

Interactive comment on “A Lagrangian model with simple primary and secondary aerosol scheme 1: comparison with UK PM₁₀ data” by K. M. Emmerson et al.

K. M. Emmerson et al.

Received and published: 13 September 2004

Author's reply to anonymous referee #2

General Remarks We thank the referee for her/his constructive comments, especially in the light of her/his misgivings about the simplicity of the model used in our study. Although some of the simplifications discussed below are due to the inevitably finite resources during the project, other simplifications are present because we demonstrate that improving the model physics in these areas would not improve the model-data comparison. We have modified the text in the paper to make clearer when either of these reasons for model simplicity occur.

Comment 1. The authors were not aware of a comprehensive NAEI VOC speciation splitting template being available on the web when the work was conducted. We

Full Screen / Esc

Print Version

Interactive Discussion

Discussion Paper

have examined the latest NAEI speciation splitting template, which details the 50 most abundantly emitted VOCs in Great Britain. Of the aromatics, benzene, toluene, ethylbenzene, xylene, methylethylbenzene and the trimethylbenzenes are present. The first four of these six aromatic species were included in our study. The PORG speciation we used contains more species than the NAEI speciation, though not a greater array of aromatic species. Of a total NMVOC emission rate of 94.5×10^6 kg yr⁻¹, CiTTYCAT received 50%.

The following text on page 3130 at line 22 will be added after the reference to (PORG, 1997). “This method of splitting the total NMVOC emission rate has been compared to the NAEI’s 50 most abundantly emitted compounds in Great Britain (the latest, year 2000 version available at <http://www.naei.org.uk/>) and found to contain similar species. From a total NMVOC emission rate of 94.5×10^6 kg yr⁻¹, the available species within CiTTYCAT received 50% of this total.”

At the time of this work, Nick Hewitt and co-workers at Lancaster University were completing an inventory of all monoterpene and isoprene emitting species in Great Britain. The inventory was compiled using literature emission values, measurements made in situ, and laboratory measurements.

The footnote at the bottom of page 3131 containing the Stewart 2004 reference can now be updated and moved to the reference section on page 3150 using the following citation: Stewart, H. E., C. N. Hewitt, R. G. H. Bunce, R. Steinbrecher, G. Smiatek, and T. Schoenemeyer: A highly spatially and temporally resolved inventory for biogenic isoprene and monoterpene emissions: Model description and application to Great Britain, *J. Geophys. Res.*, 108(D20), 4644, doi:10.1029/2002JD002694, 2003.

Text referring to this work is changed as follows: page 3131 line 7, change “Stewart et al., submitted 2004” to “Stewart et al., 2003”

The final inventory was not available at the time this work was done (see page 3131 line 12), but we were able to base our emission rates on their preliminary findings. In

[Full Screen / Esc](#)[Print Version](#)[Interactive Discussion](#)[Discussion Paper](#)

the UK therefore, α -pinene represents approximately 50% of the total monoterpene emissions rate, and this was why this value was chosen. Griffin et al. (1999) assumes even less α -pinene (35% of total monoterpene emissions) is emitted globally. It was shown in section 4 that the model response to increasing emissions is linear, and so multiplying the α -pinene emission rate by 2 would account for 100% of the biogenic surrogate species.

We have amended the text to make these points clearer: page 3131 line 15 after “The proportion of monoterpenes emitted as α -pinene in the model is estimated to be 50%.”, add “This is a higher estimate than Griffin et al. (1999) who estimate that 35% of global monoterpene emissions are attributed to α -pinene. It should be noted that the model response to increasing emissions is linear (see section 4)”

Comment 2. The current MCM does indeed include α - and β -pinene in the chemistry scheme (see <http://www.chem.leeds.ac.uk/Atmospheric/MCM/mcmproj.html>) and the report by Mike Jenkin in 1996 did indeed provide their beginnings. However, the development paper by Jenkin et al. (1997) omitted biogenics and this reference has been updated.

The additions to the text on page 3132 beginning at line 8 are as follows “The SOA chemical scheme is described in detail in Jenkin (1996) and is a subsection of the wider Master Chemical Mechanism available at <http://www.chem.leeds.ac.uk/Atmospheric/MCM/mcmproj.html> (Jenkin et al., 1997).” is to be changed to “The SOA chemical scheme is described in detail in a report by Jenkin (1996) and has since been re-developed as part of the wider Master Chemical Mechanism available at <http://www.chem.leeds.ac.uk/Atmospheric/MCM/mcmproj.html> (Jenkin et al., 2003 and Saunders et al., 2003).”

The Jenkin et al. 1997 citation in the reference section has been removed.

The reviewer also rightly points out that the xylene and toluene schemes should be referred to as “not well known”, and the text has been changed to reflect this

[Full Screen / Esc](#)[Print Version](#)[Interactive Discussion](#)[Discussion Paper](#)

Page 3129 line 21. Change “Xylene and toluene have reasonably well established reaction mechanisms (e.g., Atkinson, 1995; Jenkin, 1996), and have produced condensable material within a smog chamber environment (Pandis et al., 1992).” to “Xylene and toluene do not have reasonably well established reaction mechanisms (e.g., Calvert et al., 2002), yet have produced condensable material within a smog chamber environment (Pandis et al., 1992).”

The Atkinson, 1995 citation on page 3147 line 16 has been removed.

Comment 3. We realise that gas to aerosol transfer upon reaching supersaturation will represent a lower limit to particle production, as partitioning appears to begin at partial pressures less than the compound vapour pressure. On page 3135 line 4, we refer to a sensitivity test, whereby all the available condensable material was transferred into the particle phase (where the vapour pressure was given a value of 0 Pa). This was shown not to improve the concentration modelled significantly as the SOA mass concentrations were less than 1 $\mu\text{g m}^{-3}$. Introduction of a complicated scheme, as suggested by the references given by the reviewer, could not therefore be justified. We are not ignorant of these works, but state that if there is little material available in the gas phase to begin with, then there will be little material in the particle phase. A subsequent paper referred to on page 3135 line 4 as EMO in preparation 2004, will show this study.

Other comments Page 3134, HNO_3 formation. As stated in the manuscript, the nitrogen and sulphur schemes used in our study are gas-phase only, with rate constants from the IUPAC and JPL evaluations. All products originally reside in the gas-phase, therefore. We simply partition all HNO_3 and H_2SO_4 into the particle phase subsequent to their production. We discuss the weaknesses in this approach in the manuscript (p3135, lines 10-15).

Page 3134, H_2SO_4 formation. The referee is correct; we had inadvertently conflated our discussion of gas-phase production of SO_3 and heterogeneous production of sul-

[Full Screen / Esc](#)[Print Version](#)[Interactive Discussion](#)[Discussion Paper](#)

phate. The sentences at line 22ff on page 3133 – "The final reaction under-predicted." – have been deleted.

Page 3136, lines 16-20 The justification for the different particle diameters between primary and secondary particles is that we felt a newly condensed particle would be a lot smaller than established PM10, and an arbitrary factor of 10 was used. The text on page 3135, line 18 will be updated to include the word "smaller" as in "equivalent to smaller particles with diameters"

Deposition velocity The aerosol was treated by size only, each being given the same density of 1.6 g cm⁻³. The reader can work out the velocity of a particle with diameter 10 µm, as all the information is given on page 3130. speed = distance/time thus 1km/2days ≈ 0.6 cm s⁻¹

The particle diameters used in the parameterisation will dictate the values of the diffusion coefficient and Cunningham slip correction factors, which are then used in within the equation for dry deposition velocity, V_d . This is an analogy to the electrical resistance equation, $V_d = (1/(R_c + R_d + R_c R_d V_s)) V_s$ Where R_c is the aerodynamic resistance and R_d is the surface layer resistance and V_s is the gravitational settling velocity by Stoke's law. However to avoid confusion the text will be updated on page 3130 at line 17 from "A particle of 10mm diameter, this has a lifetime of approximately 2 days within a 1km boundary layer." To "For a particle of 10mm diameter with a deposition rate of 0.6 cm s⁻¹, this has a lifetime of approximately 2 days within a 1km boundary layer."

Page 3136, model calculations. 4 trajectories per day were used ending at midnight, 6am, 12 noon and 6pm. As the measurements were provided as 24 hour averages the modelled data was averaged to provide 1 data point per day.

The text on page 3136 at line 1 has been adjusted to include the following sentence after the web reference <http://www.badc.rl.ac.uk>. "4 trajectories per day were used ending at midnight, 6am, 12 noon and 6pm. As the measurements were provided as 24 hour averages the modelled data was averaged to provide 1 data point per day."

Full Screen / Esc

Print Version

Interactive Discussion

Discussion Paper

Page 3136, benchmark composition These were estimated based on the ratio between organic and elemental carbon in both urban and rural areas, available in the European literature. Three such published references were given in the text, those of Kuhlbusch et al., 1999, Zappolli et al., 1999 and Harrison et al., 1997 on page 3136. The values used e.g. the primary fraction of organic carbon being 40% of the total PM₁₀ are averages calculated from these data. There were no clear patterns between urban and rural sites to suggest that primary/secondary ratio is much larger at urban locations.

The text on page 3136 at line 22 will be updated so that the words “Urban and rural” are inserted before “Measurements”. This sentence has been added on page 3136 at line 27 after “10%”. “There were no clear patterns between urban and rural sites to suggest that primary/secondary ratio is much larger at urban locations.”

Page 3137, line 24. It is true that the simple chemistry scheme does not produce pinonic acid per se, and this biogenic surrogate species will be re-labelled as the “secondary biogenic component” in the edited text.

Page 3132 line 20. Change “The condensable product, pinonic acid (C₁₀H₁₆O₃ and represented here by “PINONIC”) is a carboxylic acid and has a molecular weight of 184 g mol⁻¹.” to “The condensable product, represented here as the “secondary biogenic component”, is a carboxylic acid possibly related to pinonic acid (C₁₀H₁₆O₃), and has been assigned a molecular weight of 184 g mol⁻¹.”

Page 3132 line 22. “Pinonic acid” changed in the text to “the secondary biogenic component”

Page 3134 line 25. Change “The vapour pressure of pinonic acid is treated separately” to “The vapour pressure of the secondary biogenic component is treated separately”

Page 3137 line 24. Change “Pinonic acid contributes most of the mass (98%)” to “The secondary biogenic component contributes most of the mass (98%)”

Page 3138 line 3. Change “The maximum in modelled pinonic acid of 0.8 ug m⁻³

[Full Screen / Esc](#)[Print Version](#)[Interactive Discussion](#)[Discussion Paper](#)

occurs” to “The maximum in the modelled secondary biogenic component of 0.8 ug m-3 occurs”

Page 3139 line 8. Change “A peak in model parameter PINONIC, of 1.5 ug m-3” to “A peak in the secondary biogenic component of 1.5 ug m-3”

Page 3140 line 17. Change “pinonic acid forms the greatest fraction of total modelled SOA,” to “the secondary biogenic component forms the greatest fraction of total modelled SOA,”

Page 3142 line 13. Change “entirely composed of pinonic acid.” To “entirely composed of the secondary biogenic component.”

Additional references used In light of these changes the following references should be included in the reference section:

Calvert, J.G., Atkinson, R., Becker, K.H., Seinfeld, J.H., Wallington, T.J., Yarwood, G. The mechanism of atmospheric oxidation of aromatic hydrocarbons. Oxford University Press, New York, ISBN 0-19-524628-X, 2002.

Griffin, R.J., Cocker, D.R.III., Seinfeld, J.H., Dabdub, R. Estimate of global organic aerosol from oxidation of biogenic hydrocarbons. Geophys. Res. Lett. 26. 2721-2724, 1999.

Jenkin, M.E., Saunders, S.M., Wagner, V., Pilling, M.J. Protocol for the development of the Master Chemical Mechanism, MCM v3 (Part B): Tropospheric degradation of aromatic volatile organic compounds. Atmos. Chem. Phys. 3, 181-193, 2003.

Saunders, S.M., Jenkin, M.E., Derwent, R.G., Pilling, M.J. Protocol for the development of the Master Chemical Mechanism, MCM v3 (Part A): Tropospheric degradation of non-aromatic volatile organic compounds. Atmos. Chem. Phys. 3, 161-180, 2003.

Interactive comment on Atmos. Chem. Phys. Discuss., 4, 3127, 2004.

Full Screen / Esc

Print Version

Interactive Discussion

Discussion Paper