Anthropogenic control over wintertime oxidation of atmospheric pollutants:

the importance of incorporating atypical radical precursors

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Relative importance of radical production from HCHO, ClNO$_2$, HCHO increases
Research Flight 8:

CINO₂ (ppbv) & J O₃ (10⁻⁵ s⁻¹)

3/1/15 6:38am EST
Research Flight 8: *Observed Instantaneous Production of Radicals*

- $\text{ClNO}_2$ 60-80% of the total primary radical source throughout the morning in MBL
• ClNO₂ 60-80% of the total primary radical source throughout the morning in MBL

• Steep drop off in ClNO₂ radical source at altitudes > 1000 m
Modeling the day following peak ClNO$_2$ observations:

- Initialize model at 6:40am, with WINTER measurements, simulation with & without Cl$_y$ chemistry (Riedel et al., 2013)
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- Excluding reactions with Cl$_y$ causes underestimate in the integrated daily radical budget the following day of 1.8 ppbv, or a factor of 3.75
Local secondary impacts of Cl• Chemistry on O₃ and HCHO:
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Including Cl_y reactions causes:

- **114% (0.6 ppbv)** enhancement in HCHO
- **60% (4.7 ppbv)** enhancement in O₃
GEOS-Chem Simulations:

1. **“Standard” emissions & chemistry**
   - Updated $\text{N}_2\text{O}_5$ production following (Shah et al., 2018;).
   - No ClNO$_2$ formation ($\phi_{\text{ClNO}_2}=0$).

**GEOS-Chem v10-01:**
- GEOS - FP: $0.25 \times 0.3125^\circ$
- Simulation period January 16 – March 31, 2015 (Jaeglé et al., 2018)
- Simple SOA scheme

![Map of HCHO: Standard Emissions](image)
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1. **“Standard” emissions & chemistry**
   - Updated N$_2$O$_5$ production following (Shah et al., 2018;)
   - No ClNO$_2$ formation ($\phi_{ClNO_2}$=0)

2. **“High-Oxidant”:**
   - Increased anthropogenic emissions of HCHO (constrained to WINTER obs.)
   - Allow production of CINO$_2$
Global impacts of neglecting, *incorrectly estimating* atypical radical precursors:

- 16.5% - 50% underestimates in OH
- 1-5% underestimates in $O_3$ (~2 ppbv)

*All impacts are underestimated given factor of 2 underestimate in simulated $[\text{ClNO}_2]$*
Global impacts of neglecting, *incorrectly estimating* atypical radical precursors:

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Key Conclusions:

- In the polluted winter BL, ClNO$_2$ is *the* dominant radical source, with significant primary & secondary chemical impacts
- Critical to include & correctly estimate atypical radical precursors in models