Reply to comments of Anonymous Referee # 1:

Original comments are in *italic*, replies in blue and proposed new text is in normal font.

This paper presents a series of sensitivity tests with varying volatility and emission parameters to assess the performance of the CAMx model with VBS, regarding OA over Europe. The innovative elements of this paper can be significantly enriched and this work could provide an useful insight into the VBS approach. The first part of the paper is well-written but several issues emerge in the second part. The aim of the paper stated in the introduction (OA model performance with the use of VBS) is not served properly in the discussion section.

Thank you for your comments and suggestions to improve our manuscript. Our answers to questions follow below:

General comments

1. The main part of the discussion is performed over the base case S3. I recommend changing the base case to S1 and build S2 and S3 upon that. Emissions scenarios applied in section 3.3.2 could be named S1a and S1b. The authors could skip the re-naming if the structure of the manuscript changes to focus on OA performance with and without VBS. In that context the S1 (no VBS) to S3 (VBS) sequence is proper in that it shows the improvement when utilizing volatility schemes (see Figure 7).

We changed the naming convention of the different scenarios throughout the manuscript as also suggested by Referee 2. The new nomenclature follows below:

S1: NOVBS (without VBS, two-product organic aerosol scheme based on Strader, 1999)
S2: VBS_ROB (VBS organic scheme with volatility distribution proposed by Robinson et al., 2007)
S3: VBS_BC (Base case, VBS organic scheme with volatility distribution proposed by Tsimpidi et al., 2010 and Shrivastava et al., 2011)
S4: VBS_BC_2xBVOC (Doubled biogenic emissions based on VBS_BC)
S5: VBS_BC_2xBBOA (Doubled biomass burning emissions based on VBS_BC)

2. The statistical analysis of the model performance could be enhanced by metrics that show the evolution of a process. Time series and correlation could add to the manuscript.

We included correlation coefficients of all the species in Table 2 for all the investigated periods. In addition, time series of NO_2 and SO_2 were shown as well (Fig. S1) and discussed in the reply to the next comment (3).

Table 2. Model gas phase and $PM_{2.5}$ performance for the EDIII field campaigns (based on VBS_BC).

Species	Number of sites	Observed mean (ppb) ($\mu g\ m^{-3}$ for $PM_{2.5}$)	Modelled mean (ppb) ($\mu g\ m^{-3}$ for $PM_{2.5}$)	MB (ppb) ($\mu g\ m^{-3}$ for $PM_{2.5}$)	ME (ppb) ($\mu g\ m^{-3}$ for $PM_{2.5}$)	MFB [-]	MFE [-]	r
June 2006								
CO	36	192.0	158.0	-34.2	80.7	-0.12	0.36	0.20
NO_2	320	4.1	2.3	-1.9	2.2	-0.54	0.68	0.55
O_3	460	42.3	51.2	8.9	10.8	0.21	0.24	0.57
$PM_{2.5}$	48	12.0	11.7	-0.3	4.5	-0.07	0.39	0.55
SO_2	263	1.0	1.2	0.2	0.7	0.14	0.67	0.52
Jan-Feb 2007								
CO	45	248.0	191.0	-57.8	107.0	-0.11	0.37	0.21
NO_2	337	6.5	4.4	-2.2	3.2	-0.28	0.57	0.68
O_3	455	23.5	35.8	12.3	12.6	0.48	0.49	0.61
$PM_{2.5}$	56	11.7	12.8	1.0	6.1	-0.04	0.56	0.69
SO_2	271	1.3	1.7	0.4	1.1	0.36	0.75	0.46
Sep-Oct 2008								
CO	53	208.0	136.0	-72.0	91.4	-0.31	0.48	0.27
NO_2	370	5.3	3.7	-1.7	2.5	-0.28	0.56	0.62
O_3	465	24.3	32.5	8.2	9.6	0.32	0.37	0.50
$PM_{2.5}$	90	13.0	14.1	1.0	5.7	<0.01	0.46	0.76
SO_2	256	0.9	1.1	0.2	0.8	0.25	0.74	0.37
Feb-Mar 2009								
CO	57	262.0	170.0	-91.6	119.0	-0.26	0.48	0.37
NO_2	380	6.0	3.9	-2.0	2.8	-0.33	0.56	0.61
O_3	488	32.7	33.0	0.2	7.1	0.02	0.23	0.55
$PM_{2.5}$	110	15.1	13.0	-2.1	6.4	-0.13	0.50	0.71
SO_2	257	1.0	1.3	0.3	0.9	0.23	0.76	0.45

3. Figure 1 of supplemental material denotes several areas of poor performance like complex terrain areas, coastal zones, Eastern Europe (specially of SO_2) and heavily industrialized/populated areas. The emissions are named as the culprit for the poor performance of the model regarding all gaseous species but O_3. This leads to thoughts about the quality of the emission dataset and/or model resolution. Either which, this has to be somehow elaborated on, because the limitations of the emissions also affect the OA discussion and the overall aim of the paper. Other reasons could be nitrates overestimation in the case of NO_2 (if the results shown in figure 5 can be generalized) and insufficient conversion to sulfates in the case of SO_2 or even transport, wet and dry deposition of aged aerosols

Thank you for this remark which was also stressed by Referee 2. We elaborate more on this in section 3.1. We replaced Figure 1 of the supplemental material with daily average time series of NO_2 and SO_2 for the period in Feb-Mar 2009 (below). Moreover we reported daily average time series of NO_2 at stations not exceeding 5 ppb (~92% of the stations used in the top panel in Fig. S1) in order to remove the influence of polluted areas and local events in the proximity of rural-background stations which might be difficult to resolve (middle-panel in Fig. S1). The model performance improved significantly giving more confidence regarding the emissions dataset, with the NO_2 concentration still being under-predicted. We also included an emission map of NO for 1 March 2009 at 6 AM as an example (Figure S2). The spatial distribution of emissions looks reasonable and in line with other model exercises. High emissions of NO are predicted in the Benelux area, Po Valley, Germany and in some of the eastern European countries. High NO emissions due to ship traffic are also visible especially in the Mediterranean Sea. We added daily variations of modelled and measured SO_2 concentrations as well (lower-panel) for all available stations. In general also the daily variation of modeled and measured SO_2 concentrations agrees relatively well with each other with slight overestimation during the day. We agree with the referee that insufficient conversion to sulfate or too low deposition processes might indeed also explain the over-prediction of the SO_2. Paragraph 3.1 was extensively revisited to include the discussion above for the investigated species.

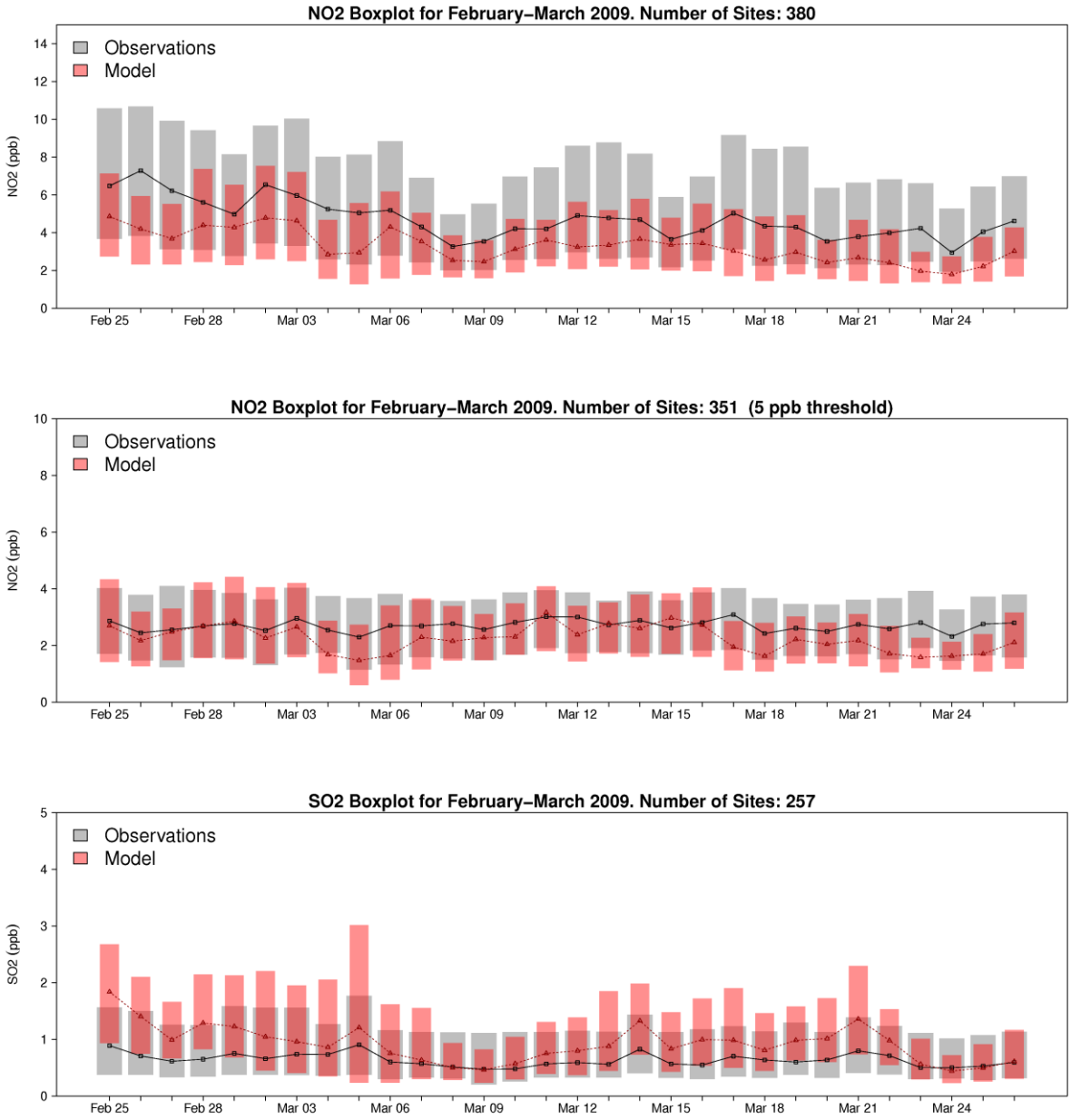

Figure S1. Comparison of modelled (VBS_BC) (red) and measured (grey) NO_2 (upper panel) and SO_2 (lower panel) concentrations at AirBase rural background sites (as in Table 2). The middle panel shows the comparison at stations where NO_2 concentrations do not exceed 5ppb. The extent of the bars indicates the 25th and 75th percentile. The black and red lines represent measured and modelled medians, respectively.

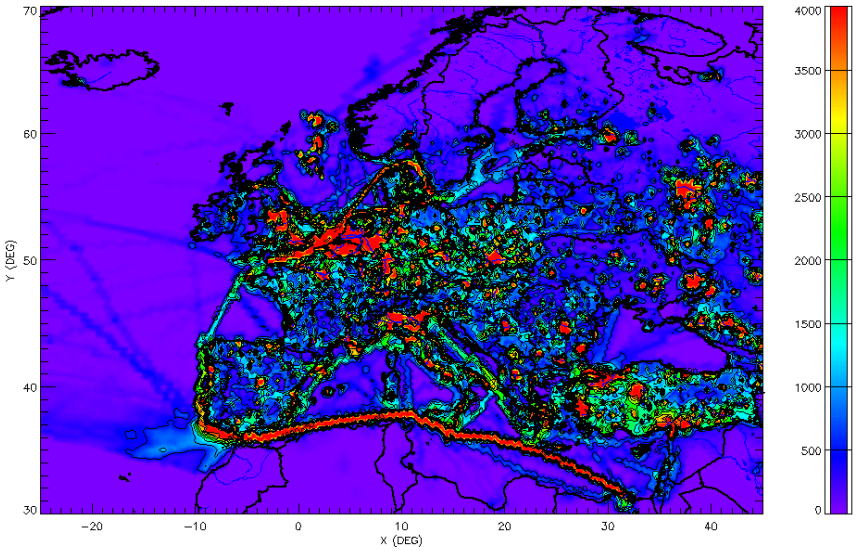

Figure S2. NO emissions in [mol/(h cell)] for 1 March 2009, at 6:00 AM

4. From the moment that the authors have discovered the reason for the 'good' performance of total PM2.5 (overestimation of inorganic aerosol fraction and underestimation of the organic one) I believe there is no merit in focusing on it in the discussion section (second paragraph of 3.1). This also goes for the abstract and conclusions section.

We agree and revised Section 3 as well as the abstract and conclusions as reviewer suggested. Paragraph 3.1 was extensively revisited by splitting it according to the different investigated species and shortened by removing figure 4 and the analysis at the stations of Casirate D'Adda and Ayia Marina.

5. The compensating effect (inorganic versus organic) has been confirmed for the period February - March 2009. Can the authors provide some arguments on whether this model behavior is effective on the other periods too and therefore affecting $PM_{2.5}$ performance throughout the year?

We included an evaluation of nitrate, sulfate, ammonium and organics for all the 4 periods at the rural station Payerne (Figure S4 below). There was a general tendency of overestimating the inorganic aerosol fraction and underestimating the organics in all periods. The bias for OA was approximately constant (~-60%) while the bias for SIA varied between 20% and 60%, being highest in spring and in fall (where high ammonia emissions are expected) causing a compensation effect during all the periods (difference of ±20% to from June 2006 to February-March 2009. Figure S5).

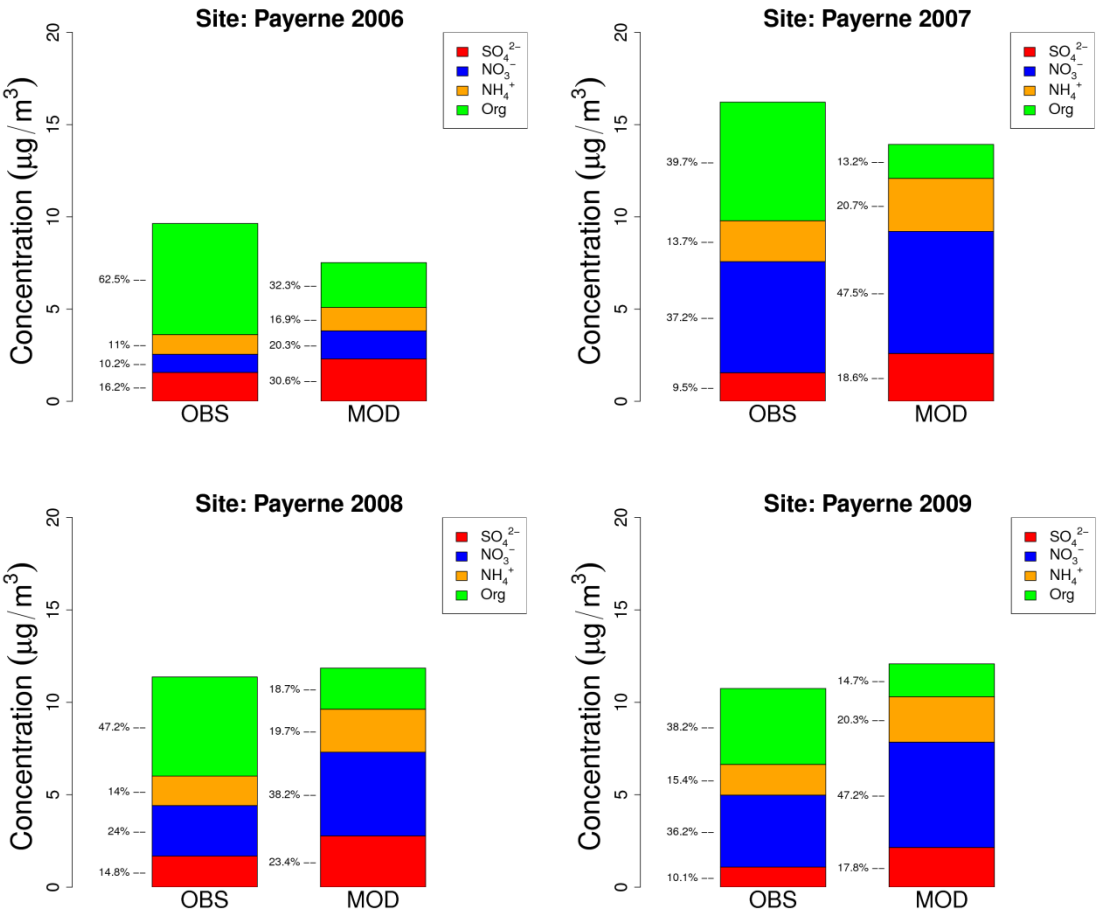

Figure S4. Comparison of observed (OBS) non-refractory PM_1 and modelled (MOD) $PM_{2.5}$ components at Payerne for all the investigated periods.

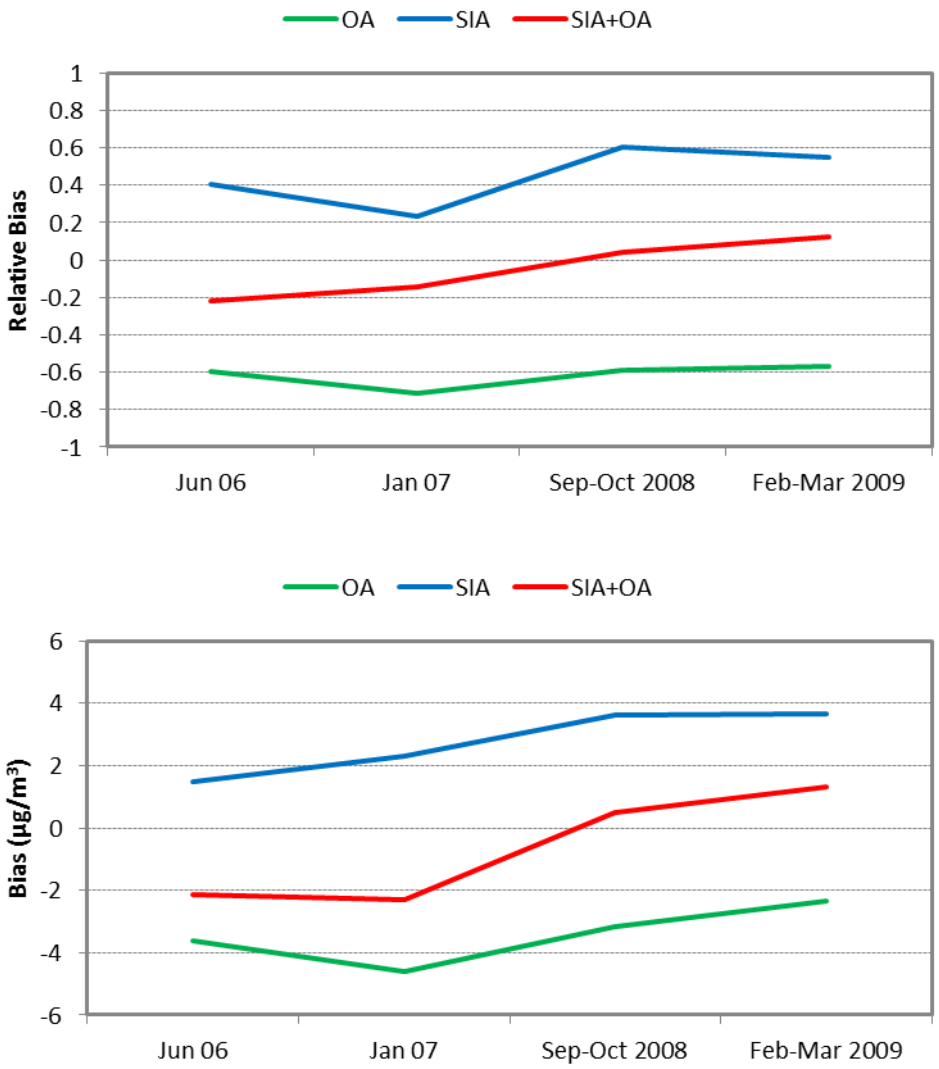

Figure S5. Absolute and relative bias for organic aerosol (OA), secondary organic aerosol (SIA) and OA+SIA in Payerne for all the investigated periods.

6. Paragraph 3.2 includes a discussion on the PM2.5 performance and sensitivity to ammonia and NOx emissions, large parts of which can be seen in Aksoyoglu et al, 2011. Please consider omitting parts or all of the analysis of paragraph 3.2 and redirect focus to the initial scope or include a satisfactory analysis of the new elements it has to offer.

We revised the section 3.2 as also suggested by Referee 2. We removed the discussion regarding the sources and annual distribution of NH_3 emissions as well as measured and modelled NH_3 comparisons at the site of Payerne. The discussion part regarding the model sensitivity to NO_x and NH_3 emission in Europe was also removed.

7. The scope of the paper is to assess what VBS scheme has to offer to OA modelling. The relative analysis is (very) limited to the small paragraph 3.3 (specifically only 3.3.1 since 3.3.2 is related to emissions).

We thank the Referee for this remark. We originally kept this section short because more detailed analysis of OA modeling with VBS is being prepared for a follow-up paper. We agree however with the referee and add section 3.3.3 to the revised manuscript.

3.3.3 OA components in summer and winter

Comparisons of primary organic fraction and secondary organic fraction at the rural site of Payerne during summer (June 2006) and winter (February-March 2009) periods are reported in Figure 10. During the winter period the VBS scheme better reproduced the primary and secondary organic aerosol components compared to the NOVBS case. In particular, For the VBS_ROB base case, total OA concentrations were lower compared to the NOVBS case, consistent with the study of Woody et al. (2016) where the same VBS scheme was applied to the US domain. The total OA concentrations in the base case (VBS_BC) and in the scenario with increased biomass burning emissions (VBS_BC_2xBBOA) were higher compared to NOVBS case, even though SOA and POA fractions were not correctly reproduced. Higher contribution from the primary fraction during winter periods was also predicted by the study of Koo et al. (2014) which deployed the same VBS scheme. Eventually, this might indicate that biomass burning precursors might be missing in this study, or that the oxidation pathways of primary organic material need to be improved in the model (up to 86% of the reacted primary organic material is still allocated in the primary set as oxidation proceeds, directly increasing the POA fraction).

Different behavior was observed for the summer period where the larger contribution of SOA to the total OA retrieved from measurements is also reproduced by the model, even though the total OA concentration was still underestimated. These results for summer are also in line with the study of Koo et al. (2014) for summer periods in the US domain carrying the same VBS scheme.

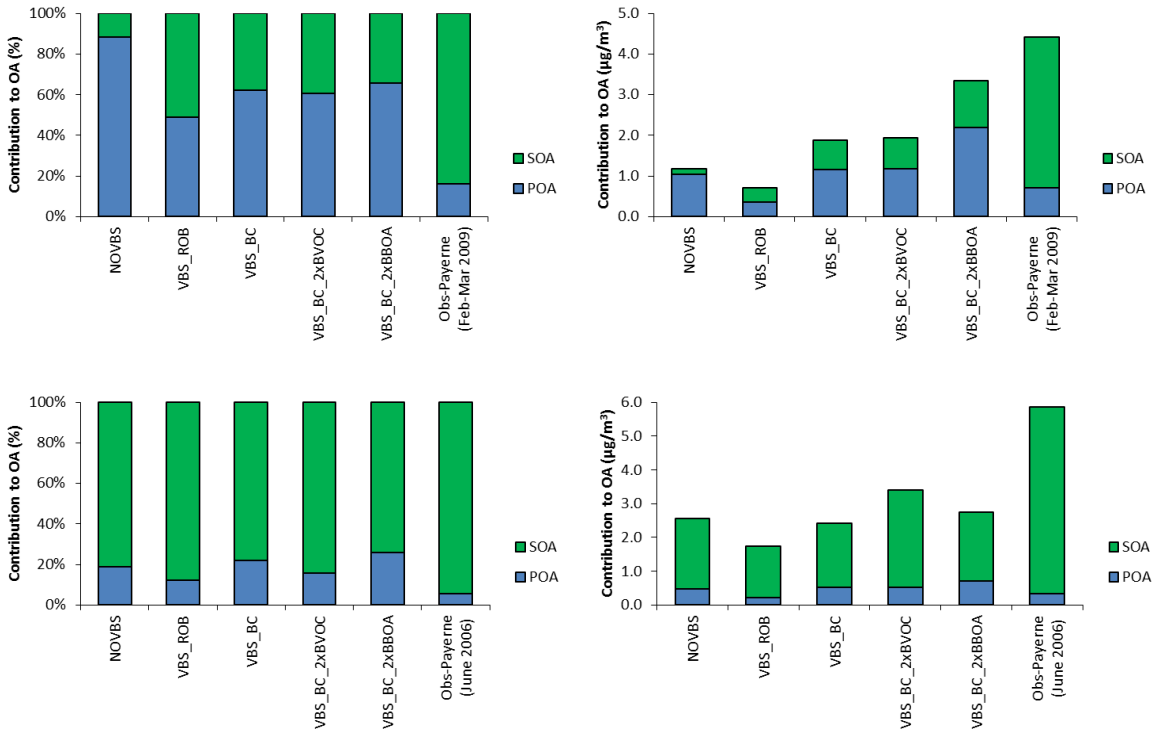

Figure 10. Relative (left) and absolute (right) contributions of predicted and measured POA and SOA fractions to the total OA mass at Payerne for February-March 2009 winter period (upper-panel) and June 2006 (lower-panel) and different model scenarios. NOVBS: (traditional non-volatile POA), VBS_ROB (Robinson et al., 2007), VBS_BC (Tsimpidi et al., 2010, Shrivastava et al., 2011), VBS_BC_2xBVOC (increased biogenic emissions relative to VBS_BC), VBS_BC_2xBBOA (increased biomass burning emissions relative to VBS_BC), Obs-Payerne: AMS-PMF.

Specific comments:

1. Definition of the statistical metrics can be put in appendix if needed. 2.

We agree and eliminated the formula in the main text.

2. Paragraph 3.1 needs splitting depending on the species. Also more discussion on the performance is needed (now based only on MB and ME).

We revised the section 3.1 as also suggested by Referee 2. We split the paragraph according to the species and added more discussion regarding model performance.

3. Figure 1 could be left out as it gives a schematic display of statistics already arithmetically mentioned in Table 2 (column 3 and 4 - observed and modelled means).

We agree and removed Figure 1 from the manuscript.

4. Please specify the time period that Figure 5 refers to (in figure caption).

We modified the caption as the following:

Figure 3. Comparison of modelled $PM_{2.5}$ (MOD) and observed non-refractory PM_1 (OBS) at 10 AMS sites in Europe during February-March 2009. Mace Head is reported only in Table 3 since the ammonium component is not available.

5. P35659 line 4. Please change 'Cypro' to 'Cyprus'

We removed the sentence containing the word.

6. Please restructure paragraph 3.2 if considered necessary to be included in the manuscript. It is very large and hard to follow.

We restructured the paragraph 3.2

7. Figure 6 Please increase the font (Axis, numbers)

We enlarged Figure in order to increase the readability.

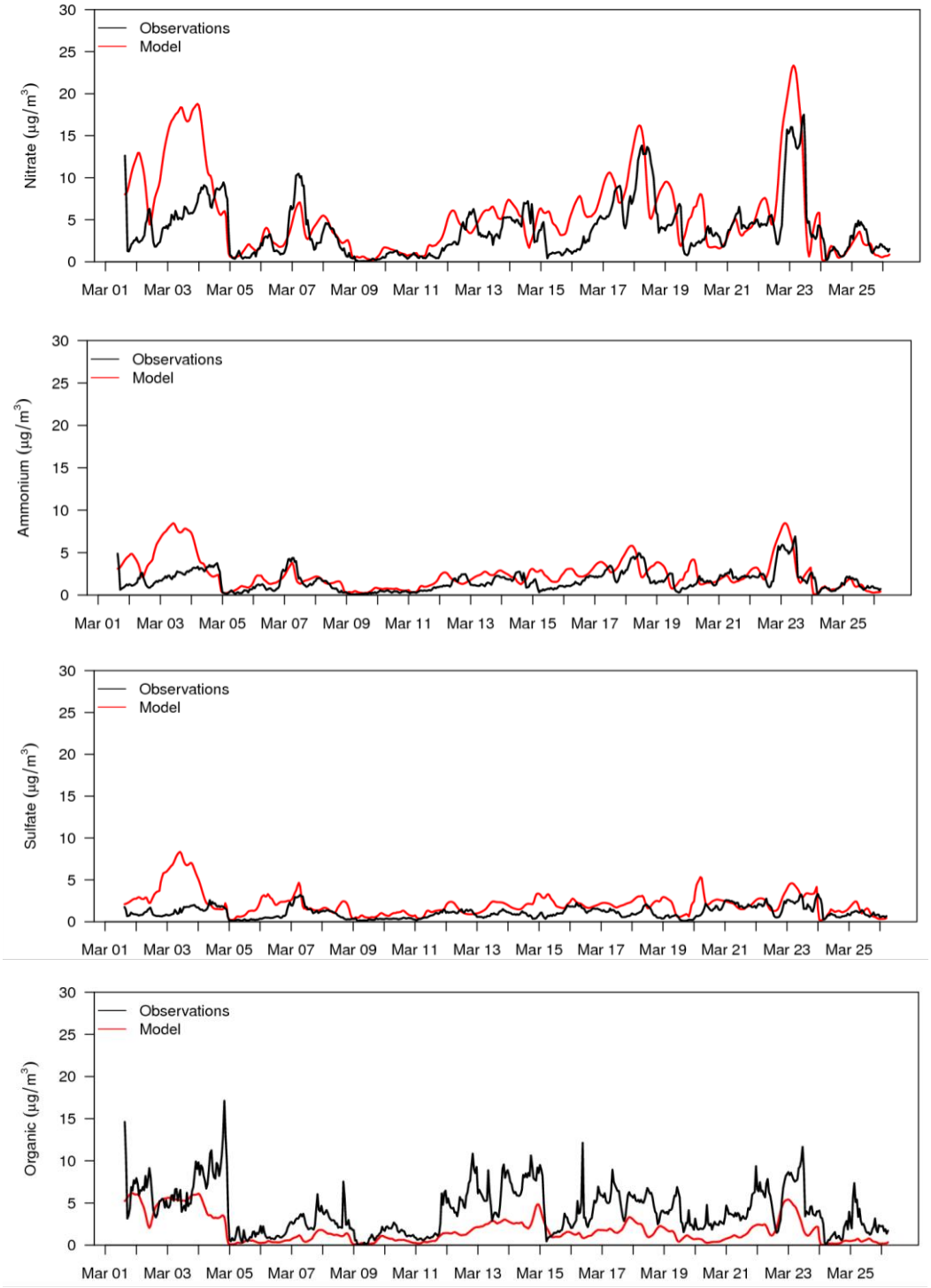

Figure 4. Comparison of observed and modelled nitrate, ammonium, sulfate and organic aerosol at Payerne for March 2009.

References

Koo, B., Knipping, E., Yarwood, G.: 1.5-Dimensional volatility basis set approach for modeling organic aerosol in CAMx and CMAQ, Atmos Environ., 95: 158-164., 2014.

Robinson, A. L., Donahue, N. M., Shrivastava, M. K., Weitkamp, E. A., Sage, A. M., Grieshop, A. P., Lane, T. E., Pierce, J. R., and Pandis, S. N.: Rethinking Organic Aerosols: Semivolatile Emissions and Photochemical Aging, Science, 315, 1259–1262, doi:10.1126/science.1133061, 2007.

Shrivastava, M., Fast, J., Easter, R., Gustafson Jr., W. I., Zaveri, R. A., Jimenez, J. L., Saide, P., and Hodzic, A.: Modeling organic aerosols in a megacity: comparison of simple and complex representations of the volatility basis set approach, Atmos. Chem. Phys., 11, 6639–6662, doi:10.5194/acp-11-6639-2011, 2011.

Strader, R., Lurmann, F., and Pandis, S. N.: Evaluation of secondary organic aerosol formation in winter, Atmos. Environ., 33, 4849– 4863, 1999.

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, doi:10.5194/acp-10-525-2010, 2010.

Woody, M. C., Baker, K. R., Hayes, P. L., Jimenez, J. L., Koo, B., and Pye, H. O. T.: Understanding sources of organic aerosol during CalNex-2010 using the CMAQ-VBS, Atmos. Chem. Phys., 16, 4081-4100, doi:10.5194/acp-16-4081-2016, 2016.