

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

M. A. J. Harrison et al.

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We thank the referee for their input and are pleased to note their recommendation of publication of the work following consideration of their comments.

A number of reaction pathways to form nitrophenol from benzene and phenol exist in addition to those included in our model. Although a review of the potential pathways has recently been published (Harrison et al., 2005), these authors did not analyse or comment quantitatively on which pathways, in addition to those in our model, are likely to be competitive under atmospheric (as opposed to laboratory) conditions of reagent

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availability and concentrations. In their study of phenol oxidation/nitration, Barzaghi and Herrmann (2002) considered the possibility of nitrophenol formation from phenol via reaction with OH to form a dihydroxycyclohexadienyl radical (followed by NO₂ addition) in addition to the mechanism via reaction with NO₃ to form a phenoxy radical as first step. Although these authors included modelling work suggesting that the reaction via OH could account for about 25% of the observed nitrophenol compounds in their experiments, they went on to conclude that the more important pathway is via the phenoxy radical. The simplification in our model of assuming all aqueous-phase reaction of phenol with OH leads to non-nitrophenol-forming loss of phenol, rather than allowing for the possibility that some of the phenol + OH reaction yields nitrophenol product, will have the effect of underestimating the magnitude of the phenol-to-nitrophenol production rate in the aqueous-phase.

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. (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.

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The revised manuscript will include greater discussion and description of the points raised by this referee.

Cited references

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