Constraining modeled remote oxidation capacity with ATom observations

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Global oxidation capacity is generally defined by the global mean concentration of OH

- Models tend to overestimate OH/underestimate the CH₄ lifetime (~11 yrs).
- Main sinks = CO and CH₄.
- Models are also biased low in CO (Shindell et al., 2006).
- GEOS-Chem has a low bias in CO (~7 ppb in the Northern Hemisphere against NOAA flasks).

Monthly methane lifetime across 8 POLMIP models

Nicely et al., 2017
ATom provides a unique dataset to constrain global models

ATom-1: Jul-Aug 2016  ATom-3: Sep-Oct 2017
ATom-2: Jan-Feb 2017  ATom-4: Apr-May 2018

100+ measurements: CO, CH$_4$, H$_2$O, ozone, NO$_x$, OH reactivity, VOCs, halogens

Interpret observations with GEOS-Chem 12.3.0 at 2°x2.5°
Anticipated biases in OH are not generally present during ATom

- Model captures seasonality.
- Hemispheric ratio during ATom-1 and ATom-2 (4 & 0.5) are well-simulated.
- Uncertainties in measurement are large.

P.I. B. Brune
Wintertime NO\textsubscript{y} is biased, but does not reflect emissions biases

- Maximum NO\textsubscript{y} in the UT summer due to lightning.
- Little variability between winter and summer NO\textsubscript{y}.
- Model overestimates NH wintertime NO\textsubscript{y} by 2x.
- Scaling US and Asian inventories does not improve this bias.
- Sea salt chloride is displaced to HCl by HNO\textsubscript{3} (Wang et al, 2018).
- Reduces global OH, but results in low ozone against observations.
- Photolysis of sea salt nitrate (Kasibhatla et al, 2018) mitigates this effect.
- Key drivers of OH (water vapor, photolysis, ozone, NO\textsubscript{y}) during are well-simulated.
Calculated OH reactivity (cOHR) is well represented in the model except for acetaldehyde.

- Model captures seasonality.
- Underestimates cOHR by ~15%.
- Observed OVOC = 36%.
- Model OVOC = 24%.

*Other= ethanol, C₃H₆, C₂H₆, acetone, >C₃ aldehydes, MEK, MVK/MACR, benzene, toluene, >C₄ alkanes, NOₓ, HNO₃, DMS

Measurement groups: Harvard QCLS, NOAA Picarro, Caltech CIMS, NASA ISAF, NCAR TOGA, NOAA NOyO3, UCATS, ATHOS, UCI WAS
Underestimate in acetaldehyde throughout the troposphere despite short lifetime (< 1 day)

Pl. E. Apel
Acetaldehyde underestimate is consistent with observed peroxyacetic acid (PAA)

Acetaldehyde is a major precursor of peroxyacetyl radical (MCO3).
• MCO3 + HO₂ → PAA
• MCO3 + NO₂ → PAN
Could an unknown long-lived precursor resolve acetaldehyde bias?

- Add 100 Tg yr\(^{-1}\) of an unknown VOC from biomass burning, anthropogenic activity, or ocean emission.
- Can’t resolve summertime bias in the Northern Hemisphere.
- Would need a much larger perturbation in summer.
- “Mystery VOC” concentrations range from 2-10 ppb.
Conclusions

• Model simulation of remote OH is generally unbiased with the exception of overestimated \( \text{NO}_y \) attributed to a missing sink of \( \text{HNO}_3 \) on seasalt aerosol.
  • Photolysis of particulate nitrate may counter the impact of this sink on ozone & OH.

• OVOC makes up > 25% of remote calculated OH reactivity.

• The model underestimates OVOC reactivity largely due to acetaldehyde. ATom provides new evidence that this bias is real from measurements of peroxyacetic acid.

• As previously suggested, a large, diffuse VOC would be required to produce this acetaldehyde. A constant source from biomass burning, anthropogenic emissions, or the ocean can’t resolve the summertime NH bias.

• It appears likely that model biases in OH must be due to excessive OH over land.
Northern Hemisphere

Altitude, km

HCHO, ppt

Southern Hemisphere

Altitude, km

HCHO, ppt

ATom-1 (Summer)

ATom-2 (Winter)

ATom-1 (Winter)

ATom-2 (Summer)

Observation

Model

Improve Ocean VOCs

+Add Fire VOC

+Add Ocean VOC

+Add Anth VOC

+Photolyze OA
NO_y bias may be resolved with chlorine chemistry

ATom-2 Northern Hemisphere

Observations
Model
+Chlorine
+Photolyze NITs

Altitude, km
HNO_3, ppt
O_3, ppb
NO_y, ppt
GEOS-Chem vs. MOPITT