

## ***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.”***

### **Anonymous Referee #2**

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The study by Williams et al addresses an interesting aspect of atmospheric aqueous phase chemistry, being relevant for the stratocumulus topped boundary layer. The model is quite comprehensive, and the aqueous chemical scheme is state-of-the-art, constructed together with laboratory researchers (excellent team work). I recommend publication of this study after clarifying some ambiguities, and after revising the manuscript according to the following remarks.

The model description (section 2) does not discuss the numerical method applied to solve the (stiff) differential equations of the chemical reactions. Considering the large range of time scales involved, I suggest that such a discussion is added. It should be questioned if a study of a single cloud system justifies conclusions about the "ozone

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budget of the MBL". The relatively high acidity (pH=4.5) biases the results toward a "fairly polluted" MBL. In the clean MBL the pH is higher and NO<sub>x</sub> more than an order of magnitude lower. On the other hand, in the polluted continental boundary layer, the pH can be substantially lower than 4.5, so that the HONO formation mechanism becomes inefficient. Therefore it seems that the conditions chosen are rather optimal for the HONO effect rather than being representative of the globe. The study would gain "global significance" by simulating a number of conditions/locations associated with persistent Sc cloud decks. Wintertime conditions are also interesting considering the generally enhanced solubility of the reactants. Initial and boundary conditions could be obtained from the global model of Dentener, Williams and Metzger (2001). Considering the importance of heterogeneous HONO formation, as mentioned in the introduction, it is hard to understand why this process has been neglected in the model. A sensitivity study of its role is recommended (in section 4). Thus I have some doubt that the conditions selected for the study are really representative of the MBL. This limits the general relevance of the conclusions.

Abstract: The final conclusion that previous studies may have overestimated the cloud effects on OHg and O<sub>3</sub>g are hardly substantiated by the stated 10% and 2% changes, especially because the uncertainties regarding heterogeneous chemistry are very large. In fact, the 2% difference for O<sub>3</sub>g is almost negligible. It would be quite interesting to discuss why the differences are so small, in spite of the added influence of HNO<sub>4</sub> chemistry.

p.279, l.3: 10 uM (I assume 10 um is meant); 10 um particles are large aerosols (cloud droplet size).

p.280, l.15: How can nitrate be "re-oxidised" into NO<sub>x</sub>? l.18: Please indicate what F2 is.

p.282, l.17/18: This remark is misplaced since HO<sub>2</sub> reduction into OH does not oxidise CO. Only the remark that HO<sub>2</sub> to OH conversion does not produce O<sub>3</sub> is relevant.

p.285, l.16-19: Why is the deposition process assumed to be unimportant? Aerosol deposition is strongly dependent on size and gas deposition on solubility.

I.25: Why is the location west of Spain selected? Is this representative for the MBL? I would think that these conditions represent a fairly polluted case (100 ppt NO<sub>x</sub>).

I.27. It could be mentioned that persistent Sc clouds are common in the MBL. It might help the reader, putting the study into context, to indicate where and when such cloud decks are most common.

p.287, I.12. Is it possible to estimate the effect of neglecting activity coefficients for aerosol reactions? Some "educated guesses" should be possible.

I.26. It could also be argued that copper induced chemistry can be neglected since such pollutants hardly reach the MBL.

p.288, end of section 2: Please mention how the boundary conditions that represent advection and entrainment are treated in the model.

Table 6: Are these conditions representative of the Atlantic MBL west of Spain? Please justify the choice of these parameters.

Table 10: parenthesis, not paranthesis

p.292, I.16: To what extent does dissolution of PA play a role (e.g. as compared to PAN dissolution, being less efficient)? This process could prevent PAN formation. The reason provided to not further analyse PAN is rather strange.

p. 297, I.22/23: The result that the change in NO<sub>x</sub> chemistry affects O<sub>3</sub> rather than halogen chemistry may be valid for the present conditions (which I would describe as fairly polluted rather than relatively unpolluted -see I.20-). Most of the MBL contains less NO<sub>x</sub> than in the present case, which limits the global significance of such results. It would be interesting to also study a case with low NO<sub>x</sub> (e.g. <10 ppt). It might also be interesting to see more of a comparison between cloud and deliquesced aerosol chemistry (e.g. following up on the study of van den Berg et al. (2000).

p.299, I.15: The global cloud fraction of 30% is wrong. A more likely number is 60%. Or do you mean a stratocumulus cloud fraction of 30%?

p. 304, I.5/6: Here it is more clearly articulated that the study applies to rather limited conditions (again I would call them rather polluted than the "unpolluted MBL").

I.15: Please delete the confusing remark on "compensation point".

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I.17/18: The remark about the influence of clouds on the overall oxidising capacity of the MBL is misplaced given the limited relevance of the selected conditions. Please rephrase.

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

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