Two-way ecosystem-atmosphere exchange of VOCs: New observational constraints from PROPHET-AMOS

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2-way flux of VOCs between land and atmosphere is an important uncertainty in current models.
• How well can we capture the main processes driving emissions and deposition?
• Are we missing a significant portion of the flux?
H$_3$O$^+$ ionization w/ quadrupole interface + high-res TOF

→ highly sensitive high-res mass spectra @ 10Hz

PROPHET 2016
~650 ions detected

Net flux measurements for full mass spectra by eddy covariance

Canopy profiling to assess source/sink distributions

Soil flux measurements via automated chamber
ISOPRENE + MONOTERPENES MORE THAN HALF OF TOTAL UPWARD VOC FLUX

\[ F_{MT}:F_{IS} \] OVERESTIMATED IN MODEL

**Isoprene fluxes ~ 15-25\times monoterpane fluxes**

**Diel isoprene emission**

- Measured
- Modeled

**Diel monoterpene emission**

- Measured
- Modeled

**Compare to 25km nested GEOS-Chem prediction:**
- Model flux underestimated
- But partly due to model temperature bias (~1ºC)

**Daytime monoterpene fluxes well-captured**
- Model overestimates \( F_{MT}:F_{IS} \) by 2\times
- Mismatch in diel cycle
GEOS-Chem UNDERESTIMATES LIGHT DEPENDENCE OF MONOTERPENE FLUX

Temperature dependence of MT flux:
- Statistically consistent between measurement and model
- Temperature + light dependence
- Consistent with prior branch measurements
  - t-β-ocimene major component of MT flux (Ortega, 2007)
- Model underestimates this light dependence
- Overestimate of low-light fluxes
- Implications for daytime vs. nighttime chemistry and VOC fate

Measured
Modeled

Daytime Monoterpene Flux

Model – Measurement Difference
HOW MUCH DO THE FLUXES OF OTHER VOCs MATTER?

**650 ions detected in the mass spectra**

**421 had detectable emission, deposition, or bi-directional flux**

GEOS-Chem: currently tracks ~30 VOC species (some are lumped).

Question: how many of those 421 actually matter for atmospheric chemistry?

**Fraction of nominal flux unaccounted for vs. cumulative number of ions**

Deposition flux carried by much larger suite of species

Very large # of ions with small individual fluxes; what is their cumulative importance?

# of ions to account for cumulative upward flux:
- 10 (90%) 91 (99%) 274 (99.9%)

# of ions to account for cumulative downward flux:
- 36 (90%), 234 (99%), 377 (99.9%)
OXYGENATED VOC: MODEL UNDERESTIMATES BOTH SIDES OF BIDIRECTIONAL FLUX

Mean diel flux for OVOC integrated to date
* caveat: approximate calibration for some!

As an ensemble:
• Emission ~ isoprene
• Daytime flux ↑, nighttime ↓

Example gradient: Formic acid

Model tendency to underestimate the diurnal flux amplitude
• Underestimating gross emissions & gross uptake

Daytime OVOC Flux

Model – Measurement Difference

• Model underestimates magnitude of both

Overall, OVOC fluxes more T- and light-dependent than predicted