

## ***Interactive comment on “The influence of cloud chemistry on HO<sub>x</sub> and NO<sub>x</sub> 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 "Major Remarks" by Anonymous Referee 3 :**

(i) Regarding the comments on the figures : The units used for concentration in the figures are those recommended by IUPAC and a definition of UTC has been included in the text (section 3).

(ii) Regarding the remark concerning the electronic supplement : this is now available at [www.atmos-chem-phys.org/acpd/1/277/supplement.pdf](http://www.atmos-chem-phys.org/acpd/1/277/supplement.pdf).

(iii) Regarding the comment on the overall length of the paper : tables 2 to 5, 7 and 8 have all been moved into the online electronic supplement which accompanies this

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paper and the remaining tables have been renumbered. Moreover, certain sections of the text have been shortened (e.g. Section 3.2).

(iv) Regarding the comment on the typographical errors we have rechecked and corrected the entire manuscript (e.g. legend for table 10a).

(v) Regarding the remark on other modelling studies (p298 ln13-15) : The references of Leriche et al. (2000 and 2001) have been added to section 5.1. and the text reworded in line with the referees suggestions.

(vi) Regarding the remark on " what is the difference between a deliquescent aerosol and cloud droplet " : The difference is that the chemistry transport model utilized here accounts for two distinct aqueous phases, these being cloud and aerosol associated water (c.f. van den Berg et al. (2000)). The main differences between these two phases is the radius of the particles on which they reside and molarity. We acknowledge that neglecting activity co-efficients ( $\gamma$  values) is a rather simplistic approach but the main focus of this paper is predominantly the effects introduced by clouds, as suggested in the title, meaning that only case(IV) has the aerosol associated water chemically active. The main reason that this approach was adopted was that computational limitations placed severe restrictions on the number of species for which a full pitzer treatment could be applied. Moreover, large uncertainties exist concerning the appropriate activity values which can be used for many soluble species (e.g.  $\text{HNO}_2^-$ ). Therefore, case (IV) is simply used here to establish that increasing the reactive surface area below the cloud layer does not negate the effects simulated by a gas plus cloud run (case (III)). Our model accounts for the size resolved chemistry of the cloud droplets which we feel is important given the nature of the study. We now provide more clarity regarding this in section 2.

(vii) Regarding the cloud LWC (p288, ln22) : the average liquid water content has now been included in the text rather than the previous value of  $1.0 \text{ g cm}^{-3}$  which relates to the maximum threshold that is allowed in the model.

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(viii) Regarding the remark on R25 (p287, ln8) : The reaction of  $\text{HNO}_{4(aq)} + \text{HSO}_{3(aq)}^-$  is treated in an identical manner to that given in Herrmann et al. (2000b) ([www.tropos.de/CHEMIE/multimod/CAPRAM/capram.html](http://www.tropos.de/CHEMIE/multimod/CAPRAM/capram.html)). Moreover, details of this reaction are also available in the electronic supplement.

(ix) Regarding the phase transfer of  $\text{HNO}_4$  : due to the extremely low solubility of  $\text{NO}_{2(aq)}$  in aqueous solution we feel R25 will be rather negligible under our conditions if the phase transfer of  $\text{HNO}_{4(g)}$  did not occur. Unfortunately, because our model does not calculate chemical fluxes, the contribution of R25 to sulphate production cannot be quantified. In view of the referees concern we have modified the text accordingly.

(x) Regarding the discussion on the conversion of  $\text{NO}_2$  to  $\text{NO}$  : this has been modified in line with the referees suggestions to provide more clarity. In the interests of brevity we do not feel adding any discussion concerning the role of VOC's for our scenario will improve the clarity of this section.

(xi) Regarding the comment on P299, ln11 : We acknowledge that under more polluted conditions the influence of the  $\text{HNO}_{4(aq)}$  mechanism will be diminished and discuss this in section 5.4 . The statement concerning greenhouse gases has been removed.

(xii) Regarding the value used for  $\text{pKa}(\text{HNO}_{4(aq)})$  : this was taken directly from the CAPRAM 2.4 chemical mechanism, which was constructed from a critically assessed literature review. Moreover, one of the aims of this work was to implement a 1-D model with a state-of-the-art aqueous phase mechanism rather than mechanism development. Although we have modified the text according to the referees concern, we feel that the uncertainties in the model have been discussed in depth in sections 5.3 and 5.4., where we state that more work is needed regarding a number of the parameters associated with the  $\text{HNO}_{4(aq)}$  reaction cycle. If the value of  $\text{pKa}(\text{HNO}_{4(aq)})$  does increase, as suggested by the study of Logager and Sehested (1993), then we acknowledge that the influence of cloud on  $\text{HONO}_g$  could be minimal under the moderately polluted conditions chosen here.

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