

# Evaluation of novel routes for NO<sub>x</sub> formation in remote regions, and the impact on ozone.

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Troposphere ozone (O<sub>3</sub>) is a major atmospheric oxidant and greenhouse gas, and an important precursor of the hydroxyl radical (OH), which determines the atmospheric lifetime of ‘primary’ gaseous pollutants, such as methane (CH<sub>4</sub>), volatile organic carbon species (VOCs) and carbon monoxide (CO). During the catalytic oxidation of these primary pollutants in the presence of reactive nitrogen (NO<sub>x</sub> = NO + NO<sub>2</sub>), ozone is generated. Although a general understanding of tropospheric O<sub>3</sub> chemistry has been reached, there is still a discrepancy between measured and calculated O<sub>3</sub> abundance in remote locations, which is large enough to have captured the attention of the atmospheric chemistry community<sup>1</sup>. Specifically, the failure of current global models to calculate NO<sub>x</sub>, and also difficulties in performing direct NO<sub>x</sub> measurements between several and several tens p.p.t.v. in remote locations, prohibit a complete understanding of O<sub>3</sub> chemistry. Here, we use the near-explicit Master Chemical Mechanism (MCM v3.2) within a box-model framework<sup>2</sup>, to describe the chemistry of NO<sub>x</sub> and O<sub>3</sub> chemistry in remote regions. We explore the impact of a recently discovered renoxification mechanism, namely the photolysis of particulate nitrate<sup>3</sup>, on the abundance of NO<sub>x</sub> and thus the abundance of O<sub>3</sub>. The model was constrained to observations of long-lived species, meteorological parameters and photolysis frequencies. Simulated levels of NO, NO<sub>2</sub>, and delta (O<sub>3</sub>) (change in O<sub>3</sub> concentration during daylight hours) was compared with observations. The model is able to reproduce the NO<sub>x</sub> abundance and delta (O<sub>3</sub>) within the model uncertainty of 20%. Sensitivity tests suggest total reactive nitrogen (NO<sub>y</sub>) abundance, particulate nitrate photolysis rate, halogen chemistry<sup>4</sup> and O<sub>3</sub> abundance could all impact both the diurnal profile of NO<sub>x</sub> abundance, and the NO/NO<sub>2</sub> ratio. The NO abundance, mainly controlled by the new reactive nitrogen cycling mechanism, was always a major, if not dominant, factor controlling the perturbation of the O<sub>3</sub> budget. Our results infer that inclusion of this new NO<sub>x</sub> source in model simulations could improve O<sub>3</sub> predictions in remote regions.

## References

- (1) Parrish, D.D. et al. Long-term changes in lower tropospheric baseline ozone concentrations: Comparing chemistry-climate models and observations at northern mid-latitudes *J. Geophys. Res. Atmos.*, **2013**, 119, 5719–5736, doi:10.1002/2013JD021435.
- (2) Whalley, L.K. et al., The chemistry of OH and HO<sub>2</sub> radicals in the boundary layer over the tropical Atlantic Ocean. *Atmos. Chem. Phys.*, **2010**, 10, 1555–1576.
- (3) Ye, C. et al., Rapid cycling of reactive nitrogen in the marine boundary layer *Nature*, **2016**, doi:10.1038/nature17195.
- (4) Read, K. A. et al., Extensive halogen-mediated ozone destruction over the tropical Atlantic Ocean. *Nature*, **2008**, 453, 1232, doi:10.1038/nature07035.