**Atmospheric
Chemistry
and Physics
Discussions**

Interactive comment on **"Simulating regional scale secondary organic aerosol formation during the TORCH 2003 campaign in the southern UK"** *by* **D. Johnson et al.**

D. Johnson et al.

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We are grateful to referee 1 for his/her general supportive comments on this paper. He/she raises a large 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 1, comment 1: "Section 3.2, first paragraph: The Goodwin et al. (2001) speciation for the UK (since it is based on NAEI) is valid also for the other European countries? Especially for the industrial emissions, one will expect major differences between different countries, since their industrial activity is not expected to be the same. Do you

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have a feeling on how much this assumption will affect the results?"

Author response: The VOC emissions speciation provided by the NAEI is the most comprehensive information available. To our knowledge, the same level of detail is not readily available for other countries, such that there is no practical alternative to the assumption made for coupling emissions with the detailed chemical mechanisms applied.

Whereas some differences in speciation between different countries in NW Europe almost certainly exist, the major source categories are, in fact, similar for those countries which mainly influence the conditions experienced in the TORCH 2003 campaign (i.e. those in NW Europe). In practice, therefore, the differences are likely to be comparatively subtle, and the assumption is believed to be reasonable. Support for this comes from the associated model-measurement comparisons for emitted hydrocarbons reported by Utembe et al. (2005) for species with a wide range of atmospheric lifetimes. That study demonstrated that the relative and absolute concentrations of anthropogenic VOC were generally well described.

In addition to this, there is no doubt that the approach adopted is a major improvement on the use of emissions lumped into a limited number species, as used in numerous previous studies, and which therefore provides a vastly improved representation of the structural and reactivity range of the emitted compounds.

Referee 1, comment 2: "Page 7837, equation 1: Do you expect that this relationship will be the same non-urban locations? This is a major assumption, since POA also come from biomass burning and from the oceans, while there are also NOx emissions from soils. By assuming that the aerosol emissions are always proportional to NOx, when simulating rural atmosphere, you will get (low, but existent) POA emissions. Furthermore, by the constant value of 0.012 you assume that e.g. cars, industries and emit the same amount of POA for a specific amount of emitted NOx, which is clearly not correct."

Author response: It is recognised that defining POA emissions in this way is an approximation, and this is discussed in the paper in relation to a variety of sources. However, we do believe that it provides a practical method which provides a good representation for the region of study, i.e., one in which anthropogenic NOX emissions dominate and with road transport being the major source. Thus, even in the 'rural' areas of relevance to the study region, the major source of NOX is still road transport, either emitted on local roads or transported from urban areas. In comparison, emissions from soils and oceans are really very minor indeed in this area.

The proportionality constant of 0.012 is defined on the basis of observations close to source, and is shown to be consistent with the relative emissions of fine particle mass and NOX from combustions sources in the NAEI. Furthermore, we believe that this adopted approach is a significant improvement on the alternative procedure, which would involve implementing PM10 emissions maps and making assumptions about the proportion of emissions which are organic from the variety of different source sectors, a rather uncertain procedure which has been used in other published studies.

Finally, the concentrations of POA we simulate show striking agreement with the observations of McFiggans et al. (2005) for a wide variety of conditions in the campaign period, confirming that the approach provides a good representation for the region and conditions of this study. In summary, therefore, we have used an empirical method based on real observations to define the emissions of POA, have discussed possible limitations of the method in relation to sources and emissions data, and have used ambient observations to provide support for the approach. We therefore believe the approach to be more than adequately discussed and supported.

Referee 1, comment 3: "Page 7837, line 7: Can you say that the ratio of OC to EC of 1.1 observed in a UK city is representative for your whole studied area, including the trajectories that the model follows (i.e. a big area of NW Europe and the North Atlantic)?"

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Author response: The OC/EC ratio of 1.1 is used to define emitted EC relative to emitted OC from combustion sources. As stated, it is based on the observed lower limit ratio of Castro et al. (1999), which was taken to be characteristic of the emitted components. Of course the ratio will vary dramatically over the wider region, because of the contribution of secondary components to OC, as has been reported in the literature, and simulated in the present study.

It should also be pointed out that an OC/EC ratio of about this value has not only been observed as a lower limit in Birmingham (although this is most relevant for the present study), but also at three urban locations in Portugal (also reported by Castro et al., 1999), and at four different locations in the USA (Tolocka et al., 2001 - noting that their reported OC concentrations are scaled by a factor of 1.4 to correct for unmeasured elements). Once again, therefore, we believe that the adopted value is appropriate for the region of study, i.e., one which tends to be dominated by anthropogenic pollution.

Referee 1, comment 4: "Page 7837, lines 16-21: Is this assumption valid for the other countries?"

Author response: There is no stated assumption in the material on lines 16-21. This text is a discussion related to the points raised in comments 2 and 3 above.

Referee 1, comment 5: "Page 7838, line 15: How many emitted VOC does the CRI contains? The net VOC mass that the two models use are the same, after appropriate lumping?"

Author response: Both the CRI and MCM mechanisms treat the degradation of the full suite of 124 emitted VOC with no additional emissions lumping in the CRI. This will be stated more clearly in the revised manuscript.

Referee 1, comment 6: "Page 7839, 2nd paragraph: Do you have OA measurements for this kind of atmosphere? If yes, how are these measurements compared with your value of 0.7 (source (ii) in your results)? Why not assuming an initial OA mass (or

POA mass) and then use it as an initial concentration, instead of using the source ii) as mentioned in page 7847, lines 6-7?"

Author response: The paper describes the procedure which was actually adopted in which it was found that an underlying background concentration of 0.7 micro g/m3 needed to be invoked to allow a consistent analysis of the data for a variety of conditions. In fact, this figure is supported by the observations within the campaign, as presented in Figure 7. The data show that concentrations of OA lower than 0.7 micro g/m3 were very rarely observed, and that the ozone vs OA correlation for the whole dataset fully supports the existence of a small background OA concentration of about this magnitude, when the ozone background is subtracted. In essence, the background concentration is being used to initialise the model, as the referee suggests.

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). The revised manuscript will include brief discussion of, and reference to, these studies, in support of the requirement to infer the background OA concentration.

Referee 1, comment 7: "Page 7839, 2nd paragraph: Are all your trajectories start from the North Atlantic? If not, maybe you should change your initial concentrations for the trajectories, and how much will this affect the results?"

Author response: In practice, the majority of trajectories do originate over the North Atlantic, such that the initial concentrations are entirely appropriate. Irrespective of whether the trajectories originate over sea or land, the species concentrations are usu-

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ally dominated by emissions collected along the trajectory, and these build upon the representative clean air background. Sensitivity tests in previous studies (e.g. Derwent and Jenkin, 1991; Jenkin et al., 2002) have shown that the results tend to be insensitive to variations in the initial concentrations of most species, provided these are varied over reasonable ranges. The recent simulations of Utembe et al. (2005) also demonstrated that the adopted approach provides a good representation for a large number of emitted organics, with a wide variety of atmospheric lifetimes.

Referee 1, comment 8: "Page 7840, equation 3: In the original paper by Pankow (1994), there is also a factor f in the numerator that denotes the fraction of the absorptive aerosol mass. Even if you assume that this factor is unity, you should not eliminate it and add a short comment about it. It will also affect the discussion in section 5.2.2."

Author response: We understand the referee to be referring to the factor 'fom', which is usually used to represent the fraction of the aerosol mass due to the absorbing organic phase. Inclusion of this factor in equation (3) would be appropriate if the discussion in general, and the partitioning equation (5) in particular, were expressed in terms of total aerosol mass. Because it is made clear from the outset that partitioning into a condensed organic phase is being considered, and because equation (5) is expressed in terms of 'mass of the condensed organic material', 'fom' is unity by definition. On balance, therefore, we feel that the referee's suggestion would probably only serve to reduce the clarity of the section unneccesarily.

Referee 1, comment 9: "Page 7841, equation 5: Mo changes with time, while the condensation of gaseous species occur. This will affect the final partitioning of the semi-volatile species. Do you calculate the partitioning iteratively, or you just calculate the equilibrium in your timestep just once? If you assume that for every time-step the gas-to-particle transfer is being done only once, then you never reach equilibrium, and you will have more mass in the gas-phase than in the aerosol-phase, which might be an additional reason for your nessecity to increase the Kp values."

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Author response: As with our previous related studies, all quantities required in the calculation are updated iteratively.

Referee 1, comment 10: "Page 7841, line 22: Is this your uncertainty for the kin value?"

Author response: As stated in the paper, this is to demonstrate that variation in kin by an order of magnitude in either direction has no effect upon the simulated aerosol mass concentrations. This is not an estimated uncertainty but just to indicate that the result is insensitive to the precise value adopted.

Referee 1, comment 11: "Page 7843, line 29: Why do you have greater input from Utembe et al. (2005)? If there are differences between the models, they should be clearly declared."

Author response: Section 3.2 describes in some detail the updates made to the representation of biogenic emissions relative to the study of Utembe et al. (2005). That section includes the statement 'The updated representation therefore resulted in a greater simulated input of biogenic VOC during the high temperature, anticyclonic period of the campaign (period (ii)), than in the previous work.' The comparison with the results of Utembe et al. (2005), presented on page 7843, is interpreted partially in terms of these updates. We feel these updates are already very clearly stated, and that no further clarification is necessary.

Referee 1, comment 12: "Page 7844, 2nd paragraph: Since your ultimate goal is to simulate the measurements correctly, there is no reason to focus on the discrepancies between the two models, but with measurements instead. A discussion for the reasons that the two (almost similar?) models give different results is still important, but not the most important one. Additionally, if you believe that the reason of this discrepancy is the reactions mentioned and the temperature difference, these are not applicable in the Utembe et al. (2005) study?"

Author response: The study of Utembe et al. (2005) used a version of the model to

simulate the distributions of gas phase organics, some of which were compared with observations. The present study uses a version of the model which is nearly identical, but which has been updated in terms of its representation of biogenic emissions and its use of case-specific temperatures (described in section 3.2). The differences in the concentration distributions of ca. 60 carbonyls simulated in the two studies are therefore discussed in section 5.1, in terms of these model updates. Because the number of simulated species far exceeds those for which observations are available, the section focuses on explaining differences in the modelled data from the two studies. However, it is also noted that the updates improve the model-measurement comparison for the limited number of species for which observations are available, and which have been presented previously by Utembe et al. (2005). Once again, we really do feel that the section is clearly written and easy to understand, provided earlier sections of the paper have been read first.

Referee 1, comment 13: "Page 7845, line 28: How do you specify the "good consistency"? If you compare your results with Figure 12 of McFiggans et al. (2005) there are definitely similarities, but also differences. You can compare for example the agreement between the two studies for the end of July and 1/8, but the high ratio of HOA/OA in McFiggans et al. (2005) that continue to exist at 2/8 is not the case for the present study."

Author response: The simulations calculate six-hourly 'snapshots' of the POA concentration throughout the campaign. The ratios to observed OA are generally in strikingly good agreement with the observed HOA/OA ratios reported by McFiggans et al. (2005) for periods (i) and (ii) of the campaign, such that "good consistency" might even be regarded as an understatement. Contrary to the referee's assertion, the observed high HOA/OA ratio does not continue beyond the simulation on 2 August, but the drop in value at the onset of the anticyclonic period (ii) is almost perfectly synchronised. Because the observations of McFiggans et al. (2005) consider only the first part of the campaign, the time axis is presented at higher resolution, and this might be the origin

of the referee's misconception.

Referee 1, comment 14: "Page 7846, last paragraph: Jenkin (2004) has increased the Kp values by a factor of 120, and Johnson et al. (2004) by a factor of 20-80. How did you reach the 500? Although it is an arbitrary value, the reason of increasing just to match the observations is not enough. You could have a factor of 120 instead of 500, then you would get an underestimation of the OA values and finally your conclusions would be different."

Author response: The use of a scaling factor of 500, and the inference of the background concentration, were required to force the simulations into agreement with the observations. This is clearly and unequivocally stated on page 7847, in the 'abstract' and in the 'summary and conclusions'. A possible explanation of why this factor is greater than in the chamber evaluation studies is also provided on page 7847.

We disagree with the referee's opinion that 'increasing (the factor) just to match the observations is not enough', or that the conclusion would have been different if we had not. There would still be the need to explain a large underestimation of SOA formation either way. Scaling the parameters provides a quantification of the extent of underestimation, and must therefore be regarded as useful even if only for this reason. In common with the MCM chamber aerosol simulation papers (Jenkin, 2004; Johnson et al., 2004a; 2005b), the approach taken was to couple a simple representation of gas/particle partitioning to a highly-detailed chemical mechanism and to begin by discussing the short-fallings. We believe the necessity for significant scaling of the partitioning coefficients is a very significant finding, consistent with an emerging picture of SOA formation and growth.

Referee 1, comment 15: "Page 7847, source (iii) and section 5.2: One of my main concerns is increment of the Kp values. How do you compare the Kp values that you calculate with the estimated lumped values that Hoffmann et al. (1997) and Griffin et al. (1999) have calculated in chamber experiments, and are widely used in global

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modeling stud- ies? A comparison table would be very informative. The increase by a factor of 500 is extremely high and is definetly not species-independent. Some species are more favourable to accretion reactions than others, and this rate is expected differ varying aerosol chemical composition and acidity. It would be very interesting to try to make a first approach on different increments of the Kp values based, say, on species structure. Since your model is so detailed, it could do such a step ahead, rather than using the same (actually, higher by a factor of 4-25) scaling factor with the work previously published."

Author response: The referee raises a couple of points here. The first essentially relates to the role of chamber studies in elucidating SOA formation mechanisms and their representation in atmospheric models. It is clear that these mechanisms require some basis for their formulation, and there is no doubt that chamber experiments have a role to play in this process. However, we are of the opinion that it is important that the formation mechanisms are understood, and that SOA yields, or lumped partitioning parameters derived from those yields, are not simply taken from chamber experiments and applied in models. The rigorous description of the oxidation mechanisms is therefore absolutely central to the approach we have adopted.

It is becoming clear from our interpretative studies (e.g., Johnson et al., 2004a; 2005b) and elsewhere (e.g., Donahue et al., 2005), that chamber aerosol yields are highly dependent on conditions, and it is therefore apparent that any derived lumped product yields and partitioning parameters would also vary significantly with experimental conditions. Given that atmospheric conditions differ considerably from those of chamber studies, it is highly unlikely that such parameters derived from a chamber dataset will give a reliable representation of atmospheric SOA formation (i.e. they only really apply to the experimental conditions for which they were derived). A further problem with SOA mechanisms based on chamber yields is that such mechanisms assume the oxidation to a limited number of representative oxygenated products (usually two) which partition into the aerosol phase. This seriously misrepresents the complexity

of atmospheric organic chemistry, because it neglects the fact that the gas-to-particle transfer of the oxidation products occurs in competition with further oxidation in the gas phase. The further oxidation may produce species with a greater or smaller propensity to form SOA, with the sequential gas-phase oxidation ultimately generating carbon dioxide. Our approach aims to account for all these factors explicitly, whereas the idealized chamber mechanisms only consider a highly parameterized initial step. It is clear, therefore, that comparing our Kp values for 2000 partitioning species formed under simulated atmospheric conditions with lumped parameters derived from chamber studies would be a largely meaningless exercise.

The referee's second point relates to the differing abilities of species to participate in accretion reactions, and the dependence of the rates of such processes on aerosol composition. We acknowledge that the use of a single, species-independent scaling factor (in conjunction with the estimated species-dependent partitioning coefficients) to account for such reactions is only a first approximation. Indeed, one of the aims of our proposed future studies is to examine the possibility of applying species-dependent scaling factors based on the functional group content of the 2000 partitioning species. However, it should also be noted that all the major components of the simulated aerosol (presented in the companion paper) contain at least one functional group which has been implicated in mechanisms proposed for condensed phase association and accretion reactions. Thus, we would expect that some degree of scaling would be necessary in almost every case, such that the initial assumption of a species-independent factor is not unreasonable.

The referee also comments on the fact that the required scaling factor of 500 is greater by variable amounts than those derived from our chamber evaluation studies (Jenkin, 2004; Johnson et al., 2004a; 2005b). In view of the above discussion, and indeed the referee's own comments, concerning the differing conditions and the dependence of accretion reactions on aerosol composition, it seems entirely reasonable that the required amount of scaling will change notably from the chamber simulations to the

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atmospheric simulations. Indeed, we believe this is an interesting and significant finding, and is one of the main conclusions of the work. This point is clearly stated on page 7847. It is also noted that some independent support for this conclusion has recently come from the study of Heald et al. (2005) who found that concentrations of OA observed in the free troposphere were 10-100 times greater than they calculated with a global CTM using a standard two product simulation of SOA formation based on empirical fits to smog chamber data.

Referee 1, comment 16: "Page 7847, line 16: Why source (ii) is SOA and not a mixture of POA and SOA? This also applies to page 7850, line 22, where the OA background will also contain POA, from my respect, and it will not have same C:O:H:N ratio."

Author response: As explained on p7847, the formation of a persistent non-volatile SOA from the chemistry described provides an explanation for the background concentration. This assumption concurs with the fact that we do not need to invoke additional POA sources to explain the AMS compositional observations in the present study, and that the AMS data obtained more generally (McFiggans et al., 2005, Table 2) demonstrate a clear progression towards highly oxygenated components at remote sites. Although we do not totally rule out the possibility that there is a POA contribution to the inferred background, we feel that categorising the background as 'SOA' is the more reasonable first approximation. It should also be noted that throughout this work, conclusions are qualified by the statement 'for the conditions of this campaign', i.e. this study considers a summertime heatwave, with record high temperatures in a region with high levels of anthropogenic pollution, particularly from road transport. We recognise that other POA sources are likely to be more significant at other locations and under other conditions.

Referee 1, comment 17: "Page 7848, line 2: The underestimation of OA for the 8/8 can be attributed to underestimation of O3 for the same period (Figure 1)?"

Author response: The fact that both OA and ozone are notably under-simulated for

this case study, points to a common problem, most likely an underestimated emissions input in the model for this case study. As discussed on the following page (in relation to Figure 7), elevated ozone and SOA formation in the heatwave both result from regional scale VOC processing, such that a reduced VOC input will impact on both. The statement on 7848 is essentially pointing out a consistent under-simulation in the two quantities. However, it is recognised that this point could probably be more clearly made, and this will be improved in the revised manuscript.

Referee 1, comment 18: "Page 7848, 2nd paragraph: Are you sure that you have all POA sources in your model? Do you include biomass burning and an oceanic source? The "ubiquitous background concentration" is a really strange quantity, which I assume that you could be able to get rid of, if you include an initial POA concentration. The intercept in Figure 7 (page 7849, line 22) should be resolved in your model, like the O3 intercept does."

Author response: These points have essentially been raised in comments 2, 6 and 16, and are answered above.

Referee 1, comment 19: "Page 7848, last paragraph: Since the definition of non-volatile species is the ones that do not exist (mostly, if not totally) in the gas-phase, then why you have so small contribution of them to the aerosol-phase?"

Author response: We are not entirely sure of the point being made here. The semi-/non-volatile species are defined as those with estimated boiling temperatures $> 450K$, and these make up the condensed phase organic SOA material. The point being made in this paragraph is that only a comparatively small collective fraction of these species needs to be in the condensed phase to account for the observations.

Referee 1, comment 20: "Page 7853, lines 3 and 6: Aerosol formation is not a linear process, thus you can not just make a division such as 500/2.5=200."

Author response: We agree entirely that aerosol formation is not a linear process.

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However, that is not what the illustrative calculation is suggesting. It is considering the change required to the magnitude of the partitioning coefficients to yield the same quantity of OA when the amount of material available for partitioning is increased by a factor of 2.5. Because the majority of the reservoir of organic material is in the gas phase, an increase in that reservoir by a given factor requires Kp to be reduced by the same factor to maintain the same quantity of OA.

Referee 1, comment 21: "Page 7855, line 22: If 170 is your average MW, you do you use a value of 130 in equation 6?"

Author response: As stated in section 4, the reference molecular weight of 130 is an arbitrary value. It is used in equation (6) as part of the method for representing the time-evolution of Kp values. It could be any number at all, and has no impact on any other part of the calculation: and was (inevitably) assigned before we knew what the average MW of the results of the study would be! The value of 170 in the illustrative calculation on page 7855 is typical of the simulated average molecular weight of 'monomers' in the aerosol phase, as reported in the companion paper.

Referee 1, comment 22: "Page 7856, first lines: WSOC will not only partition with their Kp values but also with their Henry values, if you have enough water available on the particles (Griffin et al., 2003)."

Author response: We agree with the referee on this point. This is essentially what we are trying to say in the relevant paragraph, but agree that it could be a little clearer. This will be rewritten to include mention of Henry's constants in the revised manuscript.

Referee 1, comment 23: "A comparison of aerosol-phase species, like in figure 2 for the gas-phase species would be very interesting, if aerosol-phase measurements are available."

Author response: We agree with the referee on this point but, sadly, such detailed species information is not available.

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Referee 1, technical corrections: The referee lists a small number of technical corrections, which will be addressed in the revised manuscript.

Response references not already cited in manuscript

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