Satellite measurements of formaldehyde & what they tell us about Amazonian isoprene emissions & the terrestrial biosphere

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Why are isoprene emissions important in climate?

- Increased $O_3$ (if $NO_x$ high)
- Decreased $O_3$ (if $NO_x$ low)
- Increased $CH_4$ (due to competition for $OH$)
- $\sim$70-80% oxidised to $CO_2$
- Secondary Organic Aerosols

Impact radiative forcing & climate
Impact air quality

Emissions very sensitive to climate and air quality

Isoprene (global) emissions = 400-600 Tg C / yr

Tropics = $\sim$ 70 - 90%

Amazon $\sim$ 30-40% ?
Mapping isoprene emissions from space using HCHO

- Formaldehyde (HCHO) is a significant product of isoprene oxidation.
- Isoprene emissions are main driver of variability in HCHO columns observed from space.
- Use GEOS-Chem CTM to get transfer function to infer top-down emissions.

GOME HCHO slant columns $[\times 10^{16}$ molecules $\text{cm}^{-2}]$
GOME HCHO over the Amazon

Possible to remove pyrogenic contributions using firecount data & elevated NO$_2$ columns.
GOME isoprene emissions over the Amazon

See Barkley et al., JGR, 2008

Time window: 10-12 LT

Top-down isoprene emissions [$10^{13}$ atom C cm$^{-2}$ s$^{-1}$]

Errors ~100%
What drives the isoprene emission variability?

\[ \gamma_T = \frac{E_{\text{opt}} \cdot C_{T_2} \cdot \exp(C_{T_1} x)}{C_{T_2} - C_{T_1} (1 - \exp(C_{T_2} x))} \]

[Graph showing GOME HCHO data and equations related to isoprene emission variability.]
What drives the isoprene emission variability?

*** GOME HCHO from Harvard ***

All months

July-November

\[ \gamma_T = \frac{E_{opt} \cdot C_{T_2} \cdot \exp(C_{T_1} x)}{C_{T_2} - C_{T_1} (1 - \exp(C_{T_2} x))} \]

Guenther et al, [2005] w/out \( T_{15} \) lag
Guenther et al, [2005] \( T_{15} \) lag
Fitted \( C_{T_1} \) and \( C_{T_2} \) w/out \( T_{15} \) lag
Fitted \( C_{T_1} \) and \( C_{T_2} \) with \( T_{15} \) lag
Seasonal Variability

- Scenes contaminated by fire are excluded using firecounts & NO\textsubscript{2} columns.
- Background HCHO, from the oxidation of non-isoprene species, is taken from a GEOS-Chem simulation for the year 2000.
- Satellite data consistent with surface observations of isoprene:
  - ~30% higher in dry season.

HCHO data courtesy of Isabelle De Smedt.

Barkley et al., GRL, 2009
What’s going on?

  - Leaf flushing (new leaf growth) during onset of the dry season
- **EVI** - Huete et al., GRL, 2006.
  - Rainforests green-up with sunlight in dry season
  - Majority of isoprene emitting species undergo leaf flushing prior to dry season in anticipation of light-rich conditions
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How to improve on what’s been done before

- Improved HCHO data with better counting statistics
- High resolution nested model
  - Dual isoprene emission models
  - HCHO chemical tagging scheme
- Bayesian inversion vs. Transfer function approaches
  - Improved error characterization

Aug 2005

OMI ~150 observation per 0.666° x 0.5° grid cell / month

GOME ~15-30 observation per 2.5° x 2.0° grid cell / month

- HCHO data from OMI (20x20km²)
Summary

- **HCHO columns provide key insight to Amazonian isoprene emissions:**
  - Top-down isoprene emissions, despite being highly uncertain, are still valuable!
  - Seasonal variations of HCHO consistent with satellite observations of vegetation activity
    - Data strongly suggest large-scale leaf flushing by majority of isoprene emitters results in annual cessation of isoprene emissions

- **Outlook:**
  - Sustained **long-term** measurement programs are still essential!
  - Integration of flux and concentration measurements with satellite observations
  - Need improved HCHO retrievals:
    - Influence of aerosols on air mass factor
  - Isoprene chemistry:
    - Complex, uncertain and ever evolving
Extra slides
Cumulative HCHO yields from biogenic VOCs

A. Isoprene

\[
\begin{align*}
\text{NO}_x &= 1.0 \text{ ppb} \\
\text{NO}_x &= 0.1 \text{ ppb}
\end{align*}
\]

GEOS–CHEM: \(\cdot\cdot\cdot\)
MCM: \(-\)

B. \(\alpha\)-pinene

C. \(\beta\)-pinene

D. MBO

Palmer et al., 2006
Seasonal variations in HCHO yields

Memphis, USA (90°W 35°N; clear-sky conditions)

Etoumbi, Congo (15°E 0°N; clear-sky conditions)

Bordeaux, France (0°E 45°N; clear-sky conditions)

Manaus, Brazil (60°W 5°S; clear-sky conditions)

Si Sa Ket, Thailand (105°E 15°N; clear-sky conditions)

24-hour MCM v3.1 HCHO yields (solid lines)
Midday MCM v3.1 HCHO yields (dotted lines)

\( \text{NO}_x=0.01 \text{ ppb} \quad \text{NO}_x=0.10 \text{ ppb} \quad \text{NO}_x=0.50 \text{ ppb} \quad \text{NO}_x=1.00 \text{ ppb} \quad \text{NO}_x=5.00 \text{ ppb} \)
An alternative approach...

- **HCHO column data:**
  - New 12 year data set from BIRA-IASB (De Smedt et al., ACP, 2008)
  - GOME: 1996-2002

- **Analysis:**
  - EOF (Empirical Orthogonal Function) Analysis
    - Take a set of time evolving data and separate the variability into standing oscillation patterns (EOFs) and principal components that show how each mode varies with time
  - What does EOF analysis tell us?
    - Most important variability in HCHO columns & therefore of isoprene emissions too

- **Correlative data:**
  - GEOS-4 model temperature, PAR (diffuse & direct), precipitation
  - ATSR / AATSR firecounts
  - MODIS Leaf Area Index (LAI) ➔ size of leaves
  - MODIS Enhanced Vegetation Index (EVI) ➔ colour of leaves
  - Multivariate ENSO Index (MEI) (Wolter and Timlin, 1998)
Where

EOF pattern of mode 1

When

Principal component of mode 1 = 30% of variance

Importance

GEOS-4 Surface Temperature at 2 m altitude

ATSR Firecounts (1997-2007)

HCHO & variable correlation
Where

EOF pattern of mode 1

When

Principal component of mode 1 = 30% of variance

Importance

EOF pattern of mode 2

Principal component of mode 2 = 14% of variance
Where
When
Importance
What is HCHO correlated with over the Amazon?
Modelling overview: GEOS-Chem & MEGAN

Model Biosphere
MEGAN: Model of Emissions of Gases & Aerosols from Nature
✦ Fixed base emission factors for:
  - Isoprene
  - Monoterpenes
  - Methylbutenol
✦ Temporal variability driven by:
  - Temperature
  - PAR (5-layer canopy model)
  - Leaf age
  - Leaf area

Leaf-Area-Index
✦ Monthly AVHRR LAI

Biomass Burning
✦ Monthly estimates of biomass burning from GFEDv2 database

Chemistry
✦ Detailed chemical mechanism of isoprene oxidation

Meteorological Forcing
✦ GEOS v4 assimilation system

PAR, T

Dynamics
✦ Chemistry and transport run at 2x2.5 (lat x lon)
✦ Emissions & Chemistry hourly
✦ Transport: 15 min timestep
✦ Sampled at GOME scenes

GEOS-Chem
Inverting HCHO columns for isoprene emissions

Model Biosphere
MEGAN: Model of Emissions of Gases & Aerosols from Nature
- Fixed base emission factors for:
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GEOS-Chem

Transfer Function

\[ E_{\text{Isop}} \sim \left( \Omega_{\text{HCHO}} - B \right) / S \]
The Linear Transfer Function Approach

**Method 1:**
- Currently method:
  - \( \Omega_{HCHO} = S \times E_{Isop} + B \)
  - Where \( S = d\Omega_{HCHO} / dE_{Isop} \)
  - Simply invert to get the top-down emissions:
    - \( E_{Isop} \sim (\Omega_{HCHO} - B) / S \)

**Method 2**
- New method using tagging scheme:
  - \( \Omega_{all} = \) HCHO column from all sources
  - \( \Omega_{isop} = \) HCHO columns from isoprene oxidation only
    - Background: \( B' = \Omega_{all} - \Omega_{isop} \)
    - Gradient: \( S' = d\Omega_{isop} / dE_{Isop} \)
  - \( E_{Isop} \sim (\Omega_{HCHO} - B') / S' \)
Basic idea is to minimize the difference between the observed (satellite) & the model HCHO columns (a function of the bottom-up emissions; our state vector $x$) by using a cost function:

$$J(x) = (y - Kx)^T S_{\Sigma}^{-1} (y - Kx) + (x - x_a)^T S_{a}^{-1} (x - x_a)$$

- **Observations** = HCHO columns at region $i$
- $K = \frac{\delta HCHO_i}{\delta \text{Emissions}_j}$
- Change in model HCHO columns / change in bottom-up isoprene emissions
- **Observation errors**
  - Assume diagonal; individual error sources are spatially uncorrelated
  - $S_{\Sigma} = S_{\text{instrument (AMF)}} + S_{\text{chemistry (Box-model vs. MCM)}} + S_{\text{transport (estimate)}} + S_{\text{representation (sub-grid variability of } \Omega)}$
- **Top-down isoprene emissions from region $j$**
- **A priori errors of bottom-up isoprene emissions from region $j$**
- **A priori bottom-up isoprene emissions from region $j$**
\[
\text{RO}_2 + \text{NO} \rightarrow \text{RO} + \text{NO}_2
\]

\[
\text{OH} + \text{NO}_2 + \text{M} \rightarrow \text{HNO}_3 + \text{M}
\]

\[
\text{OH} + \text{NO}_2 \rightarrow \text{H}_2\text{O} + \text{RO}_2
\]

\[
\text{VOC} + \text{OH} \rightarrow \text{H}_2\text{O} + \text{RO}_2
\]

\[
\text{NO}_2 + \text{hv} \rightarrow \text{NO} + \text{O}
\]

\[
\text{O} + \text{O}_2 + \text{M} \rightarrow \text{O}_3 + \text{M}
\]

\[
\text{RO} + \text{O}_2 \rightarrow \text{R}^\text{CARB} + \text{HO}_2
\]

\[
\text{RC(O)OO} + \text{NO}_2 \rightarrow \text{PAN}
\]

\[
\text{O}_3 + \text{M} \rightarrow \text{O}_3 + \text{M}
\]

\[
\text{HO}_2 + \text{NO} \rightarrow \text{OH} + \text{NO}_2
\]

\[
\text{HO}_2 + \text{H}_2\text{O} \rightarrow \text{H}_2\text{O}_2 + \text{O}_2
\]

\[
\text{HCHO}
\]

\[
\text{hv}, \text{OH}
\]

\[
\text{HO}_2, \text{CO}, \text{CO}_2
\]
Satellite details

Selection of fitting window!

- Chance et al. 2000: 337.35 – 356.12 nm [GOME]
- De Smedt et al. 2008: 328.50 – 346.00 nm [GOME & SCIA]
- OMI ATBD (Kuroso): 327.50 – 356.50 nm [OMI]

<table>
<thead>
<tr>
<th>Parameter</th>
<th>GOME-2</th>
<th>Other Instruments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Spectral Resolution (Formaldehyde/glyoxal)</td>
<td>0.28/0.54 nm</td>
<td>0.17/0.29 nm - GOME 0.26/0.44 nm - SCIAMACHY 0.42/0.63 nm - OMI</td>
</tr>
<tr>
<td>Global Coverage</td>
<td>~daily</td>
<td>3 days - GOME 6 days - SCIAMACHY Daily - OMI</td>
</tr>
<tr>
<td>Ground Pixel</td>
<td>40 x 80 km²</td>
<td>40 x 320 km² - GOME 30 x 60 km² - SCIAMACHY 13 x 12 (13 x 128) km² - OMI</td>
</tr>
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