**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.
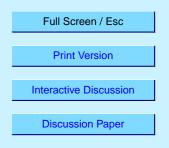
D. Johnson et al.

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We thank referee 3 for his/her general supportive comments on this paper. He/she is very complimentary concerning the scale and achievements of the study, and we are grateful for this recognition. A series of discussion points are raised by the referee, which are dealt with in detail below.

Referee 3, comment 1: "First, why do you apply always an ubiquitous background concentration of 0.7 micro g m-3 for the simulations?"

Author response: The inference of the background concentration (and the use of a scaling factor of 500 for the partitioning coefficients) was required to force the simulations

into agreement with the observations. This is stated on page 7847, in the 'abstract' and in the 'summary and conclusions'. We also refer the referee to the detailed responses to comments 6 and 16 of referee 1 (in the preceding author comment), which are of relevance to this comment.

Referee 3, comment 2: "A second question came up when reading about this 'scaling factor' of 500, with whom the calculated partitioning coefficients had to be multiplied in order to gain the observed organic aerosol mass loadings. One explanation might be the difficulty in estimating the true saturation vapour pressure of the different participating compounds. E.g. for pinic acid the saturation vapour pressure with a boiling point of 612 K [Jenkin et al., 2004] at is calculated to be 6.15 x 10ˆ2 Pa, whereas direct measurement of Bilde and Pandis [Bilde and Pandis, 2001] yields 4.36 5Pa. The discrepancy is about 1400, even larger than factor of 500 used in here. And pinic acid is usually one of the best known compounds among the huge number simulated in the accompanying paper [Johnson et al., 2005b]."

Author response: The species considered for partitioning are generally expected to be solid in their pure states at ambient temperatures, and this is certainly the case for the example of pinic acid used by the referee. However, the absorptive partitioning theory of Pankow (1994) applied in the present work makes the assumption that the depression of melting points in a complex mixture is sufficient for the aerosol to act as an amorphous liquid, such that the sub-cooled liquid vapour pressure is the appropriate quantity. It is therefore this quantity which is estimated and used in the present study, and in our previous related studies (Jenkin, 2004; Johnson et al., 2004a; 2005b). As discussed by Jenkin (2004), and in the associated ACPD discussion comment of that paper, the sub-cooled liquid vapour pressure of a non-volatile species such as pinic acid at ambient temperatures is considerably higher than its solid vapour pressure. Indeed, Jenkin (2004) also estimated solid vapour pressures for a series of pinene ozonolysis products (by use of an approximate correction to the sub-cooled liquid values), yielding a value for pinic acid which agreed with that reported by Bilde and Pandis

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(2001) to within a factor 6. We therefore believe that the estimates of sub-cooled liquid vapour pressure used in the present study are reliable.

Referee 3, comment 3 (referring to the Kp scaling factor): "But what I was confused with was that this number had to be increased from earlier smog chamber studies [Jenkin et al., 2004], which claimed it to be between 5 and 100 as stated well the present paper. If there would be an overestimation in the vapour pressure it should similar in both cases."

Author response: As indicated by our response to the previous comment, we do not believe the need for a scaling factor derives from a systematic overestimation of vapour pressures. As discussed in the paper (on page 7847, in the 'abstract' and in the 'summary and conclusions'), we believe the need for a scaling factor, and its variable value in the chamber and atmospheric simulations, is indicative of accretion chemistry in the condensed phase and the dependence of such chemistry on aerosol composition and the time available for processing. We also refer the referee to the detailed responses to comments 14 and 15 of referee 1 (in the preceding author comment).

Referee 3, comment 4: "This leads to the effect of using two surrogates for all monoterpenes and higher terpenes. Of course even a more detailed investigation would lead to an 'explosion' in number of reactions to be treated, which can't be done even in box model for this study. However, assuming even more terpenes, aromatics etc would split up number of compounds even further, leading to smaller individual concentrations and smaller partitioning of these. Consequently, this approach should overestimate the mass production slightly instead of underestimating it."

Author response: The emissions of biogenic VOC are represented by isoprene and the monoterpenes alpha- and beta-pinene. It is 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 degrada-

tion 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, as the referee points out. 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 (see page 7836). 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.

If we understand the comment, the referee also suggests that the larger number of partitioning compounds at smaller individual concentrations (which would result from a more detailed emissions speciation) would lead to lower overall partitioning of product material into the condensed phase. We do not agree with this. If a representative pinene product is replaced by a series of similar products at a comparable collective concentration and each with a similar K_p value, the partitioning methodology used in the present study would lead to a collective condensed phase concentration which is similar to that of the representative product in the simplified case. This is because the method does not require an individual species to exceed a threshold concentration for gas-to-aerosol transfer to occur: it is driven primarily by the value(s) of K_p and the amount of condensed phase material available to partition into.

The referee also mentions 'higher terpenes', which are dealt with in the response to

comment 6, below.

Referee 3, comment 5: "What about heterogeneous reactions [Jang et al., 2002; Barsanti and Pankow, 2004; Kalberer et al., 2004]? Within the assumed very long lifetime of tropospheric aerosols in here these should occur and matter, when simulating several days but not in the smog chamber studies."

Author response: We agree entirely with the referee. Indeed, this is a partial paraphrase of the explanation we give on page 7847 for the fact that the partitioning coefficient scaling factor required in the present atmospheric simulations is greater than those derived from our previous chamber studies (i.e. the referee's comment 5 effectively answers his/her comment 3).

Referee 3, comment 6: "Finally, just as a curious question, what do the authors think about the influence of larger compounds, more reactive like sesquiterpenes, which are usually extremely had to detect and below of most instrumentation detection limits. However, due to their more than 100 times faster reactivity with respect to ozone they will impact strongly on the ozone concentrations during the day and from my latest knowledge their emissions do not necessarily correlate with the one of monoterpenes. I would be interested in the impact of these on the presented results and if they could explain some of the scaling performed."

Author response: We think the referee raises an interesting point, which definitely needs further study. The atmospheric lifetime of many sesquiterpenes is exceptionally short (typically a few minutes), and is often goverened by ozonolysis. Consequently, such species are completely converted into low-volatility oxygenated products very close to the point of emission, and almost certainly contribute to rapid, local SOA formation in forested regions. The rigorous representation of such species in modelling studies is inhibited by a lack of information on their emissions and chemical processing. However, it is highly plausible that OA formation from sesquiterpenes could be a contributory factor in the need to invoke the background source in the present study.

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Response references not already cited in manuscript

Bilde, M. and Pandis, S.N. Evaporation rates and vapor pressures of individual aerosol species formed in the atmospheric oxidation of a- and b-pinene. Environmental Science and Technology, 35, 3344-3349, 2001.

Interactive comment on Atmos. Chem. Phys. Discuss., 5, 7829, 2005.

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