Ozone net production rate within the Manaus urban plume, in Central Amazonia

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Introduction
Manaus emission pattern might have changed over time:
• increase on the vehicle fleet
• moving to cleaner power plant fuels
Does the combination of BVOCs and urban emissions increase \( \text{O}_3 \) production downwind of Manaus?
Net production rate of trace gas species along the transport from Manaus to downwind areas

\[ P_{\text{net}} = P_{\text{chemistry}} + \text{Inputs} - \text{Dilution} - \text{Deposition} \] (ppb/h)

\[ P_{\text{net}} = \frac{O_3(\vec{r}, t_0 + \Delta t) - O_3(\vec{r}_0, t_0)}{\Delta t} \]

Is there significant O\(_3\) photochemical production along the transport of the urban plume, from the source to downwind areas?

\( \vec{r}_0 \): position of the source (Manaus)

\( \vec{r} \): position downwind of Manaus

\( t_0 \): when plume leaves Manaus

\( \Delta t \): transport time from \( \vec{r}_0 \) to \( \vec{r} \)
O₃ enhancement factor with respect to background conditions

\[ EF_{O3} = \frac{dO_3}{dCO} = \frac{O_3 - O_3(bkg)}{CO - CO(bkg)} \]

Evaluate the O₃ enhancement over background conditions accounting for the dilution effect

CO:
- Relatively long chemical life
- Low solubility in water
- Mostly affected by dilution (within the time frame of a day)
Methods

Ground based data
(T2 and T3 GoAmazon sites)
Urban plume detection at T3

Criteria 1: urban plume signature

\[
\frac{dCN}{dCO} = \frac{CN_i - CN_{\text{background}}}{CO_i - CO_{\text{background}}}
\]

\[
CN_{\text{background}} = 500 \text{ cm}^{-3}
\]

\[
CO_{\text{background}} = 110 \text{ ppb}
\]

Range was observed in 21% of valid data at the T3 site
Urban plume detection at T3

Criteria 2: Hysplit backtrajectories

- All points to the east of T3
- Within the boundary layer (height<1000m)

Typical transport time: 7 hours.
Requirements matched in 37% of the measurement period
Urban plume detection at T3

- Combination of criteria 1 (plume signature) and criteria 2 (backtrajectories):
  - 10% of the valid data period at the T3 site

- There is another method proposed to track the urban plume at T3 (Ryan Talman’s). Comparison between the two methods is on its way.
Methods

G1 airborne data
G1 dataset

- 35 flights
  - #1-16 wet season
  - #17-35 dry season

- Plume transects at ~constant altitudes
  - 75% <700 m;
  - 25% 900-1700 m
G1 plume/background detection

- Visual identification of plume transects: CO, CN and absorption peaks
- Acetonitrile used as a tracer for biomass burning plumes
Results

Average impacts of the Manaus urban plume over O$_3$ concentrations at T3
Average impact of the Manaus plume over O₃ concentrations at T3

Ground based measurements

O₃ peak at T0z

15 ppb

~25 ppb

~10 ppb
O₃ average diurnal cycle at T2 and at T3

Average conditions are very similar at T2 and T3 when impacted by the urban plume.
Impact of the Manaus plume at T3 at specific times of the day

- Avoided rainy days
- Morning plume only (3:00-9:00 LT, 26 days)
- Afternoon plume only (13:00-18:00 LT, 20 days)
Airborne $O_3$ X distance from Manaus

G1 data show an increase on $O_3$ as soon as the airplane leaves Manaus.
Results

O$_3$ net production rate within the plume, in reference to the urban plume source
Extreme positive values mostly in the dry season

\[ P_{net} \sim \frac{O_3(T3, t_0 + \Delta t) - O_3(T2, t_0)}{\Delta t} \]

- \( t_0 \): when plume leaves T2
- \( \Delta t \): transport time from T2 to T3

Including \( O_3 \) chemical production, dilution, deposition and inputs

Ground based measurements
O$_3$ net production rate from G1 data

Airborne measurements
### O₃ net production rate comparison

<table>
<thead>
<tr>
<th>Observation</th>
<th>Median (ppb/h)</th>
<th>p25 (ppb/h)</th>
<th>p75 (ppb/h)</th>
</tr>
</thead>
<tbody>
<tr>
<td>T3, 2014 Ground based</td>
<td>2.2</td>
<td>0.8</td>
<td>3.6</td>
</tr>
<tr>
<td>G1, 2014 Alt&lt;700m; Distance 60-75km</td>
<td>3.7</td>
<td>2.0</td>
<td>5.7</td>
</tr>
<tr>
<td>LBA/CLAIRE July 2001 Distance 40-70km; Khun et al., 2010</td>
<td>10-15</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>ABLE2B 1985 Alt~200m; Distance ~100km; Andreae et al., 1988</td>
<td>~4</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

Nowadays fast O₃ production driven by changes on Manaus emissions patterns (VOC/NOx)?
Results

$O_3$ enhancement factor with respect to background conditions
T3 enhancement factor $dO_3/dCO$

Ground based measurements (afternoon plumes)

$O_3$ and CO subtracted by background concentrations from average diurnal cycles at T3
G1 enhancement factor $dO_3/dCO$

Wet season - G1 (alt<700m)

Airborne measurements (urban plume)

Dry season - G1 (alt<700m)

10km: $y=0.02 + 2.4 \ (r^2=0.01)$
20km: $y=0.25 + 5.0 \ (r^2=0.34)$
50km: $y=0.09 + 16 \ (r^2=0.00)$
70km: $y=0.82 - 4.6 \ (r^2=0.56)$
90km: $y=0.56 + 7.2 \ (r^2=0.30)$

10km: $y=-0.01 + 6.1 \ (r^2=0.00)$
20km: $y=0.28 + 20 \ (r^2=0.35)$
50km: $y=0.56 + 10 \ (r^2=0.61)$
70km: $y=0.57 + 3.8 \ (r^2=0.42)$
90km: $y=0.34 + 13 \ (r^2=0.27)$
G1 enhancement factor $dO_3/dCO$

Enhancements from biomass burning plumes are much smaller in comparison to urban plumes.
Khun et al. (2010)

$O_3$ EF for a single flight in the dry season of 2001

- G1: slope $\frac{dO_3}{dCO} = 0.57$ in the dry season at 70km distance
- T3: slope $\frac{dO_3}{dCO} = 0.27$ in the dry season

**Fig. 7.** $\Delta O_3$ to $\Delta CO$ enhancement factors as a function of downwind distance from Manaus City during Flight #18 on 19 July 2001, 10:00–14:00 LT. Data from all transects of each vertical profile are binned. Slopes of a linear regression using the reduced-major-axis (RMA) regression method are given. Khun et al., ACP, 2010
On average, the O$_3$ peak is similar at T2 (source region) and T3 (when impacted by the urban plume).

Airborne data shows that most of O$_3$ is formed within 20 km from Manaus.

Relatively low O$_3$ net production rates, suggesting that the plume is oxidized within ~20 km from Manaus.

Greater O$_3$ enhancement factors in urban plumes in comparison to biomass burning plumes.

O$_3$ enhancements with respect to background in 2014 are smaller than observations from 2001.
Thanks for the attention!

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