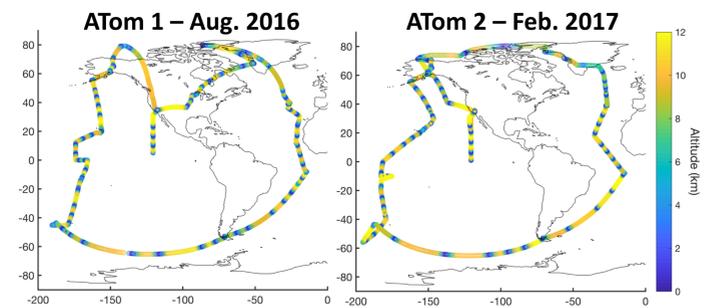


New Constraints on Remote Tropospheric Budgets of Oxidized VOCs

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Background

• NASA's **Atmospheric Tomography (ATom)** mission provides a unique opportunity to test atmospheric models against a new dataset of remote tropospheric observations.



• Here, we run simulations of ATom 1 & 2 using the chemical transport model **GEOS-Chem v11-02d1** to test species' budgets and process perturbations within the model for their effects on remote tropospheric outcomes.

• We evaluate simulated daytime averages over flight tracks and **point-by-point comparisons** with measurements of oxidized volatile organic compounds (OVOCs) from three instruments:

- Caltech Chemical Ionization Mass Spectrometer (CIMS),²
- NOAA Trace Organic Gas Analyzer (TOGA),³
- NASA In-Situ Airborne Formaldehyde instrument (ISAF).⁴

Methanol Sensitivity Studies

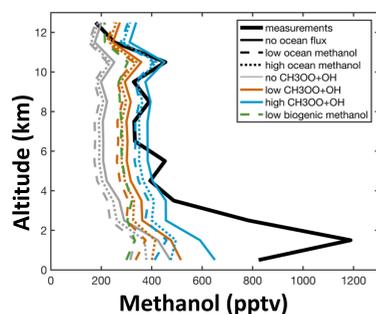
• We test the influence of aspects of methanol chemistry that have been analyzed in past studies¹¹⁻¹² by changing **biogenic emissions**,⁵ **air-sea exchange**,¹³⁻¹⁴ and **CH₃OO[•] + OH** rates and methanol yield.¹⁵⁻¹⁹

• Even the highest methanol yields tested from all three sources are together **insufficient to match high measured methanol**.

Below: Linear fits between measured (x) and modeled (y) methanol from remote samples without biomass burning influence, using 2° × 2.5° simulations with various CH₃OO[•] + OH rates and yields, seawater methanol, and biogenic emissions

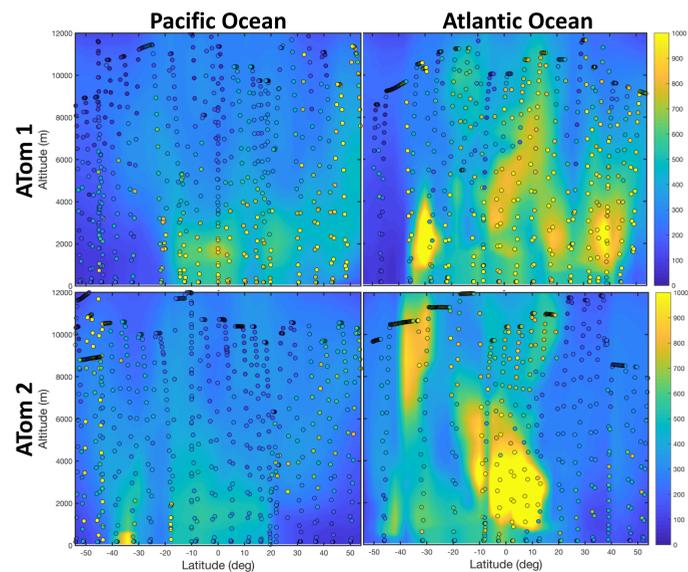
Methanol Simulation Parameters			Model-meas. fits	
CH ₃ OO [•] + OH ^a	air-sea flux ^b	biogenic ^c	Slope	R ²
none	high	base	0.47	0.66
Müller ¹⁶	high	base	0.51	0.71
new	high	base	0.55	0.73
new	low	base	0.54	0.72
new	none	base	0.59	0.72
new	high	new	0.37	0.44

^anone = no reaction; Müller = $k_{OH} = 2.8 \times 10^{-10}$, $\gamma = 10\%$; ¹⁶new = optimized with box model of ATom data, $k_{OH} = 1.6 \times 10^{-10}$, $\gamma = 30\%$. ^bnone = no exchange, low = 40 nM/L, high = 120 nM/L; ^cbase = MEGAN v2.1, new = from Wells *et al.* 2012⁵



Left: Vertical profiles of measured and modeled methanol over all of ATom 1 & 2, excluding points with biomass burning influence, with various simulation parameters

Model-Measurement Comparisons



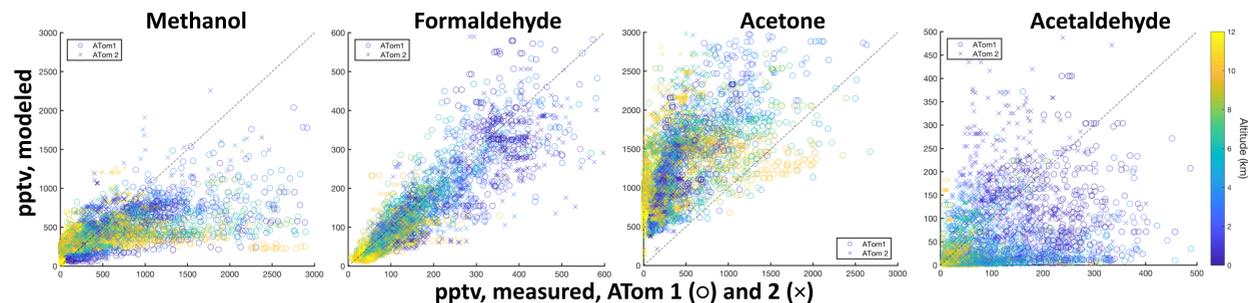
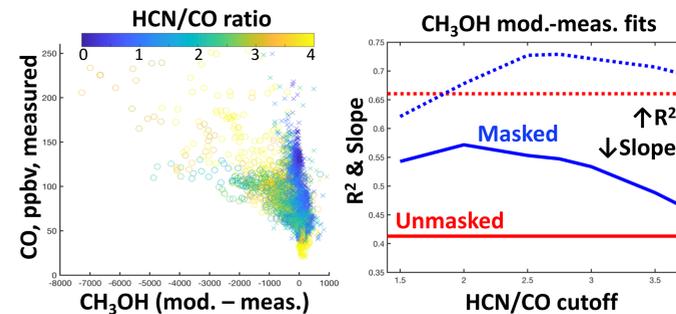
Above: spatial patterns of modeled (background, 2° × 2.5°) and measured (dots, TOGA) methanol; **Right:** correlation of model-measurement difference in methanol concentrations with HCN, a biomass burning tracer; **Far right:** improvement in model-measurement agreement (slope and R² of linear fit) when points above a given HCN/CO ratio (x axis) are excluded (blue) vs. when all points are included (red); **Below:** scatterplots of all ATom 1 and 2 measured (TOGA/ISAF) and modeled (2° × 2.5°) concentrations of methanol, formaldehyde, acetone, and acetaldehyde.

• GEOS-Chem tends to accurately capture spatial patterns (left), but **consistently underestimates methanol** and **overestimates acetone** (below).

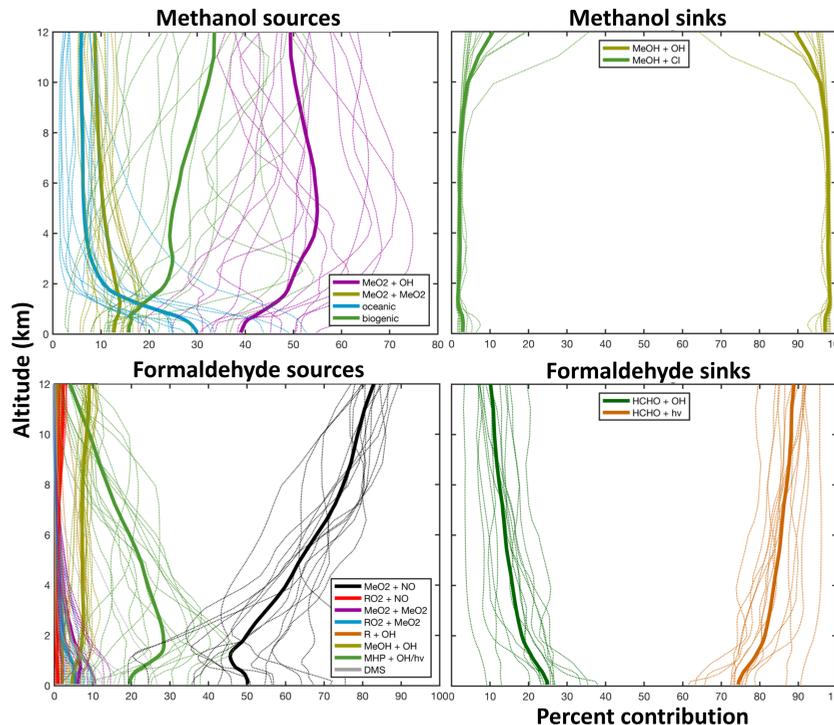
• Underestimates of CH₃OH⁵ and HCHO⁶⁻¹⁰ have been observed previously in the remote troposphere; implicated sources include organic aerosol oxidation and multigenerational chemistry of larger VOCs.

• Model-measurement differences show **strong covariances**; even OVOCs not directly connected by sources & chemistry are over/underestimated together.

• **Biomass burning** contributes substantially to model-measurement biases, especially for methanol, as observed with HCN and CH₃CN correlations (below).



Formaldehyde & Methanol Budgets



• To diagnose remote budgets of CH₃OH, HCHO, and CH₃OO[•], we compute the fraction of each compound produced and destroyed by all competing reaction along the ATom flight paths.

• The model underestimate of CH₃OH correlates most strongly with the fraction of CH₃OH from **biogenic emissions**, suggesting they are either too low in the model or insufficiently transported.

• The model underestimate of HCHO correlates most strongly with the fraction of HCHO produced in the reactions of CH₃OOH (OH and *hν*) and of CH₃OO[•] with other peroxy radicals.

Left: Percent contributions of source/sink pathways to the budgets of methanol, formaldehyde, and CH₃OO[•] along each ATom flight track (thin dotted lines) and averaged over ATom 1 and 2 (thick solid lines).

Model Resolution

• This study and previous work²⁰⁻²¹ suggest that model underestimates may be due to **insufficient transport from continental sources**, possibly due to the inability to model strong concentration gradients at low spatial resolution.

• To test this, we run simulations at various **horizontal resolutions** with the same chemical mechanism.

• Simulations run at 2° × 2.5° horizontal resolution give **increased remote oceanic concentrations** of species with continental sources relative to 4° × 5° simulations, but the difference is insufficient to explain the full model-measurement discrepancy.

Below: Parameters of linear fits between measured (x) and modeled (y) mixing ratios, from remote samples without biomass burning influence.

Species	4° × 5° Model vs. Meas.		2° × 2.5° Model vs. Meas.	
	Slope	R ²	Slope	R ²
Methanol	0.53	0.68	0.55	0.73
Formaldehyde	0.75	0.83	0.75	0.87
Acetone	1.77	0.53	1.90	0.61
Acetaldehyde	0.46	0.46	0.48	0.50
Peroxyacetyl Nitrate	0.80	0.63	0.93	0.64
Peroxyacetic Acid	0.09	0.44	0.11	0.47
CH ₃ OOH	0.49	0.82	0.49	0.83
CO	0.78	0.81	0.78	0.85

References & Acknowledgments

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- Bey, I. *et al.* 2001, *J. Geophys. Res.* - Atmos. (10.1029/2001JD000807)
- Crounse, J. D., *et al.* 2006, *Anal. Chem.* (10.1021/ja0604235)
- Apel, E., *et al.* 2003, *J. Geophys. Res.* (10.1029/2002JD003199)
- Cazorla, M., *et al.* 2015, *Atmos. Meas. Tech.* (10.5194/amt-8-541-2015)
- Wells, K. C., *et al.* 2012, *Atmos. Chem. Phys.* (10.5194/acp-12-5897-2012)
- Helkes, B., *et al.* 2001, *J. Geophys. Res.* (10.1029/2001JD000012)
- Fried, A., *et al.* 2003, *J. Geophys. Res.* (10.1029/2002JD002208)
- Riedel, K., *et al.* 2005, *J. Geophys. Res.* (10.1029/2005JD005859)
- Fried, A., *et al.* 2011, *Atmos. Chem. Phys.* (10.5194/acp-11-11867-2011)
- Anderson, D. C., *et al.* 2017, *J. Geophys. Res.* - Atmos. (10.1002/2016JD026121)
- Jacob, D. J., *et al.* 2005, *J. Geophys. Res.* - Atmos. (10.1029/2004JD005172)
- Milliet2008: Millet, D. B., *et al.* 2008, *Atmos. Chem. Phys.* (10.5194/acp-8-6887-2008)
- Singh2003: Singh, H. B., *et al.* 2003, *Atmos. Chem. Phys. Lett.* (10.5194/acpl-1-1993-2003)
- Wells2014: Wells, K. C., *et al.* 2014, *Atmos. Chem. Phys.* (10.5194/acp-14-2555-2014)
- Bossolasco, A., *et al.* 2014, *Chem. Phys. Lett.* (10.1016/j.cpl.2013.12.052)
- Müller2016: Müller, J.-F., *et al.* 2016, *Nature Comm.* (10.1038/ncomms13213)
- Yan, C., *et al.* 2016, *J. Phys. Chem. A* (10.1021/acs.jpca.6b04213)
- Assaf, E., *et al.* 2016, *J. Phys. Chem. A* (10.1021/acs.jpca.6b07704)
- Assaf, E., *et al.* 2017, *Environ. Sci. Technol.* (10.1021/acs.est.6b06265)
- Eastham, S. D. and Jacob, D. J., 2017, *Atmos. Chem. Phys.* (10.5194/acp-17-2543-2017)
- Zhuang, J., *et al.* 2018, *Atmos. Chem. Phys.* (10.5194/acp-18-6039-2018)