Winter (Dec – Jan ) 2015 - 2016

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

Utah Division of Air Quality
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Utah Basins

Cache Valley

Salt Lake Valley — medium-sized partly open valley with large urban population

Uintah Basin — large very deep basin with small population

Each basin has characteristic snow cover climatology and depth of ‘inversion’ resulting from confining topography

By Erik Crossman
LETTER

High winter ozone pollution from carbonyl photolysis in an oil and gas basin

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By Erik Crossman
Meteorological and environmental aspects of one of the worst national air pollution episodes (January, 2004) in Logan, Cache Valley, Utah, USA

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Received 15 November 2004; accepted 14 May 2005
Elevated fine PM episodes between Dec - Feb
Approximately 80% of Utahns live along the **Wasatch Front**
Factors important for SLC air pollution:
Confined topography limits horizontal mixing.

REMOTE SENSORS.

Two National Center for Atmospheric Research (NCAR) radar wind profilers, a scanning pulsed Doppler lidar, and a mini-sodar (Figs. 2d–f) provided continuous observations of winds above the SLV during PCAPS. The radar wind profilers (915 and 449 MHz), located in the valley center, characterized the wind shear within and above (~200–3,000 m AGL) each CAP as well as the occasional penetration of strong winds into the valley atmosphere. Changes in wind occurring closer to the ground (20–200 m AGL) were determined with the minisodar that was situated near the GSL to observe land and lake breezes. The lidar provided additional observations of winds aloft along the western edge of the SLV.

SURFACE METEOROLOGICAL STATIONS.

Monitoring the complete surface energy balance at seven locations distributed throughout the SLV (Fig. 1) was of fundamental importance during PCAPS. These sites were chosen to span the geographical extent of the valley and to represent varying land use, ranging from urban to agricultural. Each location housed an NCAR Integrated Surface Flux Station (ISFS) equipped with a three-dimensional (3D) sonic anemometer, fast response temperature and humidity sensors, solar and terrestrial radiometers, and soil temperature probes (Fig. 2a). Five automated weather stations (Fig. 2b) were installed at the south end of the SLV along a vertical transect of the Traverse Mountains (Fig. 1) to monitor variations in wind, temperature, and humidity during CAPs. These sites are also useful in diagnosing a cross-barrier exchange between the Utah and Salt Lake valleys (Chen et al. 2004; Pinto et al. 2006). Additional vertical profiles of temperature and humidity were established with Hobo dataloggers distributed at 50-m elevation increments along three transects: one ascending a prominent ridge on the west slope of the Wasatch Mountains and two along the east slopes of the Oquirrh Mountains. Recording measurements every 5 min, these dataloggers provide temperature pseudosoundings capable of documenting rapid changes in the vertical thermodynamic structure.

The PCAPS field campaign also benefitted from more than 100 preexisting surface meteorological
Basic Weather Features Associated with Poor Winter Air Quality: Well-Understood

Warm, clean air

High pressure

Cold, dirty air

Light winds

By Erik Crossman
PM events are closely associated with atmospheric stability

Relationship between particulate air pollution and meteorological variables in Utah's Salt Lake Valley

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HIGHLIGHTS

- PM$_{2.5}$ is closely related to integrated atmospheric stability in the valley volume.
- No long-term trends in atmospheric stability are seen in the 40-y period of record.
- PM$_{2.5}$ rises 10 ug m$^{-3}$ per day in multi-day episodes of high atmospheric stability.
- PM$_{2.5}$ is above the NAAQS on approximately 18 days per winter season.
- Snow cover is a key variable affecting PM$_{2.5}$ exceedances.

Puzzling facts:

- PM composition is quite uniform throughout the valley.
- Levels (24hr) are uniform despite sources heterogeneity; except the foothills
Major constituent of PM$_{2.5}$ during pollution episodes: NH$_4$NO$_3$

- Secondary sources dominate.
- Dominated by NH$_4$NO$_3$ (50 – 75% of the total)
- Secondary NH$_4$Cl is also a significant contributor (10-15% of the total PM$_{2.5}$) (Kelly et al., 2013)
- Chemical processes leading to PM formation are not understood well.
Long list of uncertainties

• Nitric acid formation; daytime vs. nighttime
• Sensitivity of O$_3$ and HNO$_3$ to changes in NOx and VOCs
• Which precursor limits the PM formation; NH$_3$ vs. HNO$_3$
• What are the sources of NH$_3$?
Other valleys in the intermountain west also experience cold pools and high PM2.5 ($\text{NH}_4\text{NO}_3$)

By Watson et al.

Other valleys in the intermountain west also experience cold pools and high PM2.5 (NH$_4$NO$_3$).

- Better understanding of PM pollution is important to improve wintertime air quality in the intermountain west.

Wintertime PM events: enhancements of primary pollutants, low oxidant levels near surface.

- PM$_{2.5}$ has daytime max
- CO is enhanced.
- Opposite of Uintah basin
- Both NO & NO$_2$ are enhanced.
- NOx: 100-200 ppb
- O$_3$ is titrated at night due to high NO.
- Low during the day (inefficient photolysis).
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
- Effect of Monday is seen on Tuesday
Near surface measurements suggest entrainment of PM from upper layer within the inversion during inversion Jan 23, 2013 in Hawthorne.

- PM$_{2.5}$ shows an increase.
- O$_3$ increases.
- Sharp decrease in NOx, NO, CO.
- Consistent with downward mixing of PM rich air from upper layer.
- NO$_2$ levels are sustained throughout the day; 30 – 40 ppb of NO$_2$ during the day.

At night:
- O$_3$ is depleted.
- High NOx, CO.
- PM $\sim$ 20 ug/m$^3$.

10AM - 12 PM:
- PM$_{2.5}$ shows an increase.
- O$_3$ increases.
- Sharp decrease in NOx, NO, CO.
- Consistent with downward mixing of PM rich air from upper layer.
- NO$_2$ levels are sustained throughout the day; 30 – 40 ppb of NO$_2$ during the day.
Depth of the inversion layer: \(~400 - 600\) m AGL

Nighttime

Higher O3, lower NO

\[ \text{NO}_2 + \text{O}_3 \rightarrow \text{NO}_3 + \text{O}_2 \]

\[ \text{NO}_3 + \text{NO}_2 + M \leftrightarrow \text{N}_2\text{O}_5 + M \]

\[ \text{N}_2\text{O}_5 + \text{H}_2\text{O} \rightarrow 2\text{HNO}_3 \]

O3 depleted, high NO

\[ \text{NO}_2 + \text{O}_3 \rightarrow \text{NO}_3 + \text{O}_2 \]

\[ \text{NO}_3 + \text{NO}_2 + \text{M} \leftrightarrow \text{N}_2\text{O}_5 + \text{M} \]

\[ \text{N}_2\text{O}_5 + \text{H}_2\text{O} \rightarrow 2\text{HNO}_3 \]

PM rich air

\[ \text{NH}^+\text{aq} + \text{NO}^-\text{aq} \leftrightarrow \text{NH}_3 (g) + \text{HNO}_3 (g) \]

\[ \text{NH}_4\text{NO}_3 (s) \leftrightarrow \text{NH}_3 (g) + \text{HNO}_3 (g) \]

Coupling between meteorology and chemistry.
Objectives:

• Understand the mechanism for the PM2.5 formation, in particular nitric acid formation
• Evaluate sensitivity of oxidant and nitric acid formation to changes in NOx and VOCs
• Determine limiting precursor: NH₃ vs. HNO₃

Existing measurements:
CO₂, CH₄, CO₂ isotopes, H₂O isotopes

<table>
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<tr>
<th>Species</th>
<th>Instrument (model)</th>
<th>Time resolution (response time)</th>
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<tbody>
<tr>
<td>NO₃, N₂O₅</td>
<td>Cavity Ring Down Spectrometer (CaRDs)</td>
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<td>Min</td>
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<td>Particle size distribution</td>
<td>Optical particle counter</td>
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<tr>
<td>NH₃</td>
<td>Innova photoacoustic field gas monitor</td>
<td>(&lt;2 min)</td>
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Time evolution of vertical distribution

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

O$_3$, PM$_{2.5}$, NO$_2$, met
Complementary Obs: The Mobile Lab (aka “Nerdmobile”)

Relocatable and mobile gas sampling

Capability

- Carbon dioxide
- Carbon monoxide
- Methane
- Ozone
- Flask – trace gases
- Flask – isotopes
- Flask – VOCs
- PM
- NOx
- GPS
- Temperature
- Humidity
- Wind
More Snow Cover Days in Salt Lake City and Missoula (2000-2013)

High Heat Deficit on Snow Cover Days

- Suggests importance of snow cover in PM formation
- Snow cover = higher RH & lower T; importance of hydrolysis reactions ??
- Weird snow chemistry ?? (e.g. Uintah basin)

High PM$_{2.5}$ on Snow Cover Days except for Spokane

- Normalizing PM$_{2.5}$ by heat deficit control for variations in stability.

Summary

• PM pollution is prevalent in urban mountain valleys and affects large population.
• Evidence of interplay between the dynamics and chemical processes driving the elevated PM levels measured near surface.
• Very interesting chemistry tied to the snow/RH is taking place.
• Many uncertainties regarding the chemical mechanism.
• Vertical and spatial measurements will be key for understanding the chemistry.
• Large scale studies (aircrafts etc.) are needed.