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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Simulating the detailed chemical composition of secondary organic aerosol formed on a regional scale during the TORCH 2003 campaign in the southern UK" *by* D. Johnson et al.

Anonymous Referee #2

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General Comments

This paper uses the MCM v3.1 to simulate secondary organic aerosol (SOA) formation using a Lagrangian model. It is applied to a semi-rural location in the United Kingdom during the TORCH campaign. Given the current high level of interest in SOA, this paper clearly addresses scientific questions within the scope of ACP. In general, the paper is well written, and citations of previous work are appropriate. (A couple of specific incidents of a lack of references are provided below.) The title and abstract are adequate. While the paper does not present any significantly new techniques, the model is applied to new data and to a new location. In general, some substantial conclusions are reached, but before I can recommend publication in ACP, there are numerous specific comments that must be addressed.

Specific Comments

1. Why is there such a large discrepancy in the number of anthropogenic volatile organic compounds (VOCs) that are considered (124) compared to biogenic VOCs (3)?

2. In the introduction, the authors state that primary organic aerosol emissions (POA) are linked with elemental carbon emissions in combustion sources. The authors should recognize that not all POA results from combustion and clarify this in their manuscript.

3. The authors make a relatively weak argument for use of one adjustment factor (500) for the partitioning coefficients of the semi-volatile organic oxidation products. In a sense, this value becomes a fitting parameter in their model as opposed to an adjustment factor based on science, does it not? However, the molecular structures shown in Figure 1 are very diverse, indicating that some are more likely to participate in particle-phase or gas-phase accretion reactions. This should be taken into account, especially since some work (see that of Barsanti and Pankow) has deduced the species most likely to participate in this chemistry. The assumed background organic aerosol concentration also becomes a fitting parameter in their model. Should initial conditions for a trajectory model be better known (this is mentioned in Section 2.4 as well)?

4. In the methodology section, particulate matter/POA should be included in the list of emitted species. In the same section, the authors state that observed ratios of organic aerosol to NOx are used as a ratio to determine POA emissions, based on emitted NOx. However, the observed organic aerosol will certainly include some SOA. Do the authors thus overestimate the POA emissions? It is hard to say since only total organic aerosol concentrations are reported. However, if POA emissions are, in fact,

overestimated, this means that the factor of 500 and the background aerosol level used are incorrect (which goes back to the earlier point about these being fitting parameters).

5. In Section 2.3, what method is used to estimate vapor pressure for all of the individual compounds? The method for estimating boiling points is mentioned, but that for the vapor pressures is not. Given that there are large uncertainties associated with this calculation, it should be included and potential errors discussed.

6. Also in section 2.3, more detail is required for how equations (1) and (2) are used mathematically. This should be an iterative process. Is a value for Fi,om assumed, from which Ai, Mo, and MWom are all calculated? Is the value of Fi,om iterated until the values from each equation are equal? How are these Kp values then applied? With the Kp, one needs either to know kin or kout to describe the dynamics. Is one assumed or known? Is a mass transfer calculation used? For that, a size distribution is required, but no mention of model aerosol size distribution is made here. Also, it would be appropriate to reference the kin/kout method (probably most appropriate to reference the Kamens group at UNC - Chapel Hill).

7. In the results section, the authors state that the partitioning species may well come from multiple parent VOCs; therefore, I do not think it is appropriate to attribute SOA to individual species. The authors attempt to do so by considering emissions rate of the parents. However, given that yields of the partitioning compounds may vary between the VOCs, I do not believe that this method is appropriate. The best that the authors can do is to attribute the partitioning species/SOA to parent VOC classes.

8. The authors' results indicate a mixture of over and underprediction. Is there a pattern here? What could be the cause of this, and can any indications about model uncertainties be derived from this mix?

9. I do not find the information presented in Table 3 particularly useful. Because the authors have no chemical speciation data to which to compare model result and because of the one factor (500) used to adjust partitioning coefficients, the simulated

speciated aerosol is likely inaccurate.

10. In section 4.2, I do not believe that it is appropriate to combine two individual sensitivity runs in the manner of alpha/(alpha + beta), where alpha represents the percent SOA increase in a case where anthropogenic emissions alone are increased and beta that for when biogenic emissions alone are increased. When SOA is increased because of the increase in emissions of one type of precursor, the SOA from the second type of precursor should also increase, despite no change in emissions. This is due to an increase in absorptive material. Since the aerosol is speciated, it would be of interest to look in more detail at how SOA from each precursor type responds to changes in each emissions type. In addition, I do not believe that Figure 3 really provides much additional insight. Higher values of alpha/(alpha + beta) by definition imply that the scenario is more strongly associated with anthropogenic emissions. Therefore, it is not at all surprising that this value corresponds well to the percent of SOA from anthropogenic precursors in the base case.

11. In multiple places the authors cite a companion paper by Johnson et al. (2005a) and one by Utembe et al. Based on the titles, these papers appear to be similar to the one being reviewed here. While the reviewer has not investigated the differences between the three papers, it is suggested that the editor checks this to ensure that the papers are, in fact, independent.

12. Table 1 should include a note to see Figure 1 for species molecular structures.

13. Table 2 indicates that butane is a precursor for SOA. This goes against the prevailing theory that less reactive, saturated compounds need to have larger carbon numbers in order to be SOA precursors. Can the authors provide any references that verify that butane is indeed an SOA precursor?

14. In Table 4, O3 mixing ratio is not considered in the table but is mentioned in the footnote.

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Interactive Discussion

Discussion Paper

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