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Atmospheric
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Interactive comment on "Modeling meteorological and chemical effects of secondary organic aerosol during an EUCAARI campaign" *by* E. Athanasopoulou et al.

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We appreciate the constructive comments and suggestions. We have done our best to address them in the revised manuscript.

(1) Page 21822, lines 28 onwards: Here the description of the gas/particle mass transfer is given. The reference to using the VBS approach is by lumping the condensates into fixed volatility bins that vary according to local temperature. The description goes on to state that the same gas-particle transfer method is used. Presumably this is dynamic and does not assume equilibrium partitioning? In table 1 the oxidation reactions are listed for each precursor. I presume the total mass of these compounds (generated

through oxidation) is then used to populate the four VBS volatility bins according to yields defined by table 2? If this is the case, and you have the same mass between the VBS version of SORGAM and the ‘detailed’ version, could it be that the pure component volatility used within the ‘detailed’ model are the reason for under predictions of mass? If im not mistaken, this is the only real difference in this approach...the bunching of products into specific volatility bins. Is this correct? Based on the above comment I would also point out that models such as COSMO-ART then display an inherent flexibility to test the importance of certain processes. Whilst I understand the need to use semi-empirical formulisms for correct predictions of mass for ,say, radiative transfer simulations as you have done, this dosnt remove the valuable insights gained from not getting the mass correct using a bottom up approach. This is perhaps a fundamental discussion to be had elsewhere, but it relates to the questions that should at least be addressed in the preceding paragraph.

Response: Gas/particle partitioning of the semi-volatile organic compounds in the modules used in this work is simulated assuming that the system is in thermodynamic equilibrium. In both SORGAM and the VBS approach, the partitioning is simulated as an absorption process into the particulate organic mass on the aerosol particle (Schell et al., 2001; Murphy and Pandis, 2009). The SORGAM and VBS schemes are two quite different modules for the simulation of SOA formation. Although both models use an equilibrium approach, they have numerous differences in almost every other of their aspects. The SOA yields at 298 K used in the two modules are different (the VBS approach is using values based on more recent smog chamber studies), the temperature dependence of these yields is different (different enthalpies of vaporization are used), and they also use different number of surrogate compounds, corresponding molecular weights, etc. One of the most important differences between the two approaches is the treatment of SOA chemical aging: SORGAM simulates just the first generation of chemistry, while the VBS assumes that these compounds continue to react in the gas phase with the OH radical. These chemical reactions can lead to continued SOA formation even after complete precursor consumption. This chemical aging process becomes a major SOA source in the most applications of the VBS approach (Murphy and Pandis, 2010). We have added text in Section 2.2 of the paper clarifying the use of the equilibrium approach in both models but also explaining their differences in detail.

(2) Page 21823, line 4: ‘During each time step SOA species become less volatile by one order of magnitude’. This specific assumption needs justifying. Are you assuming that the condensed material is oxidized by OH or the vapour phase? Can you really justify the order of magnitude drop in volatility across the entire volatility bins? More detail is required. For example, do the condensing organic compounds effectively build up over-time as their volatility reduces constantly?

Response: This is a parameterization of the SOA chemical aging process, through the oxidation of the corresponding compounds in the gas phase by the OH radical. This approach was originally proposed by Robinson et al. (2007) who fitted the corresponding data during SOA formation from evaporated primary organic particulate matter. It does represent a net average change in volatility in a complex reactive system where both functionalization reactions (leading to decreases in volatility by more than one order of magnitude) and fragmentation reactions (leading to an increase in volatility) are taking place. This approach has been found to give reasonable results in a variety of environments despite its simplicity. A number of more complex but also more realistic schemes has been recently tested by Murphy et al. (2012), but surprisingly this one-volatility bin shift scheme resulted in the best agreement with the observations. While it is clearly a first step in the simulating of chemical aging, it appears to capture some of the essential elements of the corresponding processes.

The overall rate of this aging process, as simulated in the current implementation of the VBS, is proportional to the gas-phase concentrations of the SOA compounds. As their volatility is reduced, their partitioning shifts towards the particulate phase and the aging rate slows down. This process effectively stops when the SOA compounds are in volatility bins with effective concentrations much lower than the ambient OA concentration. These important points are now made in the revised manuscript in

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Section 2.2.

(3) Section 3: Page 21825, line 5: 'the differences in OA concentration predictions between the SORGAM (scenario 3) and the VBS approach (base-case).' Just to clarify the point made above, the SORGAM model numerics are equal, the range of condensates, their vapour pressures and reaction rates are not?

Response: Once more we should clarify these are two different modules (SORGAM and VBS), not two variations of SORGAM. They have different numbers of surrogate compounds, yields, temperature variation of the yields, etc. The VBS also simulates SOA formation during the isoprene oxidation and the next generation of reactions; SORGAM does not describe either. The models do share though the same numerical solver of the equilibrium reactions and they also use the same rates for the reactions of the SOA precursors with the oxidants (Table 1 in paper). These differences (also discussed in our response to Comment 1) are now stressed in the revised manuscript.

(4) Page 21825, line 28: An enthalpy of vaporisation of 30 kJ/mol is low. What is the sensitivity to this? It would be useful to check more recent empirical relation by Epstein et al (2009): Epstein, S. A., Riipinen, I., and Donahue, N. M.: A Semiempirical Correlation between Enthalpy of Vaporization and Saturation Concentration for Organic Aerosol, Environ. Sci. Technol., 44, 743–748, doi:10.1021/es902497z, 2009.

Response: Our base case simulations use an effective ΔH of 75 kJ/mol. The reason that we examine a case with a low value of $\Delta H = 30$ kJ/mol as a sensitivity test is because it was the value used in the first study published for the VBS-SOA treatment in aerosol models (Lane et al., 2008) based on experimental results by Pathak et al. (2007) and Stanier et al. (2007). We have tested the sensitivity of our model results to this value for the May 2008 case. Small changes were found (5-20% of total OA) when the ΔH was reduced from 75 to 30 kJ/mol. The use of the correlation of Epstein et al. (2009) will be investigated in future work. This is now discussed in the revised paper.

(5) Conclusions: 'The inability of SORGAM to treat chemical oxidation of organic mat-

ter..' This needs stating earlier on in the paper as it may address questions posed above. 35% isn't terrible, is this averaged? I would expect a difference of 35% to be rectifiable with a revisit of composition dependent parameters. Has this been performed? Mechanistic models can underestimate by at least an order of magnitude due to insufficient carbon flux in the system.

Response: This important point is now stressed in Section 2.2 of the revised paper. This percentage (35 %) is the OA underestimation made by the SORGAM approach when comparing the 7-day averaged OA values to measurements in Cabauw. The underestimation increases up to 75 % when one examines the hourly values. This additional information has been added to the revised paper. The continued development of SORGAM is outside the scope of the current work.

Minor comments: (6) Table 1: What non highlighted species does this refer to? This isn't clear from just the table caption.

Response: We thank the reviewer for noticing this. "Non-highlighted" were the non bold species and reactions, but during the typesetting of the manuscript, all fonts became normal text. This phrase is now substituted by "Isoprene species and reactions are only treated, when COSMO-ART is coupled with VBS".

(7) Abstract: Last sentence: please consider revisiting the grammar. In the line 'while the condensation upon pre-existing, SOA-rich particles..' it should be made explicit what condensation you are referring to.

Response: This sentence has been rewritten. It now reads 'while the condensation of inorganic species upon pre-existing, SOA-rich particles results in a monthly average increase of 5 % in sulfate and ammonium formation in the accumulation mode.'

Interactive comment on Atmos. Chem. Phys. Discuss., 12, 21815, 2012.