Ozone production efficiency in plumes downwind from Houston


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- Look at ozone production in coalesced plumes from the same source under different conditions during summer of 2006

- 10 daytime flights from the NOAA WP3 with multiple crosswind transects of the combined Houston/ship channel plume

- HNO₃ loss from the atmosphere can be large. Two methods used to determine ozone production efficiencies are consistent only when HNO₃ loss is quantified and included in the comparison.
Ozone Production Efficiency

Ozone production in daylight

\[
\frac{O_3}{(\text{NOx Emitted})} \to 0 \text{ as } t \to 0 \\
\to \text{constant as } t \to \text{large}
\]

\[
\frac{O_3}{(\text{NOx Oxidized})} \to \frac{O_3}{(\text{NOx Emitted})} \text{ as } t \to \text{large}
\]

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\]

(\text{depends on VOC:NOx})
Example: NOAA WP-3 flight on September 26, 2006
Flight track below 1 km altitude colored by Ozone Mixing Ratio

Ozone produced photochemically downwind from Houston
- NOx oxidized
- HNO₃ and PAN formed
- HNO₃ >> PANs
- 9 crosswind transects
- Similar strong correlation between O₃+NO₂ and HNO₃+PANs for most transects
- Correlation slopes range from 2 to 4
Example: NOAA WP-3 flight on September 21, 2006
Flight track below 1 km altitude colored by Ozone Mixing Ratio

Markers - Maximum 1 hr Ozone at surface sites
• NOx oxidized
• HNO$_3$ and PAN formed
• HNO$_3$ $\approx$ PANs

• 7 crosswind transects
• Similar strong correlation between O$_3$+NO$_2$ and HNO$_3$+PANs
• Correlation slopes range from 12 to 15
Consider 70 crosswind transects on 10 different days

**Explanation:** HNO₃ deposition affects the slope
(this was pointed out in the paper by Trainer et al., 1993 that first examined the correlation between Ozone and NOx oxidation products)
Use CO to NOx ratio to examine HNO₃ deposition

- CO is conserved on these timescales
- Ratio of CO to (NOx + oxidation products) will be constant if reactive nitrogen conserved

- Fresh plumes (close to Houston): CO: NOx ~ 4.4 ± 1.4
- Aged plumes (far from Houston): Reactive nitrogen lost
- Observed loss of HNO₃ larger than determined from HNO₃ deposition velocity
Correct for loss of reactive nitrogen

- Compare $\text{CO/(NOx+PANs+HNO}_3)$ to Emitted CO/NOx for each transect
- Determine $\text{HNO}_3$(lost), and add to measured PANS+HNO$_3$

Example: 9/27
140 km downwind
Plume Age ~4hr
$\text{CO/NOy} = 11.4$

Account for HNO$_3$ loss and determine ozone production efficiency for every transect
• HNO$_3$ loss explains the apparent increase in OPE with wind speed

• Qualitatively consistent with HNO$_3$ deposition, which increases with wind speed, which enhances turbulent transport to the surface

• HNO$_3$ loss can have a large influence on OPE determined from O$_3$/(NOx Oxidized) slopes
Compare results to $\frac{O_3}{(NOx \text{ Emitted})}$

$\frac{O_3}{(NOx \text{ emitted})} = (\frac{O_3}{CO \text{ correlation slope}}) \times (CO/NOx \text{ Emission Ratio})$

Determine $\frac{O_3}{CO}$ correlation slopes for each plume transect, then multiply by 4.4.

As $t \to$ large, $\frac{O_3}{(NOx \text{ Emitted})} \to \frac{O_3}{(NOx \text{ oxidized})} \to$ constant

In aged coalesced plumes > 60 km from Houston:

$\frac{O_3}{(NOx \text{ oxidized})} = 3.4 \pm 1.3$

$\frac{O_3}{(NOx \text{ emitted})} = 2.2 \pm 0.9$
Texas 2000 Results (less than ~1/2 as many plume transects)

- Fresh plumes: CO/NOx $\sim 5.4 \pm 2.3$
- CO/NOy less variable compared to 2006
- Wind speeds lower and more constant
- Little correction for HNO$_3$ loss
Texas 2000: Compare results to $O_3/(NOx \text{ Emitted})$

In aged coalesced plumes > 60 km from Houston:

$O_3/(NOx \text{ oxidized}) = 4.0 \pm 1.3$

$O_3/(NOx \text{ emitted}) = 3.0 \pm 0.6$

As $t \rightarrow \text{ large}$, $O_3/(NOx \text{ Emitted}) \rightarrow O_3/(NOx \text{ oxidized}) \rightarrow \text{ constant}$
Conclusions

• HNO₃ loss can strongly affect slopes of O₃/(NOx oxidation products)

• Observed loss of reactive nitrogen not represented by HNO₃ dry deposition velocity (consistent with previous studies)

• Correcting for HNO₃ loss gives ozone production efficiency consistent with that determined from Ozone/(NOx Emitted)

• Ozone production efficiency in aged, coalesced plumes:

<table>
<thead>
<tr>
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<th>Ozone/(NOx Oxidized)</th>
<th>Ozone/(NOx Emitted)</th>
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</thead>
<tbody>
<tr>
<td>2006</td>
<td>3.4 ± 1.3</td>
<td>2.2 ± 0.9</td>
</tr>
<tr>
<td>2000</td>
<td>4.0 ± 1.3</td>
<td>3.0 ± 0.6</td>
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</tbody>
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CO is conserved, NOy is not

Example: 9/27 flight

CO remains constant
NOy drops