

Supplementary Information:

MODELING CHEMISTRY IN AND ABOVE SNOW AT SUMMIT, GREENLAND – PART 2: IMPACT OF SNOWPACK CHEMISTRY ON THE OXIDATION CAPACITY OF THE BOUNDARY LAYER

Sensitivity runs have been completed to assess the impact of additional HCHO and H₂O₂ on the budget of HO_x in the boundary layer at Summit. The initialization for concentrations of HCHO and H₂O₂ at the surface are given in SI-Table 1. The model results for all three days are shown in SI-Figures 1 and 2. This shows that the model does not sustain the high concentrations of HCHO and H₂O₂, however to approximate the impact of additional radical sources on the HO_x budget we only analyze the first 24 hours of this model run.

The OH concentration in boundary layer for the base case and the sensitivity run are compared with OH measurements made during the campaign in SI-Figure 3, indicating that additional HCHO and H₂O₂ slightly perturb the mid-day OH concentration. However, there is a significant increase in the contribution of H₂O₂ to primary OH production. The diurnal average contribution of H₂O₂ to primary OH production shifts from 22% to 41%, consistent with the study of Chen et al. (2007). The contribution of individual reactions to OH production and destruction is shown in SI-Figure 4.

This has minimal impact on the OH concentration because of the impact of recycling reactions on mid-day OH levels, including NO + HO₂.

Table 1: Surface mixing ratios for the base case and the sensitivity model run with additional HCHO and H₂O₂, initialized according to the review of Frey et al. (2009).

Species	base case (pptv)	more HCHO & H ₂ O ₂ (pptv)
HCHO	100	230
H ₂ O ₂	400	1400

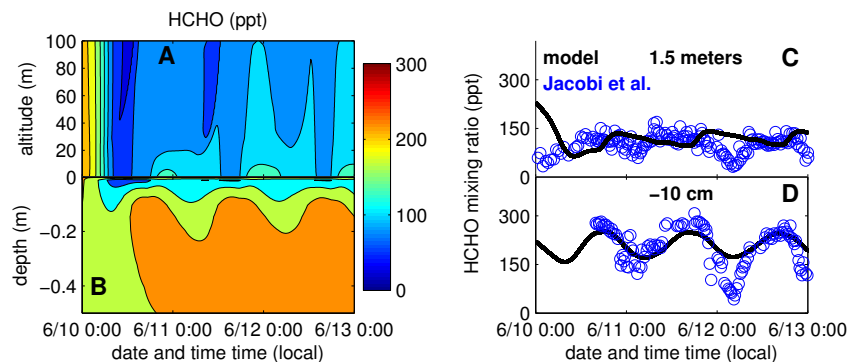


Figure 1: Model predicted HCHO for a sensitivity run with higher HCHO and H₂O₂. Model initialization is shown in SI-Table 1. Model results are compared with measurements taken in June 2000 originally published by interstitial air during shading experiments have been removed from the comparison. Measurements taken from Jacobi et al. (2004).

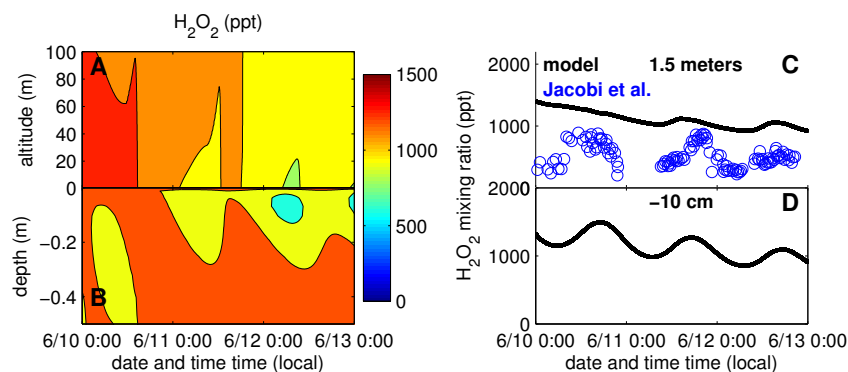


Figure 2: Model predicted H₂O₂ for a sensitivity run with higher HCHO and H₂O₂. Model initialization is shown in SI-Table 1. Model results are compared with measurements taken in June 2000 originally published by interstitial air during shading experiments have been removed from the comparison. Measurements taken from Jacobi et al. (2004).

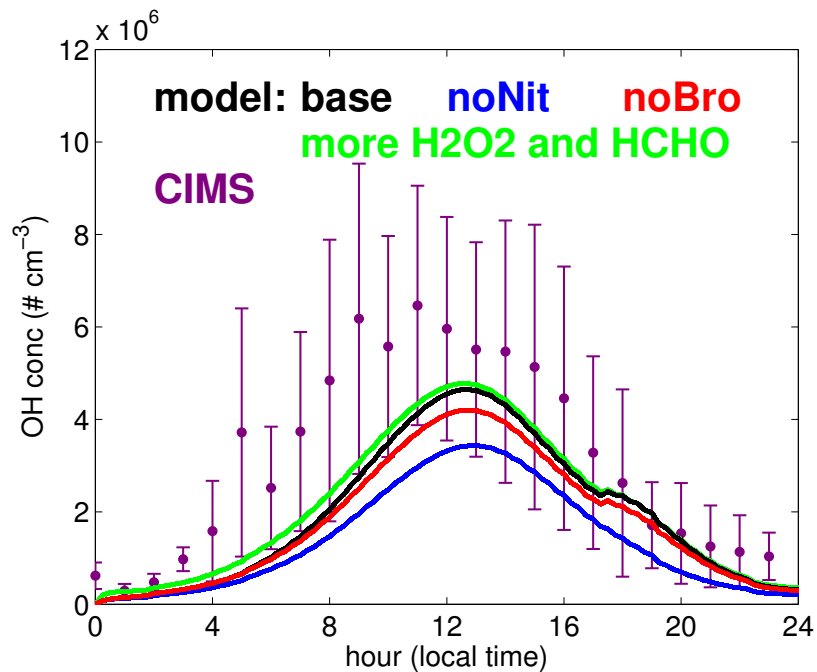


Figure 3: Model predicted OH for the base case and for the sensitivity run with higher HCHO and H₂O₂. Model initialization is shown in SI-Table 1. Model results show that the additional primary radical sources do not significantly impact the mid-day OH concentrations. However, this effect may be underestimated because the model does not sustain the high levels of HCHO and H₂O₂ seen during other years at Summit (Frey et al., 2009).

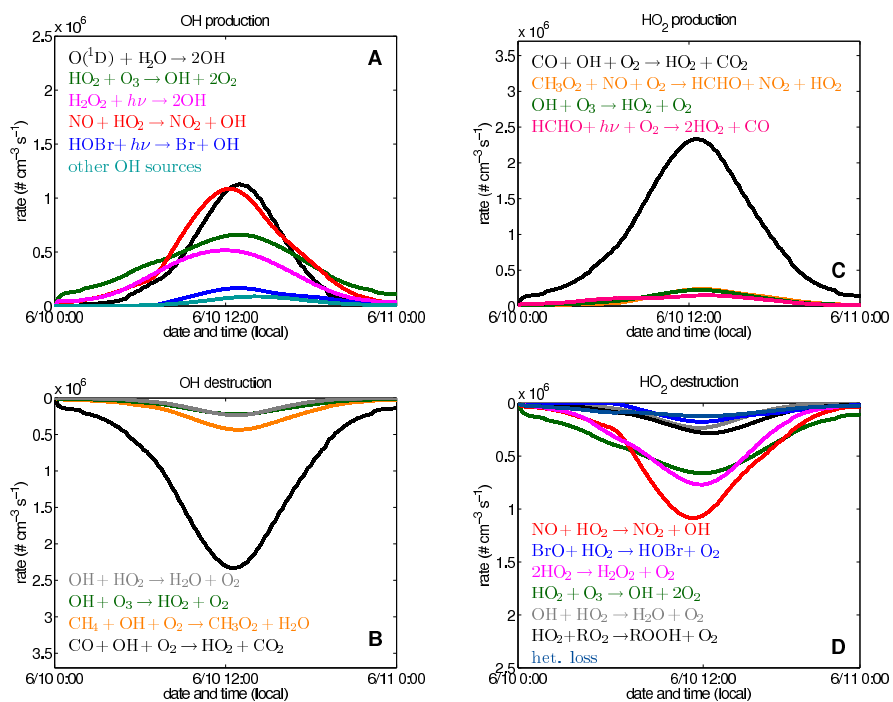


Figure 4: OH and HO₂ production and destruction reaction rates for the run with higher HCHO and H₂O₂ in panels (a–d), including primary production, HO₂ to OH cycling reactions, and terminal loss processes.

References

- Chen, G., Huey, L. G., Crawford, J. H., Olson, J. R., Hutterli, M. A., Sjostedt, S., Tanner, D., Dibb, J., Lefer, B., Blake, N., Davis, D., and Stohl, A.: An assessment of the polar HOx photochemical budget based on 2003 Summit Greenland field observations, *Atmos. Env.*, 41, 7806–7820, doi:10.1016/j.atmosenv.2007.06.014, 2007.
- Frey, M. M., Hutterli, M. A., Chen, G., Sjostedt, S. J., Burkhardt, J. F., Friel, D. K., and Bales, R. C.: Contrasting atmospheric boundary layer chemistry of methylhydroperoxide (CH_3OOH) and hydrogen peroxide (H_2O_2) above polar snow, *Atmos. Chem. Phys.*, 9, 3261–3276, 2009.
- Jacobi, H.-W., Bales, R., Honrath, R., Peterson, M., Dibb, J., Swanson, A., and Albert, M.: Reactive trace gases measured in the interstitial air of surface snow at Summit, Greenland, *Atmos. Env.*, 38, 1687–1697, doi: 10.1016/j.atmosenv.2004.01.004, 2004.