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Interactive comment on “Modelling of organic aerosols over Europe (2002–2007) using a volatility basis set (VBS) framework with application of different assumptions regarding the formation of secondary organic aerosol” by R. Bergström et al.

Anonymous Referee #1

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The manuscript by Bergstrom and coworkers presents simulations of organic aerosols over Europe using the EMEP model for 2002-07 using four different treatments of organic evaporation and chemical aging, and compares them to several types of measurements. Some conclusions appear strong, such as the underestimation of residential wood combustion emissions in winter, while the relative performance of different OA aging and SOA formation model variants is less clear. This paper represents the second application of OA models based on the “volatility basis set” (VBS) type of pa-

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parameterizations to Europe, using a different host model than the previous publication. The topic of the paper is of high current interest in the research community and fits well in ACP, and the paper is of good quality. I recommend that this paper is accepted into ACP once the following major issues have been addressed.

Major Issues

1) There appears to be major terminology error in the manuscript. On P5439 the authors describe that POA emissions are treated as semivolatile (leading to evaporation of SVOC to the gas phase) and are accompanied by a mass 1.5 times larger of intermediate volatility species (IVOC). IVOCs are never in the condensed phase (as their c^* is 1000 $\mu\text{g m}^{-3}$ or larger, e.g. Robinson et al. Science 2007). IVOCs are thus NEVER part of the POA, even though their emission rates are estimated based on the POA emission rates here. IVOC material may form SOA in the gas-phase leading to particle-phase material. However the authors appear to call this material oxidized POA (OPOA). This term is almost exclusively used in the community to refer to species whose oxidation has occurred in the particle phase due to heterogeneous or multi-phase reactions. Referring to SOA species as OPOA creates much confusion in the aerosol community. E.g. the following papers all discuss SOA formation from IVOC species, and ALL of them refer to this material as SOA:

Formation of Secondary Organic Aerosol from the Direct Photolytic Generation of Organic Radicals Kessler, SH; Nah, T; Carrasquillo, A; Jayne, JT; Worsnop, DR; Wilson, KR; Kroll, JH. JOURNAL OF PHYSICAL CHEMISTRY LETTERS 2: 1295-1300, DOI: 10.1021/jz200432n, 2011.

Effects of Molecular Structure on Aerosol Yields from OH Radical-Initiated Reactions of Linear, Branched, and Cyclic Alkanes in the Presence of NO_x. Lim Yong B.; Ziemann Paul J. ENVIRONMENTAL SCIENCE & TECHNOLOGY 43: 2328-2334, DOI: 10.1021/es803389s, 2009.

Secondary Organic Aerosol Formation from High-NO_x Photo-Oxidation of Low Volatil-

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ity Precursors: n-Alkanes. Presto, AA; Miracolo, MA; Donahue, NM; Robinson, AL. ENVIRONMENTAL SCIENCE & TECHNOLOGY 44: 2029-2034, DOI: 10.1021/es903712r, 2010.

Fragmentation vs. functionalization: chemical aging and organic aerosol formation. Chacon-Madrid, HJ; Donahue, NM. ATMOSPHERIC CHEMISTRY AND PHYSICS 11: 10553-10563, DOI: 10.5194/acp-11-10553-2011 , 2011.

Similarly the evaporation of SVOC from POA is followed by SOA formation in the gas-phase and condensation of this material. Thus it would also be objectively wrong to refer to this material as OPOA. The terminology in the manuscript needs to be modified to follow the proper definition of SOA. Some papers have referred to “non-traditional SOA” when discussing SOA formed from SVOC and IVOC. This or another term that includes “SOA” should be used to refer to this material throughout the manuscript.

2) Emissions of non-fossil carbon from urban areas, such as from cooking sources, appear to be ignored in this paper. Multiple papers using both molecular markers and aerosol mass spectrometry point to the importance of this source, which may constitute about half of the POA in urban areas. See e.g. Schauer et al. (Atmos Environ 1996); Schauer et al. (Env Sci Tech 2000), Zheng et al. (J Air Waste Manag Assoc 2007), Allan et al. (Atmos Chem Phys 2010) , Huang et al. (Atmos Chem Phys 2010), Ham and Kleeman (Atmos Environ 2011), Sun et al. (Atmos Chem Phys 2011), Minguillon et al. (Atmos Chem Phys 2011), Mohr et al. (Atmos Chem Phys 2012). For example Ham and Kleeman (2011) state that “Meat cooking was the largest identified source of PM(1.8) is organic carbon (OC) at the urban site” and Mohr et al. (2012) state that “primary OA in Barcelona contains a surprisingly high fraction (59%) of non-fossil carbon.” Omitting these sources will confuse the interpretation of non-fossil carbon measurements, and this omission should at least be discussed in the manuscript.

3) P5438-L14; the DHvap value chosen is too low. Such low values are appropriate for models with a few lumped species. However models with volatility bins every order of

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magnitude in c^* should use higher and more realistic enthalpies of vaporization. See Donahue et al. (Env Sci Tech 2006) for a discussion of this topic. The argument that Fountoukis' results did not find a strong sensitivity to this parameter is not so relevant here, as those authors only simulated the month of May, while the current study spans the whole annual cycle and thus a much wider range of ambient temperatures. Also the partitioning of semivolatile species as the air rises and cools in the atmosphere is very sensitive to this parameter.

4) The 'aging' of SOA from some biogenic and anthropogenic VOCs as used here leads to unrealistically large yields. Since the semivolatile species continue to age until they completely reside in the particle-phase (at OA concentrations of a few $\mu\text{g m}^{-3}$), we can estimate the final yields from Table 3 as $\sim 100\%$ for aromatics under high NO_x and $\sim 120\%$ under low NO_x . Similarly high yields around 100% are obtained for terpenes. Those yields are extraordinarily high and are inconsistent with current understanding of the oxidation of those species. In particular there is no experimental support for such extremely high yields in the chamber laboratory literature, as recent reevaluations find yields on the range 5-30% under atmospheric concentration levels (see e.g. Ng et al. Atmos Chem Phys 2007a, 2007b). Chamber studies are uncertain and could underestimate the yields somewhat, but not by such a large factor. Although the authors did not come up with the aging parameterizations that they are using, the fact that they produce yields 3-20 times larger than observed in chamber studies needs to be mentioned in the paper. If such a mechanism results in SOA levels that compare well with measurements it is most likely due to cancellation of errors, as this extra SOA must be compensating for precursors with similar emission footprints and formation timescales that are missing from the model.

Other Topics

The paper relies too much on tables, which makes some sections quite difficult to follow (e.g. the comparison with source apportionment studies does not have a single figure and is quite difficult to read). I strongly recommend that most of the tables are moved

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to the Supp info and the information is presented instead in graphical form.

The paper is inconsistent in the use of the terms of residential combustion, wood burning, biomass burning, vegetation burning... For example in P5447-L26 the term 'biomass burning' is used to refer to wintertime residential heating, when this term is most frequently used to refer to wildfires in the literature. I strongly recommend defining unique terms to refer to residential combustion vs open burning (the latter comprising wildfires and agricultural fires) early in the paper, and sticking to those later on, to reduce confusion.

P5430; it appears that the EMEP model does not represent the aerosol size distribution explicitly? Is a constant distribution prescribed for deriving aerosol deposition velocities, wet deposition etc? This may be described in previous papers but should be summarized in a couple of sentences here since it is important for understanding the current results.

P5431-L12; the range of deposition velocities calculated here for the higher aldehydes should be given, so that the relative effect of deposition of semivolatile organics calculated in this paper can be compared against that of future studies. Since these may depend on season and location, it may be useful to provide maps of average deposition velocities for summer and winter in the supplementary information.

P5433-L2; the recent study of Cubison et al. (Atmos Chem Phys 2011) summarizes observations of net SOA formation from forest fires and concludes that SOA formation leads to a small net amount of SOA (equivalent to 20% of the POA), with substantial variability across locations. I suggest citing this study since it provides stronger support for the limited SOA formation from wildfires, compared to the Bessagnet modeling study. Note that applying the S/IVOC VBS mechanism to wildfire emissions may lead to a great overestimation of SOA formation from these emissions, since the amount of SOA formed will be about 200-300% of the POA emissions.

P5436-L25; the units of concentration are written as $\mu\text{g m}^{-3}$, which is incorrect. Either

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ug m-3 or ug/m3 should be used throughout the paper.

P5437-L4; the location that has been studied most intensively with VBS-type models is Mexico City, with at least 9 such publications by 5 different research groups (Dzepina et al., Atmos Chem Phys 2009; Hodzic et al. Atmos Chem Phys 2010a; Tsimpidi et al. Atmos Chem Phys 2010; Hodzic et al. Atmos Chem Phys 2010b; Shrivastava et al. Atmos Chem Phys 2011; Dzepina et al. Env Sci Tech 2011; Li et al. Atmos Chem Phys 2011; Hodzic et al. Geo Mod Dev 2011; Tsimpidi et al. Atmos Chem Phys 2011) and it has been more rigorously tested there due to the availability of both ground and aircraft observations during MILAGRO and related projects. I was surprised to find no mention of any of those studies here or a comparison later between those results and the current paper.

P5437-L19; my immediate reaction was that the specified background concentration is unrealistically high. This is verified by the authors later in the paper. It is important to base the background concentration used in future studies on studies at locations such as Mace Head or during research cruises or flights in the Atlantic Ocean. Those studies are not very numerous but they do exist. I also suggest being careful with the marine OA parameterizations as there appears to be a wide diversity of results and it is not clear that the factors that drive the emission are well understood. In my opinion it is more important to compare the model results at remote locations with existing measurements in order to constrain the background OA.

P5437-L27; I am not aware of any studies showing that adsorption of semivolatile OC species to EC or dust particles makes a non-negligible contribution to OC concentrations, or of any other model that would account for this effect, and no literature reference is provided to support that point. OA partitioning is thought to be dominated by absorptive, and not adsorptive, partitioning (see for example Seinfeld and Pankow, Ann. Rev. Phys. Chem. 2003). Thus there is no basis to assume that the model should underestimate OC due to ignoring that process. If the authors want to keep this statement they should provide credible literature references that support its importance, otherwise this

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statement is unsupported and just causes confusion.

P5444-L9-11; this is too speculative, the volatility distributions of the current VBS and former Kam schemes should be compared directly in the supp. Info, so that firmer conclusions can be reached.

P5444-L13-14; here there is a cryptic reference to “boundary layer physics issues.” Has the PBL used in the EMEP model been evaluated against measurements, especially in winter? Winter inversion heights are difficult to predict, and this could also play a role in the winter OC discrepancies. I gather from the manuscript and lack of referencing of this point that this comparison has not been done; however it is critical before further progress can be made on the winter residential burning emissions (in future publications).

P5445-L23: Supp Info figures are out of order compared to their introduction in the manuscript, please re-order them.

P5446-L24; an emission algorithm for fungal PBAP has been proposed by Heald and Spracklen (Geophys Research Lett 2009). I suggest that the authors adapt this algorithm to future simulations to start to incorporate the impact of this source.

P5447-L1; it seems that R depends strongly on geographical location. A map of R in the sup info could be useful.

P5479, Fig 3: the labels of the figures do not correspond to the 4 variants of the model described in the paper.

P5457-L16; it is not clear that slower oxidation will lead to a larger influence of long range transport. Gas-phase semivolatile species dry deposit faster than submicron particles, so in the absence of wet deposition non-volatile particles should be transported farther than oxidized semivolatile species.

P5457-L21; the fact that the aging of aromatics and terpenes is not realistic and leads to too high yields should be mentioned here (i.e. the model performance is likely im-

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proved for the wrong reasons when using this SOA 'aging').

P5482 and later; the crosses are difficult to see in these figures, I recommend changing the color and potentially the shape of those to make the figures more readable. E.g. open red or blue triangles may offer more contrast with the colors used for the model results. Also the figures appear to have been squished vertically which leads to distortion of the horizontal vs vertical font. Please reformat to publication-quality figures.

Typos etc

P5427-L7; no need for dash between AMS and data

P5428-L8: 'non-refractive' should be 'non-refractory'

P5451 L23-24: awkward wording

Interactive comment on Atmos. Chem. Phys. Discuss., 12, 5425, 2012.

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