An odd oxygen framework for wintertime ammonium nitrate aerosol pollution in Salt Lake Valley

$\text{NO}_x$ and VOC control as mitigation strategies

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Wintertime PM$_{2.5}$ pollution persists in the US and elsewhere.

PM-2.5 Nonattainment Areas (2006 Standard)

Nonattainment areas are indicated by color.

When only a portion of a county is within a nonattainment area boundary, it is indicated by partial color filling.

PM-2.5 Classification
- Serious
- Moderate

Salt Lake Valley (SLV)
Cache Valley
Utah Valley

San Joaquin Valley (SJV)
South Coast Basin

Salt Lake City, USA

PM$_{2.5}$ (μg m$^{-3}$)

Day of Year

0 100 200 300

0 20 40 60 80
Salt Lake Valley pollution episodes occur during persistent cold air pools (PCAPs)

Typically more sensitive to these reductions

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

In the SLV: \( \text{PM}_{2.5} = \text{Wintertime PM}_{2.5} \approx \text{Ammonium nitrate aerosol} = \text{HNO}_3(g) \)

Some of the questions driving Utah Winter Fine Particulate Study (UWFPS 2017)

- What are the chemical mechanisms that form HNO\(_3\) during PCAPs?
- What control strategies would be most effective for limiting HNO\(_3\) production? Is NO\(_x\) control the best strategy?
Utah Winter Fine Particulate Study (UWFPS)
January 16 – February 13, 2017

Logan (L4)
- NO\textsubscript{x}, O\textsubscript{3}, PM\textsubscript{2.5}, NH\textsubscript{3}, CH\textsubscript{4}, CO\textsubscript{2}
- I\textsuperscript{-} CIMS (HONO, HNO\textsubscript{3}, ClNO\textsubscript{2}, N\textsubscript{2}O\textsubscript{5})
- AMS (pNO\textsubscript{3})

Twin Otter (TO)
- NO\textsubscript{x}, O\textsubscript{3}, NH\textsubscript{3}
- I\textsuperscript{-} CIMS (HONO, HNO\textsubscript{3}, ClNO\textsubscript{2}, N\textsubscript{2}O\textsubscript{5})
- AMS (pNO\textsubscript{3})

University of Utah (UU) and Hawthorne (HW)
- NO\textsubscript{x}, O\textsubscript{3}, CO, PM\textsubscript{2.5}
- PTR-MS (aromatics, aldehydes)

Two major PCAPs observed.
Ammonium nitrate dominated PM\textsubscript{2.5}.
Ammonia was usually in excess.
2017 was a typical winter.
Traditional
\[ O_x = O_3 + NO_2 \]
Parameter for daytime photochemical \( O_3 \) production

More general term
\[ O_{x,\text{total}} = O_3 + NO_2 + 2*NO_3 + 3*N_2O_5 + ClNO_2 + 1.5*(HNO_3 + pNO_3^-) + PANs + ANs + OH + \ldots \]
Parameter for either photochemical \( O_3 \) or \( HNO_3 \) production

"HO\textsubscript{x}-NO\textsubscript{x} cycle"
"Nighttime N\textsubscript{2}O\textsubscript{5} chemistry"
During UWFPS we observed $O_{x,\text{total}}$ growth during the PCAPs – an indicator of photochemical activity.

During UBWOS… and here?

Inversion layer height
Salt Lake Valley
Population: ~1,000,000 (~800 people/km²)
Oil & natural gas wells: 0

Uintah Basin
Population: ~50,000 (~2 people/km²)
Oil & natural gas wells: ~10,000

1) Photochemistry is important even in the winter.
2) $O_{x,\text{total}}$ describes both $O_3$ (Uintah) and $p\text{NO}_3^-$ (SLV) pollution
DSMACC modeled the O₃ growth in Uintah basin – can a similar model described Oₓ,total in the SLV?

**Initialize with observations**

- First order loss parameter (entrainment of background air, deposition)
- MCM mechanisms for VOC chemistry
- TUV model for photochemistry

**Emissions of NOx, VOCs, HONO, HCHO**

**Dynamically Simple Model of Atmospheric Chemical Complexity**

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An $O_{x,\text{total}}$ isopleth shows the NO$_x$-VOC sensitivity of the SLV

1) NO$_x$ production in the SLV is NO$_x$-saturated and VOC-limited

2) NO$_x$ reductions, in the absence of concurrent VOC reductions, will initially increase $O_{x,\text{total}}$ in the form of pNO$_3^-$ and O$_3$.

Womack et al., *GRL*, 46, 4971 (2019)
O₃ in Uintah and pNO₃⁻ in SLV can be explained by the HOₓ chain length

\[
\text{HO}_x \text{ chain length} = \frac{\sum \text{Propagation reactions}}{\sum \text{Termination reactions}}
\]

Uintah: High VOC/NOₓ propagates cycle, making O₃.

SLV: Low VOC/NOₓ quenches cycle, terminating in HNO₃.
Summary

- $O_{x,\text{total}}$ is a general parameter to describe both $O_3$ and HNO$_3$ production.
  - $O_3$ and pNO$_3^-$ pollution are closely linked, and are endpoints of the same chemical cycle
  - The NO$_x$-VOC sensitivity isopleths also apply to pNO$_3^-$.  

- The SLV is both HNO$_3$-limited, but NO$_x$-saturated. NO$_x$ reductions alone will initially *increase* pNO$_3^-$ in the valley.

- This result may be a general worldwide phenomenon, as high NO$_x$ and limited radical sources are common in wintertime boundary layers.