Fluxes of Isoprene and its Oxidation Products (and more!) over the Ozarks

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Where the Forest Meets the Sky

Chemistry & Transport

Emissions

Isoprene
Other VOC
NO$_x$

Ozone
Organic aerosol
Acids
Peroxides
Organic nitrates

Climate Coupling
Temperature
Precipitation
CO$_2$

Deposition

Ozone
NO$_y$
Oxidized VOC
CO$_2$
Major Uncertainties

Chemistry & Transport

Measured OH concentrations can exceed models by as much as a factor of 15 in high-isoprene environments (Lu et al., ACP (2012))

Emissions

Isoprene inventories (e.g. MEGAN and BEIS) can differ by factors of 2 or more (Warneke et al., JGR (2010))

Deposition

Altering deposition scheme in CESM reduced E. US summer surface $O_3$ bias by 50% (Martin et al., GRL (2014))
SEAC⁴RS Ozarks Flight

Colored by [HCHO]

Wind direction and flight path indicated.
Flux Legs

direction
E – W
W – E
E – W
W – E

altitude
320 m
430 m
800 m
1100 m
Eddy Covariance

 Flux = \langle w' c' \rangle =
What Can We Do with Fluxes?

Fluxes can provide constraints on the *rates* of boundary layer processes.

\[
\frac{\partial C}{\partial t} = E - D + P - L + \bar{u} \frac{\partial C}{\partial x} - \frac{\partial F}{\partial z}
\]

\[
F(z) = \int_0^z \left( E - D + P - L + \bar{u} \frac{\partial C}{\partial x} - \frac{\partial C}{\partial t} \right) dz
\]
Old Tricks, New Dog

Airborne fluxes are not a new idea . . .

“. . . it may be possible to study such questions as the role of natural versus anthropogenic organics and NO$_x$ in the generation and destruction of ozone . . . by careful measurements of vertical profiles of ozone mean concentration and turbulence quantities.”

- Lenschow et al., JGR (1982)

. . . but we have new questions, and new toys.

<table>
<thead>
<tr>
<th>MMS:</th>
<th>3-D winds, T</th>
<th>ISAF:</th>
<th>HCHO</th>
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<td>Isoprene, MVK+MACR</td>
<td>GTCIMS:</td>
<td>PAN</td>
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<tr>
<td>CTCIMS:</td>
<td>H$_2$O$_2$ , ISOPOOH+IEPOX, HPALD, HNO$_3$, Nitrates, PAA, HAC, . . .</td>
<td>DLH:</td>
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<td>CL:</td>
<td>O$_3$, NO, NO$_2$, NO$_y$</td>
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...Others?
Isoprene

Slope: \( L = k[\text{ISOP}][\text{OH}] \)

\([\text{OH}] = 1.6 \times 10^6 \text{ molec cm}^{-3} \) 
(0.072 ppt)

Ground intercept: Emission

\( E_0 = 964 \text{ ppt m s}^{-1} \)
Hydrogen Peroxide

\[ \text{Slope: } P = k[\text{HO}_2][\text{HO}_2] \]

\[ [\text{HO}_2] = 5.1 \times 10^8 \text{ molec cm}^{-3} \]

(23 ppt)

Ground Intercept: Deposition

\[ V_{\text{dep}} = 5.1 \text{ cm s}^{-1} \]
Ozone and $\text{NO}_x$

**O$_3$ production:**

\[
P_{O_3} = 1.2 \text{ ppb/h} \\
[\text{RO}_2] = 12 \text{ ppt}
\]

**$\text{NO}_x$ lifetime:** 5 hours

**$O_3$ Deposition:** 1.0 cm s$^{-1}$

**$\text{NO}_x$ Emission:** 6.8 ngN m$^{-2}$ s$^{-1}$
Oxidized VOC

Near-identical flux profiles for three gases measured with three separate instruments

Theoretically, we can link oVOC fluxes to isoprene oxidation, e.g. to calculate branching ratios
Spectral Clues

Can we use spectral decomposition to separate competing processes?

- Advection?
- Entrainment?
- Chemistry?
Key Parameters from Ozarks Fluxes

P_{O3} = 1.2 \text{ ppb h}^{-1} \\
\tau_{NOx} = 5 \text{ hours} \\
[OH] = 0.07 \text{ ppt} \\
[HO_2] = 23 \text{ ppt} \\
[RO_2] = 12 \text{ ppt} \\
oVOC Yields: TBD

Future Work:
• Wavelet decomposition
• CAFE 1-D Modeling

ISOP : 8 \text{ mgC m}^{-2} \text{ h}^{-1} \\
NO_x : 6.8 \text{ ngN m}^{-2} \text{ s}^{-1} \\
Ozone : 1.0 \text{ cm s}^{-1} \\
H_2O_2 : 5.1 \text{ cm s}^{-1}
One-Slide Guide to EC

1. Isoprene (ppb) vs. Time (s)
   - Data
   - Mean
   - Linear
   - Smooth

2. Detrend
   - ISOP' (ppb) vs. w' (m/s)

3. Lag covariance
   - \langle w' ISOP' \rangle (ppt m/s) vs. Lag Time (s)

4. Quality
   - Cospectral Power * F vs. Frequency (Hz)
Eddy scale: $10s \times 130 \text{ m/s} = 1300 \text{ m}$
Boundary Layer Profiles

**MIXING RATIOS**

**FLUXES**

![Graph showing mixing ratios and fluxes for Isoprene and HCHO](image)

**Boundary Layer**
Nitric Acid (HNO$_3$)

\[ F(z) = P(OH)z - D \]

**Production:**
\[ P = k[OH][NO_2] \]

**Deposition:**
\[ V_{dep}(HNO_3) = V_{dep}(H_2O_2) \]

(mass-corrected)

Discrepancy likely due to nonstationarity and inlet issues
NOy

![Graph showing NOy with various markers for different substances such as NO, NO2, PAN, HNO3, Sum, and NOy. The graph plots altitude (m agh) on the y-axis and flux (ppt m/s) on the x-axis.](image-url)
CoSpectra Comparison (Leg 1)