

## ***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.**

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We are grateful to referee 1 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 1, comment 1: “Although the model has been described in detail in the companion paper by Johnson et al. (2005), there are some important assumptions that are being made and need to be emphasized in the current paper. The assumption

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that POA emissions are relative to NO<sub>x</sub> emissions is valid only for the location that the measurements are made, and not to all countries that the air-trajectory passes through. The same applies for the POA/BC ratio. The "ubiquitous" concentration of OA, the increase of the partitioning coefficient by a factor of 500 (uniform to all species) are also factors that require more explanation."

Author response: As the referee recognises, the present paper has a preceding companion paper which describes and discusses in some detail, the various aspects of the modelling method. In preparing this 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 (and readily accessible) in the companion paper, should not be unnecessarily reproduced 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. However, the referee's particular comment about the amount of detail given concerning our methodology for representing POA emissions is reasonable, and the description of this will therefore be expanded in the revised manuscript to include some of the justification which appears in the companion paper.

Further scrutiny of the referee's comment suggests that he/she is not only criticising the amount of detail in the present paper, but also the conclusions of the preceding paper which provide the starting point. Similar points regarding POA emissions, and the need to invoke a background OA concentration and scaling factor for the K<sub>p</sub> values, were raised in a referee's comment to the companion paper, and are answered in some detail in the author responses to that paper. We therefore refer the referee to our author responses to comments 2, 6, 14 and 15 made by referee 1 in the companion paper, in which our methods and conclusions are defended and justified.

The referee also mentions the POA/BC ratio. This actually has no bearing on the

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content of the present paper, and is therefore not relevant to the present discussion.

Referee 1, comment 2: “Especially concerning uniform increment of all partitioning coefficients by a factor of 500, an explanation is needed whether or not this number comes from a scientific argument or just to fit the measured concentrations. Since there is an indication on the accretion reactions that might take place (page 7885 line 29 to page 7886 line 2), why not using different factors for different compound groups? Since the detailed chemical composition SOA is the main interest of this work, as mentioned in the title, applying different incremental factor to the partitioning coefficients multi-aldehydic compounds will change both the gas-phase chemistry and the chemical composition SOA, altering (a lot?) results. More discussion is needed on this respect, if not a couple of sensitivity model runs with different incremental factors for different types of semi-volatile compounds.”

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 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 two quantities are essentially ‘fitting parameters’, we believe their requirement is a significant finding, consistent with an emerging picture of SOA formation and growth in the atmosphere.

As the referee notes, these results are interpreted in terms of accretion reactions in the condensed phase (i.e., in the ‘abstract’, on page 7879 and in the main discussion on pages 7884-7886). The referee comments further on the differing abilities of species to participate in accretion reactions. A similar comment is also made by referee 2 (comment 2). 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, and a statement to this effect is included on page 7884. Recognising that an explicit representation of accretion reactions is impractical (even representing simple association reactions for

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the 2000 species would require 2 million reactions!), one of the aims of our proposed future studies (i.e. beyond the scope of the present study) 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 contain at least one functional group which has been implicated in mechanisms proposed for condensed phase association and accretion reactions (e.g. species with carbonyl groups react not only with carbonyls, but with alcohols and hydroperoxides). 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.

On reflection, we agree with the referees that the amount of discussion on this particular point is insufficient in the present manuscript. In the revised manuscript, we propose to incorporate the brief footnote on page 7884 into the main text, and to expand it to discuss the points made above.

Referee 1, comment 3: “Additionally to table 1, it would be very interesting to present a table with the contribution of each functional group (e.g. aldehyde, ketone, acid, alcohol, nitrate, peroxy) to the total SOA mass.”

Author response: We think this is a very good suggestion, and will include information on SOA functional group content for the various case studies in the revised manuscript.

Referee 1, comment 4: “When discussing the results, it would be more convenient to the reader to declare letters of each one of the case studies, like in the footnote of Table 1, instead of (or additionally to) the date (e.g. page 7887 line 26, page 7888 lines 6 and 14).”

Author response: We agree with the referee, and will include the case study identification letters, where appropriate.

Referee 1, comment 5: “Table 4, line 6:  $a/(a+b)$ : Since the chemistry is not linear, you

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cannot make this % contribution calculation. Instead, you can make a model run with increased both the anthropogenic and biogenic VOC emissions by 10% and use this number as the denominator.”

Author response: The referee’s point is well taken, and indeed a similar point is raised by referee 2 (comment 10). We have now investigated the effect of increasing the emissions of anthropogenic VOC (AVOC) by 10 %, biogenic VOC (BVOC) by 10 % and both by 10 % simultaneously. Although this does confirm that the results are not strictly additive, the deviation from linearity is actually very small over the considered range. The SOA increments when (AVOC+BVOC) emissions are increased by 10 % are greater by an average factor of ca. 1.06 than the sum of the SOA increments when AVOC and BVOC emissions are increased independently. As a result we conclude that the main contributor to the increase in SOA formation in each of the independent cases is the incrementally increased concentration of VOC oxidation products resulting from either AVOC or BVOC. The increased transference of material in general at the slightly higher OA concentrations is thus a secondary effect. As a result, the quantity  $a/(a+b)$  does provide an independent measure of the anthropogenic contribution to SOA formation, to a good first approximation. The discussion of the sensitivity study will be expanded to include the above points in the revised manuscript.

Referee 1, comment 6: “Figure 2: Since you assume that accretion reactions occur, I would expect that isoprene also contributes to the SOA mass. A increasing number of papers appear in the literature concerning the isoprene contribution to SOA mass, which should be taken into account in your calculations. This assumption looks even more strange when reading that benzene is also included in the precursor VOC of SOA, when literature in most (but not all) cases says the opposite.”

Author response: Isoprene oxidation products do indeed contribute to the simulated SOA mass, as indicated in Table 2, although their contribution is always less than 1 %. We are aware of the evidence in the literature for the role of isoprene as a precursor to SOA formation. However, it should be pointed out that its importance in global terms

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results to a large extent from its very high emissions, such that its efficiency as an SOA producer per unit mass emission is not necessarily particularly high. Furthermore, some of the isoprene oxidation products observed in ambient samples (e.g., 2-methylbutane-tetraols) are specifically formed at very low NO<sub>x</sub> concentrations. As discussed further below, the campaign considered in the current study was carried out in a region dominated by anthropogenic VOC emissions and with associated comparatively high NO<sub>x</sub> concentrations. It is therefore not unreasonable that isoprene products are not major contributors for the conditions of this study.

The referee's opinions concerning the role of benzene as a precursor to SOA are really quite surprising, and almost certainly guided solely by the results of the early smog chamber study of Izumi and Fukuyama (1990) in which it was reported that, unlike other aromatics, benzene photo-oxidation does not produce SOA. In a very thorough study in the EUPHORE chamber, Martin-Reviejo and Wirtz (2005) have recently examined SOA formation from benzene photo-oxidation for a range NO<sub>x</sub> concentrations in classic photo-oxidation experiments, continuous NO<sub>x</sub>-injection experiments, and with HONO or hydrogen peroxide as OH radical sources. They were thus able to demonstrate the sensitivity of SOA formation for a range of conditions, including the atmospheric NO<sub>x</sub> range. They were also able to explain why Izumi and Fukuyama (1990) did not observe SOA formation in their experiments, which was due to the high NO<sub>x</sub> regime employed and the small fractional extent of benzene oxidation considered. From the work of Martin-Reviejo and Wirtz (2005) it is now very clear than benzene is a significant precursor to SOA formation, and that SOA yields are comparable to other aromatics for which this role is well established.

In view of our understanding of aromatic degradation chemistry and the types of product believed to be involved in the SOA formation process, it is not at all surprising to us that benzene is a precursor to SOA formation. Indeed, our recent evaluation of SOA formation from the photo-oxidation of benzene, toluene, p-xylene and 1,3,5-trimethylbenzene in the EUPHORE chamber, carried out as part of the EXACT project

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and reported by Johnson et al. (2005b), was able to rationalise the observed trends in SOA formation for the series of aromatics on the basis of the types of product formed and their yields.

Finally, benzene is particularly important in the present simulations because it is a significant contributor to anthropogenic VOC emissions, which are dominant for the study region (see below).

Referee 1, comment 7: “The effort made to attribute each one of the products to specific parent VOC, although interesting, can confuse the reader. It is difficult to get clear conclusions when using at the same model 124 anthropogenic compounds and only 3 biogenic, especially when knowing that compounds like limonene are also abundant and more SOA efficient. Sesquiterpenes, even when not being so abundant, have also high SOA yields. A small discussion about the biogenic parent VOC lumping would be useful.”

Author response: The referee’s comment is very similar to one made by referee 2 (comment 1), who also queries the apparent mismatch in AVOC and BVOC speciation. There are a number of points that need to be made in response to these comments.

First, it should be noted that the 124 AVOC explicitly treated account for about 70 % of the anthropogenic mass emissions, such that the other 30 % are emitted in the form of appropriate surrogates, based on reactivity and chemical class (this is explained in the preceding companion paper). For the original nine case study events considered in the current papers (i.e. those for which OA observations are available, and which were therefore used to optimise the code), BVOC emissions collected along the associated trajectories are only between 3 % and 15 % of the AVOC emissions, as indicated in Table 1 (and Table 2 of the companion paper). It is therefore immediately apparent that the BVOC total is even lower than the initially unassigned AVOC component, such that use of only 3 representative species does not seem so unreasonable. Furthermore, it is likely that isoprene, alpha-pinene and beta-pinene actually do collectively account for

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a proportion of the BVOC emissions which is comparable to, or at least approaching, the 70 % coverage achieved by the 124 AVOC under many conditions.

Despite these comments, it is nonetheless recognised that the use of two monoterpenes to represent the large number of species actually emitted is a simplification. This is partially enforced by practical considerations. The pinenes are amongst the very limited number of monoterpenes for which at least some aspects of the degradation chemistry have been studied in the laboratory and environmental chambers, and this is able to steer and help validate the mechanism construction process. Although it is possible to construct mechanisms for other species (based on the methodology outlined in the MCM protocols), this is not a trivial undertaking. In practice, the frequency of including additional terpene mechanisms in the MCM is typically about one new species every three years.

In the absence of detailed mechanisms for a large series of monoterpenes, we believe the use of alpha- and beta-pinene as representatives is a reasonable and practical interim measure. Not only do they make significant contributions to monoterpene emissions in their own right, but they are also reasonably well-studied examples of monoterpenes containing endo-cyclic double bonds and exo-cyclic double bonds, respectively (as discussed on page 7836 of the companion paper). Current understanding of the degradation of monoterpenes indicates that there are likely to be some similarities in the degradation chemistry for species in these two classes, such that alpha- and beta-pinene are ideal representatives. We therefore believe the adopted approach allows a large proportion of monoterpene emissions to be represented in a reasonably rigorous way.

Having said all this, we are aware that there is a need to remind the reader that alpha- and beta-pinene are used to represent all monoterpenes. Although this is done at some points in the manuscript, we acknowledge that there are instances where additional mention of this could be made (e.g. Table 2; Figure 2). This will be done in the revised manuscript.

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Response references not already cited in manuscript

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