1 Response to Anonymous Referee #2

1.1 Referee comment

This paper compares the predictions organic aerosols over Europe using four different treatments described previously in the literature. Since the parameters and assumptions used by the VBS framework varies, it is useful to examine the differences in the resulting SOA and total organic matter. The paper is well-written, utilizes a wide range of data to compare with model predictions, and presents material that is suitable to ACP. Nevertheless, there are a number issues that need to be addressed before it is suitable for publication

Reply

We thank the referee for their thorough reading on the manuscript and very useful and constructive comments. We believe the paper has been much improved as a result of these comments.

1.2 General Comments:

1.2.1 Referee:

Most of the plots and statistics average the results over the five-year period (which are useful); however, some discussion on whether there is any yearly variation in the performance of the four treatments is warranted. There is some mention of important seasonal variations on page 5445, but without further discussion. In addition, the paper relies mostly on bias as the statistical metric, but it would be useful to include others, such as correlation coefficient when there is enough temporal data.

Reply

Although we have run the model for a long-period, this was mainly to encompass the various shorter-term measurement periods. Unfortunately, the measurements are too dissimilar in time-period and sampling methodology for us to investigate year-to-year variations in model performance compared to observations.

By important seasonal variations, we were referring to the summer/winter differences, as opposed to the long-term averages which were shown in the plots. We have modified the text to make this clear.

Correlation coefficients have been added to the tables (for all data sets with > 10 measurements), and to the new Figures which partly replace the Tables.

1.2.2 Referee:

The study focuses on using particulate matter data (OC, OM, EC) to evaluate the model. However, gas-phase measurements also provide useful information. Most importantly are known precursors for SOA, such as isoprene and other biogenic emissions.

Reply

We agree that the issue of BVOC emissions is very important. Indeed, Simpson et al. (2007) and the current paper stressed that more work was needed to evaluate such emissions, and we regard this as a major impediment to really being able to evaluate SOA schemes. The EMEP network has some isoprene data, and we will add some words on this in the revised manuscript, but our main need is for monoterpene measurements. We have been trying to track down suitable data in Europe, but so far without success. Unfortunately even where measurements exist, it seems to be a difficult task to interpret them for our purposes. For example Davison et al. (2009) measured isoprene and monoterpenes for Italian Macchia ecosystems. They found monoterpene emissions from flux measurements to be in reasonable agreement with estimates made from leaf-level data, but the isoprene basal emissions rates were quite different. They believed that unrepresentative sampling in the measurement area might explain some of this, but they also showed how different studies at the same site can produce quite different emissions estimates. Similarly, Seco et al. (2011) measured isoprene and terpenes near Barcelona, but the measurements were taken at 3m height in a forest gap.

In general , most BVOC data available in Europe are taken from sites very close to the canopy (e.g. extensive Finnish data sets), and cannot easily be compared to model outputs.

This task is important, and we are pursuing this as part of an ongoing project which involves explicit canopy-modelling of BVOC gradients. This is a major and difficult task, and we do not manage to present a comparison in this paper. In fact, we are not aware of any European study that has managed to show such a comparison, probably for the same reasons as given above.

We have added text to the above effect in the manuscript.

1.2.3 Referee:

Table 3 indicates that the VBS treatment will depend on high or low NOx regimes, so getting NOx correct will be important as well. Where there no measurements at all of these quantities over the 5-year period? Very little is said regarding gas-phase precursors. Since SOA is often correlated with ozone in the summer time, an evaluation of predicted ozone would shed some additional light on the performance of the model. The authors discuss many of the uncertainties associated with primary particulate emissions which is important, but neglect discussion on gas-phase chemistry.

Reply

This was an omission. In general, the EMEP model performs quite well for compounds such as NO_2 and ozone, and comparison of the model with EMEP station data is presented every

year in EMEP reports. For example, for NO_2 the mean bias for 2009 was just 3%, with maps of normalised mean bias showing values lower than 18% across most of Europe (Fagerli et al. 2011).

In general, the model performs far better for these 'traditional' species than for OA, so we assume that discrepancies for OA are related to the unique problems of that class of compounds - large uncertainties in the whole chain: emissions, formation and degradation. We will add text at relevant points in the manuscript to make this clear. See also the answer to a related point below.

1.3 Referee Specific Comments:

1. Acronyms in general: There are too many acronyms used in the manuscript and at times it is difficult to follow the points in the text. The authors should reduce the number of acronyms. Some could easily be written out (e.g. PCM) so that the text would be more readable.

   Answer: We have tried to reduce the density (or at least increase the clarity) of acronyms where possible, although with so many OA components it is not easy. We have however simplified the names of model versions (e.g. just PAA, instead of VBS-PAA) and used a new sub and superscript notation with OA components, which we hope makes things clearer.

2. Page 5427, abstract: Most of the acronyms could be written out in the abstract, although I understand that some acronyms are necessary in the main text.

   Answer: We have written out most of the acronyms in the revised abstract.

3. Page 5429, lines 5–11: The VBS framework has been widely used and evaluated by many regional modeling studies now. It would be useful to include some references here.

   Answer: We have included a number of references to other regional modeling studies, using the VBS framework, in section 5. More references (to studies covering the Mexico City region) will be added in the revised manuscript (as also suggested by Referee #1).

4. Page 5429, lines 17-20: Emissions are often blamed, fairly or unfairly, on the uncertainties in predictions of particulates. Meteorological factors, which are not mentioned anywhere in the manuscript, affect transport, mixing, secondary formation, dry deposition, and wet removal. If these factors are simulated well by a model, they will also contribute to uncertainties in particulates. Aerosol chemistry also depends on gasphase chemistry, and SOA is often correlated with ozone formation. Uncertainties in photochemistry likely contribute to SOA as well.

   Answer: Yes. Unfortunately the list of uncertainties for SOA is very long! Our approach has been to use a model which we know works well for other (and better characterised) pollutants, for example NO_2 as discussed above. This removes some of the problems associated with meteorology. We do have evidence that wood-burning emissions are especially

problematic, as are BVOC emissions, but with current observations it is hard to unpick the causes of remaining uncertainty. As background for this work, we have added:

It is also important to note that many of the problems seen when modelling OA are not found for other components. The EMEP model has been extensively compared with measurements of sulphate, nitrate, ozone, NO_2 and other compounds (Fagerli and Aas 2008, Jonson et al. 2006, Simpson et al. 2006a,b,b, Aas et al. 2012, , see also annual EMEP reports, www.emep.int). Nitrogen oxides are probably most akin to OA, in that they have large fraction of ground-level sources, which are oxidised to both gaseous and particulate forms. Fagerli et al. (2011) showed that modelled mean NO_2 levels were very well captured by the EMEP model for the year 2009 (3% bias over all stations, maps of normalised mean bias showing values lower than 18% across most of Europe). Total nitrate in air (HNO_3 + NO_3^-) was underpredicted by about 30% (*ibid*). These evaluations give some confidence to the underlying meteorology, and physical and chemical structure of the model.

5. Page 5430, lines 6-9: I agree that comparisons with carbon-14 are important to determine whether models represent fossil and modern sources of carbon. But how uncertain are these measurements? There have been some studies with co-located measurements that indicate significantly different results. There have also been some SOA modeling studies that have already compared those results with carbon-14 data (e.g. Hodzic et al, 20xx).

   Answer: We are aware of the discrepancies pointed out by Aiken et al. (2010), and discussed in detail in Hodzic et al. (2010). The size of the discrepancy there was indeed surprising, and worrying, with average non-fossil fractions of 0.54 in the US PM1 filters versus 0.34 for the Swiss PM10 filters. There were however just four filters that could be compared, so we are are reluctant to draw too many conclusions from this case. In Europe, a number of comparisons suggest that uncertainties in ^{14}C analysis between different Laboratories (S. Szidat, pers. comm.) are far smaller than this.

   We have however added text to mention this point.

6. Page 5430, line 16: MSC-W is not defined.

   Answer: Fixed. (Meteorological Synthesizing Centre - West)

7. Page 5430, line 22: A 50 km grid spacing is used, which is very coarse. As discussed in a few places later in the text, it is problematic to compare some of the point measurements with the grid-cell values especially in urban areas. It is well known that SOA is often correlated with ozone, and ozone concentrations are usually too low near urban sources when a coarse grid spacing is used. So, SOA predictions in this study should be lower than observed at many stations, especially those in the vicinity of large variations in emission rates. If the SOA predictions were close to the observations, a higher grid spacing in the same model would likely produce positive biases which would be opposite of the

conclusions drawn in this study. Some additional discussion regarding resolution and in the implications are needed up front before the results are presented.

Answer: This is a difficult area. For aerosols though, the concentrations in cities are also often surprisingly similar to concentrations in nearby rural areas (Putaud et al., 2004, Putaud et al. 2010), reflecting the importance of long-range transport in many areas. Still, local contributions can be significant. In many European cities model predictions of O_3 from coarse-grid models tend to overpredict rather than underpredict: the NOx-titration effects is often bigger than any local ozone production.

We will add text to discuss this issue in the revised manuscript.

8. Page 5431, end of section 2: The authors need to describe how wet removal is included in the model, which is important for the long simulation periods performed in this study. Accurate predictions of organic aerosol, along with other aerosol species, will also require predictions of precipitation to be well represented. If wet removal is not included in the model for this study, an important pathway of the aerosol lifecycle is not included which affects how well the four organic aerosol treatments perform. Another factor that needs to be mentioned is how lateral boundary conditions are handled.

   Answer:

   The parameterization of the wet deposition in the model includes in-cloud and sub-cloud scavenging of gases and particles and is based on Berge and Jakobsen (1998). Further details, including scavenging ratios and collection efficiencies, are given in Simpson et al., 2012. Boundary concentrations of most long-lived model components are set using simple functions of latitude and month. For ozone more accurate boundary concentrations are needed and these are based on climatological ozone-sonde data-sets, modied monthly against clean air surface observations at Mace Head on the west coast of Ireland. See Simpson et al., 2012, for details.

   This text, along with further explanation of the background OA assumptions, has been added to the manuscript.

9. Page 5431, line 23: The day/night factors are mentioned, but do emissions have a smooth diurnal variation or is it a step function as the text implies. Please be more specific.

   Answer: The day-night variations for anthropogenic emissions used in this version of the model used simple step-functions. The model has recently been updated to use hourly factors, and we have run simulations with both methods. We found surprisingly small differences, presumably because we mostly compare daily (or longer time) average model results in this study, rather than hourly, and the relatively large grid size implies spatial as well as temporal smoothing. We will change the description of the temporal variation of emissions to be more clear:

The temporal variation of the anthropogenic emissions is source dependent and varies with month and day of the week. Simple day-night factors are also used. (Since this study, we have run the latest EMEP code with hourly factors, but found very similar OA levels to those calculated here). The details of the temporal distribution of emissions are given in Simpson et al. (2012).

10. Page 5432, line 19: Am I correct to assume that the fire emissions are an 8-day average? Fires are usually more sporadic, and it seems that such a temporal variation will introduce uncertainties into the model simulations.

    Answer: Yes, this is correct. We have added text to make this point clear.

    Page 5436, lines 15-19: The authors only present measurements from one AMS deployment. It would seem that there would be much more data available for the 2002- 2007 period (Zhang et al. 2007). Since this paper has few measurements presented, it would be useful to include the comparison in this study. Not sure why it needs to be presented elsewhere.

    There are indeed many bits and pieces of information available on OA, but in most cases the measurements provide only total OA (or OC) concentrations. As shown in earlier work with the EMEP model (Simpson et al., 2007), simple comparison of e.g. TC can give a very misleading picture, since one does not know if discrepancies are due to uncertainties in the SOA or primary emission assumptions. In that study for example, the major underpredictions found at Hungarian and Portuguese sites were shown to be completely explicable in terms of problems with wood-burning emissions. In the EUCAARI project (of which this work was a part), a number of new AMS data have been analysed with the intention of source-apportionment, but this analysis is not published yet. Comparison with this data is planned, but this will also be a major task, and beyond the scope of the present study.

    We also wish to stress that we consider all SOA modelling in Europe to be exploratory at this stage. There are too many uncertainties in the emissions and SOA processing to allow any definitive conclusions to be drawn on the best solution. Still, we believe that it is important to explore the performance of available SOA schemes against European data.

    For this paper, we elected to concentrate on measurements where we had auxiliary data (levoglucosan, 14C, etc), so that we could explore the robustness of the different model components.

11. Page 5440, line 1: Not just the PAA version can lead to overestimations, Shrivastava et al. (ACP, 2011) showed that PAP can also produce too much SOA. Recent laboratory and modeling studies (Vaden et al., PNAS, 2011) have shown that the VBS framework evaporates SOA far too quickly compared to observations. Some additional descriptions of the problems with VBS need to be discussed somewhere in this section. Although there are problems with VBS, there are few suitable alternative approaches that could be used for regional models.

Answer: It is true that also the aging of S/IVOC may lead to too high SOA (at least in high emission areas such as the Mexico City region). We have added a sentence pointing this out with a reference to Shrivastava et al. (2011). We have also added a note about the too rapid evaporation of SOA in the model compared to the results suggested by Vaden et al. (2011). We have also added comments in reply to a similar point by Referee #1.

12. Page 5443, end of section 6.3: This section discusses how OM:OC ratios vary, but fail to describe earlier on how oxygen is handled by the VBS treatments. Every VBS scheme arbitrarily assumes different numbers of oxygen atoms added per VBS bin.

    Answer: The assumptions regarding the initial OM:OC ratios for the different species in our VBS schemes were described in section 5.1. For each aging step we assume a small mass increase (7.5%) due to addition of oxygen; this was only specified for the aging of S/IVOC species in the PAP-model but the same assumption is made for the BSOA and ASOA species in the PAA and PAPA models. We will clarify this in the revised manuscript.

13. Page 5445, lines 22-26: Please include a correlation coefficient for Figs. A1 and A2. There is quite a bit of scatter in the results.

    Answer: Correlation coefficients were included in Table 4. In the revised manuscript they will be included in the plots in Figures A1 and A2 as well.

14. Page 5447, line 9: It should be relatively straight-forward to check the site location when making a assessment of its proximity to local emission sources.

    Answer: Yes, this sentence was badly formulated, and unnecessarily speculative. We will reformulate this part based on better information about the actual station locations (SPC is a rural station, but within 40km of the large city of Bologna, and the Gent measurements were done at the University of Gent, within the city)

15. Page 5448, lines 1-5: While this plot is useful, it is difficult to see any differences among three of the four treatments. This is consistent with the averages over much of Sweden shown in Fig. 3. Why show this station versus another one where there might be larger differences among the four treatments? The reasons to show this site are not stated. Where is this site located? It would be useful to include it on one of the spatial distribution plots.

    Answer: The choice of Aspreveten was arbitrary, but the revised manuscript will show maps with all stations present, and the results of the four treatments illustrated. We will also improve the quality of the time-series plot. The much larger use of Figures rather than Tables in the revised manuscript should help to place all results into context.

16. Page 5449, line 16: This is the first time I see how the boundary conditions for particulates are treated. This needs to be stated earlier in the model description section. How important will long-range transport from North America be in contributing time-varying boundary conditions for Europe? It would seem that coupling the regional model with a global model

would provide more realistic variations in particulate matter from longrange transport. Of course, the regional model would then be subject to errors from the global model. But it would be preferred than using constant values over a 5-year period.

Answer: We have now moved the information about the boundary conditions to section 2 (the model description section).

There are several reasons why we believe it better to use the fixed boundary conditions. Not least, we do not believe any model can calculate 'realistic' boundary conditions for OM. All models have problems, and this is not surprising given that there are still large uncertainties with the whole chain of OM modelling, from emissions (including knowing which precursors are really important), OA-formation mechanisms, issues of volatalisation, fragmentation, deposition, etc,. This field is evolving rapidly, and we believe it will be many years before OM models can be considered reliable. Given this, we prefer to fix the concentrations at the boundaries of the European domain, based upon measurements, and explore what happens within. Our procedure allows us to interpret our results in terms of emissions, dispersion and chemical processing from within our domain.

17. Page 5450, line 18: this is the first mention of representativeness of the measurements when comparing to the coarse model. More such discussion elsewhere is needed.

    Answer: Yes, this is an important issue. We have added some text in the Observations section, and then in connection with the individual sites while discussing the comparison of modelled and observed values.

18. Pages 5451-5452: Much of this discussion regarding performance in summer versus winter on this page is confusing. The text goes back and forth between summer and winter. Why not talk about one season first before moving to the other season? Also, the tables need to be referred to more frequently. Since the text moves back and forth, it is difficult following which table or parts of the table are being discussed.

    Answer: We have re-ordered this section and added figures to make the discussion clearer.

19. Page 5452, line 7: The authors state that OCbb is severely underestimated, but in Table 5, the observations are 0.13-0.28, and the model results are 0.13-0.24. That does not look too low to me.

    Answer: On page 5452, line 7, results for the winter campaign are discussed but Table 5 shows summer results (which are good as mentioned on page 5451, line15). The winter results are given in Table 6 and for this period the OCbb is underestimated by about a factor of three.

20. Page 5457, line 26: Long-range transport as well?

    Answer: Yes, this will be added.

21. Page 5458, lines 11-12: This sentence could be deleted. It was just mentioned earlier as the last bullet on the previous page.

    Answer: Done.

22. Figure 3, Should the lower-left panel be labeled ”PAPA”? There are 2 panels labeled

    Answer: Yes, the lower-left is the PAPA model version. Corrected.

23. Figure 4, Is it possible to have the same scale for all panels? It would enable the reader to more quickly determine the relative contributions of the sources. This would likely require a non-linear scale.

    Answer: These figures will be updated in the revised manuscript and the scales are the same for all the panels.

24. Figure 6, It is difficult to see whether there are any significant differences among PAP, PAPA, and PAA. I suggest having one panel with the observations and 4 lines with the total OC from each treatment. Then have pie charts showing the average components along with the bias and correlation coefficient. An arrow could be used to point to the period where biomass burning is significant. It is hard or next to impossible to see time variations in other components.

    Figure 7, Same comment as Figure 6 applies here.

    Answer: We have changed the time series figures (6 & 7), as suggested by the referee, to show total OC from the four different model versions and added bar charts (rather than pie charts) that show average components.

25. Table A1, The latitude and longitude of the stations are listed here. But it would also be useful to have a plot showing where the stations are.

    Answer: We have added such a plot

Extra references

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