

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.”

Anonymous Referee #3

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General comments: This paper addresses a very important question on the influence of clouds on NO_x and HO_x chemistry in the MBL. However, there are major concerns about the main conclusions of the paper that relies on an uncertain value of the pK_a for HNO₄ dissociation. Also, the reviewers did not understand the difference between deliquescent aerosols and cloud droplets in this paper. Also, many typing errors, unreadable figures make this paper difficult to understand.

Minor corrections -Legend for Table 10a is not correct (case II instead of III p. 295). Many typing errors. -Figures 3 to 7 are not readable and seem to be presented with unusual units. -The paper is too long and difficult to read. The reader gets lost with many tables and the paper needs to be reorganized. -p.298, line 13 to 15: missing

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references such as Leriche et al., (2000 and 2001) and comment is not valid since Herrmann et al. are also examining the aqueous chemistry of HOX, VOCs, ? and not only sulfate chemistry.

Major remarks -The authors should comment on the real difference between deliquescent aerosols and cloud droplets. It seems that the main difference relies on different pH conditions. -What is the point to consider fancy size resolved chemistry to finally neglect activity coefficients and consider similar reaction rates for deliquescent aerosols and cloud droplets (p.287, lines 12 and 13). -The cloud water amount is enormous and unrealistic for stratiform clouds. Is there a typing error (p.288, line 22). -Since the electronic supplement was not available, it is hard to understand how the important reaction of HNO₄ with HSO₃⁻ is treated (p.287, line 28). If it is not taken into account, discussion line 10, p. 296 has no sense. Moreover, it is not clear how efficient can still be the reaction with HNO₄(aq) if mass transfer is suppressed (case V). -The discussion concerning the conversion of NO₂ into NO due to the cloud should be clarified in page 291, line 22. This is partially done in page 295 where the authors state that the net production of O₃(g) is mainly driven by NO(g) mixing ratio and do not consider the VOCs influence. The authors need to better explain the cycling of NO_x though HNO₄ reactions in aqueous phase and the release of HONO in gas phase. The overall NO_x (at least NO_y) should remain the same even though this cycling. -p.299, line 11: ?this implies?? may be in a marine case but is this statement valid in other conditions? The comment on the greenhouse gases should be removed. -In 5.3, uncertainties in reaction rates, the authors should discuss the value of pK_a of HNO₄. In CAPRAM 2.4, pK_a is given by Lammel et al. (1990) (pK_a=5) whereas the more recent study of Logager and Sehested (1993) provides a pK_a of 5.85. Such a difference will affect the efficiency of the cycle R7-R12-R13-R15-R16-R17 because the HNO₄(aq): NO₄⁻ ratio becomes (0.96: 0.04) instead of (0.60: 0.40). This will considerably change the main conclusions of the paper.

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

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