

Supplementary information

Table S1. Summary of key terms for atmospheric nitrogen in the three simulations.

| | No pNO ₃ + hv | Shah et al. 2023 | This study |
|-----------------------------------------------------------------------|--------------------------|------------------|------------|
| Emissions (TgN yr⁻¹) | | | |
| Total NO _x | 53.98 | 53.80 | 53.46 |
| Anthropogenic NO _x | 30.86 | 30.86 | 30.86 |
| Soil NO _x | 7.52 | 7.52 | 7.52 |
| Biomass Burning NO _x | 6.67 | 6.67 | 6.67 |
| Lightning NO _x | 6.13 | 6.13 | 6.13 |
| Shipping NO _x | 2.80 | 2.62 | 2.32 |
| Shipping HNO ₃ | 3.09 | 3.26 | 2.21 |
| Deposition (TgN yr⁻¹) | | | |
| HNO ₃ | 35.20 | 37.62 | 36.09 |
| pNO ₃ | 15.37 | 12.53 | 12.71 |
| PAN | 1.26 | 1.38 | 2.32 |
| NO ₂ | 1.73 | 1.76 | 1.67 |
| XNO ₂ / XNO ₃ | 0.29 | 0.33 | 0.38 |
| HONO | 0.07 | 0.14 | 0.20 |
| Photolysis Reactions (s⁻¹) | | | |
| pNO ₃ + hv → HONO | 0.00 | 7.96 | 32.89 |
| pNO ₃ + hv → NO ₂ | 0.00 | 3.98 | 16.44 |
| HONO + hv → OH + NO | 16.90 | 27.89 | 68.05 |
| HNO ₃ + hv → OH + NO ₂ | 2.07 | 2.14 | 1.81 |
| Gas-Phase Reactions (TgN yr⁻¹) | | | |
| OH + NO → HONO | 17.05 | 20.32 | 36.20 |
| OH + NO ₂ → HNO ₃ | 27.13 | 34.49 | 59.73 |
| NO ₂ + MCO ₃ → PAN | 117.57 | 133.84 | 150.17 |
| PAN → NO ₂ + MCO ₃ | 114.69 | 130.67 | 145.21 |
| HNO ₃ + OH → NO ₃ | 3.44 | 3.85 | 3.84 |
| HNO ₂ + OH → H ₂ O + NO ₂ | 0.19 | 0.37 | 0.98 |
| O ₃ + NO ₂ → NO ₃ + O ₂ | 41.53 | 49.07 | 67.31 |
| Heterogeneous Reactions (TgN yr⁻¹) | | | |
| N ₂ O ₅ (+ H ₂ O) → HNO ₃ | 10.08 | 11.52 | 16.17 |
| NO ₃ → HNO ₃ | 2.59 | 3.08 | 3.59 |
| NO ₂ → HNO ₃ | 0.98. | 1.06 | 1.07 |
| Tropospheric Burdens (Tg X) | | | |
| O ₃ | 309 | 332 | 393 |
| NO _x | 0.36 | 0.43 | 0.57 |
| HNO ₃ | 1.21 | | 1.23 |
| pNO ₃ ⁻ | 0.43 | 0.38 | 0.30 |
| HONO (Gg) | 1.64 | | 6.21 |
| CO | 326 | 306 | 271 |

Figure S1. Location and value in ppt of all available HONO measurements, from aircraft and ship campaigns (coloured by HONO concentration in pptv) and in-situ measurements (red markers).

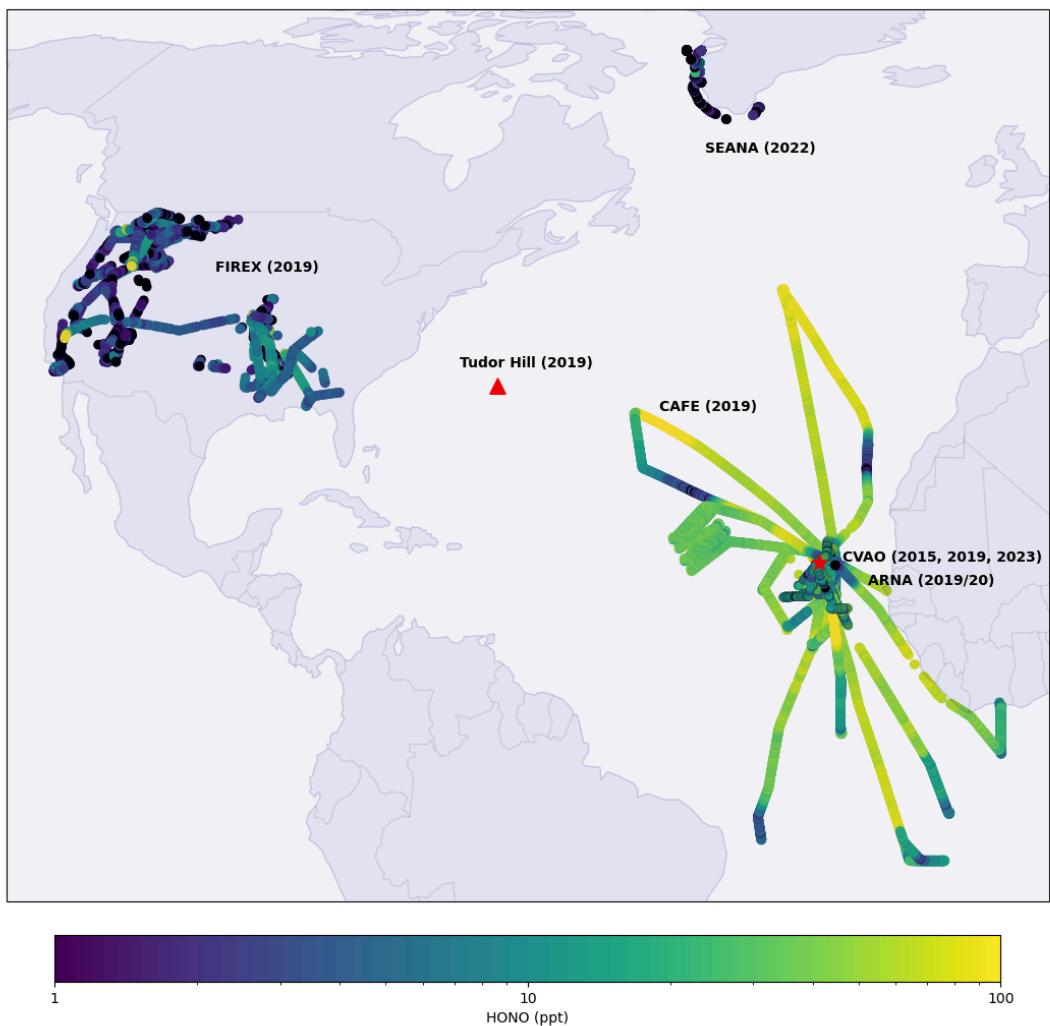


Figure S2. Nitrate aerosol photolysis enhancement factor necessary to balance the observed HONO against its photolytic loss as a function of the nitrate aerosol concentration, including parameterisations generated with additional dependencies on RH and Cl (see Methods).

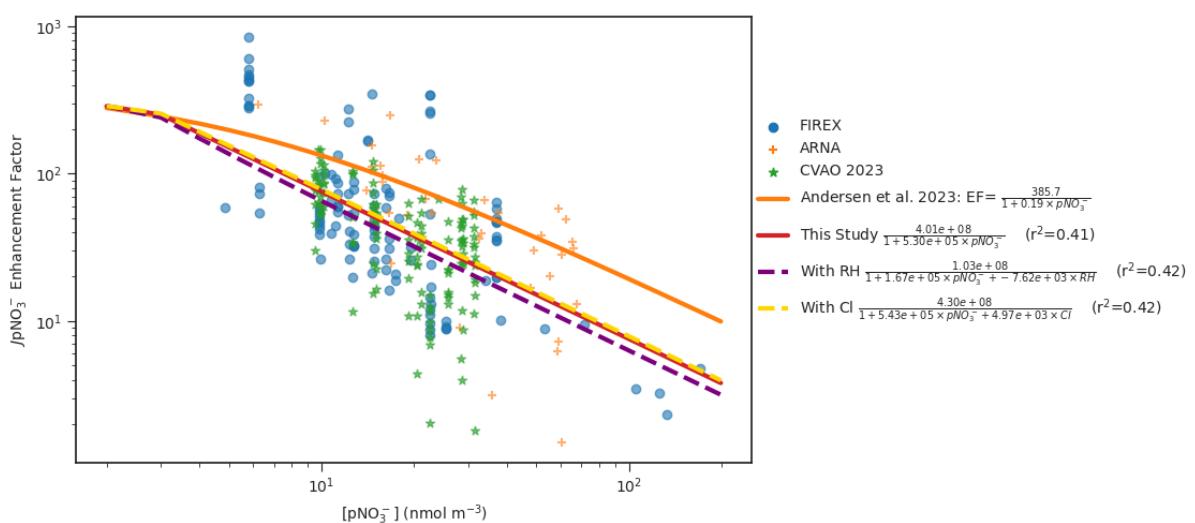


Figure S3. Comparison of FIREX-AQ AMS fine-mode nitrate (black) with simulated fine-mode nitrate from the base model version without nitrate photolysis (blue). Data is split into Western and Eastern USA (at -115°W), and averaged over 500m altitude bins. Horizontal grey lines represent 1 standard deviation on the measurements.

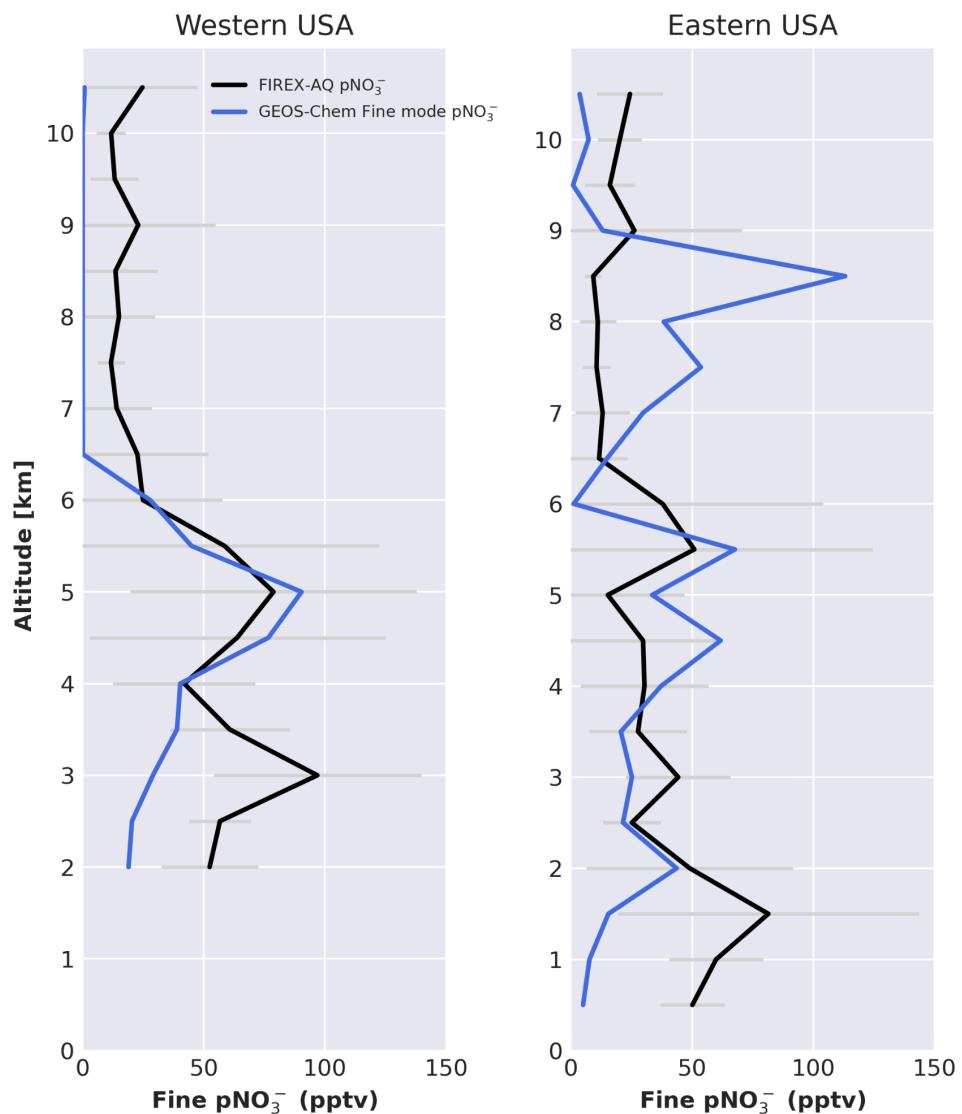


Figure S4. Monthly mean O_3 from Global Atmospheric Watch (GAW) sites (black) compared with simulated O_3 from the 3 simulations.

