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) (µg m^{-3} for PM $_{2.5}$)	Modelled mean (ppb) (µg m^{-3} for PM $_{2.5}$)	MB (ppb) (µg m^{-3} for PM $_{2.5}$)	ME (ppb) (µg 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.

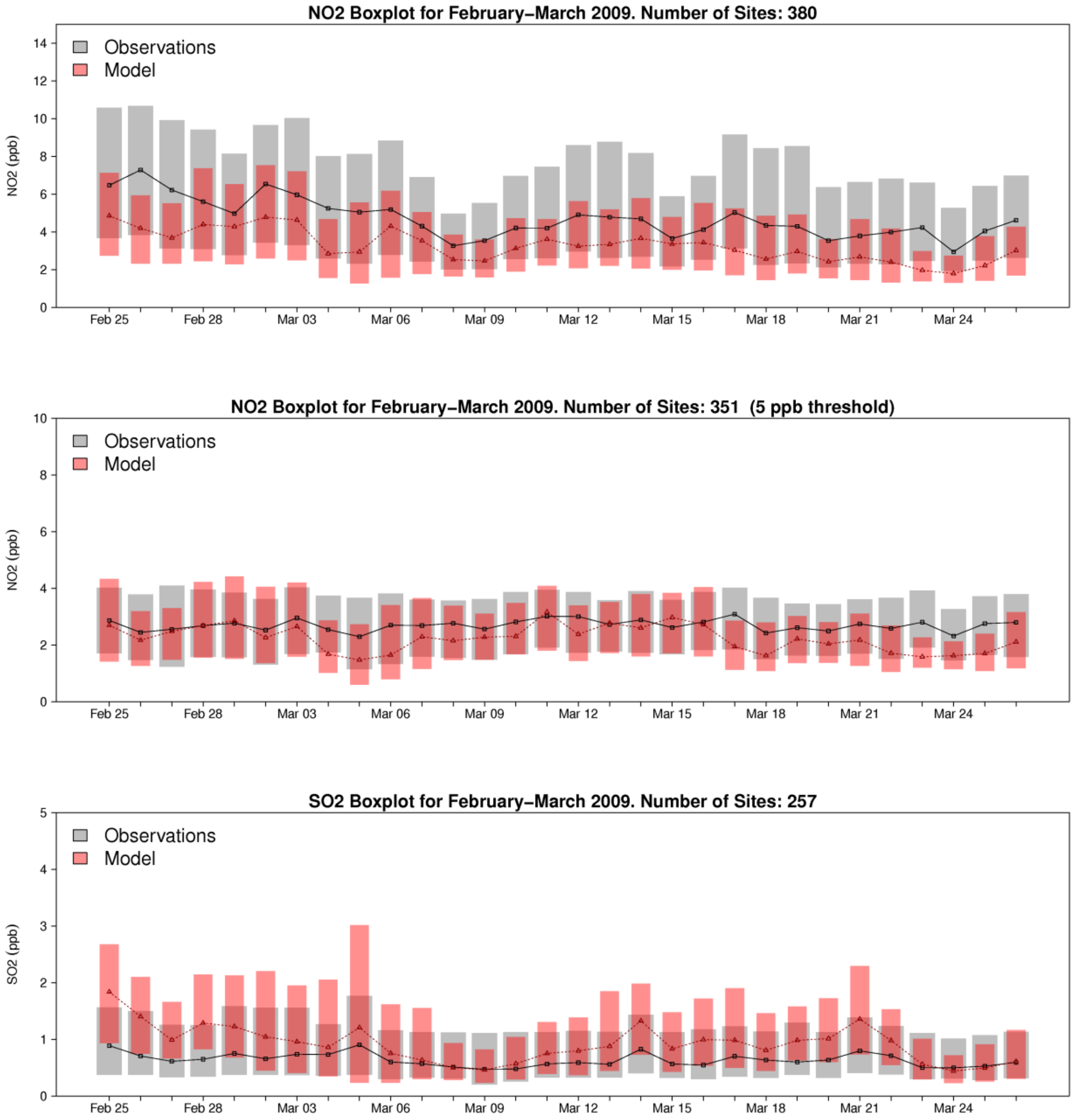


Figure S1. Comparison of modelled (VBS_BC) (red) and measured (grey) NO_2 (upper panel) and SO_2 (lower panel) concentrations at AirBase rural background sites (as in Table 2). The middle panel shows the comparison at stations where NO_2 concentrations do not exceed 5ppb. The extent of the bars indicates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

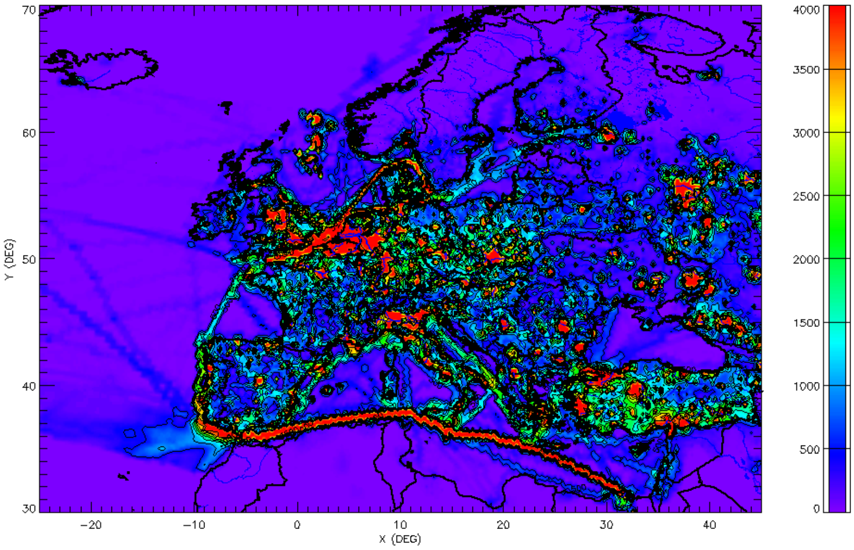


Figure S2. NO emissions in [mol/(h cell)] for 1 March 2009, at 6:00 AM

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).

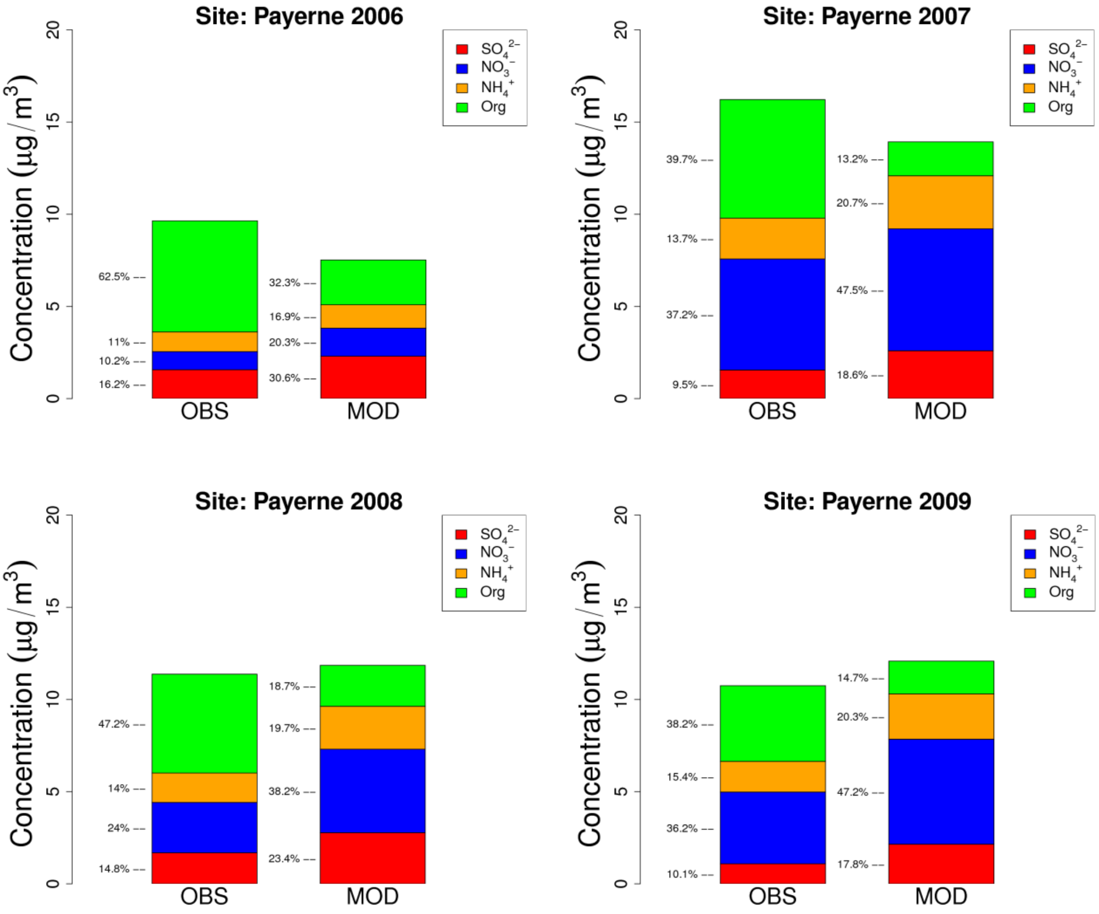
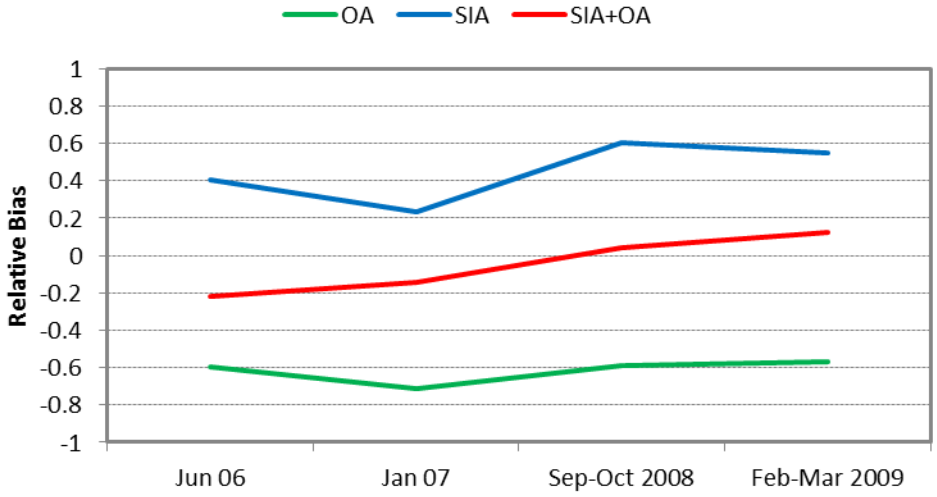


Figure S4. Comparison of observed (OBS) non-refractory PM_1 and modelled (MOD) $PM_{2.5}$ components at Payerne for all the investigated periods.



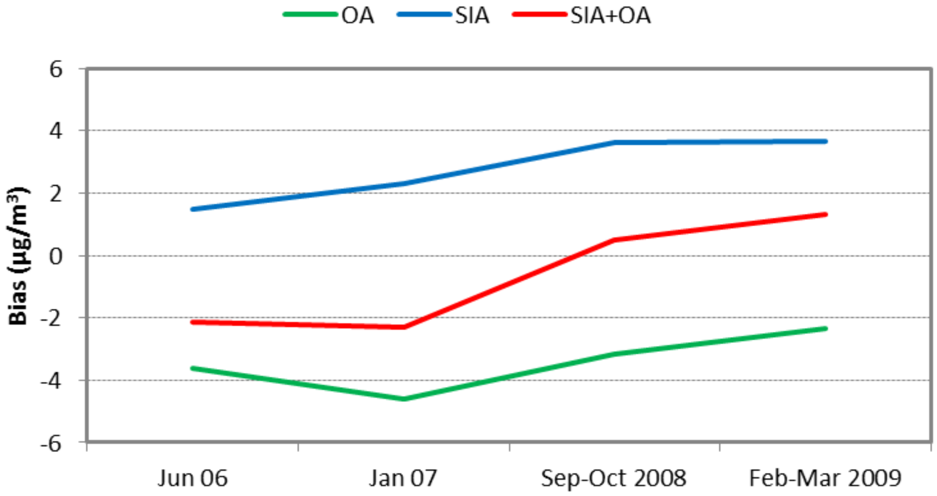


Figure S5. Absolute and relative bias for organic aerosol (OA), secondary organic aerosol (SIA) and OA+SIA in Payerne for all the investigated periods.

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.

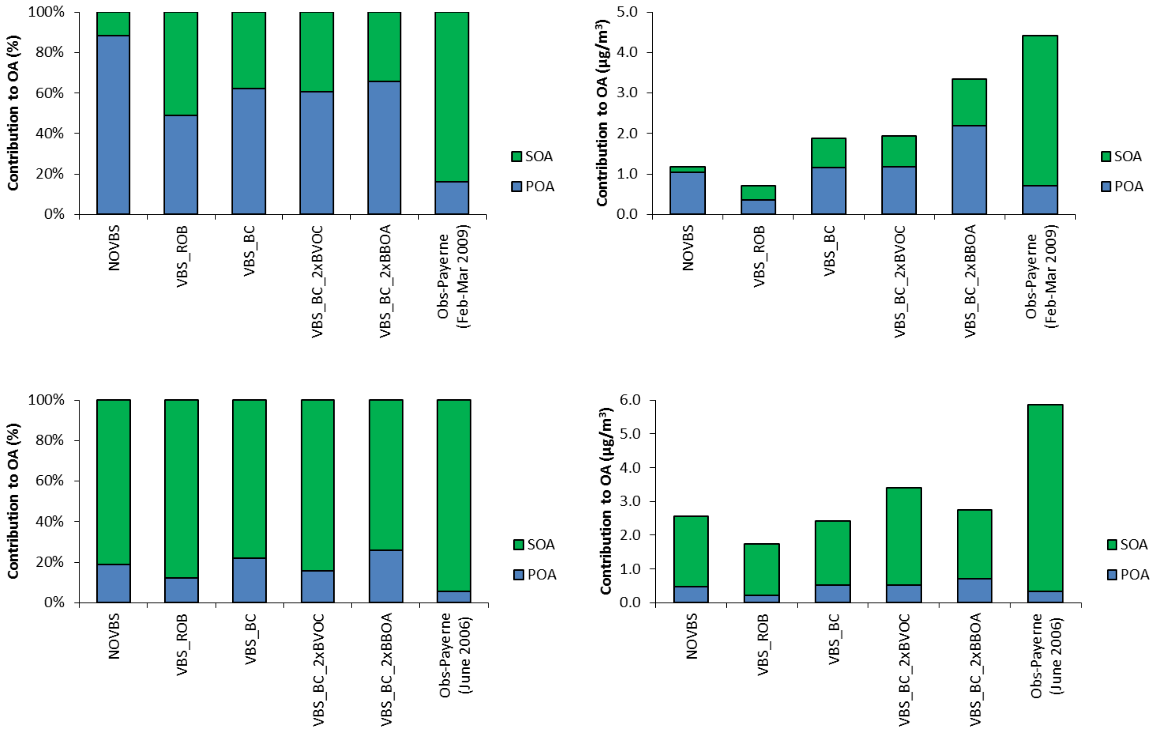


Figure 10. Relative (left) and absolute (right) contributions of predicted and measured POA and SOA fractions to the total OA mass at Payerne for February-March 2009 winter period (upper-panel) and June 2006 (lower-panel) and different model scenarios. NOVBS: (traditional non-volatile POA), VBS_ROB (Robinson 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.

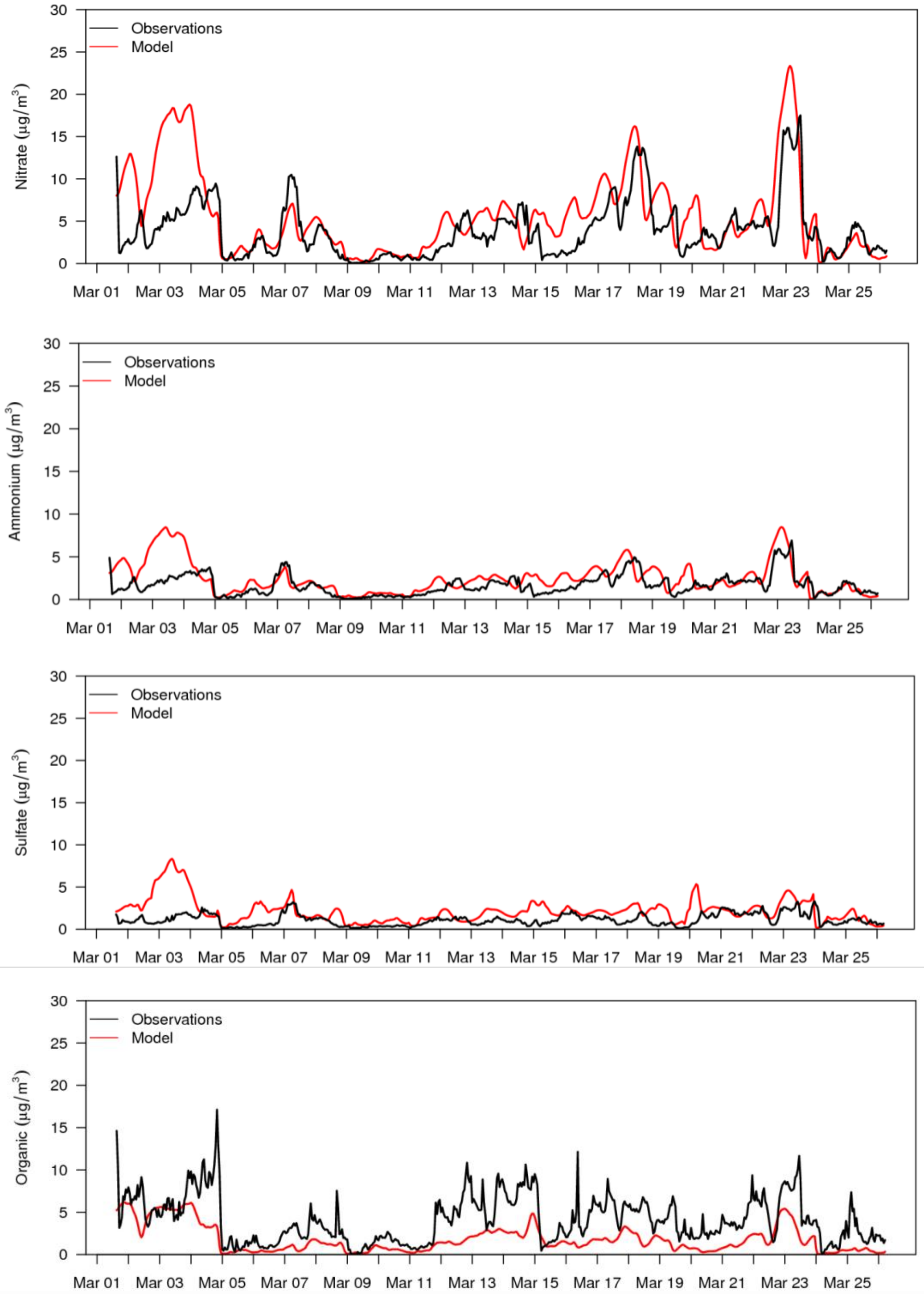


Figure 4. Comparison of observed and modelled nitrate, ammonium, sulfate and organic aerosol at Payerne for March 2009.

References

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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.

Reply to comments of Anonymous Referee # 2:

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

The paper describes the application and evaluation of the CAMx model with the Volatility Basis Set scheme used for formation of secondary organic aerosols. The study includes several sensitivity simulations varying the volatility and emission parameters of the organic species. In-general, the study goes along the same lines of several existing applications, some quoted by the authors in the introduction. In that sense, I found little new or innovative pieces in the paper. From the other side, such evaluation exercises are useful for collecting experience with the VBS approach. Till now, it falls short of demonstrating a major breakthrough in the models performance as a reward for high complexity and bulkiness.

The paper is comparatively well written except for the results section 3.

I however noticed a few omissions, some with potentially heavy consequences, which should be brought up.

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

General comments

1.The most-important omission is the analysis of the emission dataset. A potentially woeful problem, for instance, is seen from Figure 8, the S1 scenario. The concentration map evidently reproduces the emission distribution, which almost completely misses half of the countries. This is a major caveat of the input dataset, which, if confirmed by the explicit emission analysis, would disqualify the whole exercise: the authors would have to switch to another emission dataset.

Thank you for this remark. We improved the color scale as shown below in order to facilitate the visualization of countries where low OA concentrations are predicted, e.g. over Germany, Spain and UK. Emissions used in this study are based on the main European inventories TNO-MACC and EMEP which are widely used in European modelling studies. Details of the construction of emission inventory, improvements and uncertainties are discussed in Kuenen et al. (2014). We believe that the emission inventory used in this study is the best available in Europe, however, one should bear in mind its limitations. Using the same emission inventory, Bergström et al. (2012) showed that wood burning emissions in Sweden were underestimated during winter as also suggested by our results in this study.

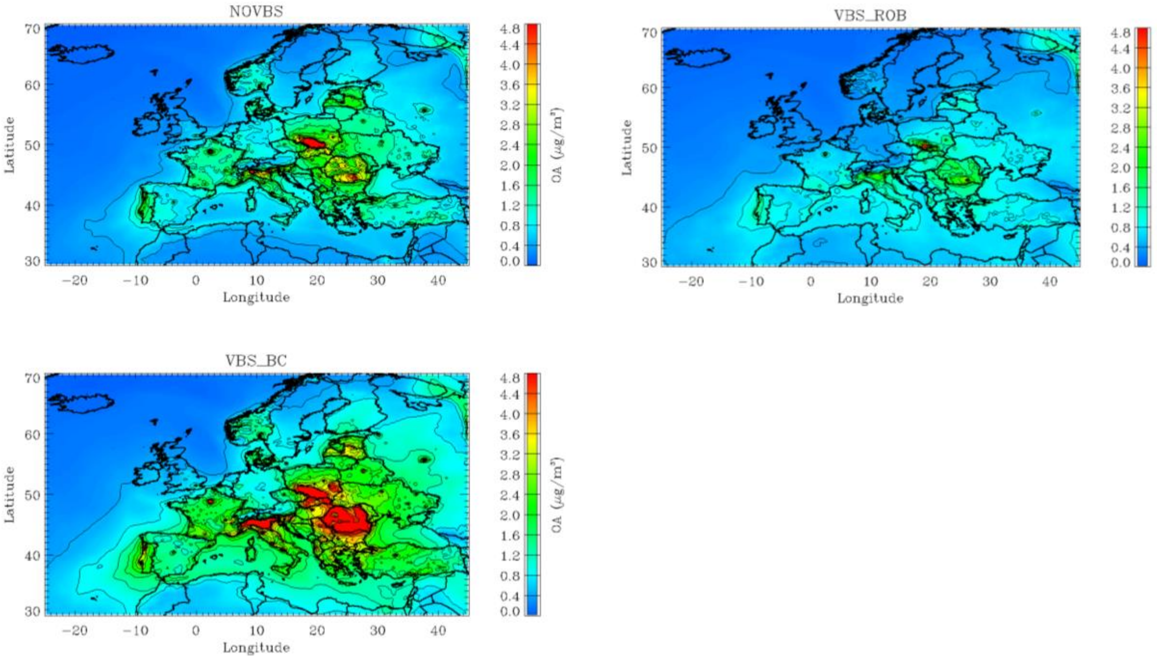


Figure 6. Predicted OA concentrations over Europe for the NOVBS, VBS_ROB and VBS_BC scenario in February-March 2009. Note that the color scale was limited to a maximum of 4.8 μg m^{-3} to facilitate comparison of the panels.

2. From the other side, the authors fell to a frequent modeller's trap of blaming emission for poor model performance, often with thin supporting analysis. Some of these blames may be justified, some may be not. For instance, I found it hard to believe the long discussion in p. 35657, where the authors try to explain the strong systematic NO2 under-estimation – and blamed emission. I found an alternative and much simpler potential explanation: nitrates are strongly over-estimated in most of cases, which would probably make-up for the deficit and suggest problems in the model chemistry rather than emission.

Thank you for this remark. We revised Section 3.1 to make it clear that there might be more than one reason for the discrepancy between modeled and measured NO_2 concentrations. One of them is the difficulty in reproducing the PBL height correctly as discussed in detail by Bessagnet et al. (2016). On the other hand, although NO_x emission estimates in Europe are thought to have an uncertainty of about ± 20%, the complete data set used in the inventories has much higher uncertainty (Kuenen et al., 2014). A recent study identified a significant discrepancy between emission estimates and actual flux measurements, with the highest underestimation being a factor of two in central London mainly due to under-representation of real world road traffic emissions (Vaughan et al., 2016). Most of the models within the EURODELTA III exercise underestimated NO_2 concentrations during the modeled periods (Bessagnet et al., 2016) especially during day time. The referee's potential explanation as over-estimated nitrate making up the deficit for NO_2 might certainly be a sound one. In addition to uncertainties in NO_2 emissions, there might also be too much HNO_3 in the model due to not enough deposition. Wet deposition of oxidized nitrogen was underestimated supporting the hypothesis of insufficient deposition leading to overestimation of nitrate.

We added daily average time series of NO_2 for the period of Feb-Mar 2009 for the stations used in Table2 (Figure S1, 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 order to remove the influence of polluted areas in the proximity of rural-background stations that might be difficult to resolve (middle panel in Fig. S1). The model performance improved significantly giving more confidence regarding the emissions. One should also bear in mind that measurements might have interferences from other oxidized nitrogen compounds leading to too high NO_2 concentrations (Villena et al., 2012). We also included emission map of NO for 1 March 2009 at 6 AM as an example (Figure S2). Spatial distribution of emissions looks reasonable and in line with other model exercises. High emission 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.

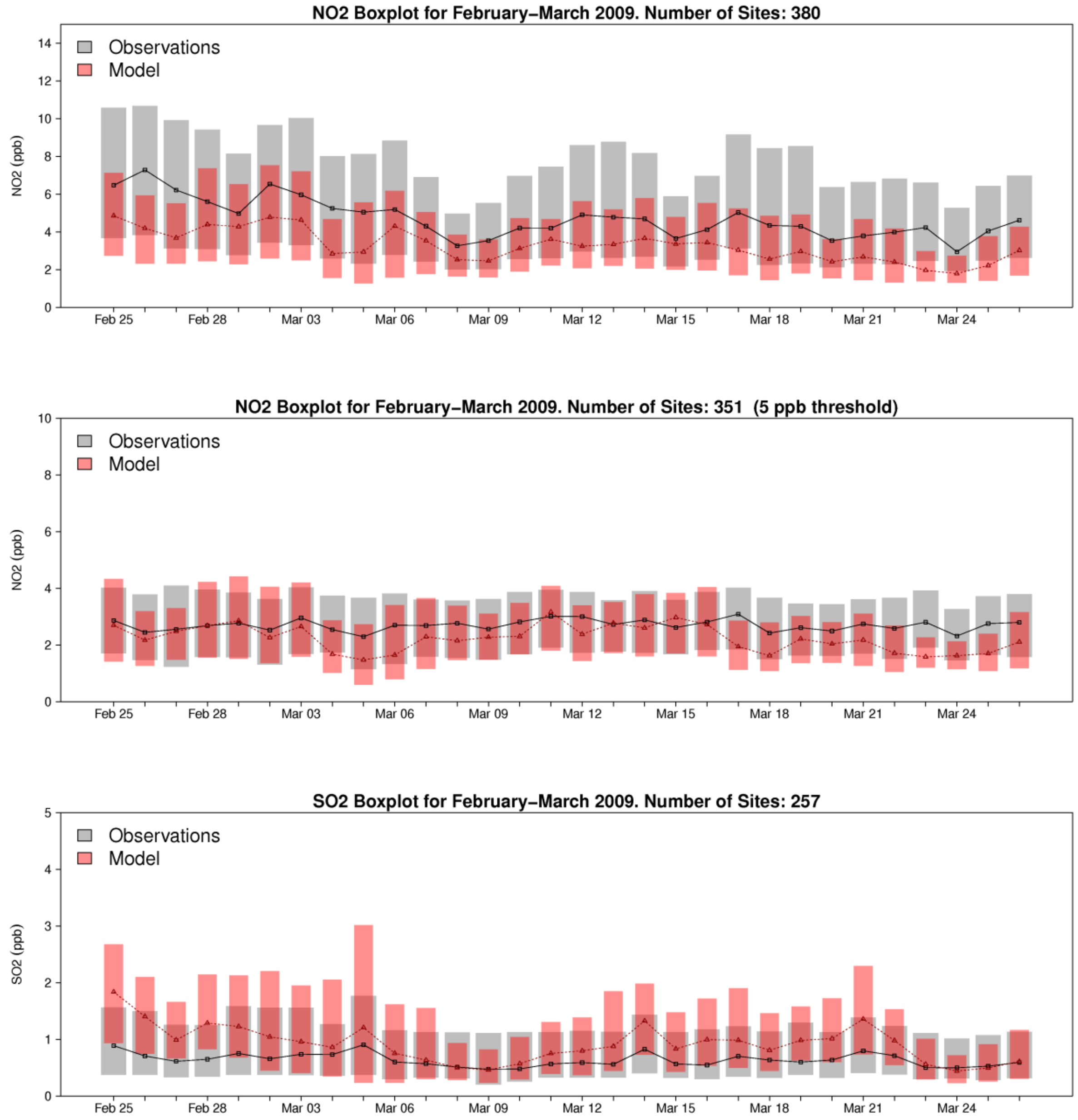


Figure S1. Comparison of modelled (red) and measured (grey) NO_2 and SO_2 concentrations at AirBase rural background sites and station not exceeding 5ppb of NO_2 concentration (central panel). The extent of the bars indicates the 25th and 75th percentile. The black and red lines are observed and modelled median, respectively. Based on base case (VBS_BC).

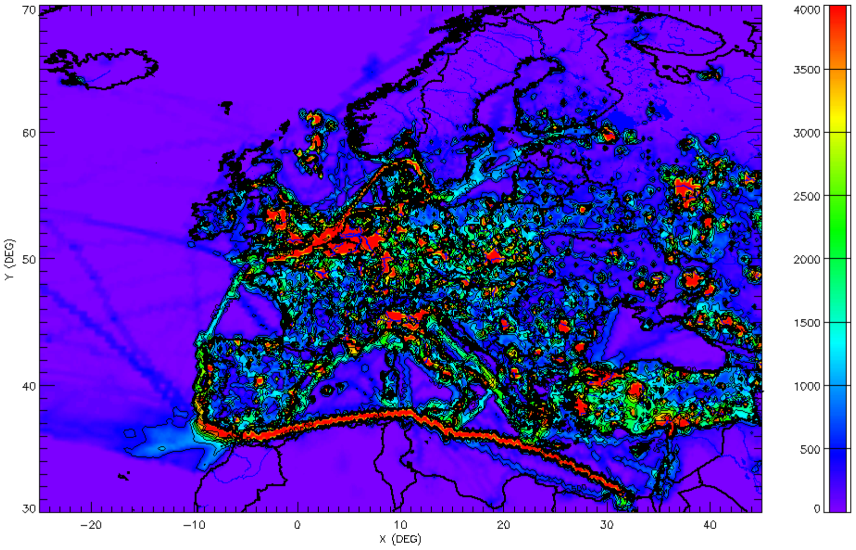


Figure S2. NO emissions in [mol/(h cell)] for 1 March 2009, at 6:00 AM

3. Another weakly presented component is the comparison with other studies. The TNO-MACC emission, EURODELTA, EUCAARI and Airbase archives are usual sources of information for numerous model exercises, not to mention MACC project itself, which covered the considered period with the ensemble of seven models and performed a detailed evaluation against the same Airbase. Numerical results and model scores are available. How does CAMx compare to these? In a couple of places, the authors mention conclusions of other studies but it has to be in a numerical form and made much more systematic.

It is true that comparison with other models was not emphasized strongly in the manuscript. This is because a very detailed evaluation of several models including CAMx for the same periods within EURODELTA III exercise is already available (Bessagnet et al., 2016). We agree, however with the referee's comment and added some more information in the revised manuscript.

Evaluation of the EURODELTA III model inter-comparison exercise showed that all models performed similarly for NO_2 in terms of correlation with values in the range 0.6-0.7, and the spatial correlation was much higher in the range 0.7-0.9 for all models (Bessagnet et al., 2016). There was a general underestimation in the afternoon. Additional analyses showed that NO_2 concentrations within the Paris area were well reproduced by CAMx showing a bias lower than 2 ppb, corresponding to less than 20% of the observed median concentration (Fig. 19 in Bessagnet et al., 2016). At the Po valley sites, on the other hand, NO_2 values were systematically underestimated. These analyses suggest that local emission sources and meteorological conditions such as reconstruction of the PBL diurnal cycle strongly influence NO_2 performance.

4. Among smaller things, I am missing the time correlation coefficient in the list of parameters. It is not only the absolute level that is to be verified, the expensive and complicated VBS mechanism is supposed to deliver better representation of the processes, thus improving the patterns and their evolution. The temporal correlation coefficient is arguably the best parameter to reflect it. Fractional error is good but less straightforward and intuitive parameter, also affected by bias.

We included correlation of determination for the three scenarios (NOVBS, VBS_ROB, VBS_BC) in Figure 5 caption excluding the elevated sites of Puy de Dome and Montseny. R^2 values are improved when the VBS approach is taken into account (VBS_ROB and VBS_BC) with respect to the non-volatile organic scheme (NOVBS). The values are reported in the caption of Figure 5:

Figure 5. OA daily average scatter plots for S1, S2 and S3 scenarios for February-March 2009 for stations in Table 3. Solid lines indicate the 1:1 line. Dotted lines are the 1:2 and 2:1 lines. Boxplots indicate medians, 5th, 25th, 75th and 95th quantiles for observations (black) and sensitivity tests (red). The crosses represent the arithmetic means. R^2 is 0.55 for NOVBS, 0.64 for VBS_ROB and 0.59 for VBS_BC.

5. The naming convention is confusing. The base case is usually number one, from which the sensitivity cases are made. It may look like a small thing but while reading I had to again and again remind myself that S3 is, in fact, the base case.

We changed the naming convention of the different scenarios throughout the manuscript as also suggested by Referee 1. 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 (Double biogenic emission based on VBS_BC)
S5: VBS_BC_2xBBOA (Double biomass burning emission based on VBS_BC)

6. Section 3 is the problematic one from the presentation standpoint. The text is not structured, subsections are routinely comprised of just one huge paragraph without much logic. I would strongly recommend heavy editing of this section.

We agree and revised Section 3.

Specific comments

1. The title does not reflect the paper content. This is the model evaluation exercise, not the AQ assessment.

We changed the title of the paper to read:

Evaluation of European air quality by CAMx including the volatility basis set scheme

2. p. 35647, l.15. I found it strange to praise the model for PM2.5 score, which, as shown already in the next lines, is a result of error compensation (l.20).

We changed the sentence to the following:

CAMx reproduced both total concentrations and monthly variations of measured PM2.5 for all the four periods with average biases ranging from −2.1 to 1.0 $\mu g m^{-3}$

3. p. 35648, l.1-3. No, it does not. The only piece shown is that the model appeared sensitive to scaling of the biogenic emission fluxes in one case and anthropogenic in another. The residential combustion is a hypothesis of the authors not directly supported by the study. It still sounds plausible and can be brought up in discussion but not in the abstract and not in the so categorical form.

Thanks for this remark. We will change the text p. 35647, l.15 of the paper to the following:

Further sensitivity tests with increased biogenic and anthropogenic emissions suggest that OA concentrations in Payerne were affected by changes in emissions from residential heating during the period of February–March 2009 whereas they were more sensitive to biogenic emissions in June 2006.

Moreover, the hypothesis of high contribution to OA from residential combustion in winter is supported by a recent modelling study performed in Europe by Denier van der Gon et al., 2015 for the same winter period (February-March 2009). In this study, an improved inventory with higher emissions from residential combustion by a factor of 2-3 compared to previously used inventories (EUCAARI) was tested in two CTMs with the VBS scheme (PMCAMx and EMEP). Authors concluded that the model performance for OA was improved when using the revisited wood burning emission inventory (Denier van der Gon et al., 2015. Figure8).

4. P. 35651, l.12-13. I did not understand: were the CAMx levels the same as the ones of IFS or not? If they were different, I would challenge the idea of neglecting the interpolation from the IFS levels. The issue should be clarified and explanations provided.

CAMx levels were the same as the ones in IFS. We modified the sentence as follows:

CAMx simulations used 33 terrain-following σ- levels up to about 8000 m a.g.l. as in the original IFS data

5. P. 35652- 35653. The emission discussion is unstructured and difficult to comprehend. Splitting the paragraphs to "main" species available from TNO-MACC, biogenics, etc, would help.

We agree and we split the paragraphs as suggested by the referee.

6. P.35652, l.14-17. How was the split made? As follows from the rest of the paper, amount of organic matter is one of the primary parameters of the study. This vague sentence is part of the most-important weakness of the paper mentioned above: the emission dataset is not analyzed and, as follows from this sentence, is not even presented properly.

Thanks for this remark. We added the following sentence to the manuscript:

$PM_{2.5}$ and PM_{10} emissions were provided by EMEP and they were split to Elemental Carbon and Organic Matter using the fractions given by IIASA (International Institute for Applied Systems Analysis) per each source and country.

7. P.35653, l.1-10. I did not understand: did the authors run MEGAN themselves, including preparation of the land use specifications, emission factors, etc? From the text it seems so ("were prepared for this study") but then, what was wrong in the native MEGAN setup? And how the *changes suggested in this study modified/improved its performance? Did the authors make this analysis?*

We regret the misunderstanding concerning biogenic emission calculations. We used the MEGAN model without any change of the model itself. The data needed to run the model (emission factors of relevant vegetation for our model domain) were retrieved from the MEGAN website (http://lar.wsu.edu/megan/), from MODIS satellite data (leaf area index, LAI) and adapted to the model domain resolution. The same meteorological variables as for CAMx simulations were used to run MEGAN.

8. P. 35654, l.4. "Further aging" from what stage? And why was the ageing stopped? Just because then the model over-estimates the SOA, as stated in the paper? But this cannot be the reason, it is artificial and model-dependent. Is there any physical/chemical ground or hypothesis?

Further reactions of gas-phase products from the first oxidation of biogenic and biomass burning precursors were not considered in the original version of the CAMx-VBS model because of some studies showing over-prediction of SOA especially in rural-areas due to ageing of biogenic SOA (Lane et al., 2008 and Murphy and Pandis, 2009). In this study our aim is to validate the original CAMx-VBS model and compare the results with previous studies performed in North America sharing the same setup (Koo et al., 2014). We will include and investigate the effect of ageing of BSOA in a follow-up study.

9. P. 35655, Statistical methods. These formulas are from textbook. One can put them to appendix for the sake of completeness but this sub-section definitely should be eliminated from the main paper.

We agree and we eliminated the formulas from the main text.

10. P. 35656- 35658. Almost two pages of plain unstructured text, all in one (!) paragraph. I tried several times and still had problems in pushing myself through it.

Paragraph 3.1 was extensively revisited by splitting it according to the different investigated species and shortened as also suggested by Referee 1.

11. P. 35656- 35658. It also looks like the authors do not really pay attention to the physical and statistical meaning of the metrics used. As said in the general comments, mean error is heavily controlled by bias when the latter is large. An independent quantity would be correlation coefficient.

We added correlation coefficients in Table 2 and revised the paragraph, as also suggested by Referee 1.

12. P. 35659, l.13. Another praising the model for meeting totals by a mere error compensation. Not sure if this is a big achievement.

We could not find the above comment in the text. We will change the text p. 35659, l.16 to l.18 of the paper to the following:

The modelled average total non-refractory PM2.5 (sum of nitrate, sulfate, ammonium and OA) concentrations match the measurements with a few exceptions (Fig. 5 and Table 3).

13. P. 35659 – 35661. . . and another 2.5 pages in a single-paragraph of unstructured text.

We modified and shorten the Section 3.2 as also suggested by Referee 1.

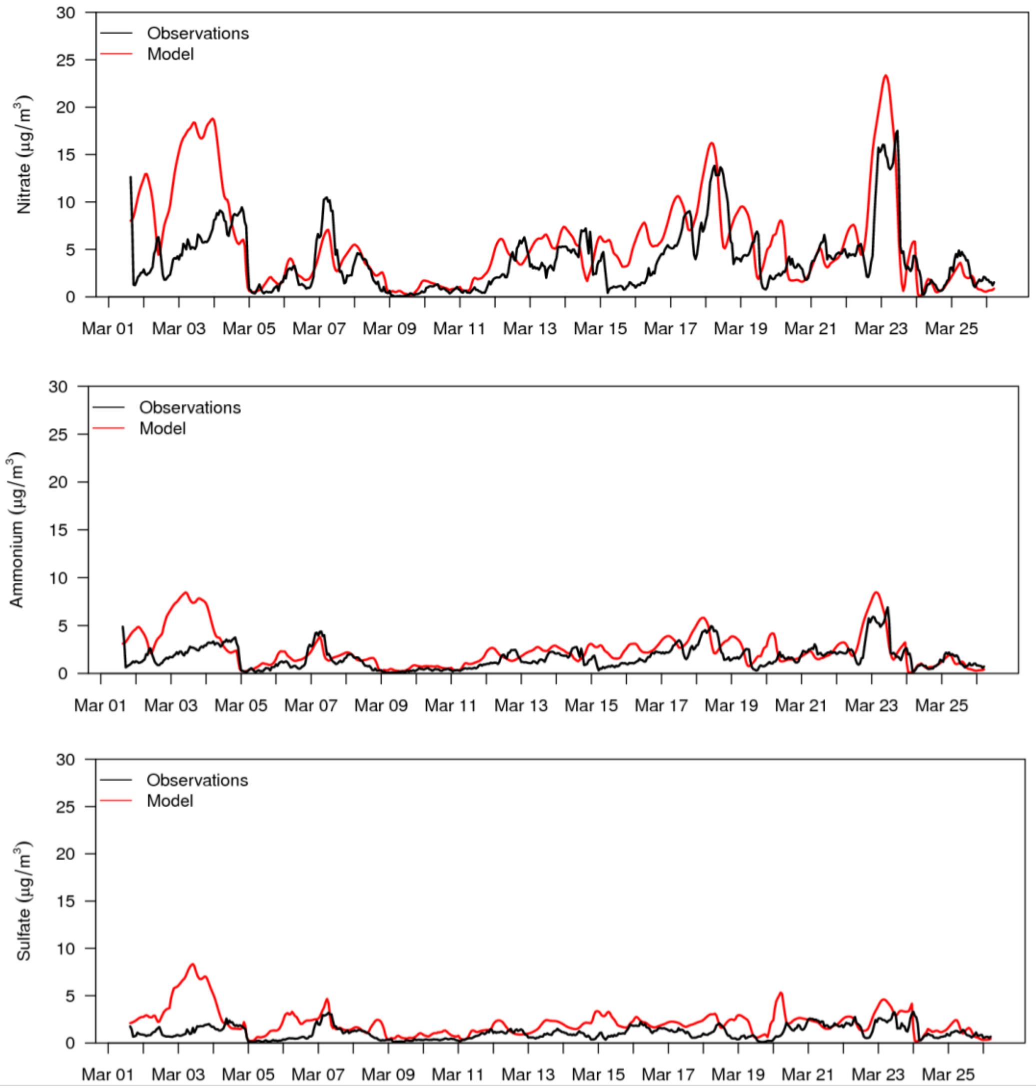
14. P. 35665, l.20. . . .and again "total PM2.5 was modelled very well", for a change without a reference to error compensation. I have strong difficulties with such presentation style.

We revised that part in the Conclusions by merging points 1 and 3 together as shown below:

Although total $PM_{2.5}$ mass concentrations and its variations were well reproduced by the model in all four periods, comparisons with AMS measurements for the February–March 2009 period revealed that the good agreement between model and measurements was most of the time due to overestimation of the inorganic fraction, especially NO_3^-, and underestimation of OA. Sensitivity tests with reduced NH_3 emissions generally reduced the positive bias in NO_3^- suggesting potential uncertainties in NH_3 emissions and their seasonal variability.

15. Figure 6: what panels are for what parameter? The axis font is much too small to figure it out.

We increased the fonts.



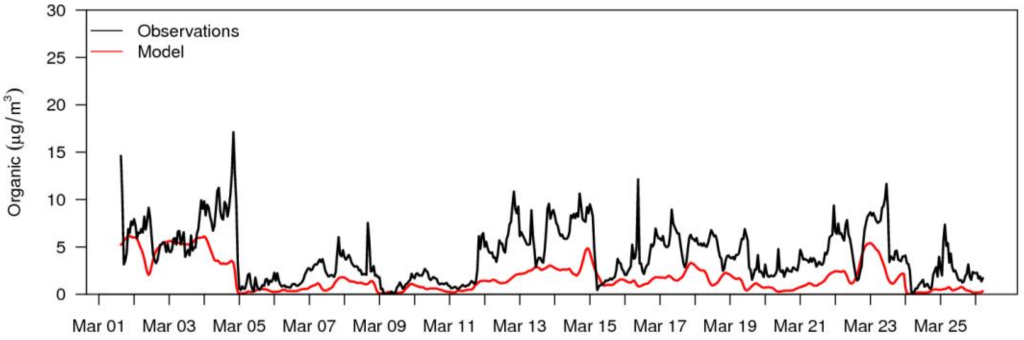


Figure 4. Comparison of observed and modelled nitrate, ammonium, sulfate and organic aerosol at Payerne for March 2009.

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Evaluation of European air quality modelled by CAMx including the volatility basis set scheme

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Abstract

Four periods of EMEP (European Monitoring and Evaluation Programme) intensive measurement campaigns (June 2006, January 2007, September-October 2008 and February-March 2009) were modelled using the regional air quality model CAMx with VBS (Volatility Basis Set) approach for the first time in Europe within the framework of the EURODELTA-III model intercomparison exercise. More detailed analysis and sensitivity tests were performed for the period of February-March 2009 and June 2006 to investigate the uncertainties in emissions as well as to improve the modelling of organic aerosols (OA). Model performance for selected gas phase species and $PM_{2.5}$ was evaluated using the European air quality database Airbase. Sulfur dioxide (SO_2) and ozone (O_3) were found to be overestimated for all the four periods with O_3 having the largest mean bias during June 2006 and January-February 2007 periods (8.9~~3~~ pbb and 12.3~~0~~ ppb mean biases, respectively). In contrast, nitrogen dioxide (NO_2) and carbon monoxide (CO) were found to be underestimated for all the four periods. CAMx reproduced both total concentrations and monthly variations of $PM_{2.5}$ ~~very well~~ for all the four periods with average biases ranging from -2.1~~3~~ µg m^{-3} to 1.0~~4~~ µg m^{-3}. Comparisons with AMS (a~~A~~erosol m~~M~~ass s~~S~~pectrometer) measurements at different sites in Europe during February-March 2009~~,~~ showed that in general the model over-predicts the inorganic aerosol fraction and under-predicts the organic one, such that the good agreement for $PM_{2.5}$ is partly due to compensation of errors. The effect of the choice of volatility basis set scheme (VBS) on OA was investigated as well. Two sensitivity tests with volatility distributions based on previous chamber and ambient measurements data were performed. For February-March 2009 the chamber-case reduced the total OA concentrations by about 43% on average. On the other hand, a test based on ambient measurement data increased OA concentrations by about 47% for the same period bringing model and observations into better agreement. Comparison with the AMS data at the rural Swiss site Payerne in June 2006 shows no significant improvement in modelled OA concentration. Further sensitivity tests with increased biogenic and anthropogenic emissions suggest that OA in Payerne ~~was largely~~were affected ~~dominated~~ by changes in emissions from residential heating ~~emissions~~ during the February-March 2009 whereas it was more sensitive to ~~period and by~~ biogenic precursors in June 2006.

1 Introduction

Air pollution is known to cause damage to human health, vegetation and ecosystems. It is one of the main environmental causes of premature death. Only in Europe, more than 400,000 premature deaths were estimated in 2011 with $PM_{2.5}$ (particles less than 2.5 μm in aerodynamic diameter) having the highest relative risk for health damage (WHO, 2014a). Air quality models help understanding the processes taking place between emission sources and pollutant concentrations at receptor sites. They are very useful to define control strategies for future legislation. In spite of large improvements in recent years, Chemical Transport Models (CTMs) have still some uncertainties (Solazzo et al., 2012a). Various air quality model intercomparison exercises were successfully carried out over the last decades to determine uncertainties in chemical and physical processes governing particulate matter and its precursors (Solazzo et al., 2012a; Bessagnet et al., 2014). However, a large variability in particulate matter concentrations was found between different models indicating process parameterization as one of the main reasons for such discrepancies. Moreover, recent studies based on AMS (Aerosol Mass Spectrometer) measurements at different sites in Europe, revealed that the organic fraction dominates the non-refractory PM_1 composition (Crippa et al., 2014). Organic aerosol (OA) can be found in the atmosphere from direct emission by various sources, such as fossil fuel combustion by road vehicle engines or residential wood combustion. Direct emissions of OA are typically referred to as primary organic aerosol (POA) whereas gas-to-particle conversion is referred to as secondary organic aerosol (SOA). Formation mechanisms of SOAs are not very well known yet and their representation in CTMs is still challenging (Hallquist et al. 2009; Fountoukis et al., 2011; Bergstrom et al., 2012; Li et al., 2013; Langmann et al., 2014; Tsigaridis et al., 2014). In one of our recent aerosol modelling studies we compared model $PM_{2.5}$ prediction with PM_1 AMS measurements for different sites (Payerne and Zürich) and periods (summer and winter) in Switzerland. We found that particulate matter was generally well reproduced by the model with the SOA fraction being under-predicted and POA over-predicted (Aksoyoglu et al., 2011). Traditional CTMs treat POA as non-volatile. Some studies however have revealed the semi-volatile nature of POA, through its dynamic equilibrium of organic aerosol with its gas phase, and the importance of semi-volatile (SVOC) and intermediate volatility (IVOC) organic compounds as SOA precursors (Donahue et al., 2006; Robinson et al., 2007; Cappa and Jimenez, 2010). To describe the absorptive partitioning and ongoing oxidation of the atmospheric material, a volatility basis set (VBS) where organic species are organized into surrogates according to their volatility was developed (Donahue et al., 2011, 2012a,b). Air quality models updated with VBS scheme started being used (Lane et al., 2008; Murphy and Pandis, 2009; Hodzic et al., 2010; Fountoukis et al., 2011; Bergström et al., 2012; Murphy et al., 2012; Jo et al., 2013; Zhang et al., 2013; Athanasopoulou et al., 2013; Fountoukis et al., 2014). Bergström et al. (2012) reported an EMEP model study over Europe for the 2002-2007 period using different assumptions regarding partitioning and aging processes. They could not reproduce the measured OA levels in winter suggesting that residential wood combustion inventories might be underestimated in different parts of Europe. Fountoukis et al. (2014) applied the PMCAMx model to simulate EUCAARI (Kulmala et al., 2009, 2011) and EMEP (Tørseth et al., 2012) campaigns in Europe. They could reproduce most of PM_1 daily average OA observations within a factor of two, with the February-March 2009 period having the largest discrepancies. Zhang et al. (2013) deployed the CHIMERE model with the VBS framework during the MEGAPOLI summer campaign in the Greater Paris region for July 2009. They found a considerable improvement in predicted SOA concentrations which might be even overestimated depending on the emission inventory used. In our study, we applied the regional air quality model CAMx with the VBS scheme for the first time in Europe within the framework of EURODELTA-III model intercomparison exercise. In addition to the base case configuration used in the exercise, more sensitivity tests with the VBS scheme for winter and summer episodes were performed together with a general evaluation of the four EMEP field measurement campaigns.

2 Method

2.1 The EURODELTA-III exercise

The EURODELTA-III (EDIII) framework is a European model intercomparison exercise between several modelling teams sharing both efforts and technical knowledge in order to reduce model uncertainties and to improve understanding of the performances. It contributes to the scientific work of the United Nations Economic Commission for Europe (UNECE) Task Force on Measurement and Modelling (TFMM) within the Convention on Long-range Transboundary Air Pollution (CLRTAP). In the first phase of the EDIII exercise, 4 periods of the EMEP field measurement campaigns were chosen in order to evaluate the model results:

- 1 June – 30 June 2006
- 8 January – 4 February 2007
- 17 September – 15 October 2008

- 25 February – 26 March 2009

Multiple models were applied on a common domain and driven with the same input data provided by the National Institute for Industrial Environment and Risks (INERIS). However, for some models, different meteorology, boundary conditions and emissions data such as biogenic emissions were used (Bessagnet et al., 2014).

2.2 Modelling method

2.2.1 CAMx

The Comprehensive Air quality Model with extensions, CAMx-VBS (CAMx5.41_VBS, kindly provided by ENVIRON before its public release) was used in this study. The model domain consisted of one grid with a horizontal resolution of 0.25° x 0.25°. The latitude and longitude grid extended from 25.125°W to 45.125°E and 29.875°N to 70.125°N resulting in 281 x 161 grid cells covering the whole of Europe. Hourly four-dimensional meteorological fields for wind speed and direction, pressure, temperature, specific humidity, cloud cover and rain required by CAMx simulations were calculated from ECMWF IFS (Integrated Forecast System) data at 0.2° resolution. Vertical diffusivity coefficients were estimated following the Kz approach of O'Brien (1970) using PBL depth profiles as available in IFS data. CAMx simulations used 33 terrain-following σ-levels up to about 8000 m above ground level, as in the original IFS data.~~. No vertical interpolation of the original IFS data was performed.~~ The lowest layer was about 20 m thick. MACC (Monitoring Atmospheric Composition and Climate) reanalysis data were used to initialize initial and the boundary condition fields (Benedetti et al., 2009; Inness et al., 2013). Elemental carbon, organic aerosol, dust and sulfate were used to model aerosol species at the boundaries of the domain. One half of the OA was assumed to be secondary organic aerosol (SOA) and the other half primary organic aerosol (POA), as recommended in the EDIII exercise. Photolysis rate inputs were calculated using the TUV radiative transfer and photolysis model (Madronich, 2002). The required ozone column densities to determine the spatial and temporal variation of the photolysis rates were extracted from TOMS data (NASA/GSFC, 2005). Removal processes as dry and wet deposition were simulated using the Zhang resistance model (Zhang et al., 2003) and a scavenging model approach for both gases and aerosols (ENVIRON, 2011), respectively. For the gas phase chemistry the Carbon Bond (CB05) mechanism (Yarwood et al., 2005) with 156 reactions and up to 89 species was used. Partitioning of inorganic aerosols (sulfate, nitrate, ammonium, sodium and chloride) was performed using the ISORROPIA thermodynamic model (Nenes et al., 1998). Aqueous sulfate and nitrate formation in cloud water was simulated as well using the RADM aqueous chemistry algorithm (Chang et al., 1987).

2.2.2 Emissions

Anthropogenic emissions

Annual total gridded anthropogenic emissions were prepared and provided by INERIS for the EDIII exercise, which is based on a merging process of data-bases from different sources, i.e. TNO-MACC (Kuenen et al., 2011), EMEP (Vestreng et al., 2007), GAINS (The Greenhouse Gas and Air Pollution Interactions and Synergies). For specific countries where TNO-MACC emissions were missing (Iceland, Liechtenstein, Malta and Asian countries), the EMEP 0.5° × 0.5° emissions were used and re-gridded using adequate proxies such as “artificial land-use” and EPER (European Pollutant Emission Register) data (http://www.eea.europa.eu/) for industries. Total primary particle emissions were made available by EMEP in two different size ranges: below 2.5µm (fine) and between 2.5µm and 10µm (coarse). Total emissions were later split to estimate the amount of elemental carbon, and organic matter for each of the 10 SNAP codes (Selected Nomenclature for Air Pollution) and country. The final emission inventory thus compiled consisted of 6 gas species namely methane, carbon monoxide, ammonia, sulfur oxides, non-methane volatile organic compounds and nitrogen oxides and 6 categories of particulate matter classes: fine elemental carbon (EC2.5), coarse elemental carbon (EC10), fine primary organic material (fine POA), coarse primary organic material (coarse POA), fine other primary particulate material (non-carbonaceous) and coarse other primary particulate material (non-carbonaceous). $PM_{2.5}$ and PM_{10} emissions were provided by EMEP and they were split to elemental carbon and organic matter using the fractions given by IIASA (International Institute for Applied Systems Analysis) for each source and country. Total non-methane volatile organic compounds were split for the CB05 mechanism using the recommendations of Passant (2002). Hourly, weekly and monthly time profiles as in the EURODELTAII exercise were applied to total annual anthropogenic emissions.

Biogenic emissions

Biogenic VOC emissions were calculated using the Model of Emissions of Gases and Aerosols from Nature MEGANv2.1 (Guenther et al., 2012). This model is driven by meteorological variables such as hourly temperature, solar radiation, humidity, wind speed, soil moisture and land cover data including leaf area index (LAI) and plant function type (PFT) as available in the Community Land Model 4.0. 8-Days average satellite data at 0.25° x 0.25° resolution were pre-processed and made available from the TERRA/MODIS satellite system. Sixteen plant function types including needle-leaved evergreen, needle-leaved deciduous, broad-leaved evergreen, broad-leaved deciduous, grass and crop for different climatic zones were prepared for this study at 0.25° x 0.25° resolution together with the global emission factors of α-pinene, β-pinene, 3-carene, isoprene, limonene, 232-methylbutenol, myrcene, NO_x, *t-β*-ocimene and sabinene. Common BVOC species such as isoprene, terpene, sesquiterpene, xylene and toluene were obtained for each hour and cell in the domain.

2.2.3 VBS scheme

A new volatility basis set (VBS) scheme is available in the CAMx model to describe changes in oxidation state and volatility. A total of four basis set simulates the evolution of organic aerosol in the atmosphere (Koo et al., 2014). POA emissions were split in HOA-like and BBOA-like emissions and allocated in two different basis sets. HOA-like emissions include emissions from all SNAP sectors except SNAP2 (non-industrial combustion plants) and SNAP10 (agriculture) which were assigned to BBOA-like emissions. Two other sets were used in the model to allocate secondary organic aerosol from anthropogenic (i.e. xylene and toluene) (ASOA) and biogenic (i.e. isoprene, monoterpene and sesquiterpene) (BSOA) gaseous precursors. These two sets also allocate oxidation products of POA vapours, from each of the two primary sets (HOA-like and BBOA-like). The 2D volatility space retrieved by Donahue et al. (2011; 2012a,b) was used to distribute the organic molecular structures for each of the volatility bins and different sets (Table S1). Five volatility bins represent the range of semi-volatile organic compounds (SVOCs) ranging from 10^{-1} µg m^{-3} to 10^{3} µg m^{-3} in saturation concentrations (C*). Oxidation processes are modelled by shifting C* by a factor of 10 in the next lower volatility bin, increasing the oxidation state and reducing the carbon number to account for fragmentation. OH reaction rates are assumed to be 4 x 10^{-11} cm^{3} $molecule^{-1}$ s^{-1} for the reaction of semi-volatile primary vapors with OH and 2 x 10^{-11} for further aging of ASOA and POA vapours from HOA-like emissions. More details about the

VBS parameterization in CAMx can be found in Koo et al. (2014). Further aging of BSOA is not considered in this study based on previous modelling results showing over-prediction of OA when such process is taken into account (Lane et al., 2008; Murphy and Pandis, 2009). This implies that also further aging of POA vapours from BBOA-like emissions was not considered since it is performed in the same basis set. In this work we focus on the effects of a VBS framework on the total OA fraction. Aging processes and alternative VBS implementations will be discussed together with SOA and POA components in a following paper (Ciarelli et al. in prep). Three sensitivity tests were performed with different assumptions on the volatility distributions (Table 1):

- **~~S1~~NOVBS:** Primary organic aerosol was assumed to be non-volatile. Biogenic (isoprene, monoterpenes and sesquiterpenes) and anthropogenic (xylene, toluene and other aromatics) volatile organic compounds (VOCs) were used as precursors for secondary organic aerosol. Partitioning of condensable gases to secondary organic aerosol was calculated using a semi-volatile equilibrium approach (Strader, 1999).

- **~~S2~~VBS_ROB:** Primary organic aerosol was assumed to be volatile and undergo chemical oxidation. The volatility distribution estimated by Robinson et al. (2007) was applied to HOA-like and BBOA-like emissions. Emissions of intermediate volatility organic compounds (IVOCs) were assumed to be 1.5 times those of primary organic aerosol (POA) as suggested by Robinson et al. (2007).

- **~~S3~~VBS_BC:** Primary organic aerosol was assumed to be volatile and undergo chemical oxidation using the approach of Shrivastava et al. (2011) and Tsimpidi et al. (2010). The total primary emissions are roughly 3 times higher than in **~~S2~~VBS_ROB.** Different volatility distributions were applied for HOA and BBOA-like emissions. IVOCs were assumed to be 1.5 times the amount of POA. This implies that for this scenario the SVOC + IVOC mass added is equal to 7.5 times the initial amount of POA. This represents the base case scenario used to evaluate gas phase and $PM_{2.5}$ model performance.

Based on the ~~S3~~**VBS_BC** ~~-~~base case scenario, two other sensitivity tests were performed with respect to emissions:

- **~~S4~~VBS_BC_2xBVOC:** Increased BVOCs emissions by a factor of 2.

- **~~S5~~VBS_BC_2xBBOA:** Increased BBOA-like emissions by a factor of 2.

2.3 Statistical methods

Statistical procedures as available in the Atmospheric Model Evaluation Tool (AMET, Appel et al., 2010) were used in this study to evaluate model performance. Daily ambient measurements of main gas phase species i.e. O_3, NO_2, CO, SO_2 and fine particulate matter ($PM_{2.5}$) were extracted from the Airbase database in Europe and statistics reported in terms of mean bias (MB), mean error (ME), mean fractional bias (MFB) ~~and~~ mean fractional error (MFE) and correlation coefficient (r).~~:~~

~~$MB = \frac{1}{n}\sum_{i=1}^{n}(M_i - O_i)$, (1)~~

~~$ME = \frac{1}{n}\sum_{i=1}^{n}(|M_i - O_i|)$, (2)~~

~~$MFB = \frac{2}{n}\sum_{i=1}^{n}(\frac{M_i - O_i}{M_i + O_i})$, (3)~~

~~$MFE = \frac{2}{n}\sum_{i=1}^{n}(\frac{|M_i - O_i|}{M_i + O_i})$. (4)~~

~~where M_i presents the modelled value, O_i the observations and n the total number of data points.~~ Due to the coarse grid resolution, only rural-background stations, defined as stations far from city sources of air pollution with pollution levels determined by the integrated contribution from all sources upwind of the station (ETC/ACC, 2004/7), with at least 80% daily average observations available were considered for the statistical analysis. For $PM_{2.5}$ this resulted~~s~~ in 48 stations available for June 2006, 56 for January-February 2007, 90 for September-October 2008 and 110 stations for February-March 2009. $PM_{2.5}$ components were further evaluated for the February-March 2009 period where comprehensive high resolution AMS measurements at 11 European sites were available, i.e., at Barcelona, Cabauw, Chilbolton, Helsinki, Hyytiälä, Mace Head, Melpitz, Montseny, Payerne, Puy de Dôme and Vavihill (Crippa et al., 2014).

3 Results and discussions

3.1 Model evaluation

Model performance metrics for gas phase species CO, NO_2, O_3 and SO_2 as well as for $PM_{2.5}$ are reported in ~~Fig.1 and~~ Table 2 and they refer to the base case VBS_BC~~S3~~.

NO_2 and O_3

~~SO_2 and O_3 concentrations were found to be over-predicted for all the four periods with a mean fractional bias ranging from 14% to 36% for SO_2 and from 2% to 48% for O_3. Both O_3 and SO_2 over-predictions were higher during the January-February 2007 periods. The mean error (ME) in SO_2 concentrations increases at stations located close to coastal areas, especially near large harbors such as Lisbon, Marseille, Barcelona and in Eastern countries of the domain (Fig. S1). Most of the SO_2 emissions arise from high stack point sources which have injection heights of few hundred meters. It might be that the vertical distribution of SO_2 might affect the model performance in particular near the harbors and coastal areas where ship emissions were allocated in the second layer of the model domain (extending from ~20 to 50 m above ground level) whereas they can reach up to 58 meters in deep draft vessels (SCG, 2004) and also undergo plume rise. On the other hand~~ NO_2 ~~and CO were~~was found to be under-predicted for all the four periods with mean fractional bias between -54% and -28%~~ for NO_2 and -31% and -11% for CO.~~ and NO_2 concentrations ~~was~~being particularly under-predicted during June 2006. ~~whereas CO had the largest bias during the September-October 2008 simulation.~~ Evaluation of the EURODELTA III model inter-comparison exercise showed that all models performed similarly for NO_2 in terms of correlation with *r* values in the range 0.6-0.7 and the spatial correlation was much higher in the range 0.7-0.9 for all models (Bessagnet et al., 2016) with a general underestimation in the afternoon. The ~~under-prediction in~~ NO_2 ~~concentrations~~ performance could be influenced by several factors:

- Uncertainties in the emission inventories. Although NO_x emission estimates in Europe are thought to have an uncertainty of about ± 20%, the complete data set used in the inventories has much higher uncertainty (Kuenen et al., 2014). A recent study identified a significant discrepancy between emission estimates and actual flux measurements, with the highest underestimation being a factor of two in central London mainly due to under-representation of real world road traffic emissions (Vaughan et al., 2016)

- ~~t~~The relatively coarse resolution of the domain which may result in too low NO_x emissions or isolated local events that the model cannot resolve. We report daily average time series of NO_2 for the period of Feb-Mar 2009 for stations in Table 2 as well as daily average time series of NO_2 for stations not exceeding 5 ppb (which represents 92% of the stations in Table 2) (Figure S1). The model performance for NO_2 significantly improved when the 5 ppb threshold was applied to the dataset. An emission map of NO for 1 March 2009 at 6 AM is reported in Figure S2. 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

- Possible positive artefacts in the chemiluminescence methods for measuring NO_2 may also occur when NO_2 is catalytically converted to NO on the molybdenum surface leading to an over-prediction of measured NO_2 concentrations (Steinbacher et al., 2007; Villena et al., 2012)~~.~~

- Moreover, an evaluation of planetary boundary layer height (PBLH) within the EDIII shows that although the PBLH was quite well represented in general in the ECMWF IFS meteorological fields, CAMx tends to under-estimate the night-time minima and to over-estimate some daytime peaks, over-predicting the dilution of day time NO_2 concentrations, whereas the wind speed was relatively well reproduced (Bessagnet et al., 2016).

~~Especially in June 2006, when the photochemical activity is higher, the general under-prediction of NO_x in the whole domain reduces the O_3 titration potential during the night time.~~ O_3 concentrations were found to be over-predicted for all the four periods with a mean fractional bias ranging from 2% to 48%. Especially in June 2006, when the photochemical activity is higher, the general under-prediction of NO_x in the whole domain reduces the O_3 titration potential during night time.

Model performance for O_3 is also strongly influenced by long-range transport especially during the winter periods when the local chemical production of O_3 is limited. ~~MACC analysis data at 1.125° x 1.125° were used in this study to map O_3 four-dimensional data at the boundary of the domain.~~ Figure S3~~2~~ shows the model performance at the Mace Head station located on the west coast of Ireland for all the four periods. Especially in January-February 2007 O_3 concentrations were found to be over-predicted by about 10 to 20 ppb indicating that boundary conditions for O_3 were probably not well represented. In June 2006 and September-October 2008 O_3 was relatively well captured at Mace Head suggesting that the observed positive bias in O_3 concentrations might arise from insufficient NO_x emissions to undergo titration during night time as well as not correctly represented planetary boundary layer dynamics. In February-March 2009 the model tends to under-predict the O_3 concentration at Mace Head and overall the O_3 model performance shows the lowest bias (2%). Eventually, the under-prediction of O_3 in the boundary condition may counteract the already mentioned deficiencies related to insufficient NO_x emissions. ~~Evaluation of O_3 vertical profiles at stations located near the boundaries of the domain show that even though the model follows the measured O_3 vertical profiles, it has difficulties to catch the inversion between the low and middle troposphere around 2-3 km above ground levels with O_3 concentrations under 2 km being over-predicted (Bessagnet et al., 2014).~~

SO_2 and CO

SO_2 concentrations were found to be slightly over-predicted for all the four periods with a mean fractional bias ranging from 14% to 36% for SO_2. The daily variations of modelled and measured SO_2 concentrations for February-March 2009 are reported as well in Figure S1 (lower-panel) for the stations in Table 2. In general, the daily variations of modelled and measured SO_2 concentrations agree relatively well with each other throughout the period.

Most of the SO_2 emissions arise from high stack point sources which have injection heights of a few hundred meters. It might be that the vertical distribution of SO_2 might affect the model performance in particular near the harbors and coastal areas where ship emissions were allocated in the second layer of the model domain (extending from ~20 to 50 m above ground level) whereas they can reach up to 58 meters in deep draft vessels (SCG, 2004) and also undergo plume rise. Insufficient conversion to sulfate or too low deposition processes might also positively bias the model performance for SO_2.

~~Finally,~~ CO was slightly under-predicted for all periods (mean fractional bias between -11% and -31%), with highest values during the September-October 2008 period (-31%). The late summer-fall period is known to be influenced by agricultural open field burning activities which might be missing from standard emission inventories.

In general, for both SO_2 and CO, the model showed lower correlation coefficients with respect to other gas-phase species (*r* values from 0.20 and 0.37 for CO and from 0.37 to 0.52 for SO_2).

$PM_{2.5}$

Of all investigated variables, CAMx shows the best statistical performance for $PM_{2.5}$. For all four periods the acceptable model performance criteria recommended by Boylan and Russell (2006) for aerosols were met (MFE ≤ +75 % and −60 % < MFB < +60 %). The fractional bias ranges from less than 1% in September-October 2008 up to -13% in February-March 2009. Also the recommended model performance goals (MFE ≤ +50% and -30% < MFB < +30%) were met for all periods except for January 2007. Modelled average $PM_{2.5}$ concentrations are shown in Fig. ~~2~~1. A different spatial distribution is seen for summer and winter. In June 2006 the model predicts higher concentrations in the southern part of the domain especially over the Mediterranean Sea and North Africa (up to 35 µg m^{-3}). On the other hand, the highest concentrations were predicted in the Po valley area (above 40 µg m^{-3}) and in the southern part of Poland during January-February 2007. During the two colder periods (2007 and 2009) elevated concentrations of around 15 µg m^{-3} are also visible close to urban areas such as Paris and Moscow. Figure ~~3~~ 2 shows $PM_{2.5}$ variations at Airbase rural-background sites in terms of medians, 25th and 75th percentiles. In all the four periods CAMx is able to reproduce the observed monthly variation very well with some over-prediction occurring mainly from the 14th to the 17th of January 2007 and towards the end of 2008 period. ~~Figure 4 shows $PM_{2.5}$ comparisons in terms of daily average scatterplots. CAMx is able to capture the concentration differences between the four periods with lower peak concentrations of around 40 µg m^{-3} in June 2006 and several high pollution events with concentrations around 60-70 µg m^{-3} for the other periods. For some days in January-February 2007 CAMx strongly over-predicts $PM_{2.5}$ with predicted concentrations around 100 µg m^{-3}. The latter occurs mainly at one station located in Italy i.e. Casirate d'Adda (Airbase code IT1464A) with the highest over prediction on the 17th of January. During the 7th and 8th of March 2009 CAMx strongly under predicts at the EMEP stations of Ayia Marina in Cyprus (Airbase code CY0002R), most likely due to a Saharan dust event not captured by the model (Fig. S3). A similar situation was found at Viznar in Southern Spain (Airbase code ES0007R) on the 11th and 12th of October 2008 with observed $PM_{2.5}$ concentration above 100 µg m^{-3}. This time CAMx was able to capture the Saharan dust episode but not its magnitude (Fig. S3).~~

3.2 Detailed evaluation of $PM_{2.5}$ components in February-March 2009

The modelled concentrations of non-refractory $PM_{2.5}$ components were compared against aerosol mass spectrometer measurements at eleven European sites for the February-March

2009 period (Crippa et al., 2014). Even though the AMS measures particles with a diameter *D* < 1 µm, the difference between the non-refractory PM_1 and total $PM_{2.5}$ mass is in general rather small as shown in Aksoyoglu et al. (2011), at least for situations without exceedingly high air pollution and situations when sea salt makes large relative contribution to $PM_{2.5}$. The modelled average total non-refractory $PM_{2.5}$ (sum of nitrate, sulfate, ammonium and OA) concentrations match the measurements quite well with a few exceptions (Fig. ~~5~~ 3 and Table 3). The model is able to reproduce both high concentrations observed at the urban site Barcelona and low ones at remote sites like Hyytiälä, Finland. Concentrations of inorganic aerosols are over-predicted and OA are under-predicted at most of the stations (with similar behavior during the other investigated periods, Figure S4 and Figure S5). Very similar results were also presented by other recent studies (Knote et al., 2011). The effect of different schemes to treat OA is discussed in Sect. 3.3. At the Cabauw site nitrate was the most dominant species (Mensah et al., 2012). Especially at this site the model strongly over-predicts in particular the nitrate (NO_3^-) fraction (by a factor of 3). ~~This site is located in a high NH_3 and NO_x emission area. Emissions of NH_3 mainly arise from agricultural activities and just a minor fraction from the transportation sectors. Figure S4 shows the seasonal distribution of the annual NH_3 emissions from agriculture, as provided in the EDIII exercise for Switzerland. High NH_3 emissions are therefore expected in March-April. A comparison with ammonia measurements (available at http://www.bafu.admin.ch/luft/00585/10770/index.html?lang=de) at the Payerne site revealed that the model predicts ammonia reasonably well in June 2006 but that there is a significant overestimation in March 2009 suggesting that the modelled emissions might be too high in spring (Table S2).~~ A sensitivity test with 50% reduction in ammonia emissions significantly improved the modelled NO_3^- concentrations at almost all sites (Table ~~S3~~S2) suggesting potential uncertainties in NH_3 emissions and their seasonal variability. ~~The lowest effect was found at Payerne, in Switzerland where reducing ammonia emissions by half led to a decrease in NO_3^- by about 12%. These results are in line with previous studies suggesting that aerosol formation during winter is more sensitive to NH_3 emissions in most of Europe whereas in the Swiss Plateau it is more limited by NO_x emissions (Aksoyoglu et al. 2011). Indeed, o~~Other potential reasons for the over-prediction of NO_3^- could be related to uncertainties in removal process of HNO_3 as well as dry deposition velocity of NH_3. Substantial over-predictions were found at the higher altitude site of Montseny and Puy de Dôme when compared with first model layer concentrations (ca. 200 and 800 meters a.s.l. respectively at these sites). These

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sites located at about 720 and 1465 meters a.s.l., are sometimes not within the PBLH during winter periods. At the Montseny site, the relatively coarse resolution of the model could also influence model performance since the site is located in a complex area about 50 km north-east of Barcelona (Pandolfi et al., 2014). Sulfate concentrations (SO_4^{2-}) were over-predicted at almost all sites and especially at Mace Head suggesting that long-range transport of SO_4^{2-} might be positively biased.

Modelled and observed hourly concentrations of NO_3^-, SO_4^{2-}, ammonium (NH_4~~$^-$~~$^+$) and OA at Payerne are reported in Fig. ~~6~~ 4 for March 2009 together with meteorological parameters in Fig. S6.~~.~~ ~~The period was characterized by south-westerly winds until the 15th of March, north-easterly winds between the 15th and 24th of March, and again by south-westerly winds until the end of the simulation (Fig. S5). Temperature was rarely above 10 °C during day-time and mostly around or slightly below 0 °C at night ,with higher temperatures observed between the 15th and 20th of March. Specific humidity was between about 4 and 5g/kg. Low wind speeds (below 2 m s^{-1}) were observed during the first part of the simulation and higher values exceeding 6 m s^{-1} around the 9th of March and throughout the end of the simulation.~~ The model was able to reproduce the meteorological parameters very well for most of the time. The temperature was slightly under-predicted at both night and day-times (with a maximum of -2 °C) whereas both the monthly variation and the absolute values of wind speed and specific humidity were reproduced well with a few under-predictions of high wind-speed (6th and 11th of March and towards the end of the simulation). The model was able to capture the three NO_3^- and $NH_4$$^+$~~$^-$~~ peaks observed around the 7th, 18th and 23rd of March with a general slight over-prediction throughout the whole period. Indeed, the under-prediction in temperature during day and night time could partially explain the over-prediction of the NO_3^- fraction with more NO_3^- partitioning to the aerosol phase which also apply to the other stations used in this study. An evaluation of modelled temperature at the European scale for the February-March 2009 period confirmed that the model systematically under-predicted the 2 meter surface temperature (Bessagnet et al., 2014). All the inorganic components were over-predicted during the first four days of March 2009 with a peak around the 3rd of March~~. The modelled (PBLH) is reported in Fig. S6 together with the convective boundary layer (CBL) height estimated from Payerne sounding data. The model exhibits very low PBLH during the night until the 5th of March. In contrast, from the 5th of March until the 11th of March PBLH at night was relatively higher, around a few hundred meters. At the same time the NO_3^- concentration was reproduced more closely, with the peak around 7th of March being under-~~

~~estimated. From the 12th until the 19th of March the modelled PBLH again showed very low values at night with the NO$_3^-$ concentration being slightly over-predicted. This might suggests that a too shallow PBLH at night could be the reason for such over-prediction.~~ , indicating that the PBLH was probably not correctly reproduced by the model during this period. Although the temporal variation was captured, concentrations of OA were under-predicted throughout all the simulation (4.1 µg m^{-3} and 1.8 µg m^{-3} observed and modelled average concentrations). Analysis of the OA fraction is discussed in the next section.

3.3 Organic aerosols

3.3.1 Sensitivity of OA to the VBS scheme

In this section, effects of different parameterizations of the organic aerosol module on the modelled OA concentrations are discussed. The scatter plots in Fig. ~~7~~ 5 show a comparison of daily average OA concentrations against the same AMS measurements as in Table 3 during February-March 2009. Statistics for each scenario are reported in Table 4. When the semi-volatile dynamics of primary organic aerosol is not taken into account (scenario ~~S1~~NOVBS), the model under-predicts OA concentrations (MFB: -66%) with an observed and modelled average concentrations of ~~2.96~~3.0 µg m^{-3} and 1.~~18~~ 2 µg m^{-3} respectively. In the ~~S2~~ VBS_ROB scenario POA emissions are allowed to evaporate following the volatility distribution proposed by Robinson et al. (2007) and to undergo chemical oxidation. In this case modelled OA concentrations decrease by about 43% with respect to ~~S1~~NOVBS, predicting an average OA concentration of 0.7~~67~~ µg m^{-3}. On the other hand, the ~~S3~~ VBS_BC scenario improves the OA model performance increasing the OA concentrations by about 47% with respect to ~~S1~~NOVBS. Predicted OA concentrations are found to be 1.7~~3~~ µg m^{-3} on average (MFB: -47%). Similar behavior during winter periods was also shown in recent studies where the same VBS scheme was applied in the U.S. domain (Koo et al., 2014). Figure ~~8~~ 6 shows the modelled total OA concentration over Europe using ~~S1~~NOVBS, ~~S2~~ VBS_ROB and ~~S3~~ VBS_BC scenarios. The model predicts high OA values in the Eastern part of the domain as well as over Portugal, France and the Po Valley (~~S3~~VBS_BC). Some hot-spots around large urban areas are also visible, i.e., Paris and Moscow. Higher OA concentrations in the southern part of the domain are observed in the ~~S3~~ VBS_BC case, likely because of higher temperature and more OH radicals available in that part of the domain leading to an increase in the total organic mass upon reaction with organic vapours. This is in line with the results of

Fountoukis et al. (2014) for the February-March 2009 period even though their study predicts lower concentration over the Po valley. Even though model input data and parameterizations are not the same, the ~~S3~~ VBS_BC case in particularly, uses a very similar volatility distribution as in Fountoukis et al. (2014). Our study predicts relatively lower OA concentrations (MFB: -0.47, MFE: 0.79) compared to those reported by Fountoukis et al. (2014) (MFB: 0.02, MFE: 0.68) for February-March 2009. Unlike Fountoukis et al. (2014) our study does not include fire emissions and marine organic aerosol which may partially explain the differences. Figure ~~9~~ 7 shows hourly modelled and observed OA concentration at Payerne for March 2009 and June 2006. In March 2009 ~~S2~~ VBS_ROB results are lower than those in ~~S1~~ NOVBS whereas OA concentrations in ~~S3~~ VBS_BC case are higher (see Supplementary Fig. S8 and Table ~~S4~~ S3 for average concentrations and statistics). In June 2006, the OA mass in ~~S2~~ VBS_ROB is lower than those in ~~S1~~ NOVBS while ~~S3~~ VBS_BC predicts similar concentrations as the ~~S1~~ NOVBS scenario (2.4~~3~~ µg m^{-3} and 2.~~5~~6 µg m^{-3}, respectively, Fig. S9 and Table ~~S5~~S4). It has to be noted that the ~~S1~~ NOVBS scenario predicts slightly lower OA concentration for June 2006 in Payerne with respect to our previous application (Aksoyoglu et al., 2011), mainly because of a different biogenic model being used which yields lower monoterpene and sesquiterpene emissions. Since both BVOCs and BBOA-like emissions are highly uncertain, sensitivity tests with increased biogenic and anthropogenic emissions were performed and results discussed in the next section (3.3.2).

3.3.2 Sensitivity of OA to BBOA-like and BVOC emissions

Emissions of BVOCs compounds (i.e. monoterpenes, isoprene and sesquiterpenes) were doubled in scenario ~~S4~~VBS_BC_2xBVOC, whilst primary organic aerosol emissions from SNAP2 and SNAP10 (BBOA-like) were doubled in scenarios ~~S5~~VBS_BC_2xBBOA, with other emissions and processes represented as in ~~S3~~VBS_BC. Figure ~~10~~ 8 shows modelled and observed OA daily average concentrations for the ~~S3~~VBS_BC, ~~S4~~VBS_BC_2xBVOC and ~~S5~~VBS_BC_2xBBOA scenarios across the sites. Statistics for each scenario are reported in Table 5. Increasing biogenic emissions by a factor of two during February-March 2009 resulted in almost no change in the predicted total OA (1.7~~3~~ µg m^{-3} and 1.~~7~~8 µg m^{-3} for the ~~S3~~ VBS_BC and ~~S4~~ VBS_BC_2xBVOC scenarios, respectively). On the other hand, doubling the BBOA-like emissions (~~S5~~VBS_BC_2xBBOA) during the same period strongly increased the predicted OA mass (up to 2.8~~4~~ µg m^{-3} on average). As a result the mean fractional bias decreased further, from -47% to -12% averaged across the sites. This could eventually confirm other studies where substantial under-predictions in residential wood burning emissions were underlined (e.g., Bergström et al., 2012). A few points above the 2:1 lines in ~~S5~~ VBS_BC_2xBBOA mainly belong to the sites of Montseny, Puy de Dôme and Helsinki. During winter periods, it is likely that elevated stations such Montseny and Puy de Dôme are most of the time above the PBLH, as suggested by previous studies for Puy de Dôme (Freney et al., 2011), whereas model concentrations are extracted from the first layer of the model. In Helsinki, BBOA emissions seem to be overestimated or the dispersion underestimated in the model.

Comparison with a warmer period in June 2006 is reported as well for Payerne where AMS measurements were also available (Fig.~~ 11~~9). In February-March 2009 increasing BBOA-like emissions (~~S5~~VBS_BC_2xBBOA) reduced the fractional bias from -85% in ~~S3~~VBS_BC to -37% (Table S3~~4~~) with an over-prediction occurring during 1-5 of March (Fig. ~~11~~9, upper panel). As already discussed in Section 3.2, it is likely that the vertical mixing processes were not correctly represented by the model since also the inorganic components were over-predicted for the same period. Almost no change in the predicted OA mass was found when biogenic emissions were doubled (scenario ~~-S4~~VBS_BC_2xBVOC) (Fig. ~~11~~9, upper panel) due to lower BVOCs emission during winter periods. Increasing BVOCs emissions in June 2006 increased the predicted OA mass at Payerne site especially during the 12-16 June and towards the end of the simulation period, where higher concentrations and temperature (Fig. S7) were also observed (Fig. ~~11~~9, ~~-~~lower panel). In contrast, similar OA concentrations were predicted in Payerne for ~~S3~~VBS_BC and ~~S5~~VBS_BC_2xBBOA ~~-~~during June 2006 (with averages of 2.4~~3~~ μg m^{-3} and 2.8~~75~~ μg m^{-3} respectively). This is in line with a very recent source apportionment study based on ACSM (aerosol chemical speciation monitor) measurements performed in Zürich for 13 months (February 2011 - February 2012) which revealed substantial differences between the winter (February-March) and summer (June-August) f_{44} / f_{43} space (organic mass fraction measured at mass to charge ratio 44 and 43) indicating that summer OOA (oxygenated organic aerosol) is strongly influenced by biogenic emission and winter OOA by biomass burning emission (Canonaco et al., 2015). Increased OA concentrations at Payerne in June 2006 with increased biogenic emissions were also found in other modelling studies. Bergström et al. (2012) used the VBS framework with different assumptions regarding aging processes and compared the model results for June 2006 with the AMS results at Payerne. In their study the total OA was found to be under-predicted with lower bias observed when aging processes were taken into account and biogenic emissions were increased by a factor of 3. Even though their model differs from ours in various aspects (number of volatility bins, aging processes parameterization and input data) in two of their scenario without aging of biogenic SOA Bergström et al. (2012) predicted an average OA concentration ranging from 2.6 μg m^{-3} to 3.4 μg m^{-3} which is similar to our base case ~~S3~~VBS_BC and ~~S4~~ VBS_BC_2xBVOC scenario (2.4~~3~~ μg m^{-3} and ~~–~~3.4 μg m^{-3}, respectively, Table ~~S5~~S4).

3.3.3 OA components in summer and winter

Comparisons of the primary 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 using the same VBS scheme.

4 Conclusions

A modelling study using the regional air quality model CAMx with VBS (Volatility Basis Set) scheme was performed for the first time in Europe within the EURODELTA-III model intercomparison exercise. An evaluation for the main gas phase species and $PM_{2.5}$ for four different periods was performed using the European air quality database Airbase as well as AMS (Aerosol Mass Spectrometer) measurements. The period in February-March 2009 was further analyzed in more detail using different assumptions regarding the volatility of emitted organic aerosol and emissions of precursor. The main findings of this study are summarized below:

- Although total $PM_{2.5}$ mass concentrations and its variations were well reproduced by the model in all four periods, comparisons with AMS measurements for the February–March 2009 period revealed that the good agreement between model and measurements was most of the time due to overestimation of the inorganic fraction, especially NO_3^-, and underestimation of OA. Sensitivity tests with reduced NH_3 emissions generally reduced the positive bias in NO_3^- suggesting potential uncertainties in NH_3 emissions and their seasonal variability. ~~Total $PM_{2.5}$ was modelled very well. The concentration gradients between the four investigated episodes were captured by the model. A few episodes of over-prediction for $PM_{2.5}$ were found in the Po valley region. Some days with high $PM_{2.5}$ loads for stations close to the southern border of the domain were not captured by the model, probably because of missing representation of Saharan dust events.~~

- In general, for all the four periods, the model under-predicted NO_2 and CO concentrations~~ especially during winter periods likely because of insufficient emissions. ~~. On the other hand, O_3 was found to be over-predicted likely because of insufficient NO_x to undergo titration during night-time chemistry or not well captured vertical mixing processes and concentrations at the boundaries. SO_2 was over-predicted ~~especially near coastal areas, ~~presumably mainly because of uncertainties in high stack point sources ~~ships stack height ~~representation in the model or too low deposition processes~~, and in the eastern part of the domain where larger emissions are occurring~~.

- ~~Comparisons with AMS measurements for the February-March 2009 period suggested that the model is able to capture the total non-refractory PM_1 mass. However, the inorganic fraction, especially NO_3^-, being over-predicted and the OA under-predicted. Sensitivity tests with reduced NH_3 emissions generally reduced the positive bias in NO_3^- suggesting potential uncertainties in NH_3 emissions and their seasonal variability.~~

- Including evaporation and oxidation processes of primary organic particles with the volatility distribution proposed by Robinson et al. (2007) lowered the modelled OA mass both in winter and summer periods. On the other hand, the adjustment of the scheme by Robinson et al. (2007) suggested by Shrivastava et al. (2011) and Tsimpidi et al. (2010) brings model and observations into better agreement by reducing the negative bias for OA by about 29% (MFB) in winter.

- Sensitivity tests with increased BVOCs and BBOA-like emissions suggested that emissions from residential heating represent an important contributor to total OA during winter periods (February-March 2009). The model under-predicted the winter OA concentrations (MFB -47% for base case ~~S3~~VBS_BC) more than gas phase pollutants e.g. NO_2 (Table 2). Eventually, increasing BBOA-like emissions by a factor of 2 brought model and observation to a reasonably good agreement even though the model still under-predicts the OA fraction (-12% MFB). This underlines the necessity to better constrain emission inventories with a focus on residential heating. Also the implementation of the VBS scheme for domestic wood burning, which substantially influences both the primary and secondary organic aerosol, should be evaluated.

- A summer period was simulated as well and results were compared at Payerne. In June 2006, the current VBS implementation could not explain the discrepancy between modelled and observed OA. During this period the difference between the model and measurements is likely to be related to BVOCs emissions which are uncertain and difficult to constrain with measurements. In this case the model was sensitive to an increase in biogenic emissions especially during periods with higher temperature and OA concentrations. The latter could confirm the importance of BVOC precursors in summer in Payerne and the way to correctly represent their evolution in the atmosphere.

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5 Figures and Tables

Table 1. Volatility distributions used for different scenarios.

Scenarios	POA emission sources	Emission fraction for volatility bin with C* of				
		0	1	10	100	1000
~~Scenario1~~NOVBS (non-volatile CAMxv5.40)	HOA-like	1.00	-	-	-	-
	BBOA-like	1.00				
~~Scenario2~~VBS_ROB (Robinson et al., 2007)	HOA-like	0.09	0.09	0.14	0.18	0.5
	BBOA-like	0.09	0.09	0.14	0.18	0.5
~~Scenario3~~VBS_BC (Tsimpidi et al., 2010 and Shrivastava et al., 2011)	HOA-like	0.40	0.26	0.40	0.51	1.43
	BBOA-like	0.27	0.27	0.42	0.54	1.50

~~Table 2. Model gas phase and PM$_{2.5}$ performance for the EDIII field campaigns (base case S3).~~

~~Species~~	~~Number of sites~~	~~Observed mean (ppb) (µg m^{-3} for PM$_{2.5}$)~~	~~Modelled mean (ppb) (µg m^{-3} for PM$_{2.5}$)~~	~~MB (ppb) (µg m^{-3} for PM$_{2.5}$)~~	~~ME (ppb) (µg m^{-3} for PM$_{2.5}$)~~	~~MFB [-]~~	~~MFE [-]~~
~~June 2006~~							
~~CO~~	~~36~~	~~192.0~~	~~158.0~~	~~-34.20~~	~~80.70~~	~~-0.12~~	~~0.36~~
~~NO$_2$~~	~~320~~	~~4.1~~	~~2.3~~	~~-1.87~~	~~2.24~~	~~-0.54~~	~~0.68~~
~~O$_3$~~	~~460~~	~~42.3~~	~~51.2~~	~~8.93~~	~~10.80~~	~~0.21~~	~~0.24~~
~~PM$_{2.5}$~~	~~48~~	~~12.0~~	~~11.7~~	~~-0.30~~	~~4.46~~	~~-0.07~~	~~0.39~~
~~SO$_2$~~	~~263~~	~~1.0~~	~~1.2~~	~~0.20~~	~~0.74~~	~~0.14~~	~~0.67~~
~~Jan-Feb 2007~~							
~~CO~~	~~45~~	~~248.0~~	~~191.0~~	~~-57.80~~	~~107.00~~	~~-0.11~~	~~0.37~~
~~NO$_2$~~	~~337~~	~~6.5~~	~~4.4~~	~~-2.17~~	~~3.16~~	~~-0.28~~	~~0.57~~
~~O$_3$~~	~~455~~	~~23.5~~	~~35.8~~	~~12.30~~	~~12.60~~	~~0.48~~	~~0.49~~
~~PM$_{2.5}$~~	~~56~~	~~11.7~~	~~12.8~~	~~1.04~~	~~6.06~~	~~-0.04~~	~~0.56~~
~~SO$_2$~~	~~271~~	~~1.3~~	~~1.7~~	~~0.38~~	~~1.09~~	~~0.36~~	~~0.75~~
~~Sep-Oct 2008~~							
~~CO~~	~~53~~	~~208.0~~	~~136.0~~	~~-72.00~~	~~91.40~~	~~-0.31~~	~~0.48~~
~~NO$_2$~~	~~370~~	~~5.3~~	~~3.7~~	~~-1.67~~	~~2.50~~	~~-0.28~~	~~0.56~~
~~O$_3$~~	~~465~~	~~24.3~~	~~32.5~~	~~8.17~~	~~9.58~~	~~0.32~~	~~0.37~~
~~PM$_{2.5}$~~	~~90~~	~~13.0~~	~~14.1~~	~~1.03~~	~~5.69~~	~~<0.01~~	~~0.46~~
~~SO$_2$~~	~~256~~	~~0.9~~	~~1.1~~	~~0.20~~	~~0.76~~	~~0.25~~	~~0.74~~
~~Feb-Mar 2009~~							
~~CO~~	~~57~~	~~262.0~~	~~170.0~~	~~-91.60~~	~~119.00~~	~~-0.26~~	~~0.48~~
~~NO$_2$~~	~~380~~	~~6.0~~	~~3.9~~	~~-2.03~~	~~2.78~~	~~-0.33~~	~~0.56~~
~~O$_3$~~	~~488~~	~~32.7~~	~~33.0~~	~~0.22~~	~~7.14~~	~~0.02~~	~~0.23~~
~~PM$_{2.5}$~~	~~110~~	~~15.1~~	~~13.0~~	~~-2.13~~	~~6.37~~	~~-0.13~~	~~0.50~~
~~SO$_2$~~	~~257~~	~~1.0~~	~~1.3~~	~~0.31~~	~~0.86~~	~~0.23~~	~~0.76~~

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

Species	Number of sites	Observed mean (ppb) (μg m^{-3} for $PM_{2.5}$)	Modelled mean (ppb) (μg m^{-3} for $PM_{2.5}$)	MB (ppb) (μg m^{-3} for $PM_{2.5}$)	ME (ppb) (μg 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

Table 3. Statistical analysis of nitrate, ammonium, sulfate and organic aerosol in base case (~~S3~~VBS_BC) for February-March 2009 at different AMS sites.

Site	Mean observed ($\mu g/m^3$)	Mean modelled ($\mu g/m^3$)	MB $\mu g\ m^{-3}$	ME $\mu g\ m^{-3}$	MFB [-]	MFE [-]
			NO_3^-			
Barcelona	3.6	5.8	2.19	3.98	0.35	0.98
Cabauw	2.2	6.7	4.49	4.58	0.85	1.01
Chilbolton	2.7	4.0	1.33	2.21	0.02	0.76
Helsinki	1.0	1.9	0.93	1.30	0.29	0.92
Hyytiälä	0.2	1.0	0.75	0.83	0.21	1.09
Mace Head	0.6	1.7	1.11	1.12	0.14	0.70
Melpitz	3.1	4.3	1.25	2.41	0.35	0.71
Montseny	3.1	5.9	2.83	4.31	0.38	1.00
Payerne	3.9	5.7	1.81	2.83	0.34	0.61
Puy de Dôme	0.9	2.7	1.81	2.17	1.13	1.30
Vavihill	2.8	3.7	0.89	2.17	0.14	0.78
			$NH_4^{\cancel{-}+}$			
Barcelona	1.6	2.5	0.92	1.41	0.42	0.71
Cabauw	1.0	2.7	1.73	1.75	0.95	0.97
Chilbolton	1.3	2.0	0.68	1.02	0.39	0.61
Helsinki	0.8	1.3	0.52	0.59	0.51	0.60
Hyytiälä	0.4	0.8	0.43	0.48	0.55	0.70
Melpitz	1.4	2.1	0.72	1.11	0.45	0.69
Montseny	1.7	2.6	0.92	1.58	0.39	0.74
Payerne	1.7	2.5	0.80	1.15	0.36	0.56
Puy de Dôme	0.7	1.2	0.51	0.87	0.83	1.07
Vavihill	1.6	1.9	0.38	0.90	0.17	0.56
			SO_4^{2-}			
Barcelona	2.7	2.3	-0.44	1.25	-0.19	0.48
Cabauw	1.0	2.1	1.13	1.34	0.73	0.85
Chilbolton	1.3	2.2	0.91	1.33	0.45	0.70
Helsinki	2.4	2.2	-0.24	0.92	-0.04	0.43
Hyytiälä	1.4	1.7	0.26	0.73	0.09	0.58
Mace Head	0.4	1.2	0.83	0.89	1.04	1.12
Melpitz	1.1	2.2	1.15	1.40	0.54	0.76
Montseny	1.4	2.3	0.97	1.19	0.55	0.64

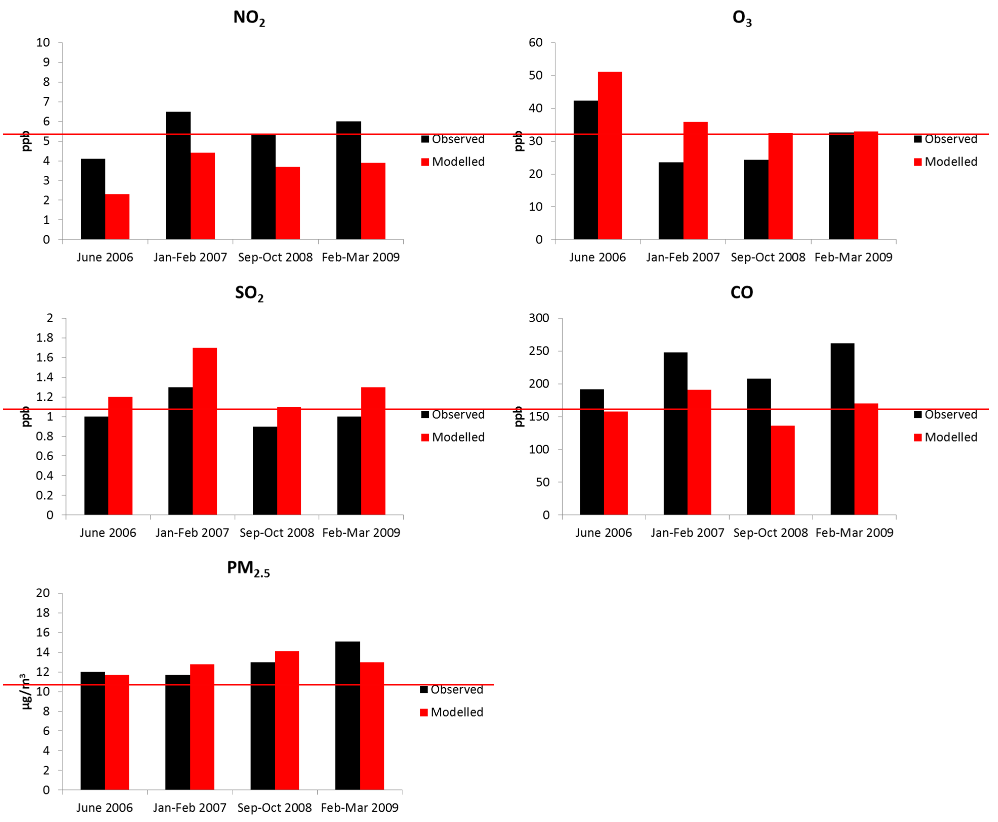
Payerne	1.1	2.1	1.06	1.16	0.62	0.70
Puy de Dôme	0.4	1.1	0.77	0.82	1.14	1.19
Vavihill	1.6	2.3	0.73	1.05	0.18	0.54
			OA			
Barcelona	8.2	3.1	-5.11	5.15	-0.80	0.82
Cabauw	1.2	1.1	-0.14	0.53	-0.13	0.50
Chilbolton	2.4	0.7	-1.70	1.70	-1.09	1.10
Helsinki	2.7	2.9	0.26	1.64	0.08	0.62
Hyytiälä	1.3	1.0	-0.28	0.52	-0.48	0.60
Mace Head	0.8	0.4	-0.38	0.43	-0.29	0.70
Melpitz	1.5	0.5	-0.95	0.98	-0.94	0.97
Montseny	3.1	3.9	0.88	1.88	0.31	0.57
Payerne	4.1	1.8	-2.33	2.43	-0.85	0.90
Puy de Dôme	0.6	1.4	0.78	0.96	0.68	0.91
Vavihill	3.9	1.4	-2.53	2.53	-1.04	1.04

Table 4. Statistical analysis of OA for ~~S1~~NOVBS, ~~S2~~VBS_ROB and ~~S3~~VBS_BC scenarios for the 11 AMS sites for February-March 2009.

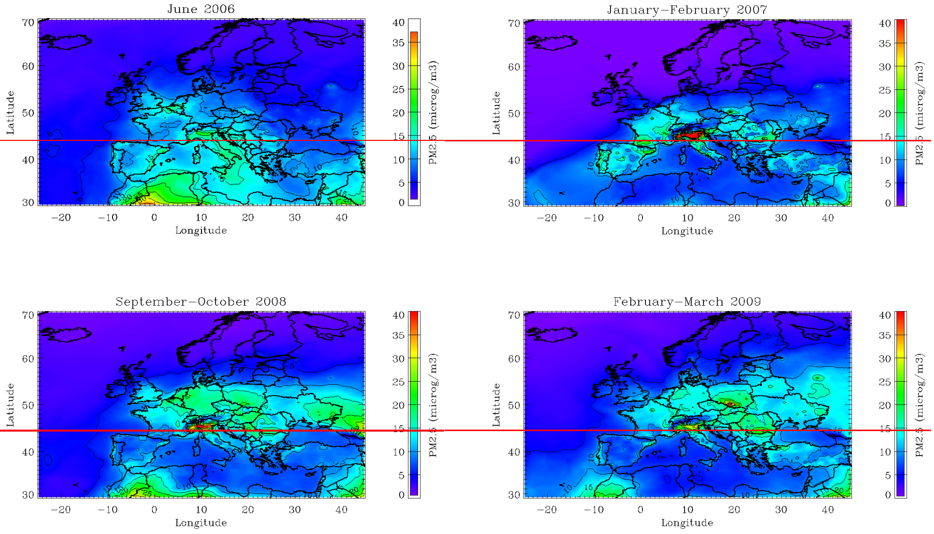
Scenario	Mean observed OA (μg m^{-3})	Mean modelled OA (μg m^{3})	MB (μg m^{-3})	ME (μg m^{-3})	MFB [-]	MFE [-]
~~S1~~NOVBS	3.0~~2.96~~	1.2~~1.18~~	-1.8~~−1.78~~	2.0~~2.04~~	−0.66	0.88
~~S2~~VBS_ROB	3.0~~2.96~~	0.7~~0.67~~	-2.3~~−2.29~~	2.4~~2.35~~	−1.08	1.19
~~S3~~VBS_BC (base case)	3.0~~2.96~~	1.7~~1.73~~	-1.2~~−1.23~~	1.8~~1.83~~	−0.47	0.79

Table ~~–~~5. ~~–~~Statistical analysis of OA for ~~–S3~~VBS_BC, ~~–S4~~VBS_BC_2xBVOC and ~~S5~~VBS_BC_2xBBOA scenarios for the 11 AMS sites for February-March 2009.

Scenario	Mean observed OA (μ~~-~~g m^{-3})	Mean modelled OA (μg m^{3})	MB (μg m^{-3})	ME (μg m^{-3})	MFB [-]	MFE [-]
~~S3~~ VBS_BC (base case)	3.0~~2.96~~	1.7~~1.73~~	-1.2~~−1.23~~	1.8~~1.83~~	−0.47	0.79
VBS_BC_2xBVOC~~S4~~	3.0~~2.96~~	1.8~~1.78~~	-1.2~~−1.17~~	1.8~~1.82~~	−0.46	0.78
VBS_BC_2xBBOA~~S5~~	3.0~~2.96~~	2.8~~2.84~~	-0.1~~−0.11~~	1.9~~1.91~~	−0.12	0.69



~~Figure 1. Observed and modelled means for NO$_2$, O$_3$, SO$_2$, CO and PM$_{2.5}$ for Airbase rural background sites with at least 80% of data available for June 2006, January-February 2007, September-October 2008 and February-March 2009. Number of sites is reported in table 2.~~



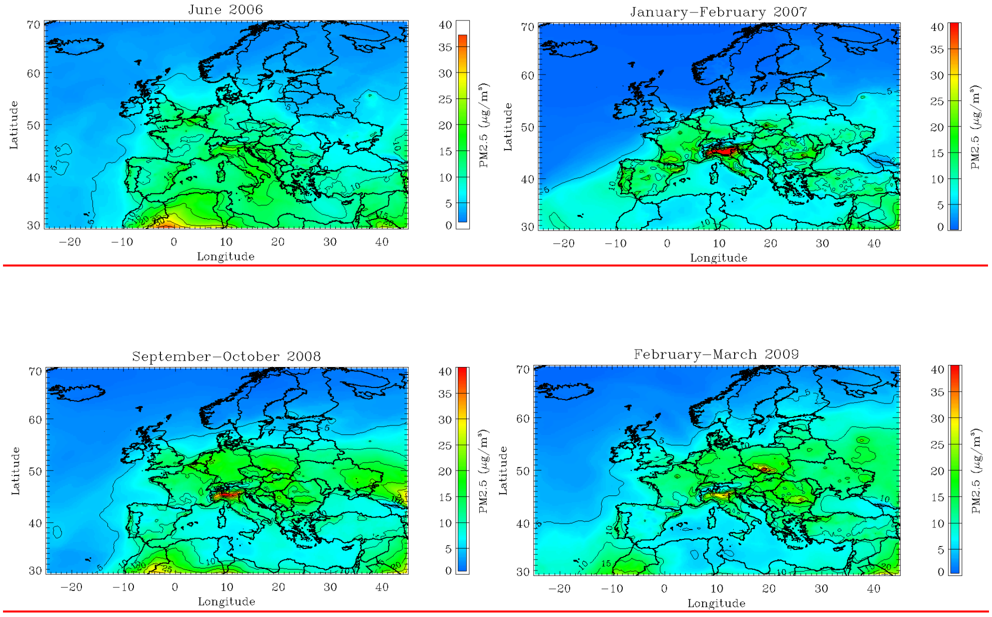


Figure 1~~2~~. Modelled average $PM_{2.5}$ concentrations for June 2006, January-February 2007, September-October 2008 and February-March 2009 (top to bottom) based on the base case (~~S3~~VBS_BC). Note that the color scale was limited to maximum of 40 µg/m^3 to facilitate comparison of the panels.

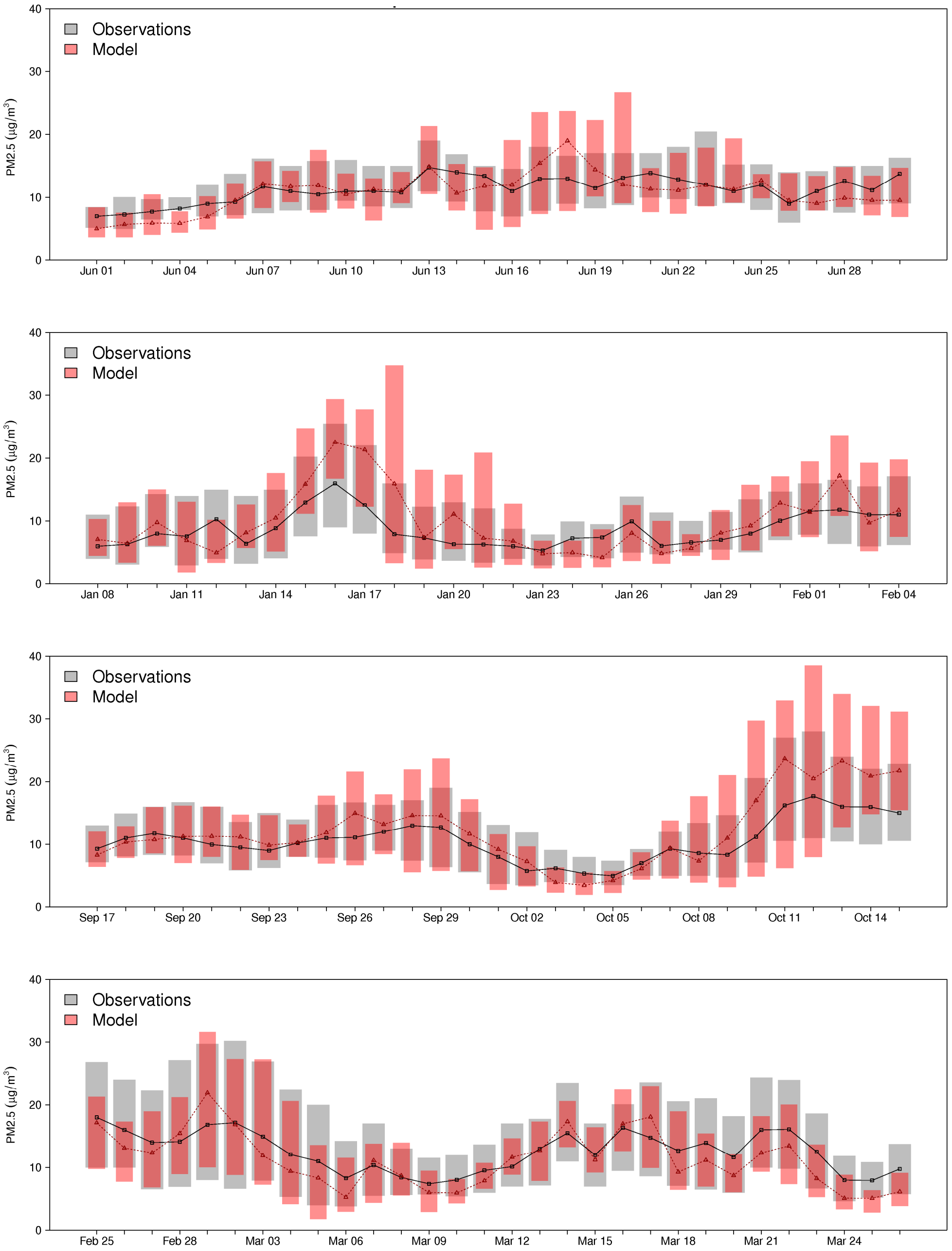
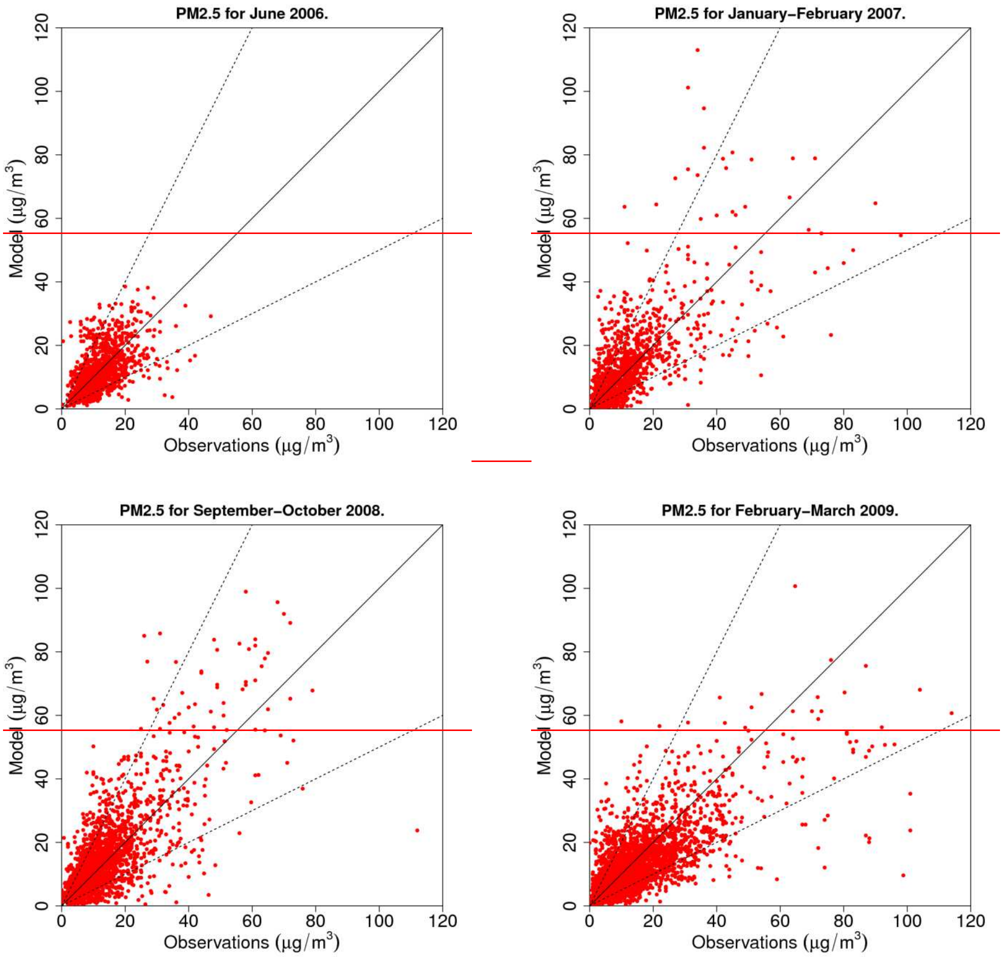


Figure 2~~3~~. Comparison of modelled (red) and measured (grey) $PM_{2.5}$ concentrations at AirBase rural background sites. The extent of the bars indicates the 25th and 75th percentile.

The black and red lines are observed and modelled median, respectively. The numbers of sites are 48, 58, 90, and 110 from top to down. Based on base case (~~S3~~VBS_BC).



~~Figure 4. Daily average scatter plots for PM$_{2.5}$ at AirBase rural background sites. Solid lines indicate the 1:1 line. Dotted lines are the 1:2 and 2:1 lines. Based on base case (S3).~~

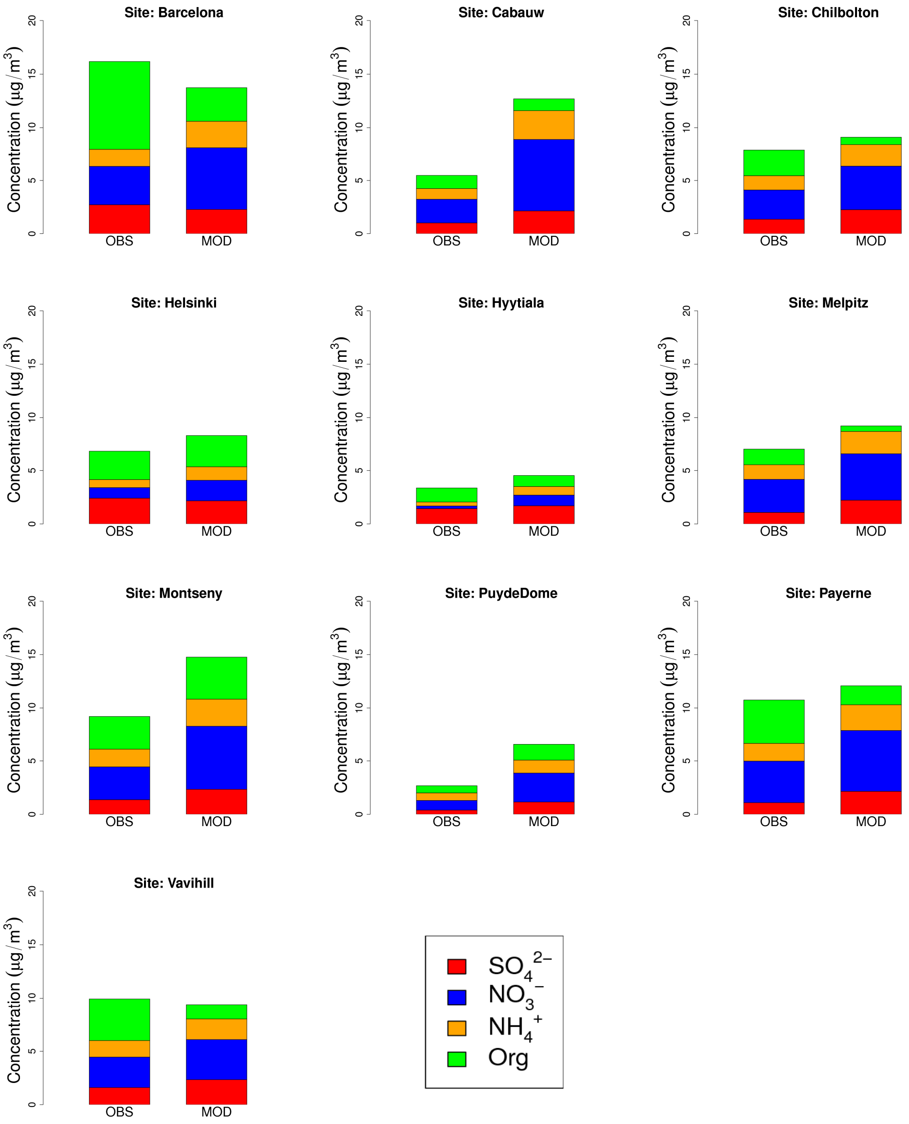


Figure 3~~5~~. Comparison of observed (OBS) non-refractory PM_1 and modelled (MOD) non-refractory $PM_{2.5}$ at 10 AMS sites in Europe during February-March 2009. Mace head is reported only in Table 3 since the ammonium component is not available.

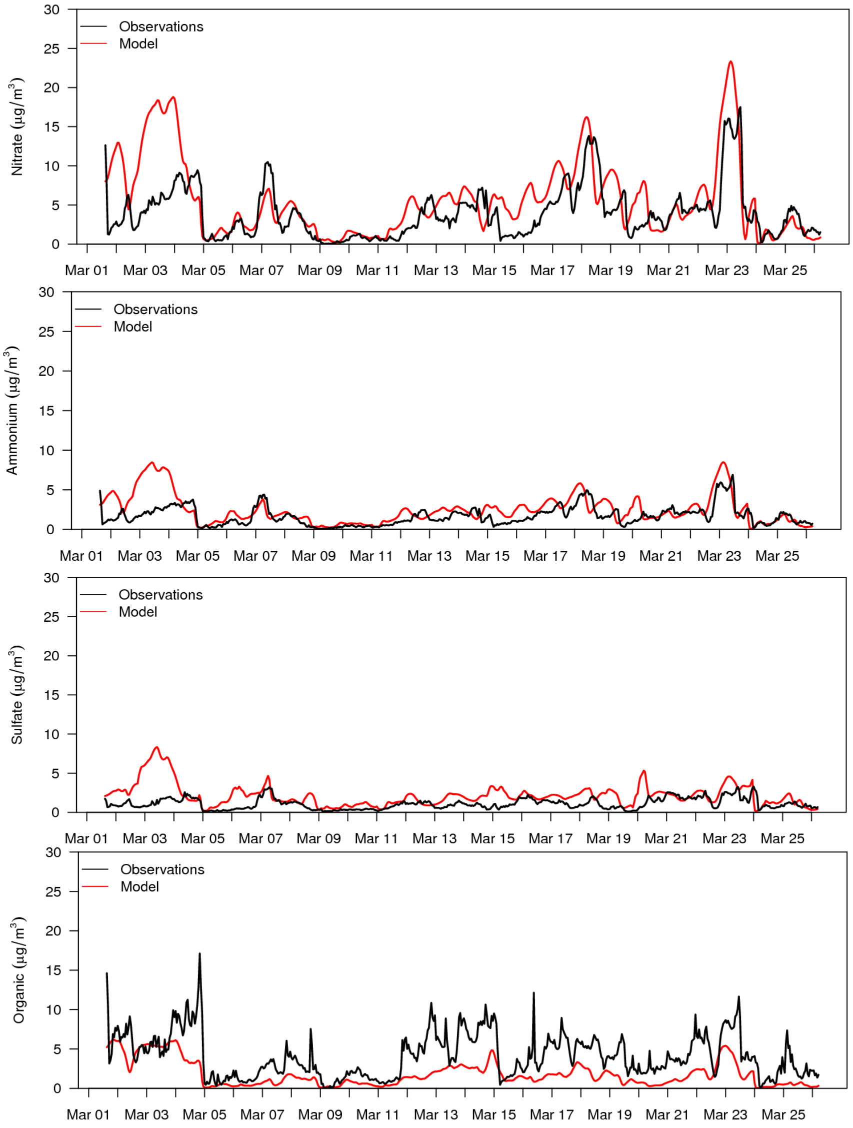
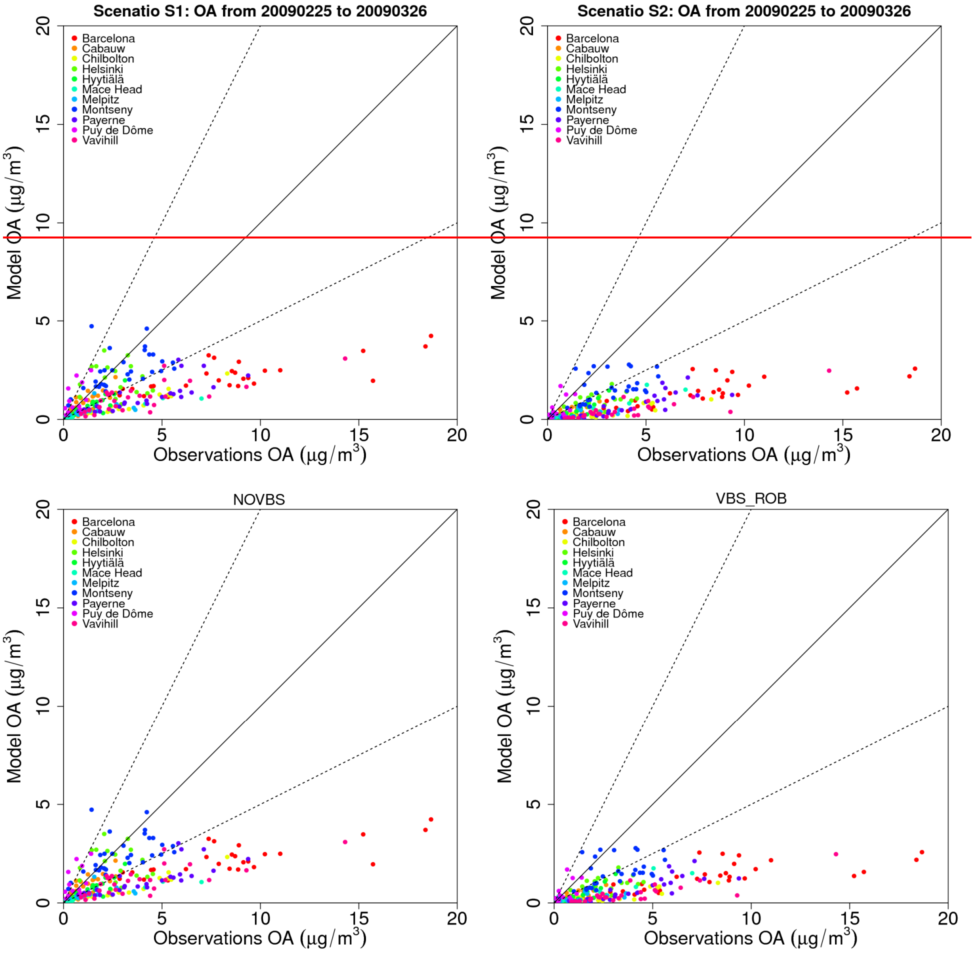


Figure 4~~6~~. Comparison of observed and modelled nitrate, ammonium, sulfate and organic aerosol at Payerne for March 2009.


Scenatio S1: OA from 20090225 to 20090326
Scenatio S2: OA from 20090225 to 20090326
NOVBS
VBS_ROB
Barcelona
Cabauw
Chilbolton
Helsinki
Hyytiälä
Mace Head
Melpitz
Montseny
Payerne
Puy de Dôme
Vavihill
Model OA (µg/m3)
Observations OA (µg/m3)
0
5
10
15
20

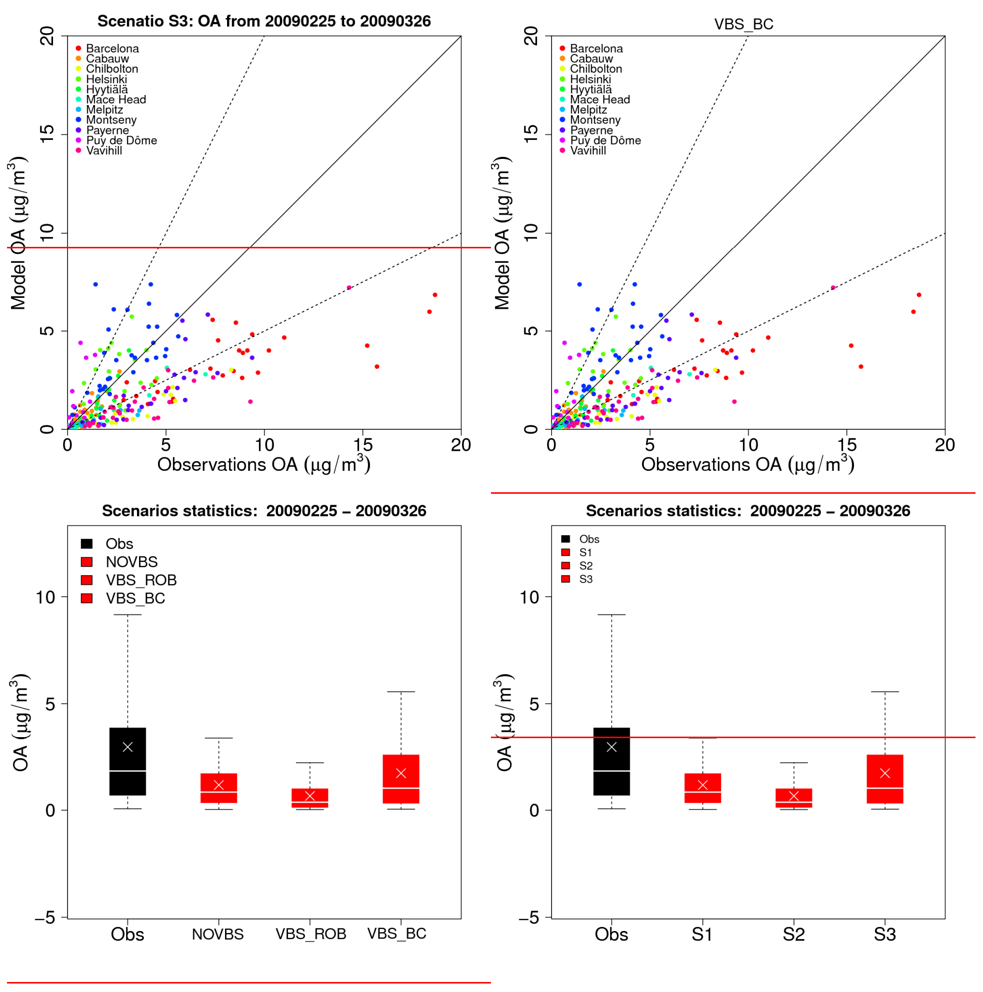
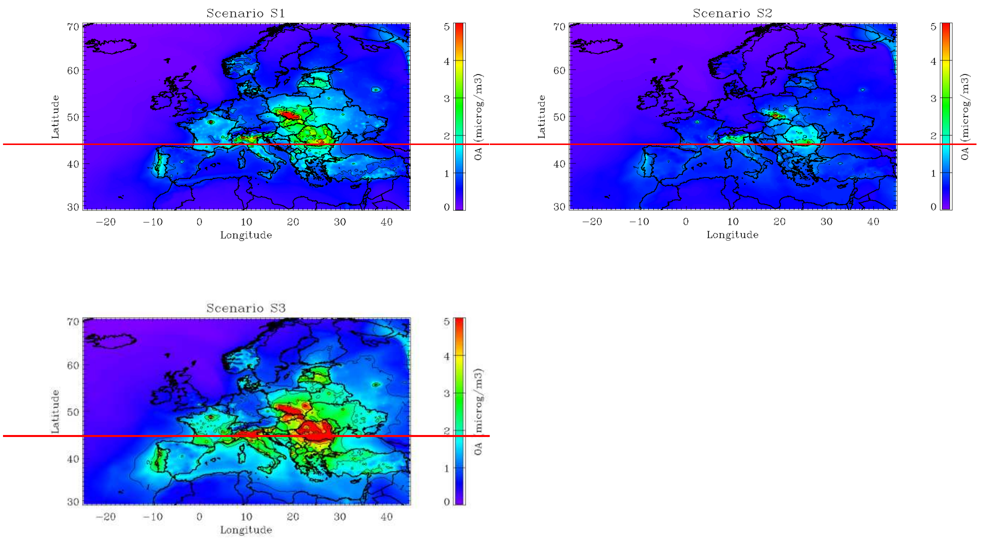


Figure 5~~7~~. OA daily average scatter plots for ~~S1~~NOVBS, ~~S2~~ VBS_ROB and ~~S3~~ VBS_BC scenarios for February-March 2009 for stations in Table 3. Solid lines indicate the 1:1 line. Dotted lines are the 1:2 and 2:1 lines. Boxplots indicate medians, 5th, 25th, 75th and 95th quantiles for observations (black) and sensitivity tests (red). The crosses represent the arithmetic means. R^2 is 0.55 for NOVBS, 0.64 for VBS_ROB and 0.59 for VBS_BC (excluding the elevated sited of Puy de Dôme and Montseny).



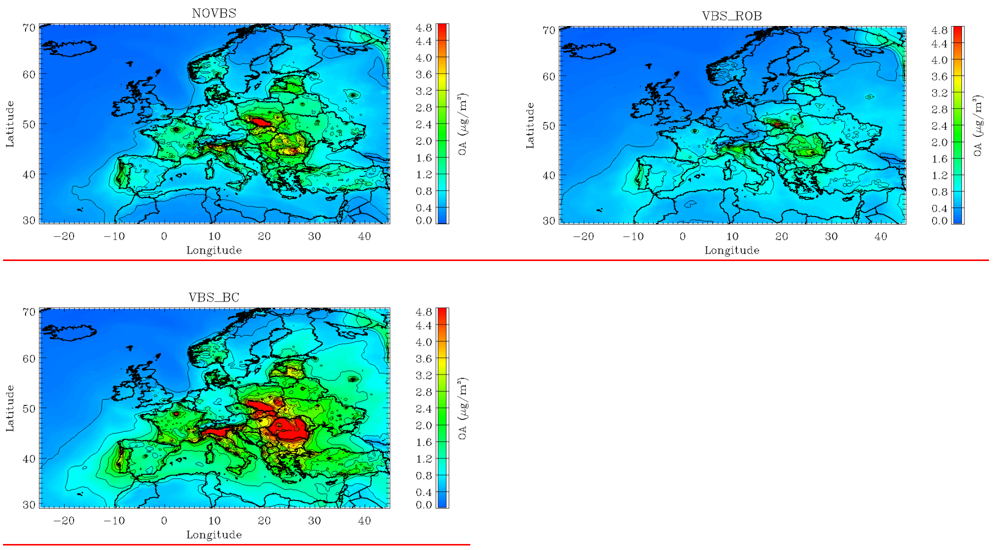
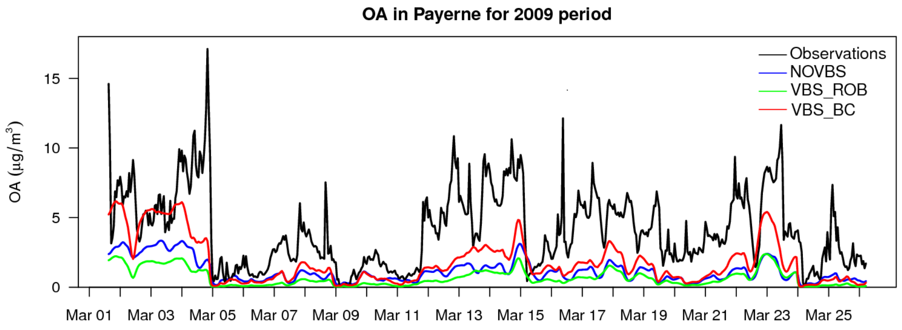
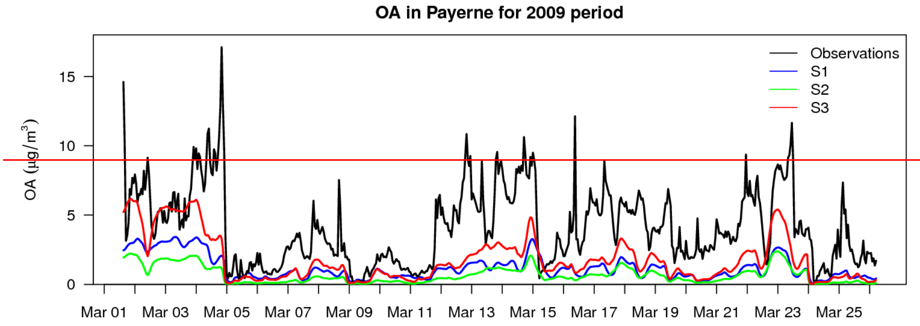
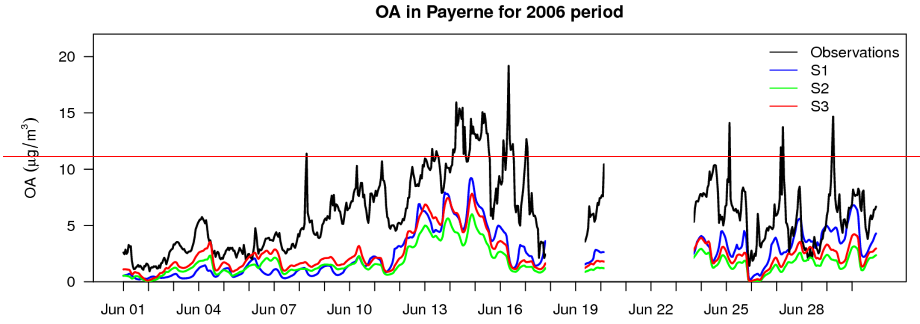


Figure 6~~8~~. Predicted OA concentrations over Europe for the ~~S1~~NOVBS, ~~S2~~VBS_ROB and ~~S3~~VBS_BC scenario in February-March 2009. Note that the color scale was limited to maximum of 4.8~~5~~ μg/m^3 to facilitate comparison of the panels.


OA in Payerne for 2009 period
OA (µg/m³)
0
5
10
15
Mar 01
Mar 03
Mar 05
Mar 07
Mar 09
Mar 11
Mar 13
Mar 15
Mar 17
Mar 19
Mar 21
Mar 23
Mar 25
Observations
NOVBS
VBS_ROB
VBS_BC


OA in Payerne for 2009 period
OA (µg/m³)
0
5
10
15
Mar 01
Mar 03
Mar 05
Mar 07
Mar 09
Mar 11
Mar 13
Mar 15
Mar 17
Mar 19
Mar 21
Mar 23
Mar 25
Observations
S1
S2
S3


OA in Payerne for 2006 period
OA (µg/m³)
0
5
10
15
20
Jun 01
Jun 04
Jun 07
Jun 10
Jun 13
Jun 16
Jun 19
Jun 22
Jun 25
Jun 28
Observations
S1
S2
S3

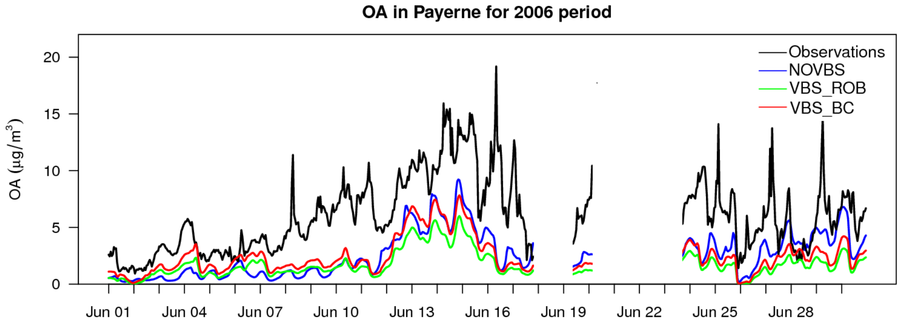
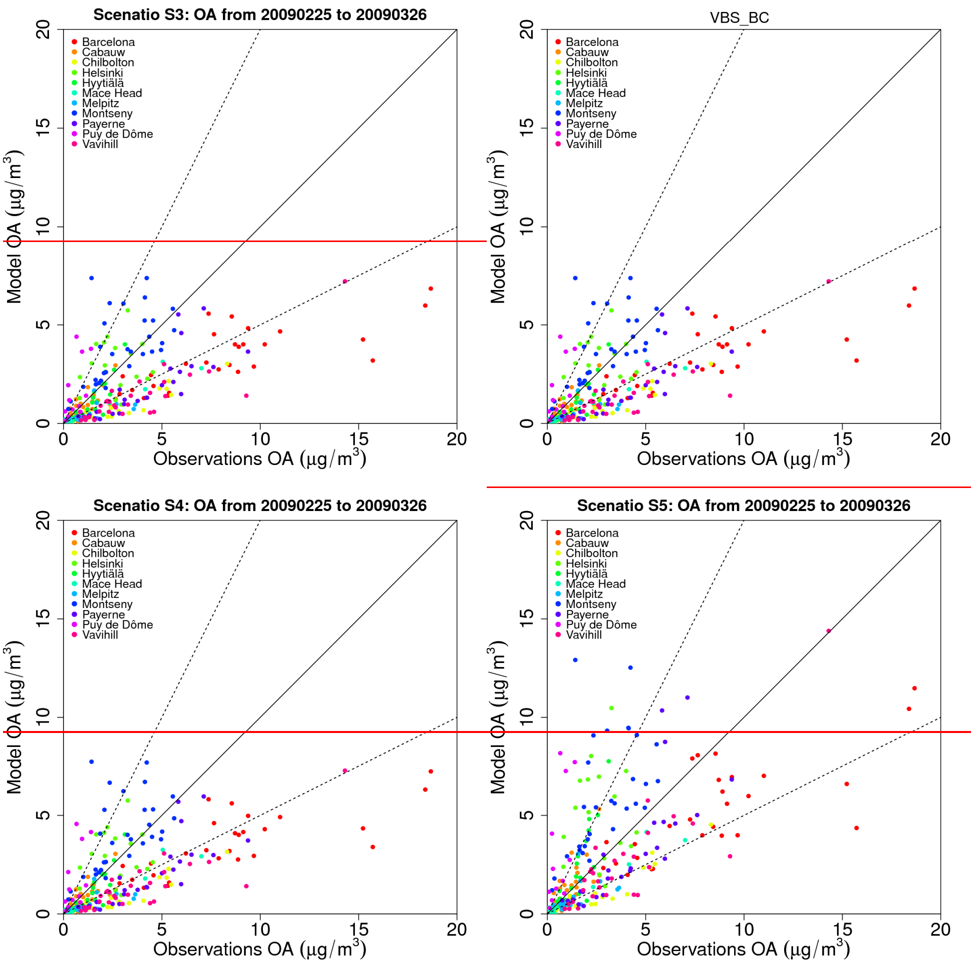

OA in Payerne for 2006 period
OA (µg/m³)
0
5
10
15
20
Jun 01
Jun 04
Jun 07
Jun 10
Jun 13
Jun 16
Jun 19
Jun 22
Jun 25
Jun 28
Observations
NOVBS
VBS_ROB
VBS_BC

Figure 7~~9~~. Predicted and observed total OA for scenarios ~~S1~~NOVBS, ~~S2~~ VBS_ROB and ~~S3~~ VBS_BC in March 2009 (upper panel) and June 2006 (lower panel) at Payerne.


Scenatio S3: OA from 20090225 to 20090326
VBS_BC
Scenatio S4: OA from 20090225 to 20090326
Scenatio S5: OA from 20090225 to 20090326
Barcelona
Cabauw
Chilbolton
Helsinki
Hyytiälä
Mace Head
Melpitz
Montseny
Payerne
Puy de Dôme
Vavihill
Model OA (µg/m3)
Observations OA (µg/m3)
0
5
10
15
20

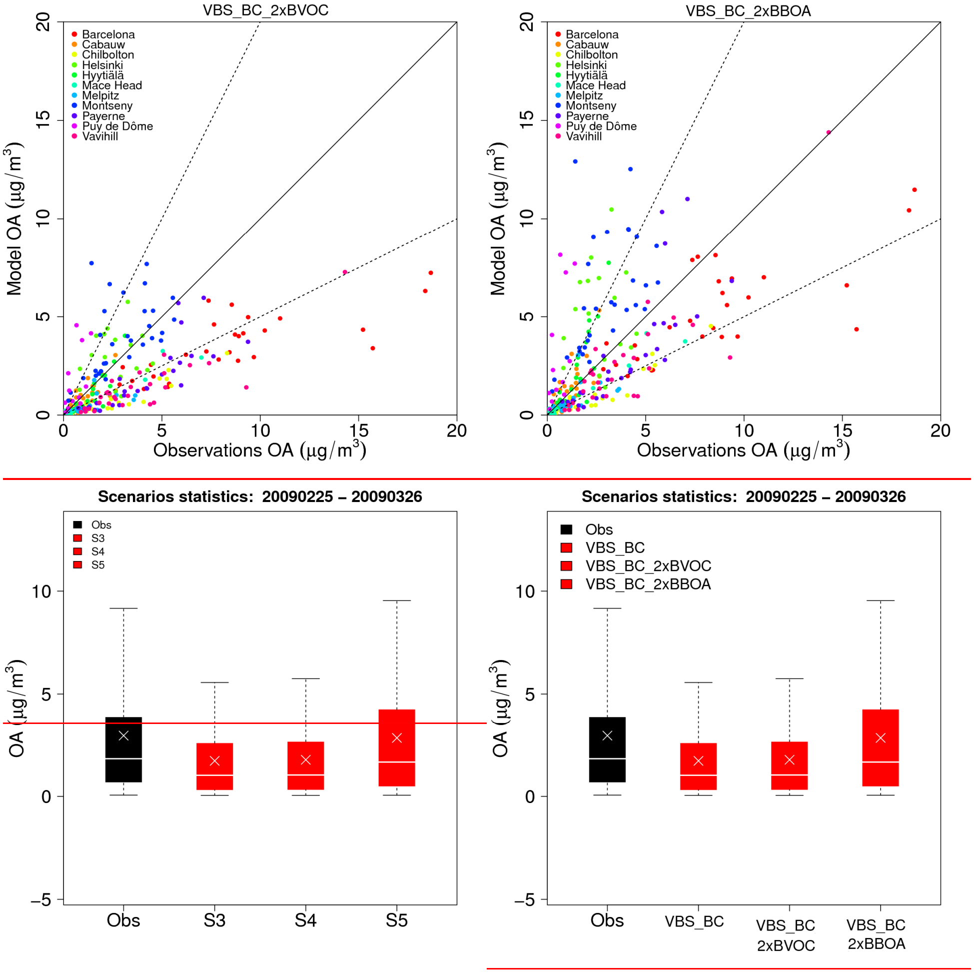
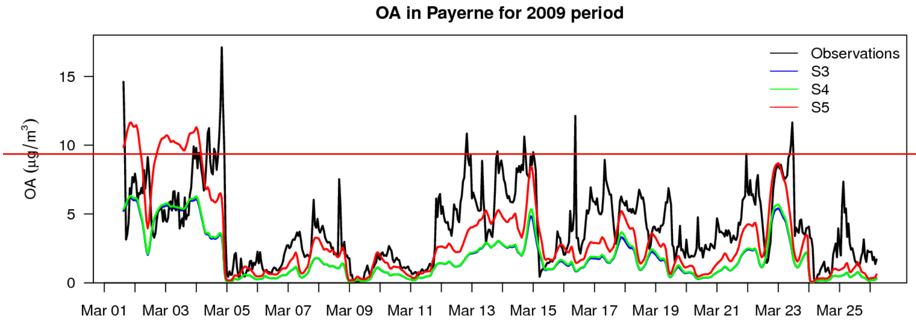
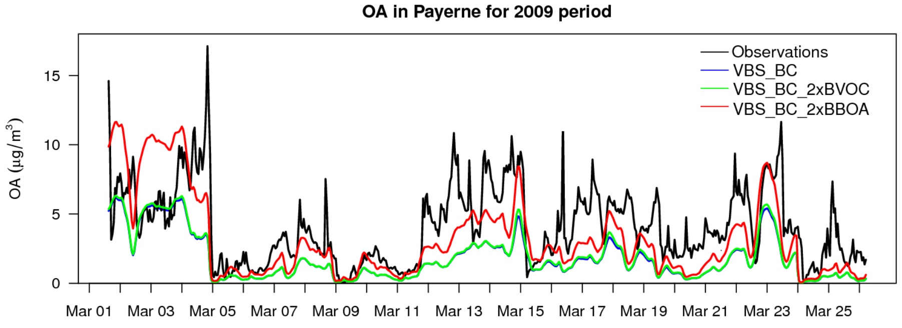
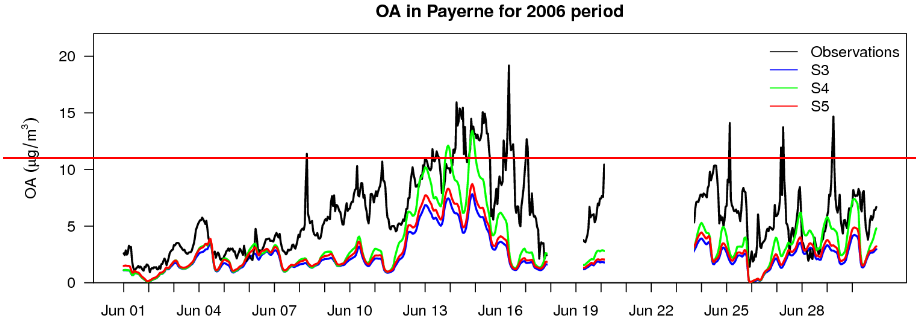


Figure ~~–~~8~~10~~. OA daily average scatter plots for ~~S3~~VBS_BC, VBS_BC_2xBVOC~~S4~~ and ~~S5~~VBS_BC_2xBBOA scenarios for February-March 2009 for stations in Table 3. Solid lines indicate the 1:1 line. Dotted lines are the 1:2 and 2:1 lines. Boxplots indicate medians, 5th, 25th, 75th and 95th quantiles for observations (black) and sensitivity tests (red). The crosses represent the arithmetic means.


OA in Payerne for 2009 period


OA in Payerne for 2009 period


OA in Payerne for 2006 period

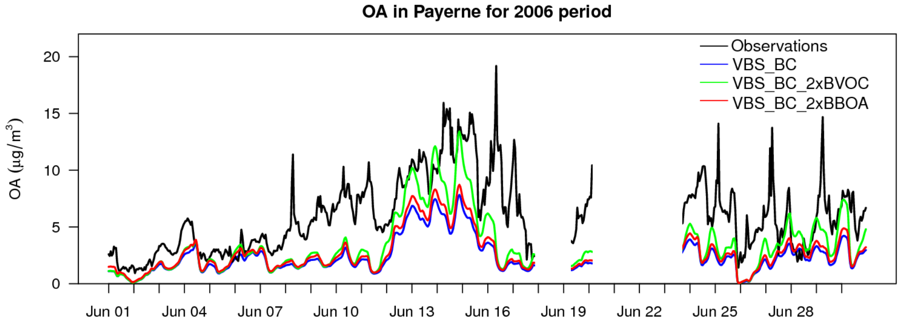

OA in Payerne for 2006 period

Figure ~~11~~9. Predicted and observed total OA for scenarios ~~S3~~VBS_BC, VBS_BC_2xBVOC~~S4~~ and VBS_BC_2xBBOA~~S5~~ in March 2009 (upper panel) and June 2006 (lower panel) at Payerne.

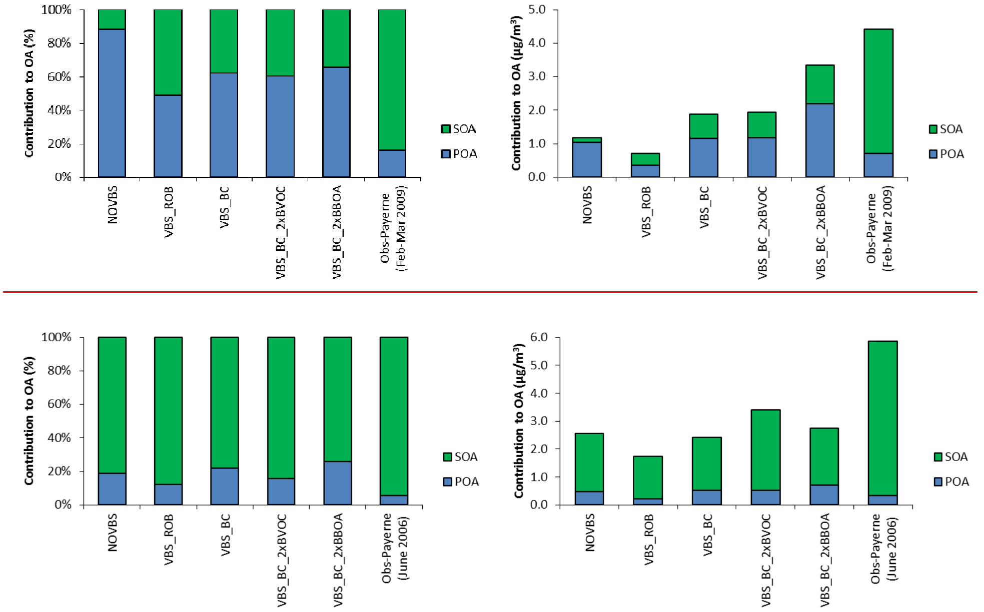


Figure 10. Relative (left) and absolute (right) contribution of predicted and measured POA and SOA fractions to the total OA mass at Payerne for February-March 2009 winter period (upper-panel) and June 2006 (lower-panel) and different model scenarios. NOVBS: (traditional non-volatile POA), VBS_ROB (Robinson 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.