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Interactive comment on "Evaluation of the pathways of tropospheric nitrophenol formation using a multiphase model" *by* M. A. J. Harrison et al.

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Authors' reply to comments by D. Vione

We thank Dr. Vione for his supportive comments.

(1) A similar comment on nitrophenol product ratios was made by Referee 2 and the following repeats part of our response. The issue of the product ratio of nitrophenol isomers formed in the aqueous phase now has greater consensus than when this modelling study was initiated. The observation by Barzaghi and Herrmann (2002) of 2NP:4NP product ratios in the range 60:40 to 50:50 (depending on reaction conditions) has been supported by a very recent study by Vione et al. (2004) which reports a

similar 60:40 2NP:4NP product ratio. Although 4-nitrophenol can form from oxidation of 4-nitrosophenol (the isomer of phenol nitrosation), the present state of knowledge is that direct phenol nitration, rather than via a nitroso intermediate, is the main route to aqueous phase nitrophenols (Harrison et al., 2005). It remains clear that aqueous phase nitration reactions of phenol do not yield the 3-nitrophenol isomer. Vione et al. (2004) observed 3-nitrophenol via aqueous-phase hydroxylation of nitrobenzene but the absence of 3-nitrophenol in field measurements implies that this potential pathway is negligible as an atmospheric source of nitrophenols. We undertook the model simulations with both a 10:90 and 90:10 product ratio for 2NP:4NP precisely in order to "bracket" the range of possible product ratios. Output from the two scenarios are always plotted together in the same figure so that it is easy to interpolate the outcome of intermediate product ratios.

(2) We will emphasise the point suggested by Dr. Vione. Since Henry's law coefficients decline markedly with increased temperature, the effect is to increase the amount of reagent, both radical and other, that is partitioned in the gas-phase which in turn increases the role of the gas-phase in reagent-to-product conversion.

(3) As in our response to a similar comment by Referee 1, we will emphasise the different atmospheric regimes that correspond to different modelled combinations of liquid water volume fraction, L_c, and droplet diameter, *d*. For the bulk of our discussion of model results we focus on the "base scenario" conditions of $L_c = 3 \times 10^{-7}$ and $d = 10\ \mu\mathrm{m}$ which are entirely realistic conditions for typical temperate cloud events, as described in Section 2.6. The smallest L_c value that was modelled (3×10^{-9}) is more typical of mist/haze. As this is unlikely to consist of droplets as large as $10\ \mu\mathrm{m}$ in diameter, our modelled scenario in which water content is assumed dispersed in droplets of diameter $1\ \mu\mathrm{m}$ is more appropriate when considering the smallest L_c values (Fig. 9b). Likewise, for the largest assumed values of L_c (3×10^{-6}), corresponding to heavy condensed phase events such as fog, then larger droplets might be expected, so our modelled scenario in which water content is assumed dispersed in droplets of

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diameter $100\ \mu\mathrm{m}$ is more appropriately considered (Fig. 9b)

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Interactive comment on Atmos. Chem. Phys. Discuss., 5, 1115, 2005.