Biogenic VOC emissions modeling: Implications for aerosol formation

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Workshop on Aerosol-Climate Interactions
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Talk Outline

1. What are VOC and where do they come from?
2. How do we model these emissions?
3. Importance for atmospheric chemistry and climate
4. Case study - Isoprene measurements during the AMMA campaign
5. Biogenic aerosol-climate feedbacks
1. VOC Introduction

What are VOC?

VOC = Volatile Organic Compounds

Hydrocarbons (C+H)
- Alkanes
- Alkenes
- Aromatics

Oxygenated Hydrocarbons (C+H+O)
- Aldehydes
- Ketones
- Alcohols

\[ R = \text{alkyl group} \quad -\text{CH}_3 \]
1. VOC Introduction

What are sources of VOC?

- Anthropogenic (caused by humans)
  - Wood-Burning Stoves
  - Power Plants
  - Cars and Trucks

- Biogenic (natural)
  - Forest Fires
  - Natural Sources
1. VOC Introduction

What are sources of VOC?

Globally, biogenic VOC are an order of magnitude greater than anthropogenic VOC.

<table>
<thead>
<tr>
<th>Emission (Tg yr(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Anthropogenic VOC</td>
</tr>
<tr>
<td>Biogenic VOC</td>
</tr>
</tbody>
</table>

Seinfeld and Pandis, 1998
1. VOC Introduction

Why do plants emit VOC?

- Different vegetation species emit different chemical species of VOC
- Examples:
  - Floral scents (blossoming trees, flowers)\(\text{\textbackslash oxygenated \textit{VOC}}\)
  - Pine needles \(\text{\textbackslash hydrocarbons (terpenes)}}\)

- Different chemical species have different emission mechanisms - no one-size-fits-all answer!
- Several biogenic VOC emissions that are atmospherically important…
1. VOC Introduction

**Species of Biogenic VOC**

Biogenic VOC = natural VOC emissions from vegetation

<table>
<thead>
<tr>
<th>Species</th>
<th>Emission (Tg yr⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Isoprene</td>
<td>503</td>
</tr>
<tr>
<td>Monoterpenes</td>
<td>127</td>
</tr>
<tr>
<td>Other reactive VOC</td>
<td>260</td>
</tr>
<tr>
<td>Isoprene (a monoterpene)</td>
<td>β-pinene</td>
</tr>
<tr>
<td>Other VOC</td>
<td>260</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td><strong>1150</strong></td>
</tr>
</tbody>
</table>

Seinfeld and Pandis, 1998
1. VOC Introduction

Biogenic VOC Emissions

Emissions are dependent on environmental factors

**LIGHT**

**TEMPERATURE**

**LAND COVER (vegetation type)**
1. VOC Introduction

Biogenic VOC Emissions

- Isoprene ($C_5H_8$)
  - Deciduous trees
  - Light and temperature dependent
  - Emissions linked to photosynthesis

- Terpenes ($C_{10}$ compounds)
  - Coniferous trees and shrubs
  - Temperature dependent
  - Emitted from resin pools on needle leaves

- Methylbutenol (MBO)
  - Coniferous trees
  - Light and temperature dependent

- Other VOCs
  - Methanol
  - Acetone
  - Acetaldehyde
2. Modeling BVOC Emissions
Initial modeling method

\[ Flux = EF \cdot D \cdot f(T) \cdot f(L) \]

EF = Emission factor
D = Foliar density
f(T) = Temperature dependence
f(L) = Light dependence
2. Modeling BVOC Emissions

MEGAN Model (Guenther et al., 1996)

\[ Flux = \varepsilon \cdot \gamma \cdot \rho \]

\[ \gamma = \text{LAI} \cdot \gamma_P \cdot \gamma_T \cdot \gamma_{age} \cdot \gamma_{sm} \]

\(\varepsilon\) = emission factor map (mg m\(^{-2}\) hr\(^{-1}\))
\(\gamma\) = activity factor
\(\rho\) = production and loss within the canopy

Or, emissions are a function of:
1. LAI (leaf area index)
2. Light (P=PPFD=photosynthetic photon flux density)
3. Temperature (T)
4. Leaf age
5. Soil moisture (sm)
2. Modeling BVOC Emissions

MEGAN - Isoprene Emission Factor Map ($\varepsilon$)

Baseline isoprene emission fluxes ($\mu g m^{-2} hr^{-1}$)

Need to be modified for temperature, light, soil moisture, LAI, etc…
2. Modeling BVOC Emissions
MEGAN - LAI

Emissions increase with increasing LAI until saturation at around 5 $m^2 \cdot m^{-2}$
2. Modeling BVOC Emissions
MEGAN - Light ($\gamma_P$)
2. Modeling BVOC Emissions
MEGAN - Temperature ($\gamma_T$)
2. Modeling BVOC Emissions
MEGAN - Age ($\gamma_{\text{age}}$) and Soil Moisture ($\gamma_{\text{sm}}$)

- **Age**
  - As leaves get older, photosynthesis (and emission processes become less efficient)
  - Divide the canopy into new (no emissions), growing (moderate emissions), mature (peak emissions) and old (reduced emissions)

- **Soil moisture**
  - emissions are reduced under soil moisture stress and cease during drought
  - couple emissions to CLM soil moisture
2. Modeling BVOC Emissions

MEGAN - Canopy loss and production ($\rho$)

- All species emitted from the canopy do not escape to the atmosphere
- Can react within the canopy before ever escaping

\[
\rho_{ISO} = 1 - \frac{D}{\lambda u^* \tau + D}
\]

$D =$ canopy depth (m)
$u^*$ = friction velocity (m/s)
$\tau =$ above canopy isoprene lifetime (s)
$\lambda =$ empirical parameter
2. Modeling BVOC Emissions

MEGAN - Global Isoprene Emissions

Guenther et al., 2006
2. Modeling BVOC Emissions
Evaluating the model vs. ground-based data

- Emission factors based on ground-based measurements
  - Leaf level enclosures
  - Branch level enclosures
- Model evaluated versus measurements
  - Flux towers
  - Ambient concentrations

Flux tower at University of Michigan Biological Station (UMBS)
2. Modeling BVOC Emissions

Diurnal cycle of Light and T dependent Emissions (MBO)

- Five days in 2000 at location in California
- Emissions go to zero at night

Steiner et al., 2007
2. Modeling BVOC Emissions

Diurnal cycle of T dependent Emissions (terpenes)
3. VOC: Chemistry and Climate

Biogenic VOC and ozone

- Near urban regions, VOC are particularly important in ozone formation
- In forested urban regions, biogenic VOC are known to contribute to ozone formation
- Anthropogenic VOC control may be less effective
3. VOC: Chemistry and Climate

Biogenic VOC and ozone

\[ \text{HOx} = \text{OH} + \text{HO}_2 + \text{RO}_2 \]

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

\[ \text{NO}_2 \rightarrow \text{HNO}_3 \]

\[ \text{RO} \rightarrow \text{ROOH} \]

\[ \text{NO}_2 + h\nu \rightarrow \text{NO} + \text{O}^{3P} \]

\[ \text{O}^{3P} + \text{O}_2 \rightarrow \text{O}_3 \]
3. VOC: Chemistry and Climate
Impact of future climate change on biogenic VOC emissions

- $T$ perturbation based on Snyder et al. (2002)
  - Regional climate model
  - Ensemble run
  - 40km resolution
  - 2xCO$_2$ scenario

- Allowed temperature to impact:
  - chemical kinetics
  - atmospheric water vapor
  - biogenic VOC emissions
3. VOC: Chemistry and Climate

Increased T increases BVOC
3. VOC: Chemistry and Climate

BVOC in high NOx regimes

\[ \Delta \text{Ozone (ppb)} \]

\[ \text{O}_3 \text{ increases in urban areas} \]

\[ \begin{align*}
\text{NO} & \rightarrow \text{OH} \\
\text{RO} & \rightarrow \text{NO} \\
\text{RO}_2 & \rightarrow \text{HO}_2 \\
\text{O}_2 & \rightarrow \text{RO} \\
\text{RH},\text{O}_2 & \rightarrow \text{O}_3
\end{align*} \]

Steiner et al., 2006
3. VOC: Chemistry and Climate

BVOC in low NOx regimes

O₃ decreases in Sierras

\[ \text{RO} \xrightarrow{\text{NO}} \text{ROOH} \]

\[ \text{RO} \xrightarrow{\text{HO}_2} \text{RO}_2 \]

\[ \text{OH} \xrightarrow{\text{RH}_2\text{O}_2} \]

Steiner et al., 2006
3. VOC: Chemistry and Climate

Secondary organic aerosols (SOA)

Isoprene
OxVOCs
Terpenes
Sesquiterpenes

Gas Phase
Oxidation products

Particle Phase
Secondary Organic Aerosol

These processes are still not well understood
3. VOC: Chemistry and Climate

Secondary organic aerosols (SOA)

As with emissions, SOA formation depends on chemical species

<table>
<thead>
<tr>
<th>Flux</th>
<th>Yield</th>
<th>Isoprene</th>
</tr>
</thead>
<tbody>
<tr>
<td>High</td>
<td>Low</td>
<td>Originally not thought to produce SOA by gas-particle conversion</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Cloud-processing (aqueous chemistry) can lead to SOA (Ervens et al. 2004; Lim et al. 2005)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Yields could be NOx dependent (Kroll et al., 2005,6)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Yields of a few percent</td>
</tr>
<tr>
<td>Terpenes</td>
<td></td>
<td></td>
</tr>
<tr>
<td>oxidation products have low enough volatility to condense to vapor phase</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Yields on the order of 10%</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Flux</th>
<th>Yield</th>
<th>Sesquiterpenes</th>
</tr>
</thead>
<tbody>
<tr>
<td>Low</td>
<td>High</td>
<td>Yields on the order of 20-30%</td>
</tr>
</tbody>
</table>
4. Case study: AMMA Campaign

The Fate of Carbon From Isoprene Over West Africa

Jennifer Murphy*, Graham Mills, Brian Bandy, David Oram, Claire Reeves
University of East Anglia, *now at University of Toronto
Gerard Capes, Hugh Coe
University of Manchester

AGU Fall 2007 Meeting Presentation
4. Case study: AMMA Campaign

AMMA-UK flight campaign

- 100 flight hours on BAe-146 between 17 July – 17 Aug, 2006
- NH ‘wet’ season
- Monsoon flow is southwesterly at surface
4. Case study: AMMA Campaign

Measured species

Measurements of Focus
- Isoprene, [MVK+MACR] – PTR-MS
- HCHO – Hantzsch/fluorescence
- Aerosol composition – Q-AMS
- NO – chemiluminescence (UEA)
- OH, HO₂ – FAGE (Leeds)
- VOC - WAS (York)
4. Case study: AMMA Campaign

Altitude profiles over forest
4. Case study: AMMA Campaign

Predicting isoprene SOA

Isoprene + OH → MVK + CH₂O → MACR + CH₂O → SOA

Yield per isoprene

15%\(^a\)
18%\(^a\)
3%\(^b\)

If \(\tau\) of SOA is comparable to MVK+MACR, or at least > residence time in BL

Isoprene-derived SOA = \([\text{MVK+MACR}] \times \frac{Y_{\text{SOA}}}{Y_{\text{MVK+MACR}}}\)

= 400 ppt \times 3% / 33%
= 200 ppt C \times 1.6 \text{ OM/OC}
= 0.16 \mu g/m\text{³}

\(^a\) Rupert and Becker, 2000  \(^b\) Kroll et al., 2006
4. Case study: AMMA Campaign
Daytime boundary layer layer concentrations

Latitude 7-13 N excluding biomass burning and urban
4. Case study: AMMA Campaign

High isoprene fluxes, low SOA

• Observations are consistent with <5% SOA yield from isoprene and with global model results\(^1\) predicting <0.3 \(\mu g \text{ m}^{-3}\) of SOA in the region

• Observations are possibly inconsistent with studies over vegetated areas with more anthropogenic influence\(^2\) Why?
  – Insufficient seed aerosol for condensation (~0.5 \(\mu g \text{ m}^{-3}\) inorg)
  – SOA could exist in >PM\(_1\) size range
  – SOA lifetime could be significantly shorter in tropics
  – Lower OH in tropical boundary layer (less NO\(_x\)) significantly reduces processing rate of product gases

*No evidence of high OA in cloud layers where isoprene was enhanced

1. Chung and Seinfeld, 2005
2. e.g. Lewis et al., 2004, Weber et al., 2007
5. Biogenic aerosol-climate feedbacks

SOA reduces direct sunlight at surface

bVOC emissions form SOA

cooling

less radiation, cooler leaf T

Warmer T, more radiation, more bVOC

cooling

cooler T, less radiation less bVOC and SOA

warming

Less SOA, more radiation reaches the Earth
Conclusions

• Different vegetation types emit various biogenic VOC species
• These are controlled by environmental factors and will significantly increase under future warming scenarios
• Impacts
  - gas phase chemistry and ozone (air quality impact)
  - secondary organic aerosol formation (climate)
• Still a lot to learn about SOA formation in the atmosphere and its relative importance for regional and global aerosol burdens…