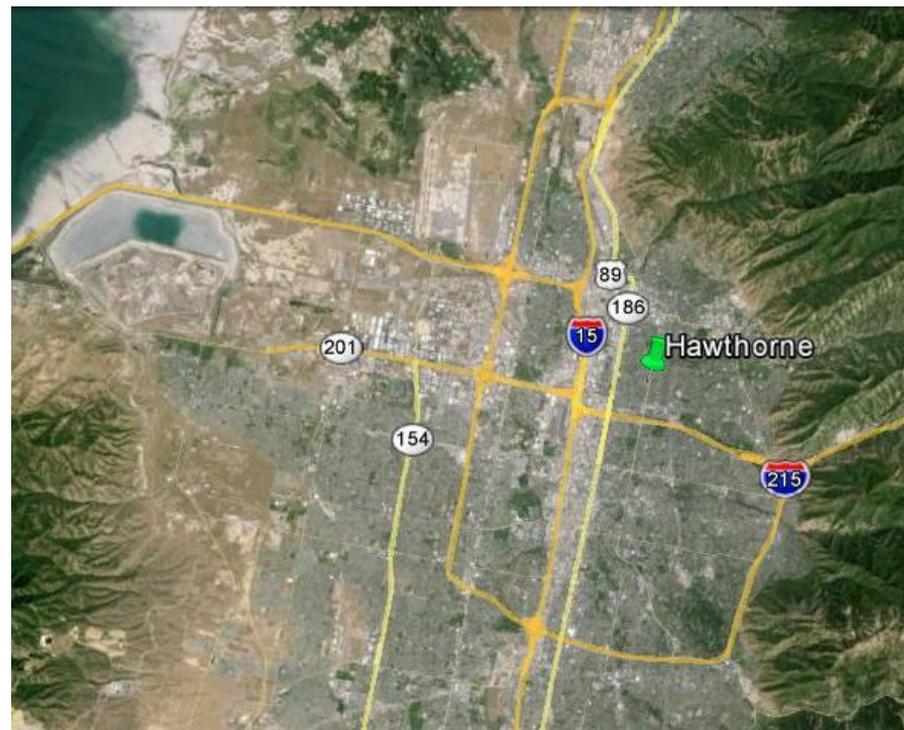


Ozone Precursor Study: Volatile Organic Compounds in Salt Lake City

Dr. Munkhbayar Baasandorj
Utah Division of Air Quality

Contact: mbaasandorj@utah.gov

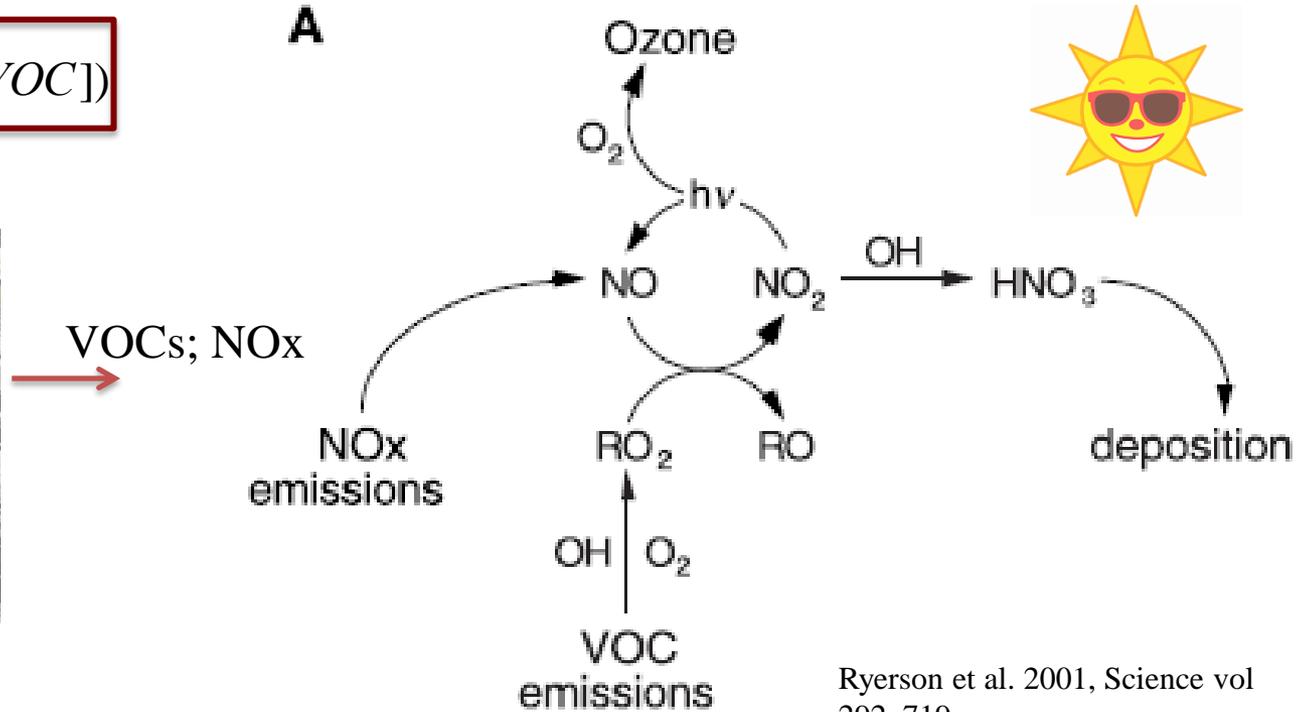


Ozone Formation: Non-linear Function of [NO_x] and [VOC]

$$R_{OH} = \dot{a} (k_{OH+VOC} * [VOC])$$



Urban



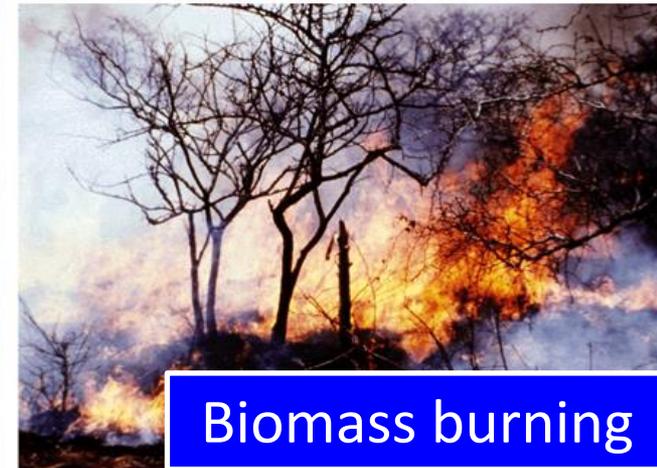
Ryerson et al. 2001, Science vol 292, 719



Biosphere



Industry



Biomass burning

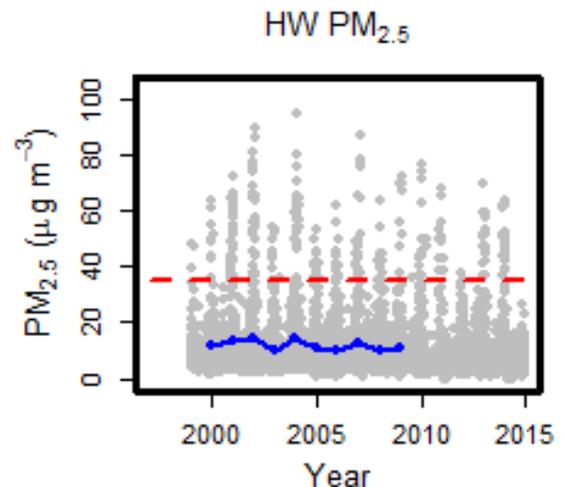
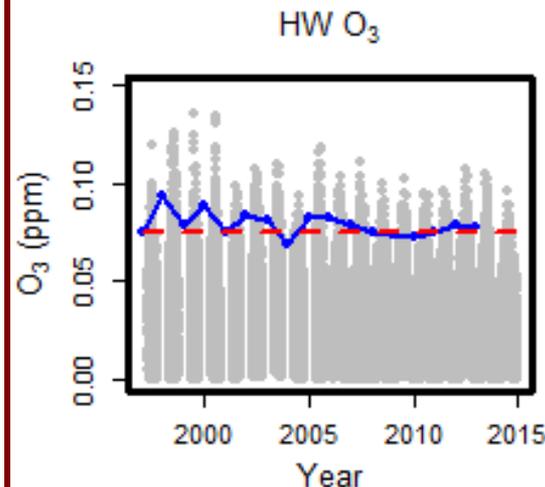
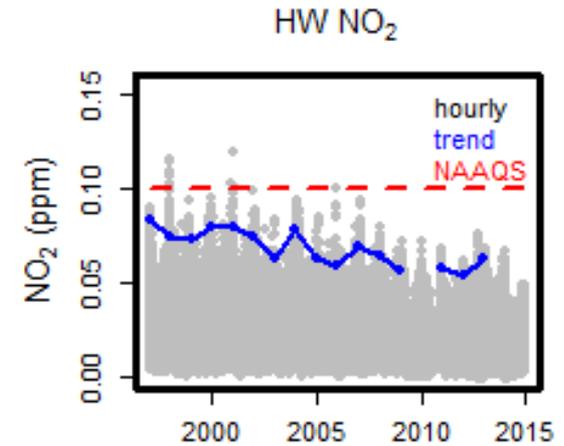
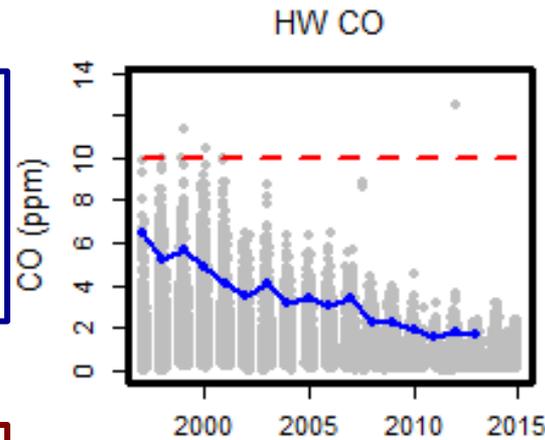
Motivation: Decrease in Precursors , But no Significant Change in O₃ and PM_{2.5}

From 1996 to 2015:

- 3 x decrease in CO
- 2 x decrease in NO_x

Secondary pollutants

- No significant change
- O₃ levels are close to the current standard
- Out of attainment with new O₃ standard
- Importance of O₃ 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

Technique (GC-FID)



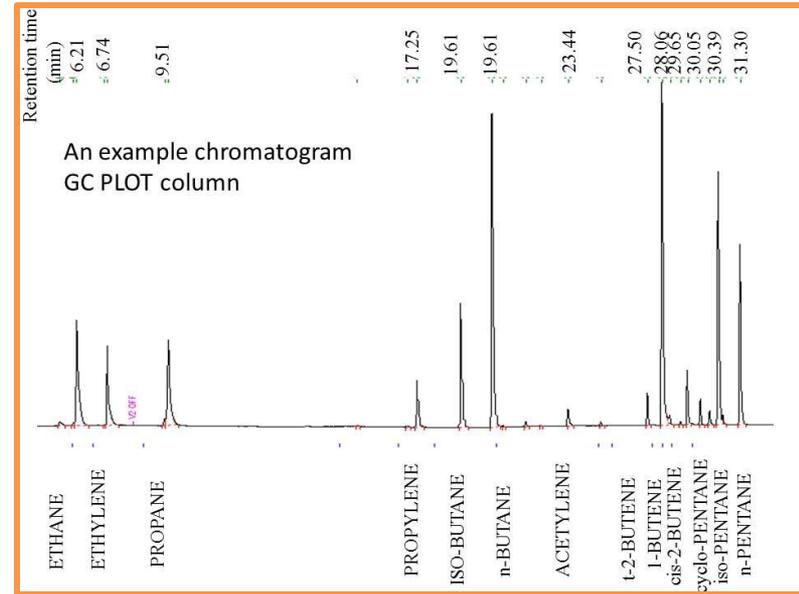
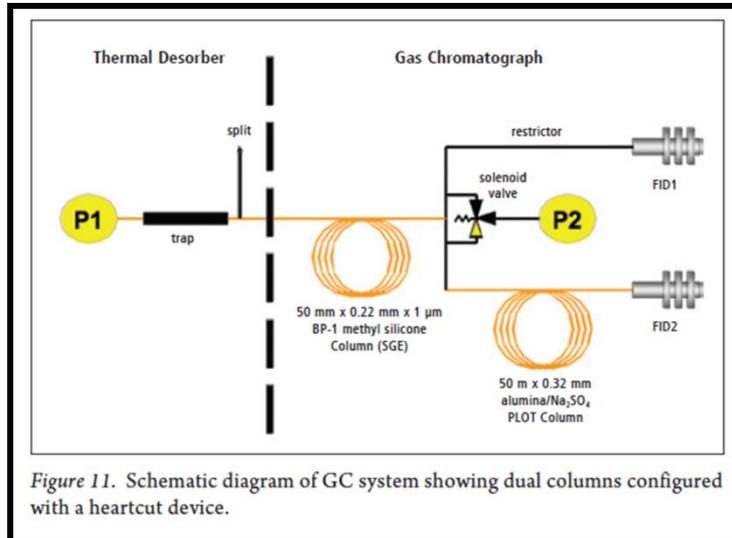
PerkinElmer ozone precursor system used for monitoring VOCs

Step I Sample collection

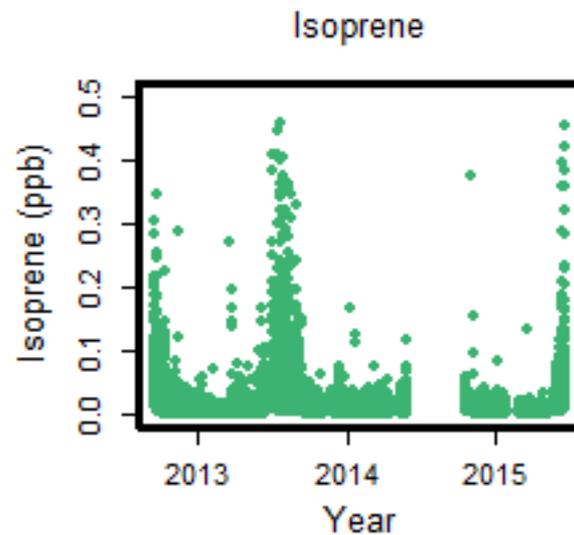
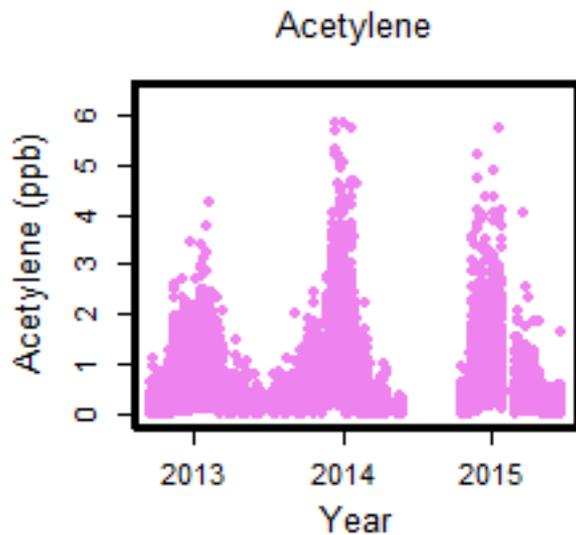
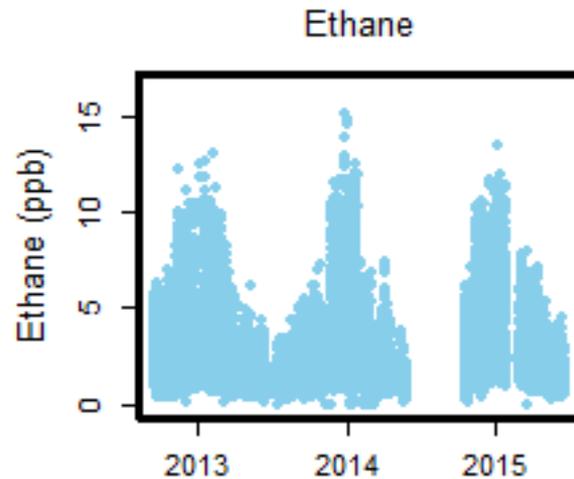
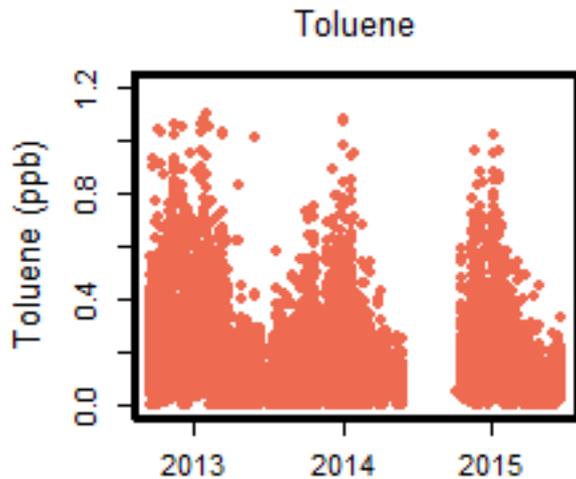
- Pre-concentrates the sample in a trap consists of adsorbent materials (carboblack & molecular sieve)
- Collects ~40 min at -30 C
- Desorbed by heating the trap fast
- Delivered to GC

Step II Sample separation

- Achieved by coupling of two columns
- Based on their volatility



Results: VOC Time Series 2012 - 2015



Most VOCs from anthropogenic sources

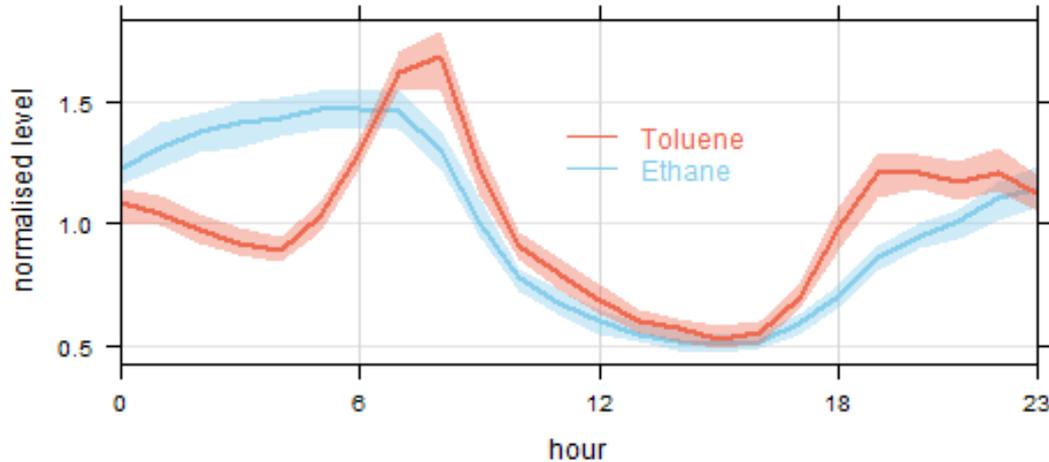
- peak in winter due to shallow PBL, change in source strength
- Lower in summer due to abundant sunlight and efficient photochemistry
3 – 6 x decrease in summer
- High levels of light alkanes

Isoprene

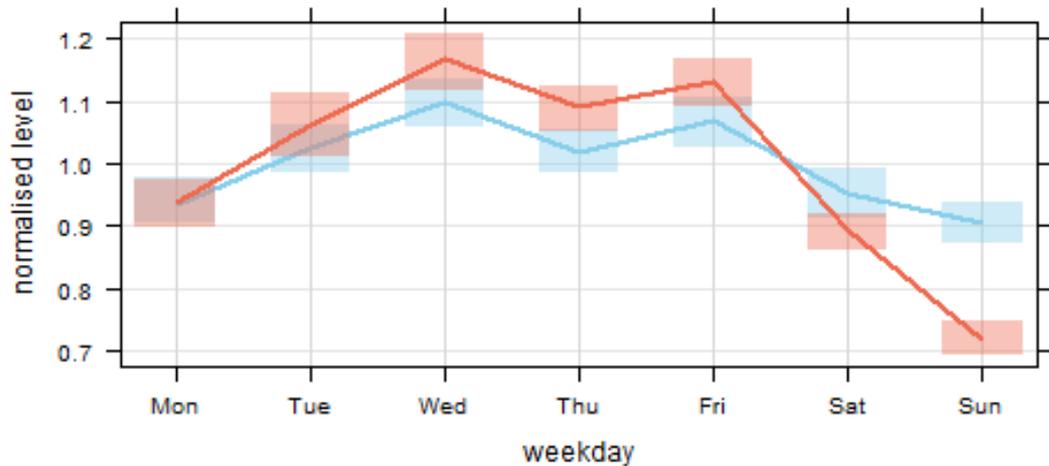
- Peaks in summer, growing season
- Low in winter

Diurnal and Weekly Trend of VOCs: driven by Sources and Sinks

Diurnal Trend of VOCs



Weekly Trend of VOCs



Trends reflect different sources of aromatics and alkanes.

Toluene

- 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

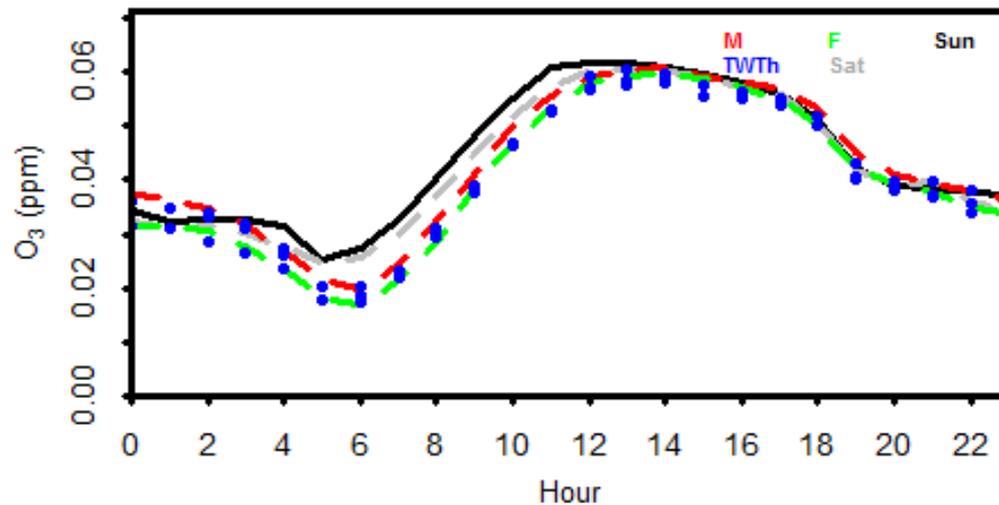
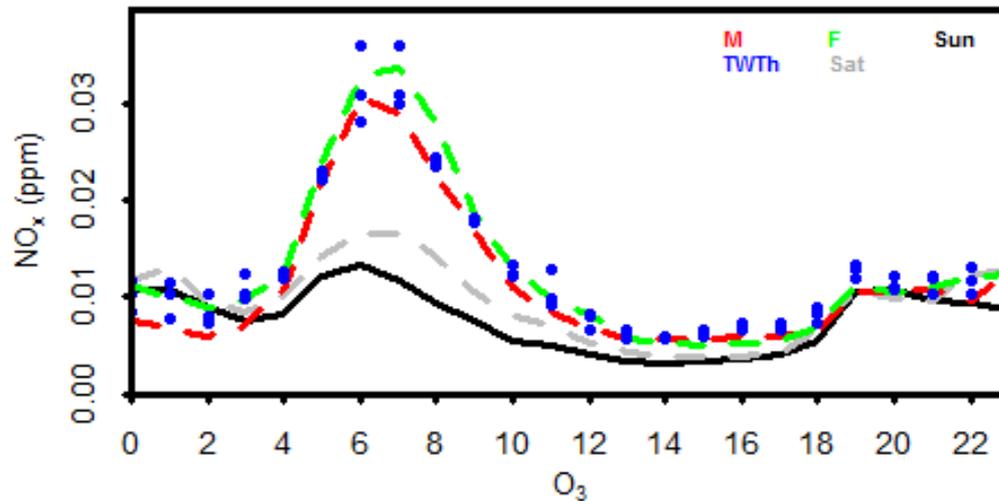
- No morning or evening peak
- Persist throughout the night due to nighttime emissions
- Larger contributions from non-road sources
- Lower on weekends; variation is less, within 20 %

Weekend Effect: Lower Precursor Emissions, Slightly Higher O₃

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

Diurnal Trend of NO_x and O₃

NO_x



Diurnal Trend in NO_x

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

O₃ trend

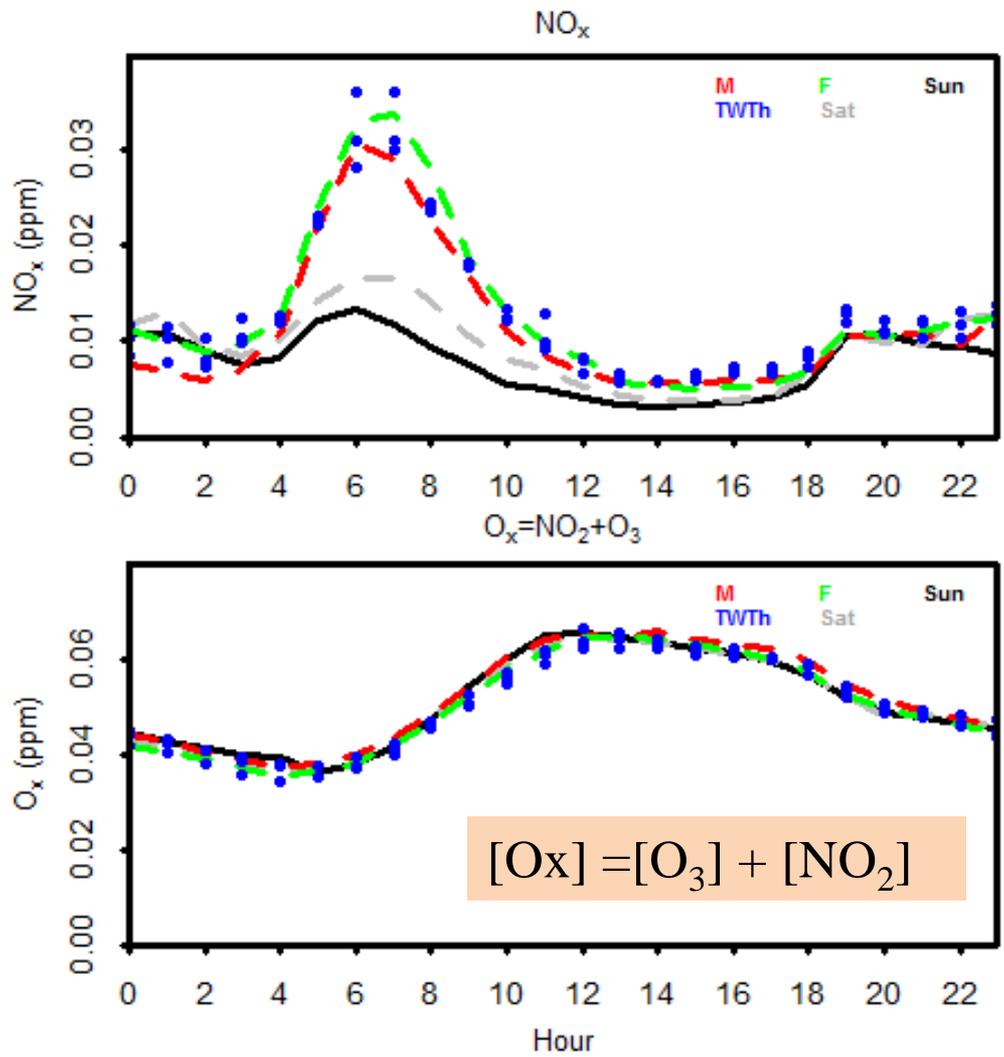
- O₃ shows opposite trend
- does not show large variation
- higher on weekends in early morning hours

Why?

- Suppressed by the high NO_x on weekday
- Slightly higher O₃ production (P_{O₃}) on weekends?

Weekend Effect: Lower Precursor Emissions, no Change in O_x

Diurnal Trend in NO_x and O_x



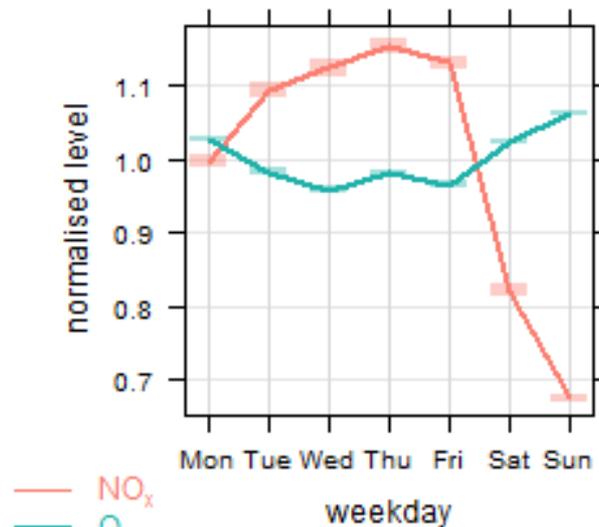
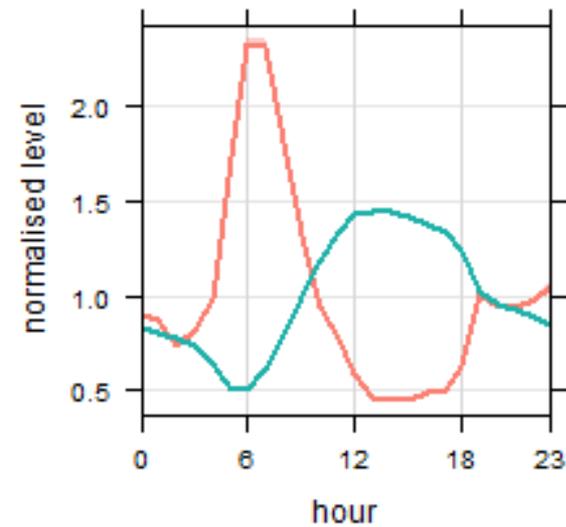
Diurnal Trend in NO_x

- Lower NO_x levels on weekends

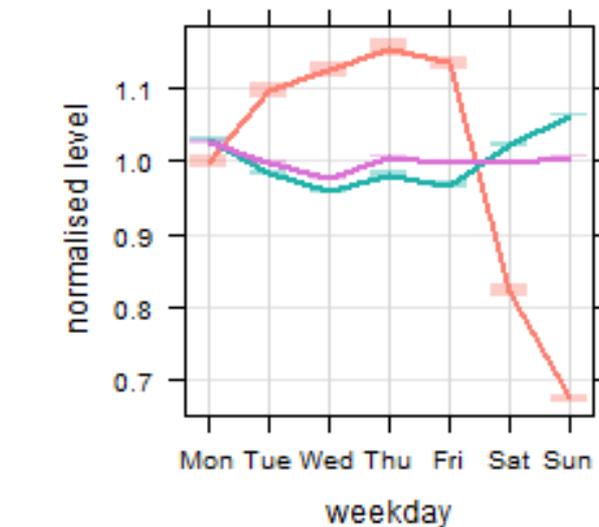
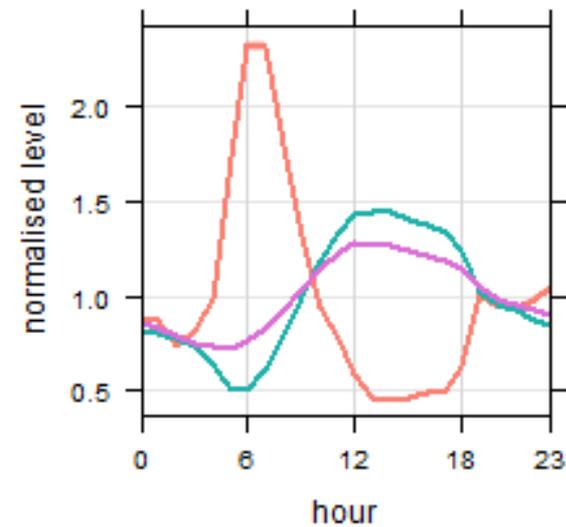
O_x trend

- O_x levels are not very sensitive to the changes in NO_x .
 - suggests NO_x saturated regime
 - O_3 is suppressed by high NO_x on weekdays
- $O_3 + NO \rightarrow NO_2 + O_2$

Weekend Effect: Slightly Higher O₃, Less Variation in Ox



— NO_x
— O₃
— O_x



NO_x

- Lower NO_x levels on weekends
- 40 % variation in NO_x

Ozone

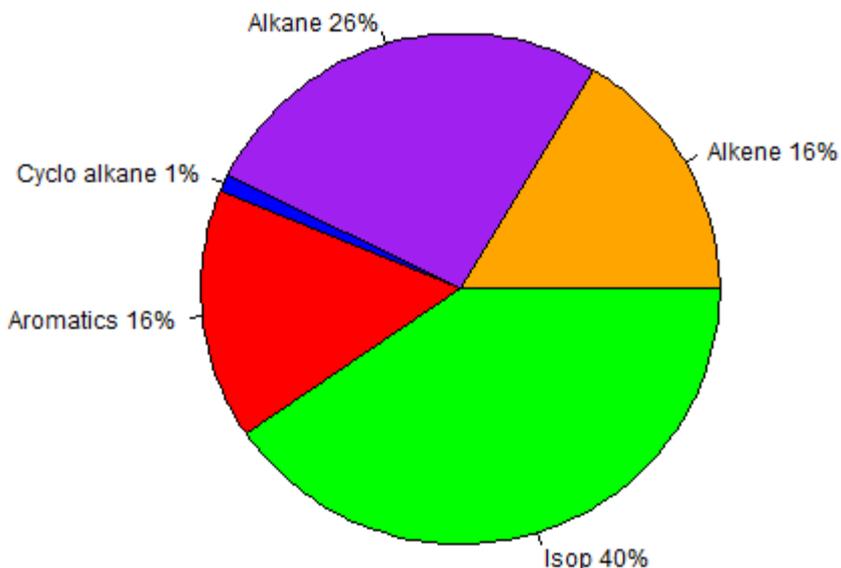
- Higher O₃ on weekends
- Variation is within 10 %

O_x = O₃ + NO₂

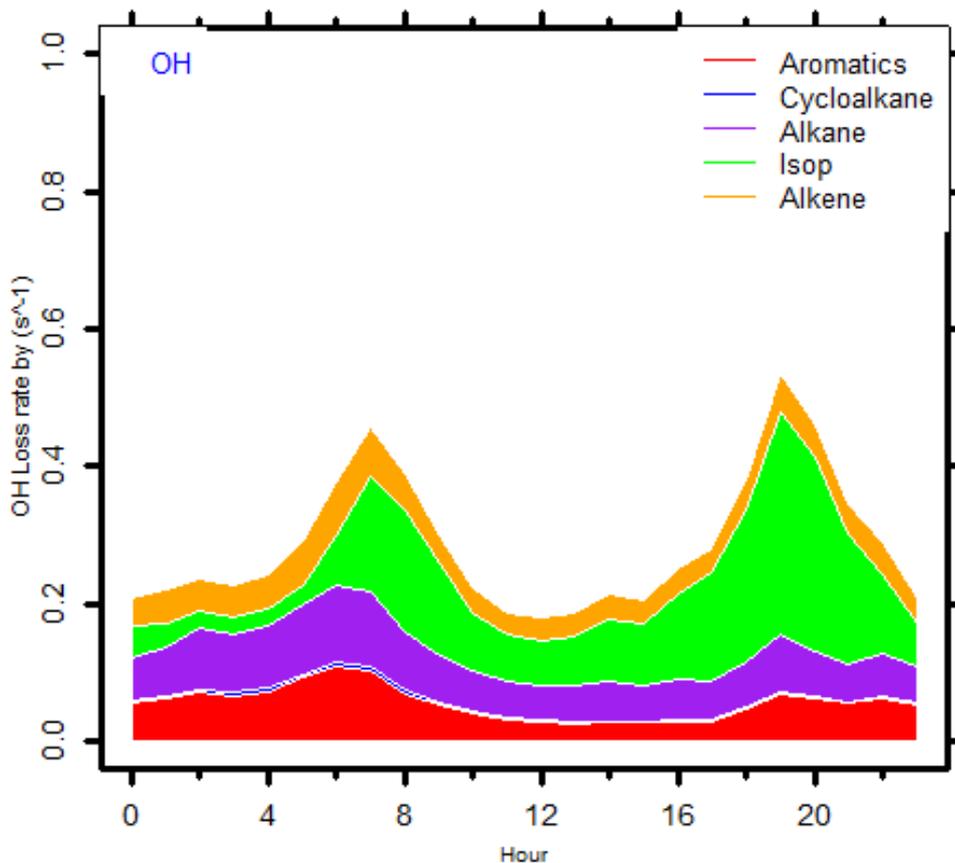
- Shows less variation
- within 5 %
- Insensitive to changes in precursors
- NO_x saturated regime
- Importance of VOCs and their speciation

VOC Contribution to OH Loss Rates in Summer: Importance of Alkanes

OH Loss Rates due to VOCs
during summer



OH reactivity = 0.21 s^{-1}

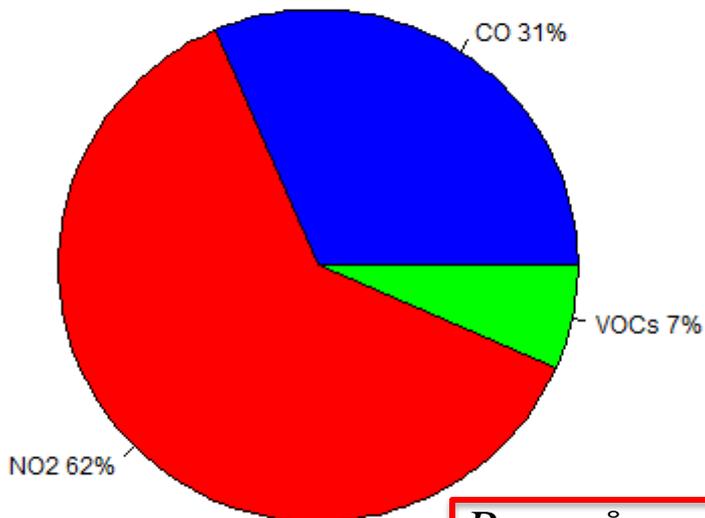


$$R_{OH} = \dot{a} (k_{OH+VOC} * [VOC])$$

- Alkanes and isoprene appear to dominate the OH loss rate.
- Not measuring all VOCs; oxygenates and monoterpenes → lower limit
- Preliminary analyses: uncertainty in the calibration factors

Contribution to OH Loss Rates in Summer: (VOCs + CO) vs. NOx

Total OH Loss Rates during summer



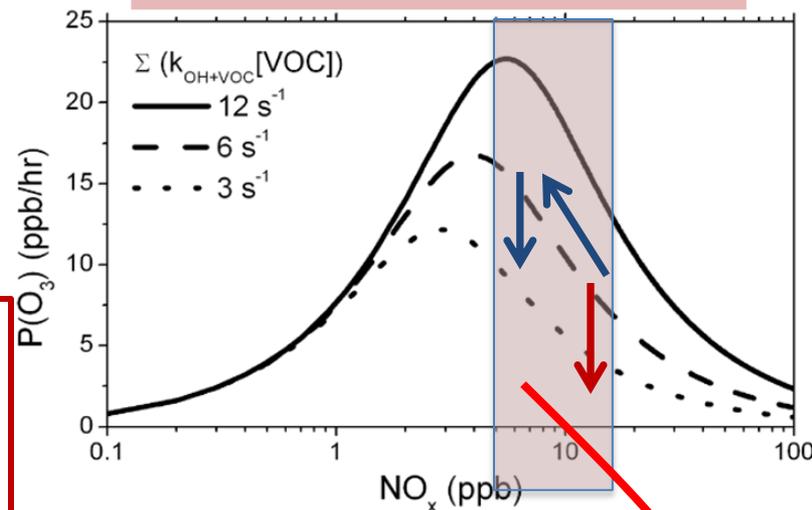
$$R_{OH} = \dot{a} (k_{OH+VOC} * [VOC])$$

OH reactivity=3.3 s⁻¹

- NO₂ dominates the OH reactivity
- NO₂ accounts for ~ 60 % of total
- VOC + CO account for ~ 40 % of the total

- Independent confirmation for “NO_x 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

Rate of ozone production



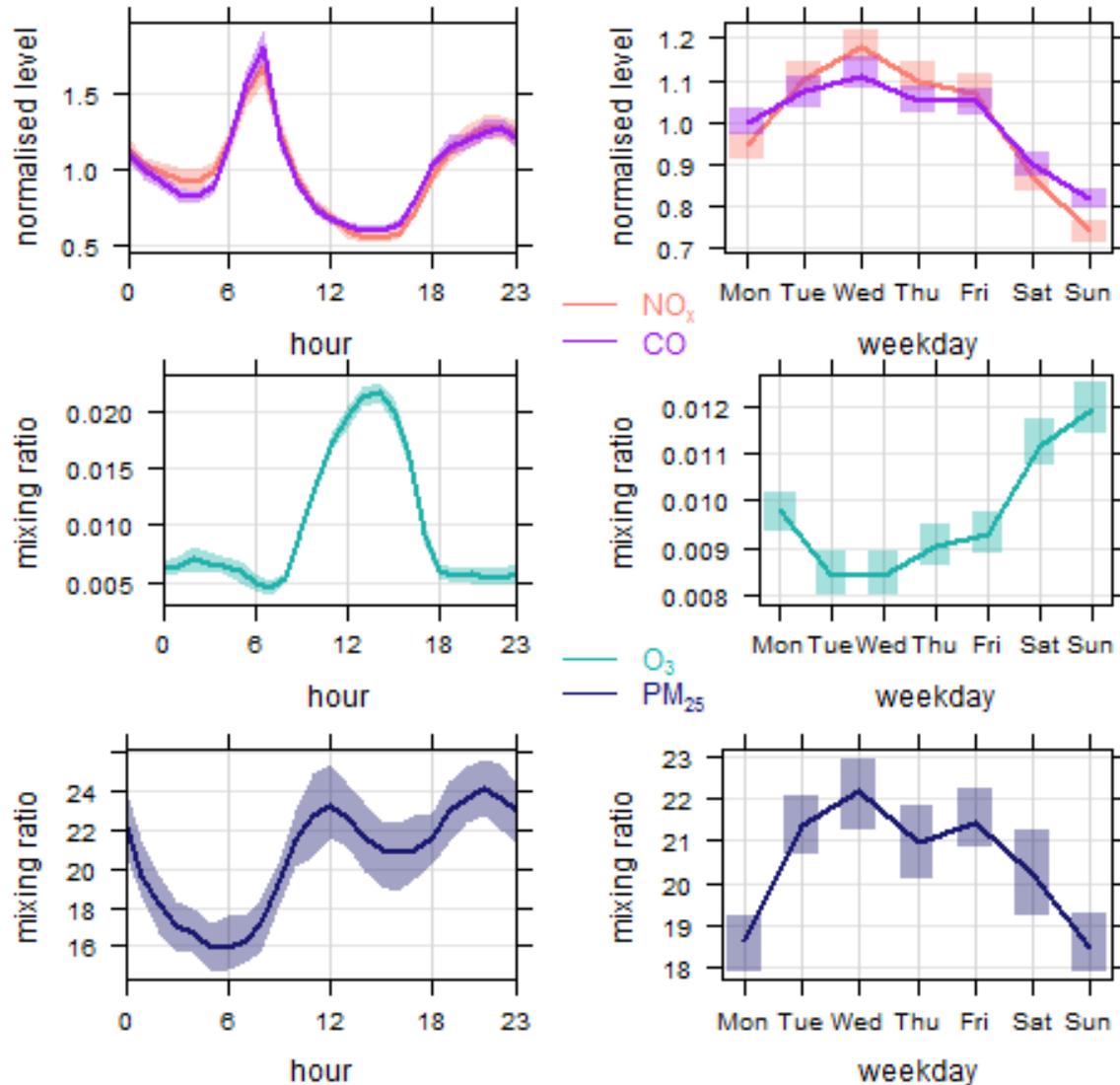
“NO_x- saturated” regime
OH + NO₂ termination dominates
 $P(O_3) \propto [VOC], 1/[NO_x]$

Summary

- Both VOCs and NO_x levels are lower on weekends.
- In contrast, ozone levels are slightly higher on weekends.
- Weekly O_x 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 NO_x limited regime).
- Analysis points to “NO_x 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}



NO_x & CO

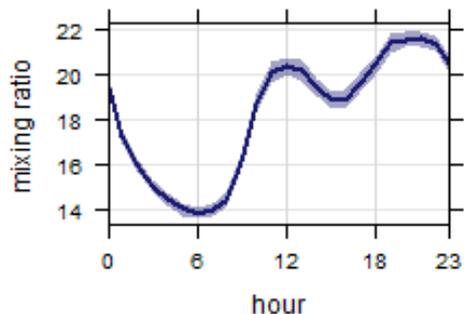
- Lower NO_x levels on weekends
- 40 % variation in NO_x

Ozone

- Higher O₃ on weekends
- Variation is large, ~ 40 %

PM_{2.5}

- Shows less variation
- 20 % lower on weekends
- Diurnal profile shows midday and nighttime peak.
- Nighttime activity



Winters (Dec – Jan) 2015 - 2016

Wintertime PM_{2.5} Study: Chemical Mechanism and Nitrate Chemistry

Utah Division of Air Quality
Contact: mbaasandorj@utah.gov



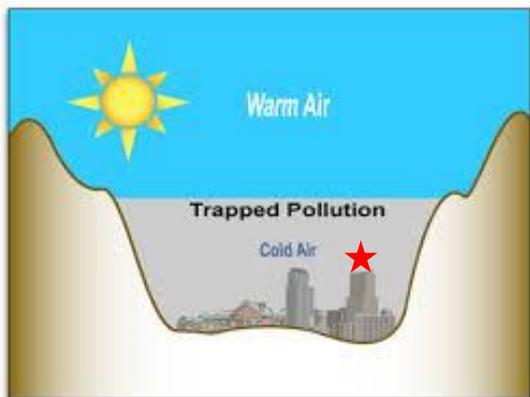
Objectives:

- Understand the mechanism for the PM_{2.5} formation, in particular nitric acid formation
- Determine limiting precursor: NH₃ vs. HNO₃



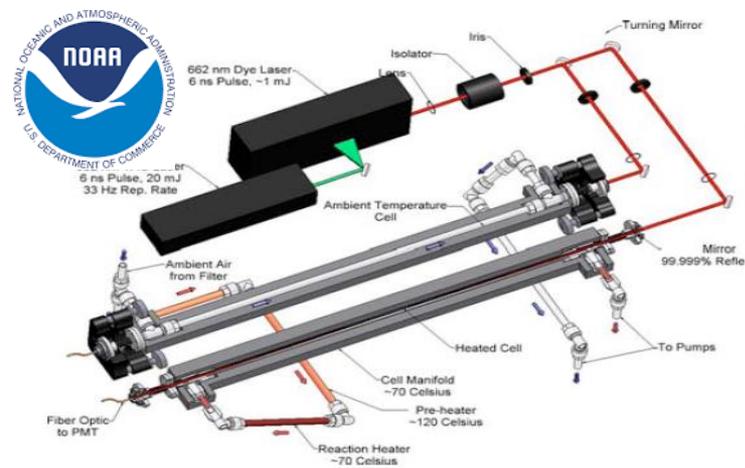
Wintertime $PM_{2.5}$ Study: Chemical Mechanism and Nitrate Chemistry

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 NO_3 and N_2O_5 , and NO_y instrument



Ammonia analyzer



Potential sites



Downtown SLC



WBB UofU



Intermountain Health Center Murray

Species

NO_3/N_2O_5

O_3

NH_3

NO_y , NO , NO_2

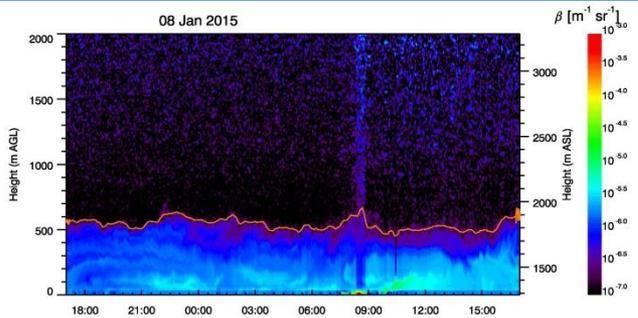
$PM_{2.5}$

Met etc.

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



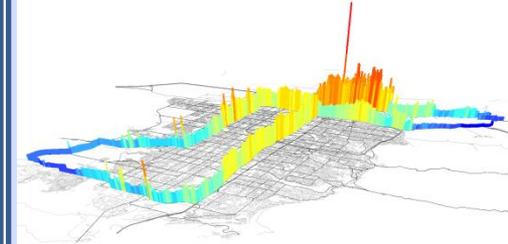
Scanning Doppler LiDAR

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



O₃, PM_{2.5}, NO₂, met

Spatial Distribution



Salt Lake Valley
CO₂ January 2013 Inversion

- CO₂ x2
- CO
- CH₄
- NO or Nox
- PM 2.5 – 10
- O₃
- GPS
- met



Dr. John Lin's group



Utah Department of
Environmental
Quality



West Valley High Time Resolution Air Toxics Monitoring Campaign

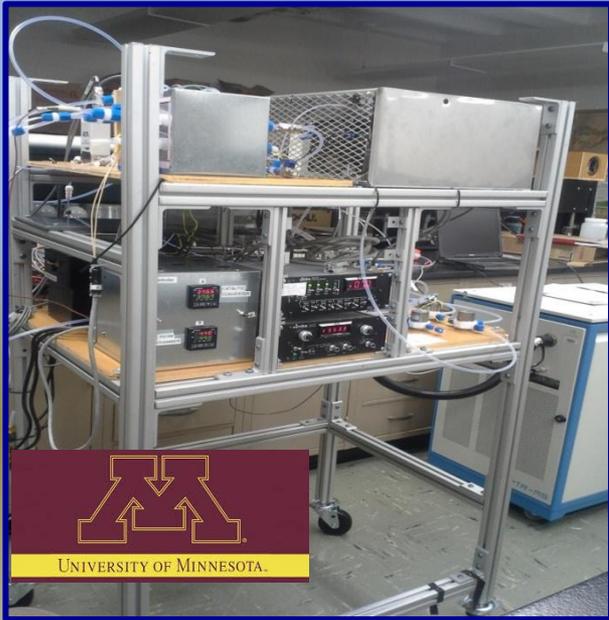
Utah Division of Air Quality
Contact: pbarickman@utah.gov
mbaasandorj@utah.gov



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

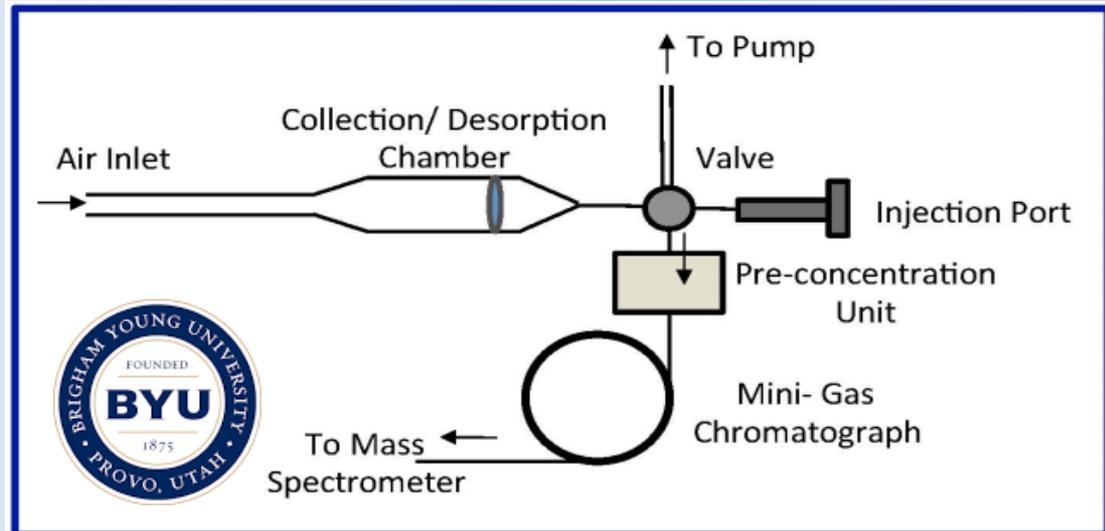
Objective: determining HAPs exposure levels and characterizing sources

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.

Two proposed sampling campaigns:
1. Dec 2015 – Feb 2016
2. June – August 2016

Acknowledgements

- State of Utah legislature for funding for air quality research
- Air monitoring group for data collection over the years
- Seth Arens, Michael Yang and others for GC-FID measurements

Questions?