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Atmospheric Chemistry and Physics Discussions

Interactive comment on "The influence of cloud chemistry on HO_x and NO_x in the Marine Boundary Layer: a 1-D modelling study" *by* J. E. Williams et al.

J. E. Williams et al.

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In response to the Interactive comment titled "Review" by Anonymous Referee 2 :

(i) Regarding the numerical method used : The numerical method used for solving the diferential equations uses a third-order Rosenbruck scheme where the solution is performed using time-splitting with a time step of 4s. Tere is a brief addition to section 2 comcerning this point.

(ii) In view of the concerns of the referee on the definition of "unpolluted" we have modified this definition throughout the text to "moderately polluted" and been more specific in the title.

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(iii) Regarding the question of "global significance" : We realise that the chosen conditions are not representative on a global scale but mearly wish to show that, in certain locations, the aqueous phase reduction of $HNO_{4(aq)}$ could be a possible source of $HONO_g$. Moreover the study of Dentener et al. (2001) was performed specifically to address the question of global impact . We acknowledge that the $HNO_{4(aq)}$ route would be rather trivial under more polluted conditions and comment on this fact in section 5.4. Moreover, we hope that this paper will provide the incentive for other heterogeneous modelling studies to include R12 to R17 in their reaction schemes over a range of atmospheric conditions. As discussed in Section 5.4 computational limitations prevent us from simulating a winter-time scenario otherwise we would have done so.

(iv) Regarding the question of "heterogeneous HONO formation" : The suggestion that we include the surface conversion route for $NO_{2(aq)}$ to $HNO_{2(g)}$ is limited by the large uncertainty associated with the reaction probability . Therefore, until a more definitive value becomes available, we feel this process should not be included.

(v) Regarding the initial conditions : One of the initial aims of this study was the successful implementation of a state-of-the-art aqueous phase chemical mechanism (e.g. CAPRAM 2.4) into a 1-D cloud model. The CAPRAM 2.4 mechanism was produced using a range of initial conditions and emission/deposition parameters thought to be representative of Europe. Therefore we chose our initial conditions using this rationale.

The more specific comments are dealt with below :

Abstract modified according to suggestion.

P279, ln13 : Amended . P280, ln15 : "re-oxidised" changed to "recycled" . F2 changed to Fluorine . P282, ln17-18 : Amended, P285, ln16-19 : The model does account for sea-salt deposition back into the ocean (c.f. van den Berg et al. (2000)). The first-order deposition terms are related to the solubility of the different species (c.f. electronic supplement). P285, ln25 : The initial conditions and location chosen here were selected to be representative of an air-mass which is influenced by continental emissions. Addi-

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tional text has been added. P285, ln27 : we infer this in ln19-25. P287, ln12 : The effect of concentrated solution on the aqueous phase rate constants is dependent on both the charges involved and becomes somewhat empirical at molarities greater than 1 M dm^{-3}. Moreover, appropriate activity values for many of the soluble species included in our aqueous phase mechanism are still speculative. P287, ln26 : In our simulations a small concentration of copper (10^{-9} M dm^{-3})) is used in the initial concentrations for the CCN. P288, end of section2 : for brevity the reader is referred to van den Berg et al. (2000). Table 6 : These initial conditions are similar to those used for the marine scenario during the construction of CAPRAM 2.4 and are thought to be representative of a European scenario. Table 10 : Amended. p292, ln16 : phase transfer of PAN is ignored in CAPRAM 2.4 as it is thought to be insignificant (c.f. Herrmann et al., 2000b). P297, ln22/23 : See comment (iii). P299, ln15 : Deleted. P304 ln15 : deleted. P304, ln17/18 : Amended.

Interactive comment on Atmos. Chem. Phys. Discuss., 1, 277, 2001.

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