Biosphere-atmosphere exchange of biogenic oxidized volatile organic compounds over a Southeastern United States forest

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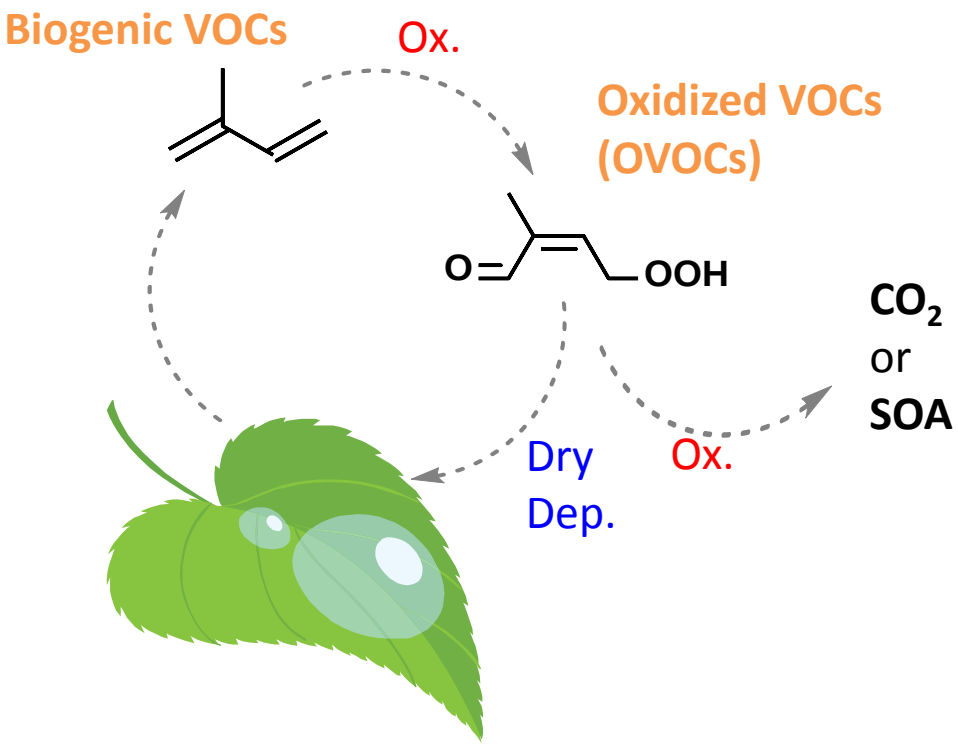
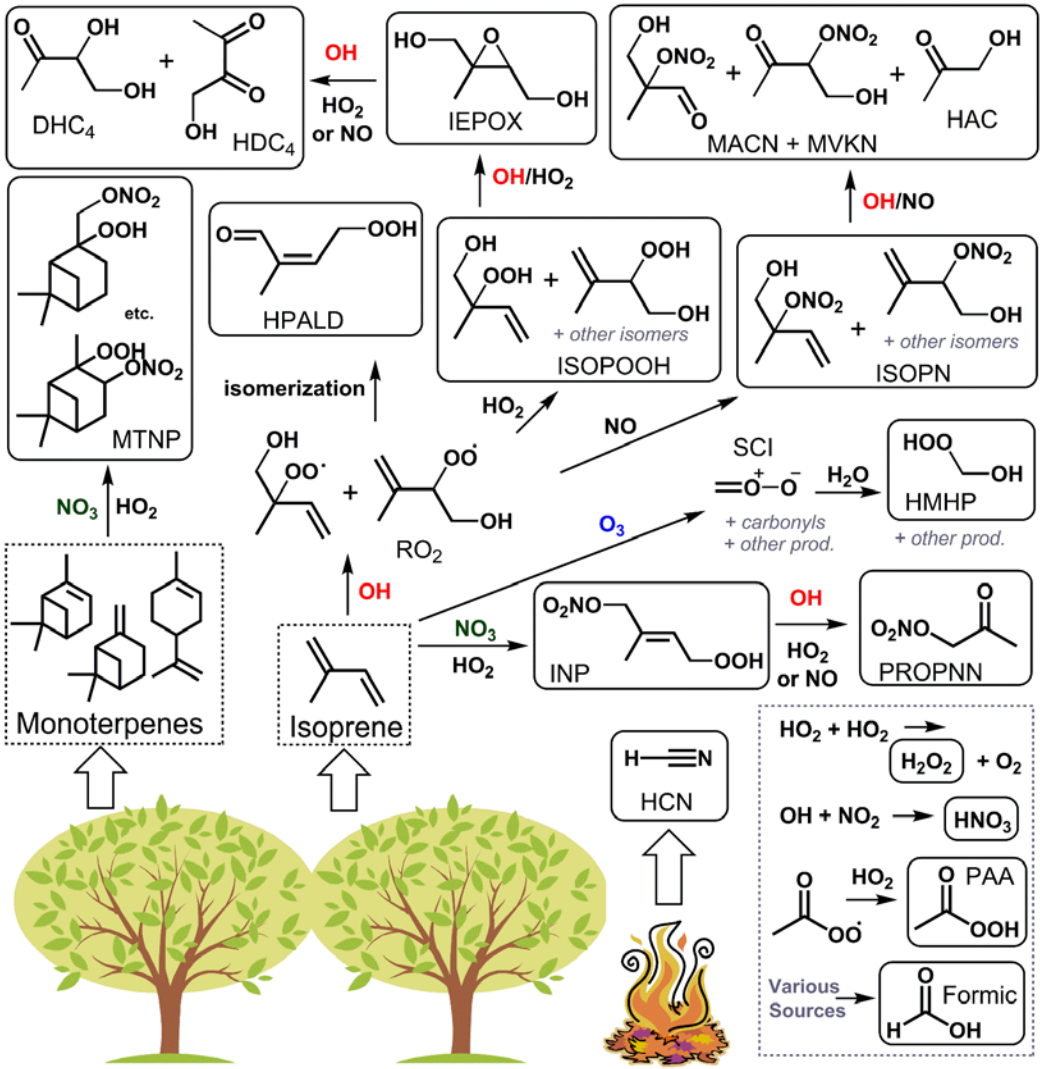
For more information: ***Nguyen et al., PNAS, 2015, 112, E392-E401***

Dry deposition data for most OVOCs are not available – our goal is to directly obtain these data for as many OVOC species as possible



- Is dry deposition of OVOCs ***fast enough*** to impact atmospheric and ecosystem processes?
- The few models that include deposition of some OVOCs do so by extrapolating from SO_2 and O_3 deposition – are they getting the right answers for the right reasons?

The instrument: a time-of-flight CF_3O^- CIMS

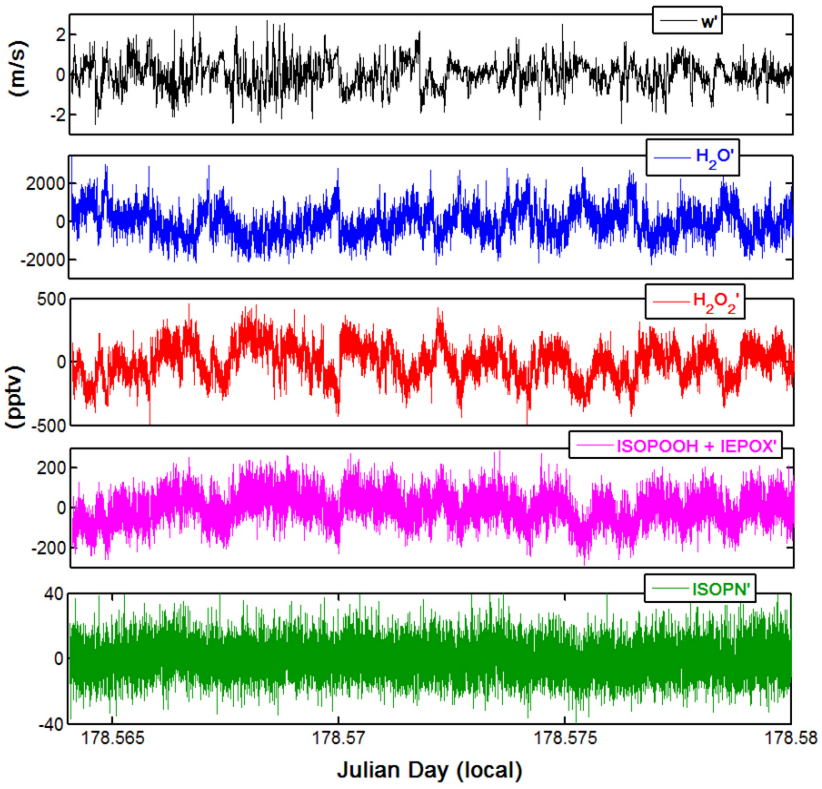


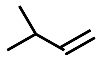
- What makes this measurement novel:
  - **Fast** enough (10 Hz) to measure fluxes via Eddy Covariance
  - Speciate and quantify dozens of OVOCs and some inorganic gases **simultaneously**
  - Measure **hard-to-detect species** like hydroperoxides and multifunctional compounds in-situ

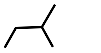
The 10Hz Caltech CIMS was deployed at the 2013 SOAS campaign **in its first attempt** to measure OVOC fluxes

- Campaign period : **Jun – Jul 2013 in Centreville, Alabama (near an NADP site)**
- 20 m tower, 10 m canopy height
- ToF-CIMS instrument, weather station, and sonic anemometer (mounted on top of box)
  - 10 hz measurements of **OVOC fluxes**, **water flux, and heat flux** using Eddy Covariance
- Inlet facing North toward the forest

Measuring canopy fluxes and deposition velocity with eddy covariance







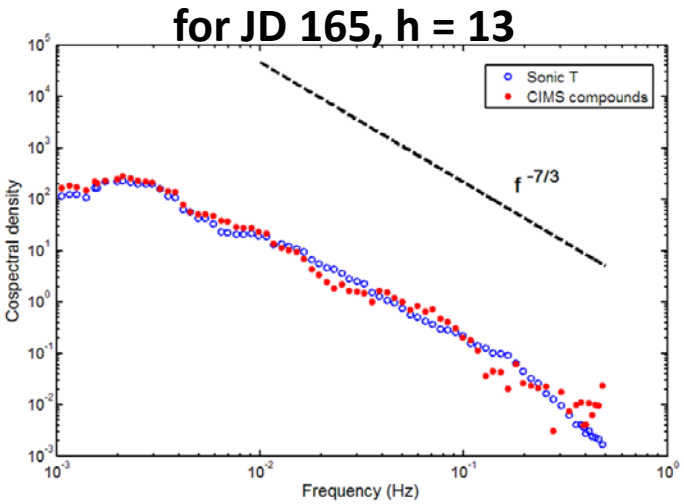
$$F = \overline{w'c'}$$

$$V_d = -\frac{F}{C}$$

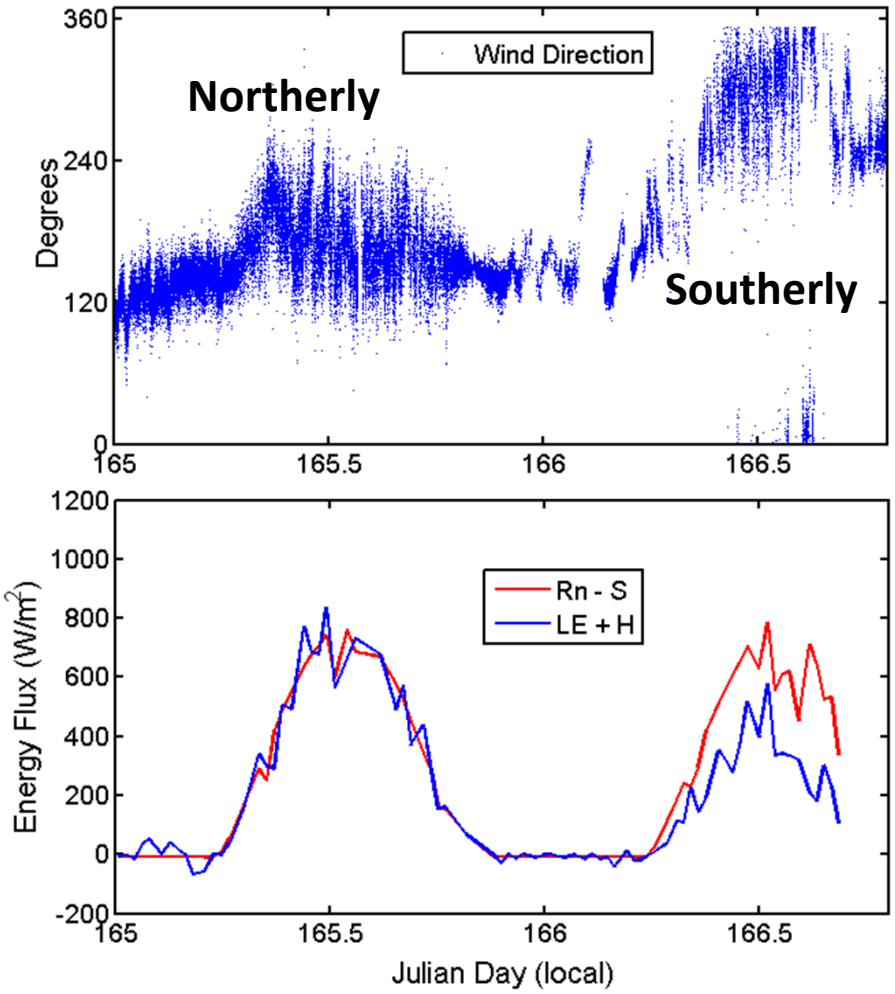
Indications of flux quality

- Out of 30+ days of continuous measurements, only approximately **5 days** were considered ideal
  - Rain, lightning, non-favorable winds, instrument failure, clogged inlets from bugs…

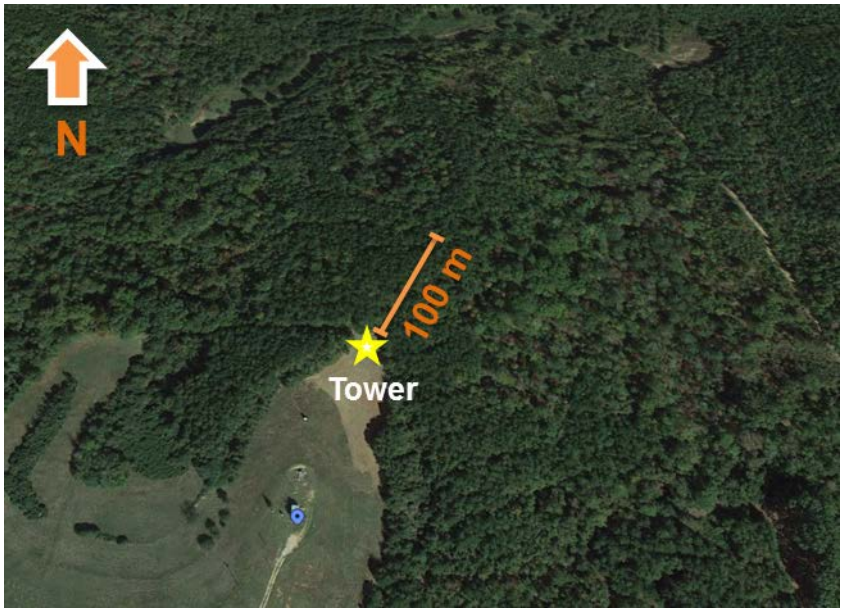
- We used spectral analyses, turbulence assessments, stationarity/intermittency tests
  - However we ended up relying on the **energy balance closure condition** to indicate when which measurements to trust

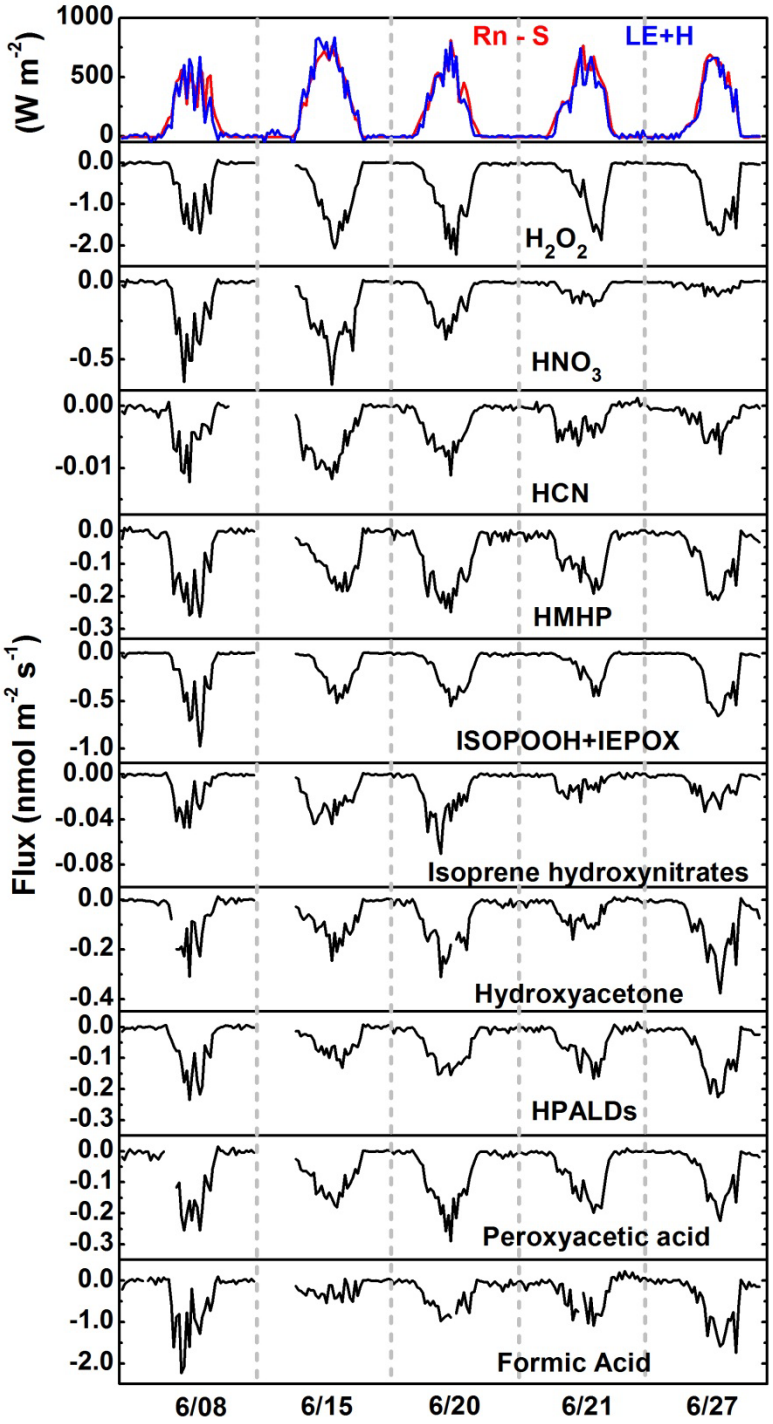


Wind direction effect on Energy Balance Closure



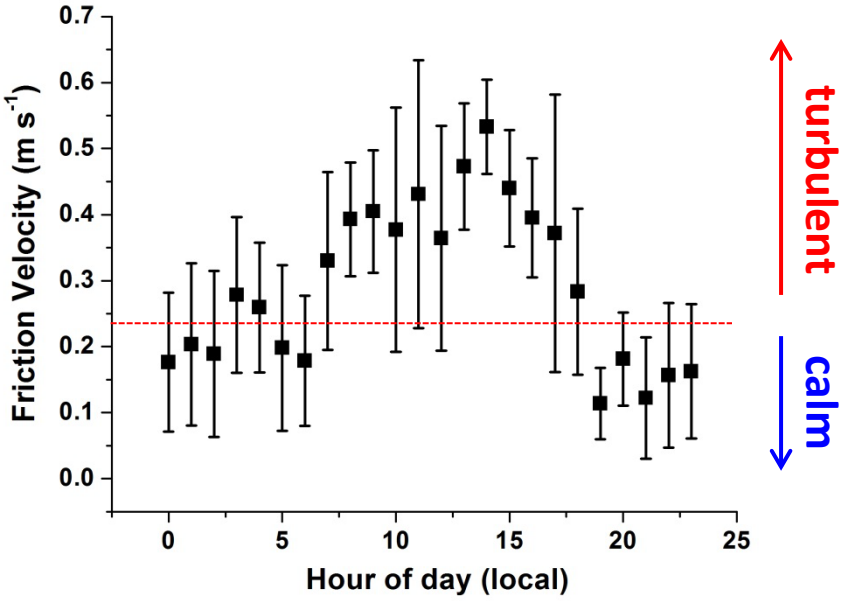
- Some factors that affect fluxes from southerly winds
  - Change in roughness element (forest → grass)
  - Change in geography (hills, forest edge)
  - Physical wind obstruction by tower and enclosure





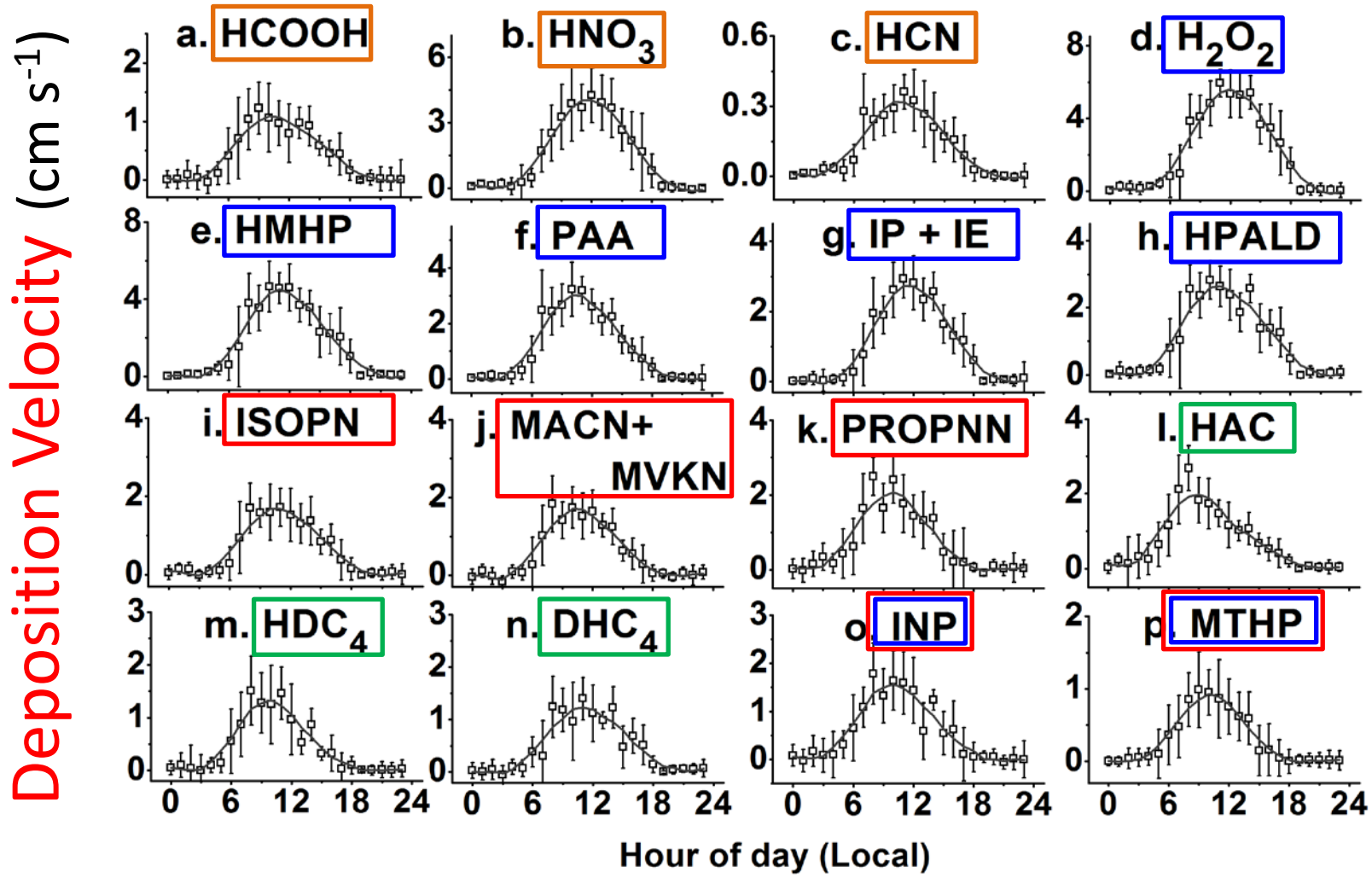
Energy and Concentration Fluxes

- **Reported for days where conditions are favorable, and surface energy balance roughly met**



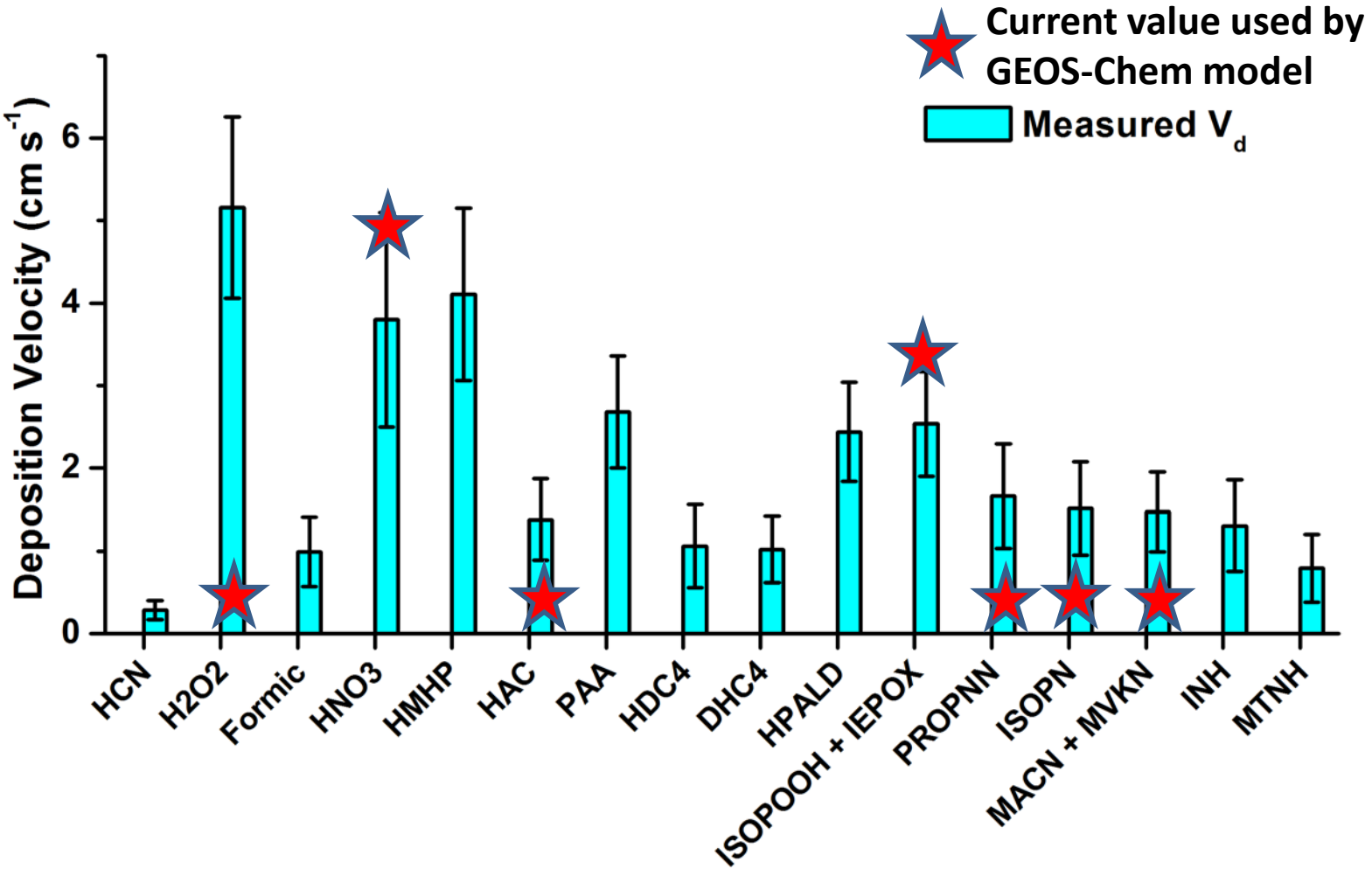
** 0.23 m/s threshold following Reichstein, et al. (2005), *Global Change Biology*, *11*(9), 1424–1439

Acids Hydroperoxides Organic nitrates Hydroxycarbonyls



All of the measured OVOCs deposited faster than ozone, and some as fast as nitric acid

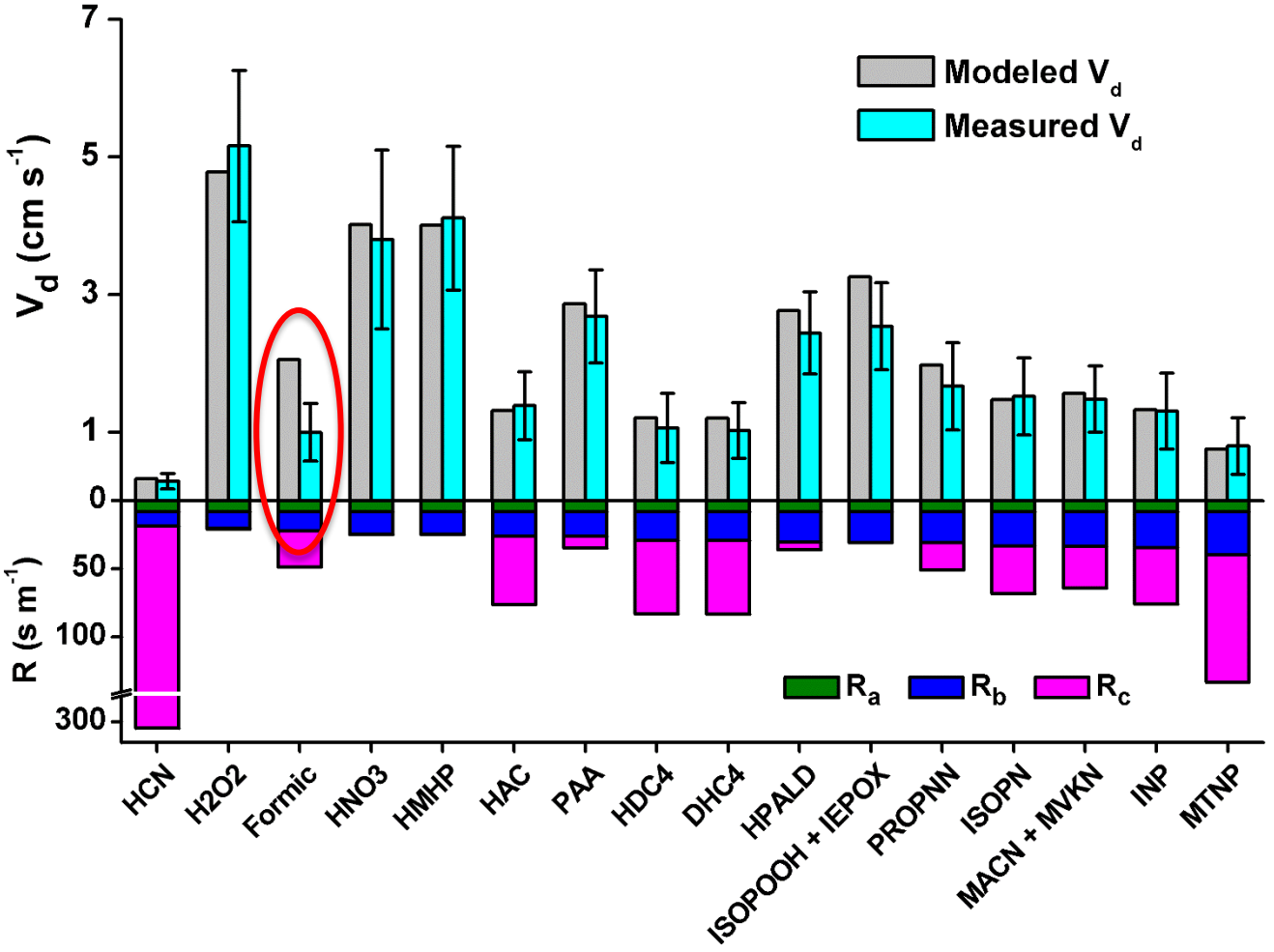
Model vs. measurements



- GEOS-Chem's current resistance-in-series Weseley scheme tends to overestimate surface resistance

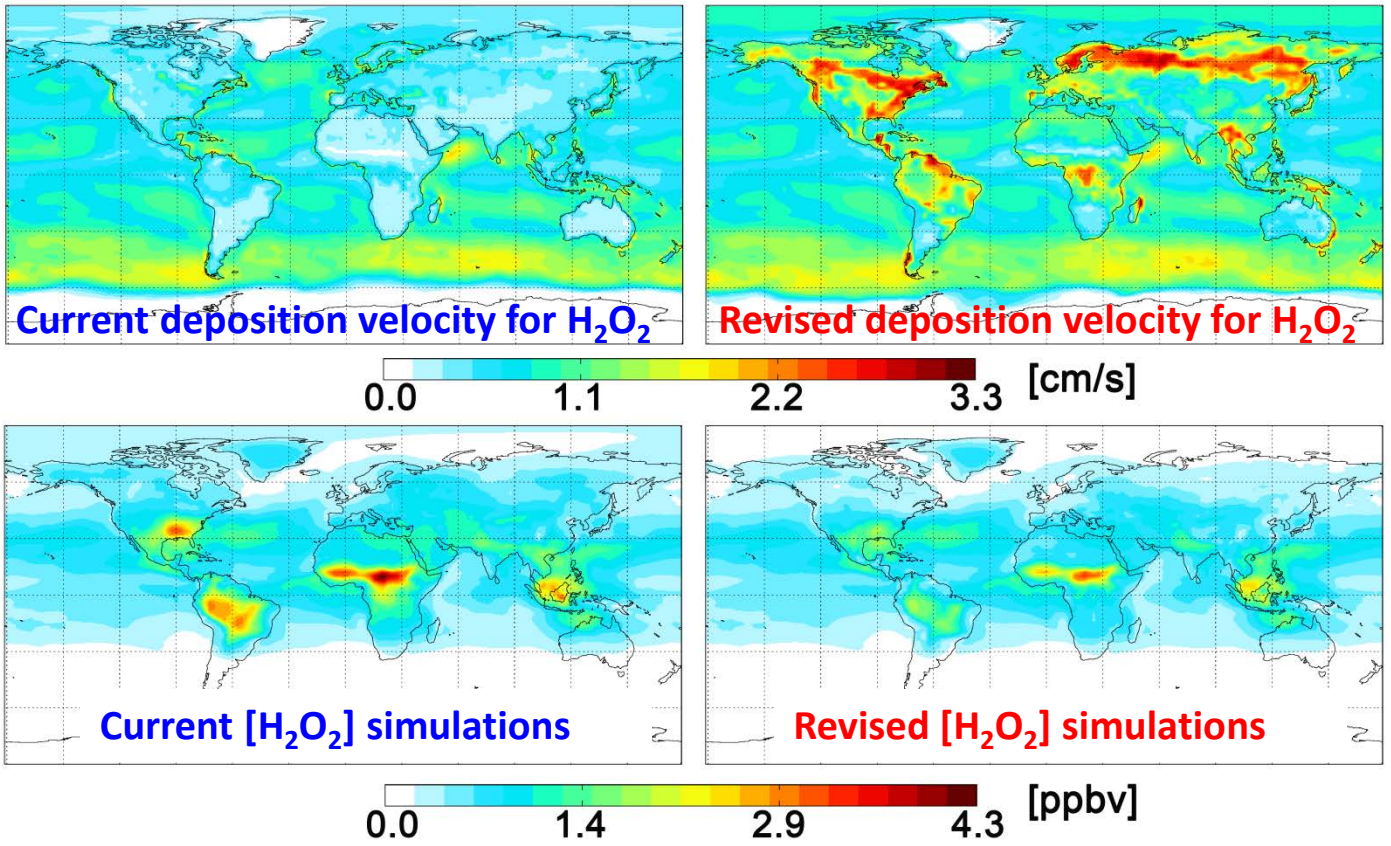
$$V_d = \frac{1}{R_a + R_b + R_c}$$

We used the new observational data to adjust the Weseley Scheme – e.g., increased sensitivity to **Henry's Law Coefficient**



- Now modeled V_d agrees fairly well with observations of both organics and inorganics (high and low H) *…except formic acid*

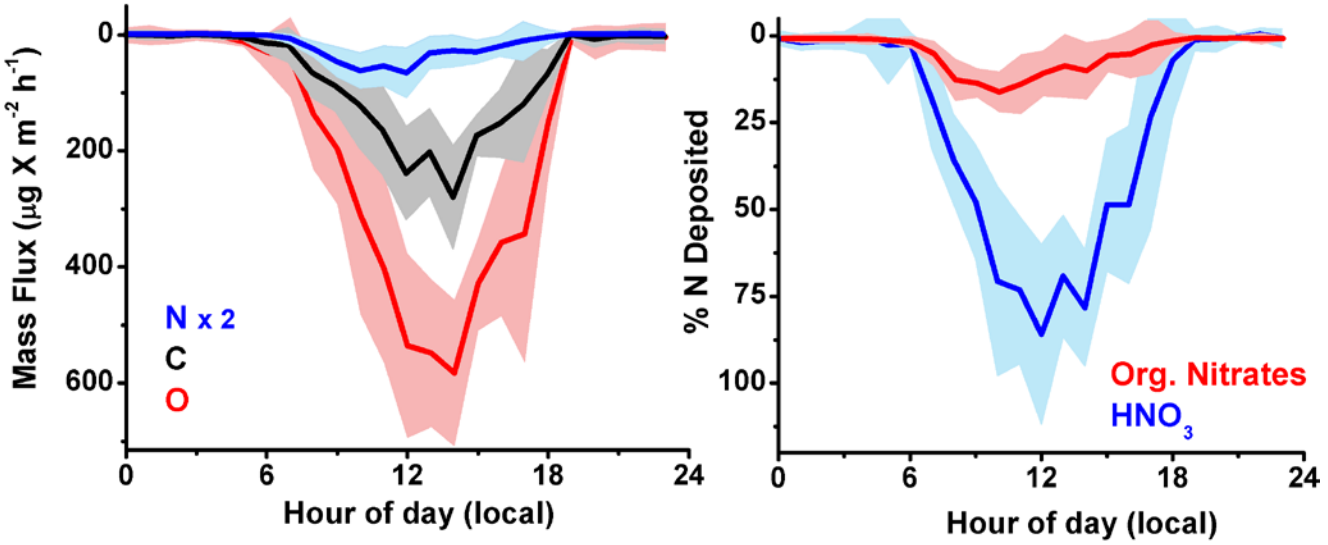
Revised deposition in GEOS-Chem model



Reduces gas phase concentrations in global model by 10 – 50%

- Factor 1 – 4 closer to ground measurements

O and **N** deposition



- O deposition: At least 13% oxidant flux is from OOH groups
- N deposition : measured species total **27 (±15) μgN m^{-2} ·h $^{-1}$**
  - ~ 15% of that is organic N that we measured, may be up to 25% if including organic N we don't measure (estimated from other sites)
- Using NADP data to supplement (AL03 site), we estimate 52% of N downward flux is from dry deposition at this site and time

Closing words

- OVOCs can deposit fairly fast (organic oxidants and nitrogen can be significant fraction of total, depending on site)
- Resistance in series framework works well for organic dry deposition, but need minor adjustments to parameters in models
- More flux data from the TOF-CIMS to come from PROPHET and other field campaigns

Thanks

- SOAS/SAS campaign organizers
- NADP for providing data
- NSF for funding
- Thanks for your attention