Factors controlling the production of secondary organic material from isoprene epoxydiols (IEPOX) in the Amazonian wet season


ACRIDICON-CHUVA Workshop, Ilha Bela, 2016
Atmospheric importance of isoprene

VOC (isoprene, terpenes, etc.)

\[ \text{Gas-phase oxidation products} \]

Condensation
Absorption
Reactive uptake

Biogenic SOA

Isoprene Emission (\(\mu\text{mol m}^{-2}\text{hr}^{-1}\))

(Adapted from Guenther et al., 2012)
Under low-NO conditions...

Isoprene

IEPOX

H+, H₂O

H+, SO₄²⁻

IEPOX-SOA

Atmospheric importance of IEPOX-SOA

IEPOX-SOA = SOA derived from isoprene epoxydiols (IEPOX)

IEPOX-SOA factor = statistical factor estimated from positive matrix factorization (PMF) of AMS organic mass spectra

[Hu et al., 2015]
In the Amazon forest...

**BACKGROUND CONDITIONS**

**Sources of NO:**
- Soils [Bakwin et al., 1990] + Manaus

**Sources of sulfate:**
- In-basin: DMS/H$_2$S
- Atlantic ocean + Manaus
- African biomass burning [Andreae et al., 1990; Chen et al., 2009]
Biogenic-anthropogenic interactions: the chemistry of IEPOX-SOA

In the Amazon forest...

**POLLUTED CONDITIONS**

**Sources of NO:**
- Soils [Bakwin et al., 1990] + Manaus

**Sources of sulfate:**
- In-basin: DMS/H$_2$S + Manaus
- Atlantic ocean + Manaus
- African biomass burning [Andreae et al., 1990; Chen et al., 2009]

How do anthropogenic emissions affect the production of IEPOX-SOA in Amazonia?
Motivating questions

1. Is sulfate mass concentration a good predictor for IEPOX-SOA factor loadings in the Amazon?

2. Can a role of NO on IEPOX-SOA factor loadings be quantified through the use of $NO_y$ as an indicator of integrated exposure of airmass to NO? 
   
   ($NO_y = NO + NO_2 + \text{reservoir species}$)

3. What is the effect of urban pollution (sulfate + NO) on the loading of IEPOX-SOA factor in the Amazon basin?
Focus:
IOP1 (wet season): Feb 1 – Mar 31 2014
Afternoon data (12:00 – 16:00 local time)
The T3 research site

Intensive Operation Periods (IOPs) - 2014

IOP1: wet season
Feb 1 – Mar 31

IOP2: dry season
Aug 15 – Oct 15
The IEPOX-SOA factor

IOP1 AMS measurements (ALL DATA)
Correlations with external tracers corroborates validity of IEPOX-SOA factor

IOP1 AMS measurements (ALL DATA)

SV-TAG measurements from A. Goldstein group
Sulfate as a predictor of IEPOX-SOA

- IOP1, afternoon data (12:00-16:00 local time)

SE U.S.
$R^2$: 0.48 – 0.60
[Xu et al., 2015, Hu et al., 2015, Budisulistiorini et al., 2013, 2015]

IEPOX-SOA factor loadings = f(sulfate), favored at ↑ sulfate
NO as a modulator of IEPOX-SOA

\[ \text{NO}_y = \text{proxy of integrated NO chemistry} \]

- IOP1, afternoon data (12:00-16:00 local time)

IEPOX-SOA factor loadings = \( f(\text{sulfate}, \text{NO}_y) \), favored at ↑ sulfate and ↓ \( \text{NO}_y \)
Quantifying the dependence on NO$_{y}$

IEPOX-SOA factor loadings change:
- Across observed sulfate range: ~10x increase
- Across observed NO$_{y}$ range: 2-3x decrease
  - Region of NO$_{y}$ < 1.5 ppb is most sensitive
Quantifying the dependence on NO$_y$

IEPOX-SOA factor loadings change:
- Across observed sulfate range: $\sim$10x increase
- Across observed NO$_y$ range: 2-3x decrease
  - Region of NO$_y$ < 1.5 ppb is most sensitive

What is the net effect of the Manaus plume?

IEPOX-SOA factor (µg m$^{-3}$)
Organic material (µg m$^{-3}$)
Case study

Background conditions vs. Polluted conditions

March 3 2014 vs. March 13 2014
March 3 2014: Background conditions

Data credit: Backward airmass trajectories: group of M. Assunção Silva Dias, USP
G1 NO\textsubscript{y} data: Stephen Springston, ARM
G1 CPC data: Fan Mei, ARM
March 13 2014: Polluted conditions

Data credit: Backward airmass trajectories: group of M. Assunção Silva Dias, USP
G1 NO$_y$ data: Stephen Springston, ARM
G1 CPC data: Fan Mei, ARM
Background conditions

Polluted conditions

Pollution indicators

Variables of interest

Explanatory variables

Met conditions

March 3 2014 UTC March 13 2014
Manaus contribution over background is more significant for $\text{NO}_y$ than for sulfate.

This is in agreement with case comparisons for polluted vs background days, where the Manaus plume is associated with lower IEPOX-SOA factor loadings.

- **Green** are PDF from other sites (background reference).
- **Red** is PDF for T3 data.
Conclusions

1. Is sulfate mass concentration a good predictor for IEPOX-SOA factor loadings in the Amazon? **Yes, to first order.**

2. Can a role of NO on IEPOX-SOA factor loadings be quantified through the use of NO\(_y\) as an indicator of integrated exposure of airmass to NO? **Yes.** For a given sulfate mass concentration, IEPOX-SOA loading is expected to decrease by 2-3x when going from NO\(_y\) ~ 0.5ppb to NO\(_y\) ~1.5ppb or higher.

3. What is the effect of urban pollution on the loading of IEPOX-SOA factor in the Amazon basin? **The observed net effect of the plume is, in general, to decrease the loading of IEPOX-SOA factor.** This is attributed to the fact that the contribution of the plume above background levels in the basin is more significant for NO\(_y\) than for sulfate (suppressing effect > enhancing effect).
Acknowledgements

- All collaborators
- ARM team
- Funding agencies
Thank you for listening!
Aerosol Mass Spectrometry

HR-ToF-AMS
Aerodyne
High-resolution
Time-of-Flight
Aerosol Mass
Spectrometer
(AMS)

Non-refractory PM1
- Mass concentrations: Organic, Sulfate, Ammonium, Nitrate, Chloride
- Chemically resolved mass-size distribution
- Mass spectra, EI → “fingerprint”

[DeCarlo et al., 2006]
### Sampling Scheme

#### AMS Ambient data:
- Every 4 out of 8 min

#### System Diagram:
- **Exhaust** ~13.7 L/min
- **Ambient air** 14.9/16.3 L/min
- **Polytube Nafion drier**
- **Cyclone PM 2.5 um**
- **Valve switching system**
  - From OFR1
  - From OFR2
- **Thermodenuder**

#### Outside of container
- RH: 20 – 35%
- 0.3/1 L/min

#### Inside of container
- RH: 40 – 80%
- 0.1 L/min
- 0.1 L/min
In light of the chemical mechanism...

- Dependence on sulfate: at higher sulfate/acidity, reactive uptake is favored.
- Dependence on NO\textsubscript{y}: at higher NO:
  (i) Direct effect: HO\textsubscript{2} pathway is suppressed
  (ii) Indirect effect: oxidation capacity increased $\rightarrow$ chemical loss enhanced
    - $\tau_{OH}(\text{IEPOX-SOA}) \sim 9$ days (See poster A13E-0395 (Weiwei Hu))
    - $\tau_{OH}(\text{IEPOX}\_g) \sim 24$ h
    - OH increase $\sim 3x$ in plume!
    - Transport time Manaus-T3 is $\sim 4$h!

IEPOX-SOA factor loadings = f(sulfate, NO\textsubscript{y}), favored at $\uparrow$ sulfate and $\downarrow$ NO\textsubscript{y}
What is the Manaus contribution?

- The Manaus plume shows a more significant increase over background concentrations for NO\textsubscript{y} than for sulfate.

- This is in agreement with the general observation of decrease in IEPOX-SOA factor loading for polluted days when compared to background days (illustrated here by Mar 13 vs Mar 3).
Atmospheric importance of isoprene

VOC (isoprene, terpenes, etc.)

\[ \text{hv} \rightarrow \text{OH, O}_3 \]

Gas-phase oxidation products

Condensation
Absorption
Reactive uptake

Biogenic SOA

(Adapted from Guenther et al., 2012)
Atmospheric importance of IEPOX-SOA

IEPOX-SOA = SOA derived from isoprene epoxydiols (IEPOX)

IEPOX-SOA factor: estimated from positive matrix factorization (PMF) of AMS organic mass spectra

[Paulot et al., 2009]

[Hu et al., 2015]
Positive Matrix Factorization (PMF)

- It can be seen as a mass balance assuming constant mass spectra for the factors
- Positively constrained problem
- Weighted least-squares method
- No a-priori information for either source or profiles
- The researcher chooses the number of factors, P
- Minimization of the sum of the weighed squared residuals, Q, for chosen P
- \( e_{ij} \) comes from an additional matrix (not shown) of 1σ measurement precisions associated with \( \text{org}_{ij} \)

\[
\text{org}_{ij} = \sum_{p=1}^{P} t_{isp} m_{spj} + e_{ij}
\]

“Q-value”, or “PMF quality-of-fit parameter”

\[
Q = \sum_{i=1}^{t} \sum_{j=1}^{m} \frac{(e_{ij}/\sigma_{ij})^2}{Q}
\]
IEPOX-SOA chemistry: the Amazon forest and Manaus

- Two fold effect of Manaus on IEPOX-SOA chemistry.
Isoprene oxidation products

C₅ alkene triols
- cis-2-methyl-1,3,4-trihydroxy-1-butene
- trans-2-methyl-1,3,4-trihydroxy-1-butene
- 3-methyl-2,3,4-trihydroxy-1-butene

2-methyltetrols
- 2-methylthreitol
- 2-methylerythritol

α-pinene oxidation products
- pinic acid
- pinonic acid
- 3-hydroxyglutaric acid
- 3-methyl-1,2,3-butanetricarboxylic acid (MBTCA)

Biomass burning tracer
- levoglucosan

• Courtesy of G. IsaacmanVanWertz, UC Berkeley (now at MIT)
Under high-NOx conditions when the isoprene peroxy radical reacts predominantly with NO, high NO2/NO ratios lead to methacryloylperoxynitrate (MPAN) and SOA. MPAN reaction with the hydroxyl radical (·OH) produces methacrylic acid epoxide (MAE)
The IEPOX-SOA factor

IOP1 AMS measurements (ALL DATA)

PMF

13% 4%

Other factors 83%

IEPOX-SOA 17%

Organic
Sulfate
Ammonium
Nitrate
Chloride

79%

3% 1%
• Normal fit, intercept constrained to zero

<table>
<thead>
<tr>
<th>Group</th>
<th>NOy med (ppb)</th>
<th>Slope of fit</th>
</tr>
</thead>
<tbody>
<tr>
<td>G1</td>
<td>0.31</td>
<td>1.33</td>
</tr>
<tr>
<td>G2</td>
<td>0.68</td>
<td>1.46</td>
</tr>
<tr>
<td>G3</td>
<td>0.90</td>
<td>1.18</td>
</tr>
<tr>
<td>G4</td>
<td>1.30</td>
<td>0.91</td>
</tr>
<tr>
<td>G5</td>
<td>2.09</td>
<td>0.62</td>
</tr>
<tr>
<td>G6</td>
<td>3.24</td>
<td>0.50</td>
</tr>
</tbody>
</table>
• Normal fit, intercept not constrained

<table>
<thead>
<tr>
<th>Group</th>
<th>NOy med (ppb)</th>
<th>Slope of fit</th>
</tr>
</thead>
<tbody>
<tr>
<td>G1</td>
<td>0.31</td>
<td>1.76</td>
</tr>
<tr>
<td>G2</td>
<td>0.68</td>
<td>1.58</td>
</tr>
<tr>
<td>G3</td>
<td>0.90</td>
<td>1.23</td>
</tr>
<tr>
<td>G4</td>
<td>1.30</td>
<td>0.76</td>
</tr>
<tr>
<td>G5</td>
<td>2.09</td>
<td>0.62</td>
</tr>
<tr>
<td>G6</td>
<td>3.24</td>
<td>0.56</td>
</tr>
</tbody>
</table>
NO as a modulator of IEPOX-SOA

$NO_y$ = proxy of integrated NO chemistry

- IOP1, afternoon data (12:00-16:00 local time)

IEPOX-SOA factor loadings = $f$(sulfate, $NO_y$), favored at ↑ sulfate and ↓ $NO_y$

<table>
<thead>
<tr>
<th></th>
<th>$NO_y$ median (ppb)</th>
<th>Fit slope</th>
</tr>
</thead>
<tbody>
<tr>
<td>G1</td>
<td>0.31</td>
<td>2.61</td>
</tr>
<tr>
<td>G2</td>
<td>0.68</td>
<td>2.39</td>
</tr>
<tr>
<td>G3</td>
<td>0.90</td>
<td>2.54</td>
</tr>
<tr>
<td>G4</td>
<td>1.30</td>
<td>1.74</td>
</tr>
<tr>
<td>G5</td>
<td>2.09</td>
<td>0.86</td>
</tr>
<tr>
<td>G6</td>
<td>3.24</td>
<td>0.65</td>
</tr>
</tbody>
</table>
Blue box encloses 23% of data.
Red box encloses 52% of data.
A map for IEPOX-SOA

IEPOX-SOA factor ($\mu$g m$^{-3}$)

Organic material ($\mu$g m$^{-3}$)

Sulfate (µg m$^{-3}$)

Sulfate (µg m$^{-3}$)
Shown case study
Polluted cases

Graphs showing various environmental data over time, including:
- Particle number concentration (cm⁻³)
- Organic concentration (µg m⁻³)
- IEPOX-SOA factor (µg m⁻³)
- Sulfate concentration (µg m⁻³)
- Rain (mm h⁻¹)
- Wind direction
- Ozone concentration (ppb)
- CO concentration (ppb)
- NOy concentration (ppb)
- Solar irradiance (W m⁻²)

Other cases
Other cases, shift of conditions
Quantifying the dependence on NOy

- Considerable effect of NOy on IEPOX-SOA loadings and mass fraction of organic material ($f_{\text{IEPOX-SOA}}$)
  - Decrease on order of 2-3x over the observed range of NOy
- Region of NOy < 1.5 ppb is most sensitive
Looking at extreme sulfate regimes... 

- Considerable effect of NO$_y$ on IEPOX-SOA loadings and mass fraction, especially for NO$_y$ < 1.5 ppb.
Summary of daytime 12-16h LT plots

[Graphs showing the relationship between NOy (ppb) and IEPOX-SOA/Sulfate and IEPOX-SOA/Organic for low and high sulfate conditions.]

Median and quartiles
Dependence on NOy...
PMF RESULTS
Particle composition at T3

IOP1 (Wet season)
- Organic: 13%
- Sulfate: 11%
- Ammonium: 4%
- Nitrate: 3%
- Chloride: 1%
- PMF: 79%
- Other factors: 21%

IOP2 (Dry season)
- Organic: 11%
- Sulfate: 3%
- Ammonium: 3%
- Nitrate: 1%
- Chloride: 1%
- PMF: 85%
- Other factors: 15%

IEPOX-SOA: 17%
Other factors: 83%
IEPOX-SOA: 15%
Other factors: 85%
IOP1: Factors profiles

- HOA: 5.8%
- 91fac: 12.6%
- BBOA: 9.1%
- LO-OOA: 25.6%
- MO-OOA: 30.0%
- IEPOX-SOA: 17.1%
IOP1: Correlations with external tracers
IOP1: Diel patterns

- HOA
- 91fac (A-OA)
- BBOA
- LO-OOA
- MO-OOA
- IEPOX-SOA
OTHER POSSIBLE PREDICTORS FOR IEPOX-SOA?
Why not use/test pH as a predictor?

1. pH estimation (E-AIM / ISORROPIA) is largely limited in this dataset by:
   - No gas phase measurements on site (NH3, HNO3, HCl)
   - Organic acids likely to contribute (high Org fraction) but not measured
   - Inorganic ion balance falls in sensitive region
   - High AMS measurements uncertainty (~30%)

2. Instantaneous pH (at T3) is not what we want to know. IEPOX-SOA is formed upwind, where the aerosol might have been acidic, and after that neutralized during transport, leading to a unrealistically lower correlation between IEPOX-SOA and pH.

3. Out of scope of this study, whose main message is actually to highlight the importance of NOy as another variable in determining IEPOX-SOA mass. i.e. thinking of the role of NOx might be more important than thinking of whether sulfate or acidity is more important, especially given that acidity is not a measured quantity, but estimated.
IOP1, T3: Inorganic ion balance

- Inorg ion balance falls in sensitive region
- No gas phase measurements on site (NH$_3$, HNO$_3$, HCl)
- Organic acids likely to contribute (high Org fraction)
- High AMS measurements uncertainty (~30%)
Looking at \([H^+]\) as a parameter
Looking at $[\text{H}^+]$ as a parameter
Diel trend of particle water

- $W_i =$ water from inorganic uptake
- $W_o =$ water from organic uptake

E-AIM results for $W_i$, kappa from R. Thalman/J. Wang CCN
Diel trend of particle water

- $W_i =$ water from inorganic uptake
- $W_o =$ water from organic uptake

RH $< 98$

PRETTY SIMILAR!! ☺️
E-AIM results (Points for which cations > anions (H+ < 0) are excluded)
Diel trend of pH

E-AIM results (Points for which cations > anions (H+ < 0) are excluded)