Uncertain Chemistry: Implications for Hemispheric Transport

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MOTIVATION

Ozone is an air quality pollutant and a short-lived climate forcer, whose impacts are primarily estimated by 3-D model simulations. Simulations are necessary because observations are too sparse in time and space to fully characterize ozone's concentration fields.

- Chemical mechanisms rely on kinetic rates with uncertainty
- Recent literature[3;4] suggests reducing the rate coefficient of $NO_2 + HO^{\cdot} \longrightarrow HNO_3$
- Decreasing k($NO_2 + HO^{\cdot} \longrightarrow HNO_3$) will
  - increase NO_x lifetimes
  - increase ozone production efficiency per unit NO_x
  - increase ozone concentrations
  - alter responsiveness of ozone to changes in emissions

We have quantified how updating $NO_2 + HO^{\cdot} \longrightarrow HNO_3$ changes ozone concentration, ozone responsiveness to emissions, and the source receptor relationships that depend on the spatial distribution of responsiveness. Quantifying the sensitivity to a chemical reaction helps to characterize the uncertainty in assessments of Hemispheric Transport of Air Polution (HTAP).

$NO_2 + HO^{\cdot} \rightarrow HNO_3$ RATE UPDATE

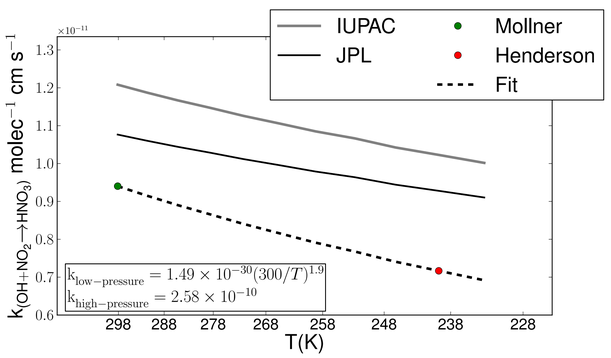
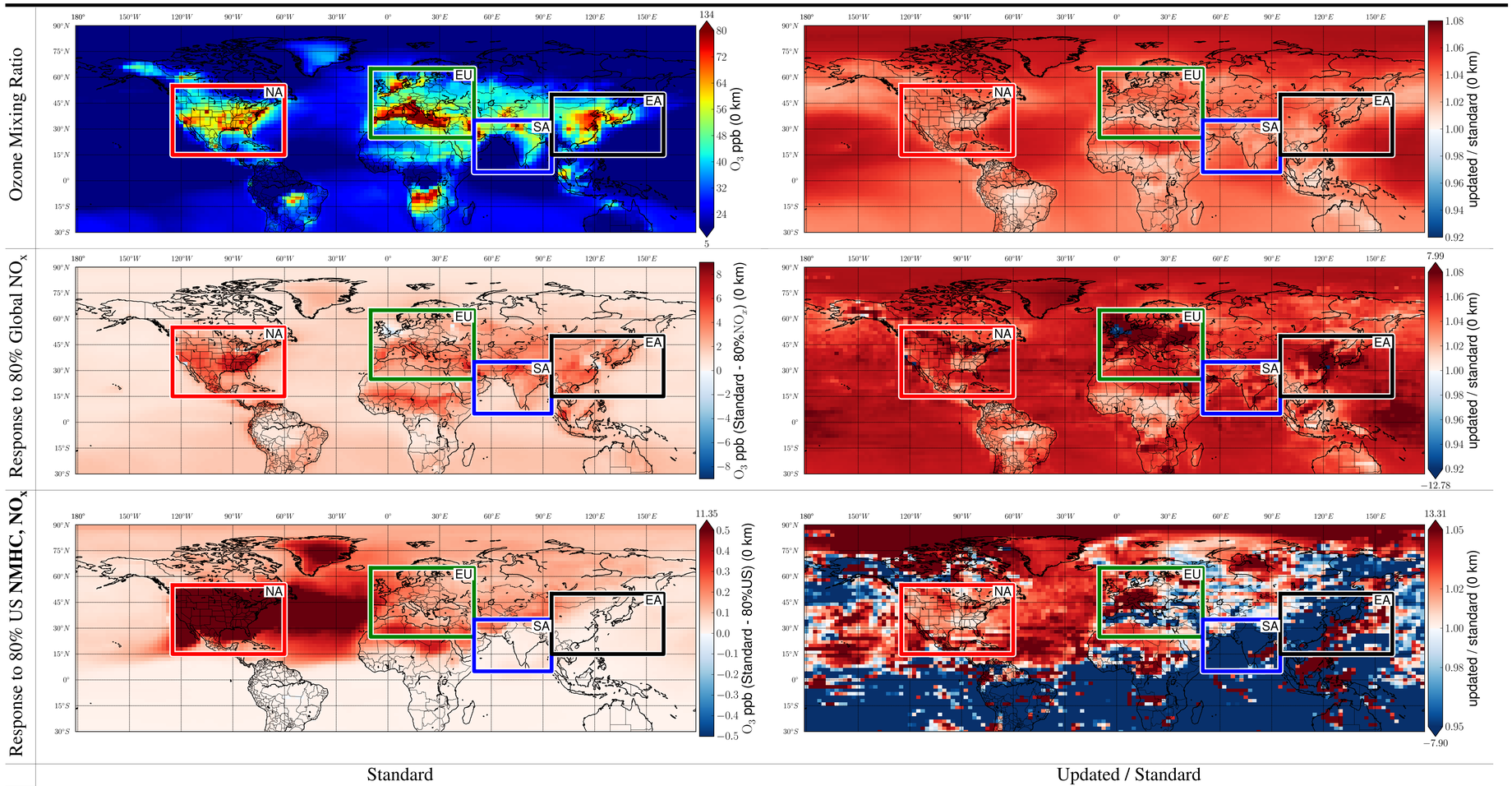


Figure 1: Rate coefficients ($NO_2 + HO^{\cdot} \longrightarrow HNO_3$; IUPAC[1]; JPL[2]; Mollner[3]; Henderson[4]) evaluated at pressures (not shown) and temperatures relevant for the troposphere. Fit line and coefficients (inset) are derived from Mollner and Henderson.

GEOS-CHEM SIMULATIONS

- GEOS-Chem v09-01-01
- 1.5-year spin up
- Results from July-August 2004
- Meteorology GEOS-5
- Standard Emissions
  - BRAVO, EDGAR, MEGAN
  - NEI with ICARTT modifications[5]
- All results are surface concentrations
- Emission Perturbations
  - 6-month perturbation spinup
  - 80%US: US Non-methane hydrocarbon, CO, NO_x set to 80%
  - 80%NO_x: Global NO_x set to 80%
- Contribution or Sensitivity
  - Δ US: BASE - 80%US
  - ΔNO_x: BASE - 80%NO_x
  - Integrated within 4 regions: North America (NA), Europe (EU), South Asia (SA), East Asia (EA)
  - Integration excludes oceans

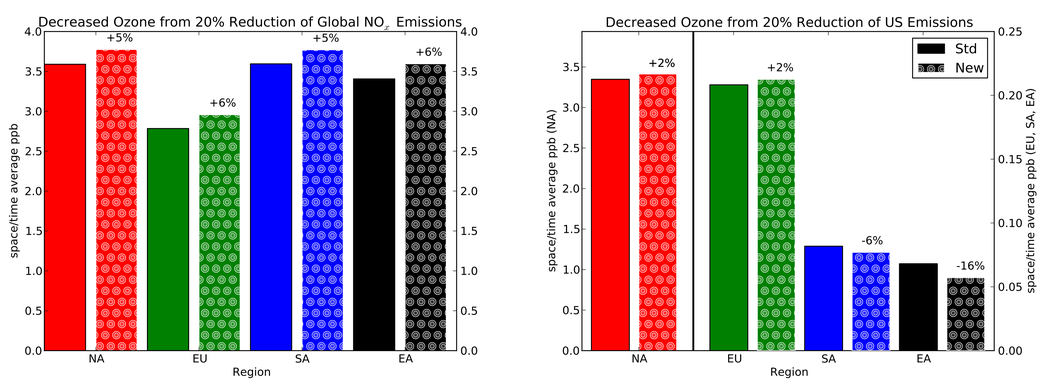
OZONE CONCENTRATION AND OZONE RESPONSES AT SURFACE



Sythesis

- Updated chemistry increases ozone concentrations
- Increases response to NO_x reductions except in large cities (e.g., Los Angeles, Shanghai)
- Increases NA and EU response to US emission reductions
- Decreases SA and EA response possibly due to increased removal of NMHC

REGIONAL MEAN RESPONSE: STANDARD AND UPDATED



SUMMARY

We have quantified the model sensitivity to uncertainty in the $NO_2 + HO^{\cdot} \longrightarrow HNO_3$ reaction rate for ozone concentrations, responsiveness emission reductions, and source/receptor relationships.

1. Ozone increased up to 8% with the largest increases over oceans
2. Regional response of ozone to global NO_x reductions, increased consistently by 5-6%
3. Regional response of ozone to US emission reductions changed by 2 to -16%, with response increasing with distance from the source.

Acknowledgments and References

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