zelenyuk, A.: Evaporation kinetics and phase of laboratory and ambient secondary organic aerosol, Proc. Natl. Acad. Sci. U. S. A., doi: 10.1073/pnas.1013391108, 2190-2195, 2011.

Virtanen, A., Joutsensaari, J., Koop, T., Kannosto, J., Yli-Pirila, P., Leskinen, J., Makela, J. M., Holopainen, J. K., Poschl, U., Kulmala, M., Worsnop, D. R., and Laaksonen, A.: An amorphous solid state of biogenic secondary organic aerosol particles, Nature, 467, 824-827, 10.1038/nature09455, 2010.

However, we think that they are not directly related to our study as almost no CTM model has all the constraints described in these papers, such as an explicit mixing state treatment of SOA and its morphology, etc. In the regional CTM, these parameters are in general more simplified than box models, thus providing reasonably good results within limited calculation capacity.

Assuming SVOC emissions as 3 times POA emissions was not necessary in our work. It was necessary for work in Mexico City, as POA emission factors there were derived under ambient conditions, and 2/3 of initial POA was supposed to appear in the gas phase (Dzepina et al. 2009). However, the emission data bases used in our study were derived under high OA conditions (as in Robinson et al. 2007‘s paper), and thus no correction factor is needed to account for the part emitted as SVOC. When air masses will dilute and OA levels will decrease, part of the POA will evaporate following partitioning theory and as a function of the POA volatility distribution (Robinson et al. 2007).

K. Dzepina, R. M. Volkamer, S. Madronich, P. Tulet, I. M. Ulbrich, Q. Zhang, C. D. Cappa, P. J. Ziemann, and J. L. Jimenez: Evaluation of recently-proposed secondary

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organic aerosol models for a case study in Mexico CityAtmos. Chem. Phys., 9, 5681-5709, 2009

2. Measurements, Section 2.1: The authors note while other instruments measure aerosols, they only use measurements from the AMS in this study. I can understand perhaps that the measurements may be redundant, but are those other measurements similar to those from the AMS? This information would be useful to know something about measurement uncertainty which will affect interpretation of model results.

Reply: There are measurements from PILS-IC and OC instruments at SIRTA and LHVP, but not at the third (GOLF) site. The AMS measurements have been compared to the PILS measurements (Freutel et al.2012). PILS-OC measurement provides only OC, not OM. This is why a direct comparisons to AMS measurements are not straightforward. Qualitatively speaking, PILS OC values showed a similar temporal variability as AMS OM measurements (Couvidat et al. 2012).

3. Model Configuration, Section 3.1: Does CHIMERE include wet removal of trace gases and aerosols? It is not clear whether this process is important or not for this study, since there is little discussion on whether precipitation is significant or not. In several places the authors introduce features of the model configuration after section 3.1, which is confusing. For example, the authors state that the model does not include an urban canopy parameterization on page 29493, which should also be included in section 3.1. They also state they set a minimum PBL height in the model of 200 m which again should be stated up-front in section 3.1.

Reply: Yes. CHIMERE includes wet removal of trace gases and aerosols, but there was no heavy precipitation happening during the campaign in the Ile de France region.

A sentence commenting on precipitation is added on p29483, line 17:

“No important precipitation happened during the campaign in the Ile-De-France region.”

A sentence concerning on deposition mechanism is added on p29484, line 10:

“Dry deposition velocity for gases and aerosol is computed by use of a resistance analogy (Wesely, 1989). Wet removal of gases and aerosol in cloud and by precipitation is taken into account (Tsyro, 2002; Loosmore and Cederwall, 2004), respectively.”

References to be added:

Loosmore, G. and Cederwall, R.: Precipitation scavenging of atmospheric aerosols for emergency response applications: testing an updated model with new real-time data. Atmos. Env., 38:993–1003, 2004

Tsyro, S.. First estimates of the effect of aerosol dynamics in the calculation of PM10 and PM2.5. EMEP report, 2002

Wesely, M.: Parameterization of surface resistances to gaseous dry deposition in regional-scale numerical models. Atmos. Environ., (23):1293–1304, 1989

The discussion on urban canopy parameterization and the minimum PBL height on page 29493, line 12 “In addition, MM5 often predicts low nighttime PBL height down to 70 m in urban regions. This is related to the fact that the urban canopy effect and urban heating effect are not taken into account in this model. Therefore, the minimum modeled PBL height 15 is set to 200 m which is close to the measurements. “

is modified and put into section 3.1, p29498, line 26:

“MM5 often predicts low nighttime PBL height down to 70 m in urban regions. This is related to the fact that the urban canopy effect and urban heating effect are not taken into account in this model. Therefore, the minimum modeled PBL height is set to 200 m which is close to the measurements.”

4. Section 3.4: Please comment if any attempt was made to include effects of anthropogenically influenced biogenic SOA. There have been recent observations suggesting that anthropogenic precursor emissions enhance biogenic SOA when these two sources mix. Paris is an environment where this is possible. Normally anthropogenic and biogenic SOA are computed separately.

Reply: The anthropogenic and biogenic SOA are computed separately. The NOx effect on SOA formation is described in section 3.4.2. The highest SOA yield under low-NOx condition is chosen. Indeed, under the conditions of the present campaign, most SOA is formed under relatively clean conditions in the rural south to west sectors upwind of the Paris agglomeration. An "anthropogenic" effect taken into account is the increase in urban OA, which favors condensation of biogenic SVOC according to the gas-particle partitioning theory.

5. Model Evaluation in General, Section 4: The evaluation of the model relies solely on surface meteorological, trace gas, and aerosol quantities. Many other modeling studies have shown that knowing whether the conditions aloft are simulated well is important since those conditions will affect surface concentrations. Where there no measurements aloft collected during MEGAPOLI that could be used to evaluate model performance? For readers not familiar with the campaign, it would be useful to state somewhere (either in the introduction or Section 2.1) that no observations were made during the campaign.

Reply: One related study (Royer et al. 2011) about "Comparison of lidar-derived PM10 with regional modeling and ground-based observations in the frame of MEGAPOLI experiment" has been published.

The following text has been added to the manuscript on p29484, line1:

"Model simulation during the MEGAPOLI campaign has previously been compared with mobile ground based lidar measurements around the Paris agglomeration from which PM10 values have been derived. Wet PM10 vertically integrated between the ground and 1 km above ground level from lidar and CHIMERE results have been compared and have shown similar results with a root-mean-square error (and mean absolute percentage error) of about 5 mg m-2 (22 %)."

References to be added:

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Royer P., Chazette P., Sartelet K., Zhang Q. J., Beekmann M., and Raut J.-C., Comparison of lidar-derived PM10 with regional modeling and ground-based observations in the frame of MEGAPOLI experiment, Atmos. Chem. Phys., 11, 10705-10726, 2011

6. Meteorological Evaluation, Section 4.1: I suggest including a time series of observed and simulated humidity. Relative humidity is an important quantity for the uptake of water on aerosols. The model underestimates daytime temperatures, as much as 5 deg C on some days which is rather large. What impact will this have on biogenic emissions that are temperature dependent, and subsequently ozone and SOA?

Reply: The uptake of water on aerosol is calculated by ISORROPIA and is not evaluated in this paper, as AMS measurements refer to dry aerosol. The daily temperature peak is underestimated by up to 5K on some days which may theoretically conduct to an underestimation of biogenic VOC emissions. However, many other uncertainties affect biogenic VOC emissions. Nevertheless, biogenic VOC levels in the Paris agglomeration are reasonably well predicted in the model as illustrated in Figure S6 which has been added to the Supplementary material.

On page 29492, line 12, a sentence commenting the underestimation of temperature on some days is added:

“The daily temperature peak is sometimes underestimated by up to 5K which may theoretically cause an underestimation of biogenic VOC emissions, and thus of ozone and SOA formation. However, many other uncertainties affect biogenic VOC emissions. Nevertheless, biogenic VOC levels in the Paris agglomeration are reasonably well predicted in the model as illustrated in Figure S6 (see section 4.2). “

7. Section 4.2: The model has not been evaluated with VOC or OH measurements. Were these available? Since the VBS approach depends on both, knowing how SAPRC performs in terms of VOCs and OH will provide evidence of whether SOA production would have been higher or lower, had the photochemistry been predicted better.

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Reply: A figure on VOC evaluation is presented as Fig. S6. For the biogenic species, the comparison is presented above. A sentence for discussion on aromatics can be added on p29496, line3 in section 4.2. Thus, the title of section 4.2 will be changed into BC, NOx and VOC evaluation.

"Predicted major VOC precursors for SOA formation are evaluated with the GC-FID and PTRMS measurements. The mean concentrations of isoprene are 0.24, 0.22 and 0.43 ppb in the model, and from GC-FID and PTRMS (m/z 69) measurements, respectively. The predicted terpenes concentration is on a similar level of the observed one from PTRMS (m/z 137). Considering measurement uncertainties, this result implies a correct average level of biogenic VOC in the model. The variability is also well represented, larger observed and predicted values occur in periods R1 and R3 when winds are low and temperature enhanced. Lumped anthropogenic aromatics are compared to the sum of the measurements of benzene, toluene, xylenes, ethylbezene, n-propylbezene, 1,3,5-TMB, o-ethyltoluene and 1,2,4-TMB from GC-FID which are the major aromatics in urban region and the sum of m/z 79, 93, 107 and 121 (which are corresponding to the sum of benzene, toluene, aromatic C8 and aromatic C9) from PTRMS (Fig. S6). The model overestimates the sum of the aromatic species by about 48% and 82% with respect to the measurements from PTRMS and GC-FID, respectively. This is partly due to an underestimation of dispersion as NOx and BC. However, measurements probably do not represent all emitted aromatic species. Thus, the aromatic species are probably reasonably well predicted.

Higher alkanes grouped in model species are not evaluated because of lack of measurements for a large part of the lumped species in the model."

The OH comparison is discussed in the Supplementary Information as OH evaluation and discussion are beyond the aim of this paper. Some sentences are added to the Supplementary Information to comment the following figure of OH comparison.

"Predicted OH concentrations are correlated (R=0.62) with the measurement at SIRTA, the driving force for correlation being the strong diurnal cycle with a noon maximum due to enhanced UV radiation. Daily maxima are mostly overestimated with a factor up to three. This overestimation could be due to a variety of reasons: OH and HOx radical sources (O3, H2O, HONO formed by heterogeneous reactions, photolysable VOC, photolysis frequencies) and sinks of HOx radicals (NO2, . . .) and in NO and VOC levels responsible for radical inter-conversion reactions. “

8. Inorganic Aerosol Evaluation, Section 4.4: The evaluation of inorganic species seems a bit of a distraction since the main purpose of the paper is to evaluate organic aerosols. I am not recommending removing the section, since it is useful for completeness. However, the rationale for inclusion up-front in the paper and some transition statements here would improve the ïňĆow of the paper.

Reply: On p29496, line22, a transition sentence is added:

“Although the focus here is on organic aerosol, for completeness also inorganic aerosol is evaluated because of its important contribution on fin PM.”

9. Organic Aerosol Evaluation, Section 4.5: The authors need to state how the model predictions of organic aerosols are compared to AMS measurements. The AMS measures aerosols up to about 1 um, as reported by the manufacturer, but they often could only be measuring up to 0.7 um if the aerosol concentrations are low. So, which size bins from CHIMERE are used to compare with AMS measurements? Also, do the AMS measurements been compared with independent aerosol size distribution data to derived collection efïňĄciency factors? What are the factors that have been employed? It would be useful to include some sort of uncertainty estimate in the data.

Reply: Yes, the AMS measures in the size range of ∼70nm - 750nm (vacuum-aerodynamic diameter). However, generally most of the aerosol mass in PM1 is within this size range, which is the reason why typically the AMS effectively gives ∼PM1. AMS measurements at LHVP and GOLF were compared to total mass measurements using TEOM-FDMS, and to aerosol size distribution measurements from an SMPS at

SIRTA (Freutel et al. 2012). Collection efficiencies used were 0.5 for all comparisons, and gave consistent results with all co-located measurements. Freutel et al. 2012 have applied a value of 30% for the overall uncertainty in AMS measurements (which is consistent with Canagaratna et al., Mass Spectrom. Rev., 2007). This includes uncertainties of collection efficiency and other calibrations and measurement uncertainties. Freutel et al. 2012 have compared the total mass measured in PM1 with the sum of mass measured with the AMS (∼PM1) and BC (PM1), and find good agreement, the fraction of the total mass covered by the AMS measurements is about 0.9 for both LHVP and the GOLF site, see their ACP-paper, Section 2.2.2. The remaining discrepancy of ∼10% is well within the uncertainty of the AMS measurement itself.

Modeled secondary aerosol is considered to appear all in the accumulation mode, thus it is directly compared to the AMS measurements regardless of its size distribution. Some sentences about AMS measurements are added on p29482, line 14: “Freutel et al. 2012 have evaluated the AMS measurements in terms of the total mass measurement (including BC measurements from MAPP) using a PM1 TEOM-FDMS at LHVP and GOLF and aerosol size distribution measurement from an SMPS at SIRTA, and find good agreement. The fraction of the total mass covered by the AMS measurements is about 0.9 for both LHVP and the GOLF site. The overall uncertainty of AMS measurements of PM different components is estimated as 30%. ”

Sentences on model evaluation are added on p29491, line 5, after “primary and secondary PM species with simulations”:

“Main fine PM components compared here to measurements (BC, OA, sulfate, nitrate, ammonium) are considered to appear in the accumulation mode or at smaller size bins. Therefore, the modeled bulk amounts (all size bins integrated) of these species can be compared to AMS (or BC) PM1 measurements.”

10. Evaluation using AMS Measurements, Section 4.6: It is good that the paper compares simulated primary and secondary organic aerosol with estimates derived from

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AMS measurements. But only one site is presented in this study, and the conclusions regarding the performance would have been much stronger if such comparisons could be made at the other sites. The modeling domain is large and only one site is available for evaluation, so the results need to be taken with a grain of salt. I certainly agree that the VBS approach is an improvement over the previous treatment, but much work remains to determine whether the model is getting a better answer for the right reason.

Reply: Here, we focus on POA and SOA prediction at one urban background site, for which the 3-factor PMF solution was available.. The 2 factor PMF available at all 3 sites leads to an larger HOA concentrations than the 3 factor PMF due to classification of an important part of cooking OA to the HOA factor, but this HOA is then not consistent to the modeled one not taking into account cooking related emissions. Therefore, only the urban LHVP site is presented. Even with only one site, a large panel of meteorological situations, transport regimes and air mass origins is sampled.

On p29500 line 17, add after ". . . and OOA factors."

"Here, we focus on POA and SOA prediction at one urban background (LHVP) site, for which the 3-factor PMF solution was available. The 2 factor PMF available at all 3 sites leads to an larger HOA concentrations than the 3 factor PMF due to classification of an important part of cooking OA to the HOA factor, but this HOA is then not consistent to the modeled one not taking into account cooking related emissions."

Specific comments:

Page 29480: line 11: Change "(Hodzic et al : : :" to "(e.g. Hodzic et al : : :" There are other papers using the VBS approach for Mexico City.

Reply: OK. This was done.

Page 29481, line 11: Change "of the Paris city" to "of Paris".

Reply: OK. This was done.

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Page 29482, line 11: Change “performed by several instruments” to “sampled by several instruments”. Change “with AMS” to “from the AMS”.

Reply: OK. This was done.

Page 29482, line 12: Suggest starting a new paragraph with the sentence “Source apportionment ...”

Reply: OK, this was done.

Page 29482, line 22: I am a bit confused by the use of PMF for model evaluation. The authors mention using only the 3-factor PMF analysis that includes cooking activities, but cooking activities are not included in the emission inventory so perhaps it would be more appropriate to compare with the other two sites. At LHVP, should we expect the model to be too low when compared to PMF POA or OOA. A bit more clarification from the authors is needed here.

Reply: The HOA factor from 3-factor PMF corresponds to POA mainly from the traffic sector, while HOA from the 2-factor PMF (representing the primary factor) may contain an important part of cooking activities. Thus, the HOA from 2-factor PMF analysis is not compared here to simulations because the cooking emissions of OA are not taken into account.

To make this clear, we have added a sentence on p29500 line 17:

“Here, we focus on POA and SOA prediction at one urban background (LHVP) site, for which the 3-factor PMF solution was available. The 2 factor PMF available at all 3 sites leads to an larger HOA concentrations than the 3 factor PMF due to classification of an important part of cooking OA to the HOA factor, but this HOA is then not consistent to the modeled one not taking into account cooking related emissions.”

Page 29488, line 28: I assume the author mean that the use of VOC species does not alter the concentration of VOC species. The current phrase is a bit confusing. Is this assumption significant?

Reply: In fact, the gas chemistry is computed with the default MELCHIOR2 scheme. The lumped SAPRC99 species are used in an off-line mode only for the purpose of SOA formation, but they do not interfere with gas phase chemistry to avoid double counting of VOC species.

Page 29495, line 8: I do not think it has been mentioned what type of instrument is used to obtain BC measurements, but it is mentioned in Table 2. What size range is included for the model evaluation? Please state this somewhere.

Reply: The inlet of BC measurements is PM2.5 at SIRTA, PM1 at GOLF and PM10 at LHVP. BC is considered to appear at size ranges corresponding to the accumulation mode and below. To answer an earlier question about this issue, we have added the following sentence on p29491, line 5:

“Main fine PM components compared here to measurements (BC, OA, sulfate, nitrate, ammonium) are considered to appear in the accumulation mode or at smaller size bins. Therefore, the modeled bulk amounts (all size bins integrated) of these species can be compared to AMS (or BC) PM1 measurements.”

Page 29499, lines 16-17: This statement is not quite correct. The model does better for total OA during these periods. While biogenic SOA is high, three are no observations of biogenic SOA to suggest that the peaks were “reproduced” for this reason.

Reply: Evidences from HULIS and oxalate measurements (not shown) provides indirect evidence that OA was due to biogenic origin. The sentence will be changed to:

“During R3, the peaks in the Greater Paris region are also reproduced, in the simulations they are related to advection of biogenic SOA (> 60 % of OA in the VBS-T2 simulations) (Figs. 11, 12, 13).”

Page 29501, line 6: Is the simulated value 1.21? The phrase with 0.34 and 1.21 is confusing.

Reply: Yes. We change this to:

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“The observed POA/BC ratio at LHVP is 0.34 while the predicted one is 1.21, and thus largely overestimated, in the CSS simulation. “

Interactive comment on Atmos. Chem. Phys. Discuss., 12, 29475, 2012.

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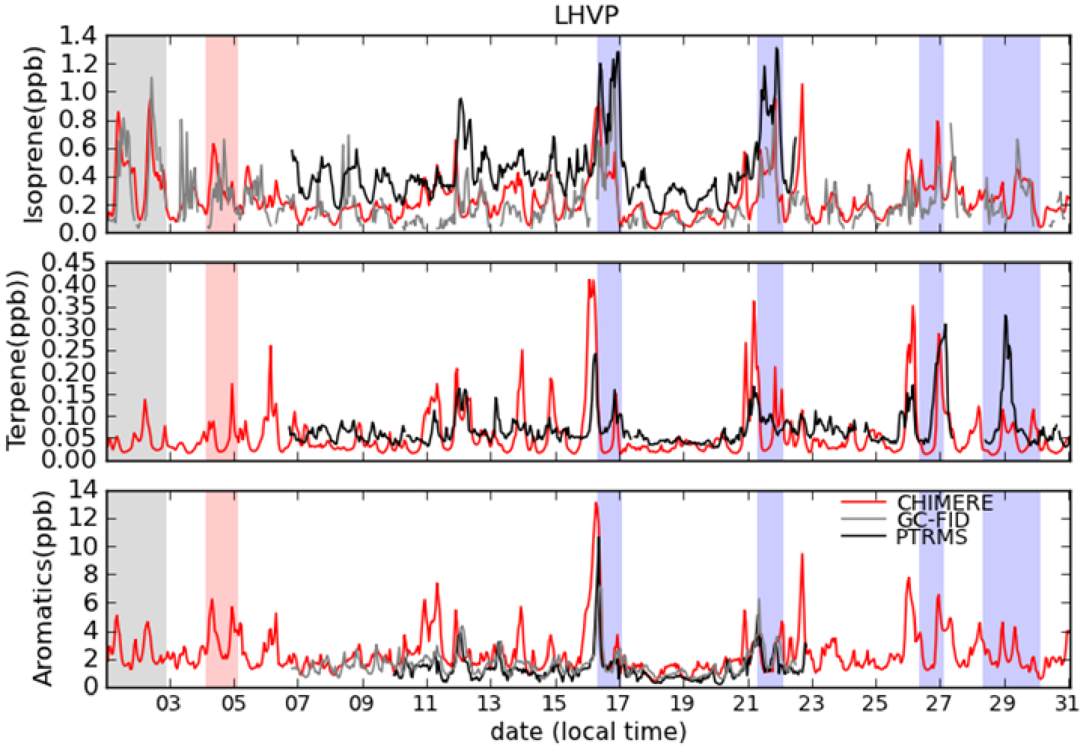

Fig. 1. Fig S6. Comparison of simulated and observed isoprene (from GC-FID and PTRMS), terpenes (from PRTMS) and aromatics (from GC-FID and PTRMS) at LHVP.

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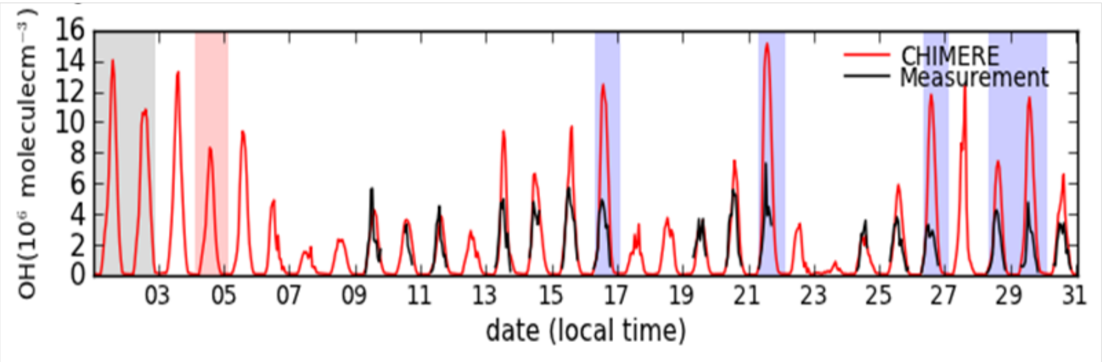

Fig. 2. Fig S7. Comparison of simulated and observed OH at SIRTA.