Ozone Precursor Study: Volatile Organic Compounds in Salt Lake City

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Ozone Formation: Non-linear Function of [NOx] and [VOC]

\[ R_{OH} = (k_{OH+VOC} \times [VOC]) \]

Ryerson et al. 2001, Science vol 292, 719

VOCs; NOx

Urban

Biosphere

Industry

Biomass burning
Motivation: Decrease in Precursors, But no Significant Change in O$_3$ and PM$_{2.5}$

**From 1996 to 2015:**
- 3 x decrease in CO
- 2 x decrease in NOx

**Secondary pollutants**
- No significant change
- O$_3$ levels are close to the current standard
- Out of attainment with new O$_3$ standard
- Importance of O$_3$ precursor study
Technique: Gas Chromatography-Flame Ionization Technique (GC-FID)

Total ~ 57 species
- Alkanes (C2 – C10)
- cycloalkanes (C6 – C7):
- alkene (C2- C6)
- aromatics (C6-C10)
- isoprene

1 hr time resolution

Step I Sample collection
- Pre-concentrates the sample in a trap consists of adsorbent materials (carboblack & molecular sieve)
- Collects ~40 min at -30 C
- Desorbed by heating the trap fast
- Delivered to GC

Step II Sample separation
- Achieved by coupling of two columns
- Based on their volatility
Most VOCs from anthropogenic sources
• peak in winter due to shallow PBL, change in source strength
• Lower in summer due to abundant sunlight and efficient photochemistry 3 – 6 x decrease in summer

Isoprene
• Peaks in summer, growing season
• Low in winter
Diurnal Trend of VOCs

- Early morning and evening peak due to traffic emissions
- Lower during day due to chemistry and PBL
- Lower levels on weekends
- 40% decrease in toluene

Ethane

- No morning or evening peak
- Persist throughout the night due to nighttime emissions
- Larger contributions from non-road sources
- Lower on weekends; variation is less, within 20%
Weekend Effect: Lower Precursor Emissions, Slightly Higher O₃

Summers (June – August) 2006 – 2015 at HW, Salt Lake City

Diurnal Trend of NOₓ and O₃

Diurnal Trend in NOₓ

- Early morning and evening peak due to traffic emissions
- Lower NOx levels on weekends

O₃ trend

- O₃ shows opposite trend
- does not show large variation
- higher on weekends in early morning hours

Why?
- Suppressed by the high NOx on weekday
- Slightly higher O₃ production (P₀₃) on weekends?
Weekend Effect:
Lower Precursor Emissions, no Change in $O_x$

Diurnal Trend in $NO_x$ and $O_x$

\[ [O_x] = [O_3] + [NO_2] \]

**Diurnal Trend in $NO_x$**

- Lower NOx levels on weekends

**$O_x$ trend**

- Ox levels are not very sensitive to the changes in NOx.
- suggests NOx saturated regime
- $O_3$ is suppressed by high NOx on weekdays

\[ O_3 + NO \rightarrow NO_2 + O_2 \]
Weekend Effect: Slightly Higher $O_3$, Less Variation in Ox

**NOx**
- Lower NOx levels on weekends
- 40% variation in NOx

**Ozone**
- Higher $O_3$ on weekends
- Variation is within 10%

**Ox = $O_3$ + NO$_2$**
- Shows less variation
- within 5%
- Insensitive to changes in precursors
- NO$_x$ saturated regime
- Importance of VOCs and their speciation
VOC Contribution to OH Loss Rates in Summer: Importance of Alkanes

\[ R_{OH} = (k_{OH+VOC} \times [VOC]) \]

- Alkanes and isoprene appear to dominate the OH loss rate.
- Not measuring all VOCs; oxygenates and monoterpenes \(\rightarrow\) lower limit
- Preliminary analyses: uncertainty in the calibration factors
Contribution to OH Loss Rates in Summer: (VOCs + CO) vs. NOx

- NO$_2$ dominates the OH reactivity
- NO$_2$ accounts for ~ 60% of total
- VOC + CO account for ~ 40% of the total

Independent confirmation for “NOx saturated regime”
Reduction in mobile sources leads to little or no change in Po3 (day of week analysis)
Importance of reducing VOCs and CO from non-mobile sources

\[ R_{OH} = (k_{OH+VOC} \times [VOC]) \]

Rate of ozone production

“NO$_x$-saturated” regime
OH + NO$_2$ termination dominates
\[ P(O_3) \propto [VOC], 1/[NO_x] \]
Summary

• Both VOCs and NOx levels are lower on weekends.
• In contrast, ozone levels are slightly higher on weekends.
• Weekly Ox trend show very little variation.
• Weekend effect shows that reducing on-road emissions will not lead to immediate O₃ reduction in SLC.
• But it will benefit the air quality in downwind areas (in NOx limited regime).
• Analysis points to “NOx saturated regime” and importance of VOC reduction.
• Alkanes contribute to OH reactivity significantly.
• Best strategy to reduce O₃: reduction of CO and VOCs (alkanes) from area and point sources.
Future Works
Diurnal Profiles and Weekend Effect: 20 % lower PM$_{2.5}$

**NOx & CO**
- Lower NOx levels on weekends
- 40 % variation in NOx

**Ozone**
- Higher O$_3$ on weekends
- Variation is large, ~ 40 %

**PM2.5**
- Shows less variation
- 20 % lower on weekends
- Diurnal profile shows midday and nighttime peak.
- Nighttime activity
Wintertime PM$_{2.5}$ Study: Chemical Mechanism and Nitrate Chemistry

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Objectives:
• Understand the mechanism for the PM$_{2.5}$ formation, in particular nitric acid formation
• Determine limiting precursor: NH$_3$ vs. HNO$_3$
Wintertime PM$_{2.5}$ Study: Chemical Mechanism and Nitrate Chemistry

Approach 1: Rooftop measurements of nitrate radicals and related species

- Radicals levels are highly altitude dependent.
- >100 m above the valley floor
- Away from emissions
- Opportunity to look into radical chemistry

Key instrument: NOAA’s CaRDS for NO3 and N2O5, and NOy instrument

Potential sites

<table>
<thead>
<tr>
<th>Species</th>
<th>Downtown SLC</th>
<th>WBB UofU</th>
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</thead>
<tbody>
<tr>
<td>NO$_3$/N$_2$O$_5$</td>
<td></td>
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<tr>
<td>O$_3$</td>
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<td>NH$_3$</td>
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<td>NOy, NO, NO$_2$</td>
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<tr>
<td>PM$_{2.5}$</td>
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<tr>
<td>Met etc.</td>
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Ammonia analyzer

Intermountain Health Center Murray
Wintertime PM$_{2.5}$ Study: Chemical Mechanism and Nitrate Chemistry

Approach 2: Time evolution of vertical distribution and spatial distribution of key species

Vertical measurements of PM$_{2.5}$ & related species

Time evolution of aerosol layer based on back scattering

Ceilometer  Scanning Doppler LiDAR
- 3-D fields of ws and wd, evolution
- Advective processes & transport
  - upward mixing/downward mixing

Spatial Distribution

Salt Lake Valley CO$_2$ January 2013 Inversion
- CO$_2$ x2
- CO
- CH4
- NO or Nox
- PM 2.5 – 10
- O$_3$
- GPS
- met Dr. John Lin’s group

O$_3$, PM$_{2.5}$, NO$_2$, met
West Valley High Time Resolution Air Toxics Monitoring Campaign

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Real-time Monitoring of HAPs in both Gas and Particle Phase: Chemical Speciation and Exposure Levels

Objective: determining HAPs exposure levels and characterizing sources

Two proposed sampling campaigns:
2. June – August 2016

PTR-MS for VOC measurements
- Time resolution: 2-3 min
- Aromatics (benzene, toluene, xylenes)
- Oxygenated (form-, acetaldehyde, acids)
- Others (isop, products)

OAM (Organic aerosol monitor) for organics in PM
- Time resolution: hourly
- Semi-volatile and non-volatile organic component in PM
- DPM, organic tracers etc.
Acknowledgements

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Questions?