

***Interactive comment on* “Multiphase modeling of nitrate photochemistry in the quasi-liquid layer (QLL): implications for NO_x release from the Arctic and coastal Antarctic snowpack” by C. S. Boxe and A. Saiz-Lopez**

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Author Response to Anonymous Referee #2 comments to “Multiphase Modeling of nitrate photochemistry in the quasi-liquid layer (QLL): implications for NO_x release from the Arctic and coastal Antarctic snowpack”; by C. S. Boxe and A. Saiz-Lopez.

C. S. Boxe and A. Saiz-Lopez

1. We are grateful and really appreciate Anonymous Referee #2’s comments

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and suggestions, which will undoubtedly improve the manuscript.

2. The specific comment pertaining to lines 11-15, page 6011 will be corrected in the revised manuscript as suggested. In addition, the reference, Hastings et al. (2004) will also be added.

3. The specific comment pertaining to line 17, page 6011 will be corrected in the revised manuscript as suggested.

4. The specific comment pertaining to lines 15-18 will be corrected to refer to the existence of the QLL;

5. In relation to the comment for page 6013, starting at line 10: in the revised version of the manuscript, the range in NO_x fluxes that have been measured in the Arctic and Antarctic will be clearly delineated.

6. (i) Sensitivity analyses showed us that the primary factors governing the release of NO_x from the snow/ice surface is the initial nitrate concentration and the photochemical reactions producing NO and NO₂ (i.e., via nitrates primary (photolysis of nitrate) and secondary (photolysis of nitrite) photochemical pathways. Concomitantly, we will provide appropriate references for sites and their respective temperature ranges as suggested by Anonymous Referee # 2. (ii) The range of temperatures mentioned on page 6014, line 10 are also apply to temperatures on and within the snowpack, which we feel is appropriate since we are modeling nitrate photochemistry in the thin film (i.e., the QLL) that exist on snow/ice surfaces and its simultaneous interplay with polar boundary layer chemistry; therefore, no drastic difference(s) in temperature are expected in comparison to air just above the snowpack.

7. Anonymous Referee #2 does bring forth an excellent point, pertaining to his/her suggestion of providing a table, which will be provided in the revised manuscript such that readers/users can utilize and interpret our investigation accordingly.

8. Page 6014, line 15: (i) This sentence will be corrected in the revised manuscript. (ii)

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The range of nitrate and nitrite concentrations applies to the surface of the snowpack (e.g., top few centimeters).

9. Page 6016, lines 11-12: A QLL thickness of $\sim 14 \mu\text{m}$ was calculated by utilizing a mean snow depth of $\sim 50 \text{ cm}$. Therefore, $50 \text{ cm} \times 1 \text{ cm}^2 = 50 \text{ cm}^3$; $50 \text{ cm}^3 / 10^{-5} = 0.00139 \text{ cm}^3$; then, $0.00139 \text{ cm}^3 / 1 \text{ cm}^2 = 13.90 \mu\text{m}$.

10. Page 6016, line 13: both old and new; refer to snow.

11. (i) Page 6016, lines 14-15: Although we are aware that there are depth variations in snowpack environments, we utilized reported mean snow depths from Sumner and Shepson (1999) and Michalowski et al. (2000) as an approximation. Still, our model shows us that photochemistry of nitrate at the surface (i.e., within the QLL) dominates the release of NO_x ; therefore, within the representative framework of our model, depth variations have a negligible impact. (ii) We do not consider the diffusion of nitrate, but the release of HNO_3 is considered since we conducted multiphase model simulations. Nitrate diffusion will be incorporated in a more refined version of the model.

12. Page 6016, line 19: The terminology throughout the text will be clarified throughout the text in the revised version of the manuscript.

13. (i) Page 6020, lines 10-16: In this section, we calculate the depth below which NO_2 photolysis will not occur ($\sim 15 \mu\text{m}$ as shown in the text), but above that depth NO_2 produced is readily released to the gas phase. So, we are consistent in the fact that we exclude NO_2 photolysis in the condensed-phase portion of the model. (ii) The estimated QLL thickness (or depth) shown in Figure 1 ($\sim 14 \mu\text{m}$) is smaller than the maximum depth for NO_2 photolysis not to occur, which makes sense since due to its diffusion timescale, the fact that any NO_2 release at the uppermost region of the snowpack is released [Dubowski et al., 2001; Boxe et al., 2005; Boxe et al., 2006], and the inclusion of NO_2 photolysis at yielded NO_x concentrations several orders of magnitude higher than ever measured in the field.

14. Page 6020, lines 20-22: Anonymous Referee #2 is correct in the statement that the inclusion of HONO in the model simulations produced unreasonably high NO/NO₂ ratios (~ 1500).

15. (i) Page 6022: Anonymous Referee #2 is correct in the assessment of the reported literature pertaining to the light attenuation in the snowpack. Although Anonymous Referee #2 is correct, the key point of our paper is that, which we will make clearer in the revised version of the manuscript, is that photochemistry at the ice-air interface (i.e., where the QLL also resides) is the dominant process governing the release of NO_x via nitrate photodecomposition. (ii) A short discussion of Lee-Taylor and Madronich (2002) will be included.

16. Page 6023, lines 1-3: This section will be rephrased as suggested in the revised manuscript.

17. Page 6023: A conclusion/summary section will be included in the revised manuscript after rearrangement of the last paragraph on page 6023 with the discussion on page 6022.

18. Given the small quantum yields of the primary photolytic pathways of nitrate photolysis, a significant change in nitrate concentrations would only be observed over long timescales (e.g., days to weeks) without replenishment of surface nitrate via HNO₃ deposition., which would affect bulk nitrate concentrations in the snow, which is a scenario that is not realistic. Therefore, over our model simulation timescales, a significant change in nitrate in the QLL was not observed. Still, we could assess this issue in the revised version of the manuscript.

19. Figure 1: This typographical mistake will be amended in the revised manuscript, where it will read as ~ 14 μm QLL thickness as calculated in the text.

20. Figure 3: We will definitely modify this figure since we do agree with Anonymous Referee #2's comment.

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21. Figure 4: We will add the phrase “above the snowpack”; at the end of the caption.

References Boxe, C. S., Colussi, A. J., Hoffmann, M. R., Murphy, J. G., Wooldridge, P. J., Betram, T. H., and Cohen, R. C.: Photochemical production and release of gaseous NO₂ from nitrate-doped water ice, *J. Phys. Chem. A*, 109, 8520-8525, 2005.

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