Atmos. Chem. Phys. Discuss., 5, S3867–S3876, 2005
www.atmos-chem-phys.org/acpd/5/S3867/
European Geosciences Union

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.

D. Johnson et al.

Received and published: 14 November 2005

We are grateful to referee 2 for his/her general supportive comments on this paper. He/she raises a series of discussion points, which are dealt with in detail below. A revised manuscript reflecting some (but not all) of the referee's suggestions will be submitted, based on the responses given below.

Referee 2, comment 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)?"

Full Screen / Esc

Print Version

Interactive Discussion

Discussion Paper

Author response: An almost identical point was raised by referee 1 (comment 7). We therefore refer the referee to the detiled response given in the preceding author comment.

Referee 2, comment 2: “In the introduction, the authors state that primary organic aerosol emissions (POA) 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.”

Author response: We agree with the referee on this point, and will clarify this introductory statement in the revised manuscript.

Referee 2, comment 3: “The authors make relatively weak argument for use 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)?”

Author response: The use of a scaling factor of 500, and the inference of the background concentration of 0.7 micro g m-3, were required to force the simulations into agreement with the observations. This is clearly stated in the ‘abstract’, on pages 7878-7879 and on page 7884 (and in the companion paper on page 7847, in the ‘abstract’ and in the ‘summary and conclusions’). Although these are essentially ‘fitting parameters’ (we do not claim otherwise), we believe their requirement is a significant finding, which can be at least rationalised in terms of the role of accretion chemistry in the condensed phase.

Concerning the referee's comments about the use of a single, species-independent scaling factor for the Kp values, we refer the referee to our detailed response to referee 1 (comment 2), in the preceding author comment. As indicated in that comment, we do intend to expand the discussion of this point.

Concerning the background OA concentration, this needed to be invoked to allow a consistent analysis of the data for a variety of case study conditions, as summarised in the present paper (pages 7878-7879 and on page 7884) and discussed in the companion paper (page 7847). This figure is supported by the observations within the campaign, as presented in Figure 7 of the companion paper. The data show that concentrations of OA lower than 0.7 micro g/m3 were very rarely observed, and a correlation of ozone vs OA concentrations for the whole dataset supports the existence of a small background OA concentration of about this magnitude, when the ozone background is subtracted. We therefore believe it is reasonable to use this background concentration to initialise the model.

In addition, there is a large and increasing body of evidence from online compositional analyses that there is a nearly ubiquitous background fine OA mass of the order of 1 micro g/m3. Representative of North-West Europe, the data from the NAMBLEX project in clean air in the west of Ireland shown in Figure 8 of Coe et al. (2005) shows median and 75th percentile organic loadings of this order. Background organic loadings were evident during Ace Asia (Topping et al., 2004) and ITCT (Allan et al., 2004) and in the Free Troposphere (measurements referenced in Heald et al., 2005 and unpublished data from the CLACE-2 and CLACE-3 experiments on the Jungfraujoch). We will include discussion of these points in the revised companion paper, and reference to this discussion in the revised current paper.

Referee 2, comment 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

Full Screen / Esc
Print Version
Interactive Discussion
Discussion Paper

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 authors thus overestimate the POA emissions? It is hard to say since only total 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).”

Author response: We agree with the referee that POA should be included in the list of emitted species, and this will be done in the revised manuscript.

We disagree with the referee that the OA measurements used to define the POA vs. NOx correlation include a significant proportion of secondary OA, and feel that the referee has no basis whatsoever for this comment. The measurements of fine organic particle mass (reported by Allan et al., 2003; Alfarra, 2004) were made close to source in urban locations (i.e. without significant time having passed for SOA formation), and correlated well with NOx, with the correlation plots tending to the origin. Good correlation with other emitted components (e.g. CO) was also observed.

Referee 2, comment 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.”

Author response: The present paper has a preceding companion paper which describes and discusses in some detail, the various aspects of the modelling method. In preparing the present paper, we were careful to include in sections 1 and 2, a summary of the findings of the companion paper and an overview of the various elements of the modelling method, with reference to the more detailed account given in the companion paper, where appropriate. We are certainly of the opinion that a large amount of material appearing in the companion paper, should not be unnecessarily reproduced

Full Screen / Esc
Print Version
Interactive Discussion
Discussion Paper

verbatim in the present paper. One the whole, we feel that we have got the balance about right, although we recognise that where the line is drawn is likely to be a matter of individual opinion.

Specifically, the method for estimating vapour pressures was provided in much more detail in section 4 of the preceding companion paper. Section 2.3 of the present paper starts with the statement ‘Again as described in more detail in the companion paper’, and we really do feel that it is unnecessary to copy portions of text from the preceding paper in the same journal which is readily and universally available on-line.

The method for estimating boiling temperatures (which is also part of the method for estimating vapour pressures) is specifically (briefly) mentioned in the current paper in relation to the criterion for identifying the 2000 partitioning species.

Concerning the errors associated with the vapour pressure estimation, these have been discussed in previous related papers (Jenkin, 2004; Johnson et al., 2004a; 2005b; the companion paper), all of which are referred to in the current paper.

Referee 2, comment 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).”

Author response: Once again, this information is all provided in the preceding companion paper, and in the earlier studies (Jenkin, 2004; Johnson et al., 2004a; 2005b). Our first use of the kin/kout method (Jenkin, 2004) did indeed include the statement ‘the partitioning process was represented dynamically as a balance between absorption and desorption, using a methodology similar to that described by Kamens et al. (1999)'. A similar phrase will be included in the revised version of the current paper.

Referee 2, comment 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."

Author response: Only a few of the product species identified in the present study have more than one significant parent VOC, and these instances are described. We believe the adopted procedure provides a valid indication of the contribution made by individual emitted VOC, and we will revise the text to provide a better justification of this.

Referee 2, comment 8: "The authors' results indicate a mixture of over and under-prediction. Is there a pattern here? What could be the cause of this, and can any indications about model uncertainties be derived from this mix?"

Author response: It is not entirely clear to us to what the referee is referring, with regard to 'over- and under-prediction'. If it is total OA for the various case studies, then this discussion is more appropriate to (and indeed appears in) the companion paper. That the model is able to provide a reasonably consistent level of agreement with observations for several different days with different prevailing meteorological conditions, and suggests that our approach is performing acceptably well.

Referee 2, comment 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."

Author response: This comment again hinges on the appropriateness of using a single species-independent scaling factor for the species-dependent partitioning coefficients for the 2000 species. As indicated in our responses above (referee 1, comment 2; referee 2, comment 2), we feel this is an acceptable first approximation. It should also be pointed out that the SOA speciation would be the same if the scaling factor was not applied, such that the calculated speciation genuinely represents that defined by the species-dependent partitioning coefficients, and the distribution of degradation products simulated with a highly detailed gas-phase chemical mechanism. We therefore feel it is of interest and value to the community to report this information.

It could be argued that the fact that observed speciation data is unavailable at this level of detail makes the results even more valuable. However, in the absence of speciated chemical data with which to make such a comparison, Suwanee River fulvic acid is a useful "working model" of the ensemble of functionalities/degree of oxidation observed for real ambient OA samples and, as discussed in the paper, our simulated compositions compare well with this.

Referee 2, comment 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 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 the base case.”

Author response: The referee's point is well taken, and indeed a similar point is raised by referee 1 (comment 5). We therefore refer the referee to our detailed response to that comment in the preceding author comment, which describes the steps we have taken to inverstigate this issue and the changes we propose to make in the revised manuscript.

Referee 2, comment 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 the one being reviewed here. While the reviewer has not investigated the differences between three papers, it is suggested that the editor checks this to ensure that the papers are, fact, independent."

Author response: We do not feel that this comment warrants a response. However, we note that it is very clear from several of the referee's above comments that he/she has not read the companion paper.

Referee 2, comment 12: "Table 1 should include a note to see Figure 1 for species molecular structures."

Author response: We agree with the referee on this point, and will include the note in the revised manuscript.

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

Author response: To put the situation in perspective, butane oxidation products are simulated to make a very small contribution (0.16 %) to the SOA in just one of the eleven case studies, i.e., that with the highest simulated OA mass. This is very clear from Table 2. The results do not suggest, therefore, that it is a major contributor. The result simply reflects that butane oxidation does yield products with estimated boiling

Full Screen / Esc

Print Version

Interactive Discussion

Discussion Paper

temperatures $>$ 450 K (e.g., 4-hydroxy-butanoic acid, 514 K) and that such products are generated at sufficiently high concentration in one case study to be simulated to be present (albeit to a very small extent) in the aerosol phase. Butane is the anthropogenic VOC with the single greatest emissions (accounting for ca. 10 % of the total, on a mass basis), such that this result is driven mainly by its large contribution to the emitted material, rather than a high propensity to generate SOA. Further inspection of Table 2 reveals that a number of larger alkanes with much lower emissions make greater simulated contributions to the SOA. The result does not really therefore contradict prevailing understanding.

Referee 2, comment 14: “In Table 4, O3 mixing ratio is not considered in the table but is mentioned in footnote.”

Author response: We thank the referee for pointing out this error, which will be corrected in the revised manuscript.

Response references not already cited in manuscript

Allan, James D., Keith N. Bower, Hugh Coe, Hacene Boudries, John T. Jayne, Manjula R. Canagaratna, Dylan B. Millet, Allen H. Goldstein, Patricia K. Quinn, Rodney J. Weber, and Douglas R. Worsnop. Submicron aerosol composition at Trinidad Head, CA during ITCT 2K2, its relationship with gas phase volatile organic carbon and assessment of instrument performance. Journal of Geophysical Research Atmospheres, Vol. 109, D23S24, doi:10.1029/2003JD004208, 2004

Coe, H., J. D. Allan, M. R. Alfarra, K. N. Bower, M. J. Flynn, G. McFiggans, D. O. Topping, P. I. Williams, C. D. O’Dowd, M. Dall’Osto, D. C. S. Beddows and R. M. Harrison, Chemical and Physical Characteristics of Aerosol Particles at a remote Coastal location, Mace Head, Ireland, during NAMBLEX, submitted to Atmos. Chem. Phys., 2005

Heald, Colette L., Daniel J. Jacob, Rokjin J. Park, Lynn M. Russell, Barry J. Huebert,

Full Screen / Esc

Print Version

Interactive Discussion

Discussion Paper

John H. Seinfeld, Hong Liao, and Rodney J. Weber, A large organic aerosol source in the free troposphere missing from current models, Geophys. Res. Letts., 32, L18809, doi:10.1029/2005GL023831, 2005.

Kamens, R.M., Jang, M., Chien, C-J and Leach, K. Aerosol formation from the reaction of a-pinene and ozone using a gas-phase kinetics-aerosol partitioning model. Environmental Science and Technology, 33, 1430-1438, 1999.

Topping, D. O., H. Coe, G. McFiggans, R. A. Burgess, J. D. Allan, M. R. Alfarra, K. N. Bower, T. W. Choularton, S. Decesari and M-C. Facchini, Aerosol chemical characteristics from sampling conducted on the island of Jeju, Korea, during ACE Asia, Atmos. Env., 38, 2111-2123, 2004.

Interactive comment on Atmos. Chem. Phys. Discuss., 5, 7875, 2005.

Full Screen / Esc

Print Version

Interactive Discussion

Discussion Paper