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

NO_x and VOC control as mitigation strategies

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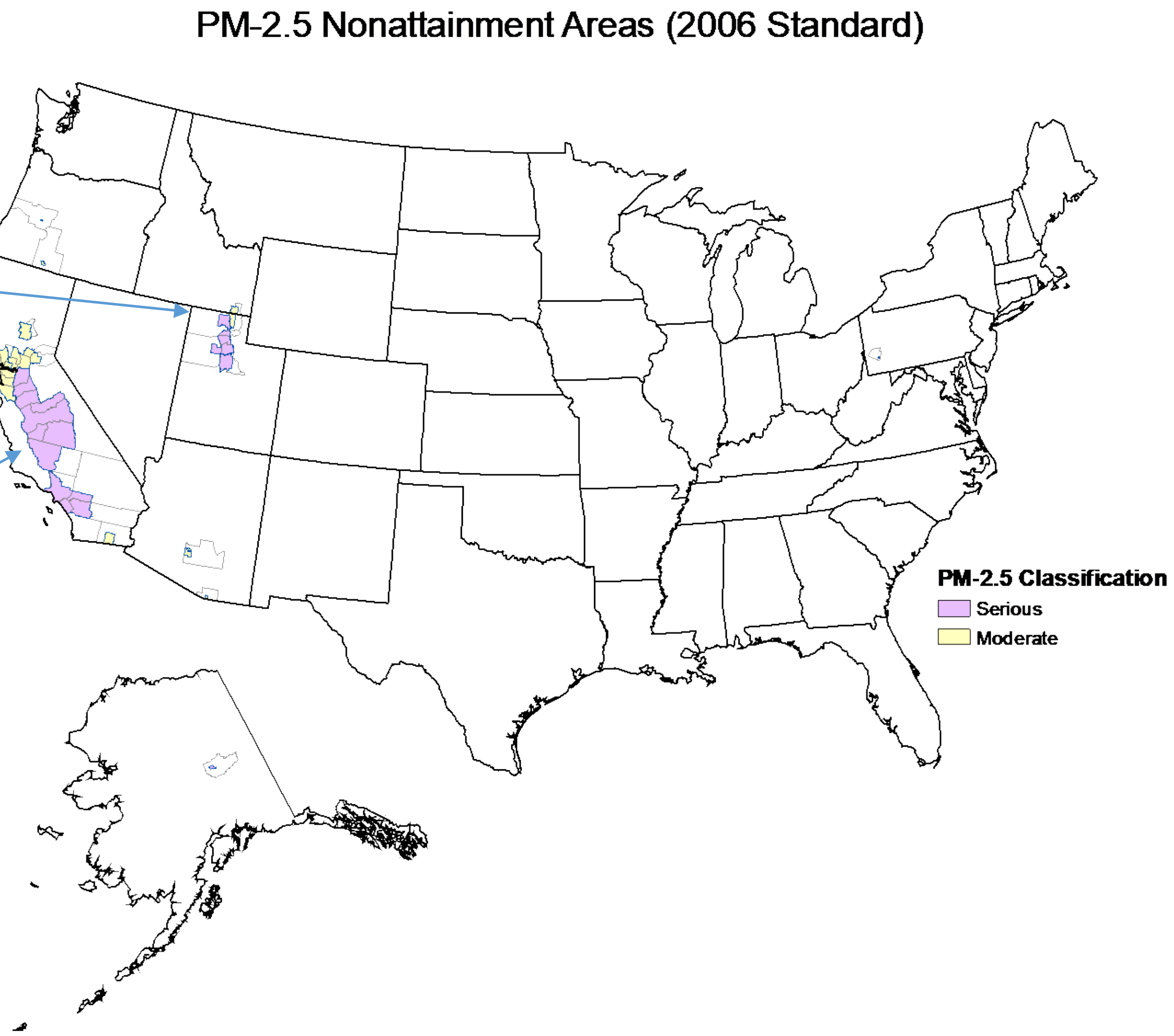
UBWOS Team

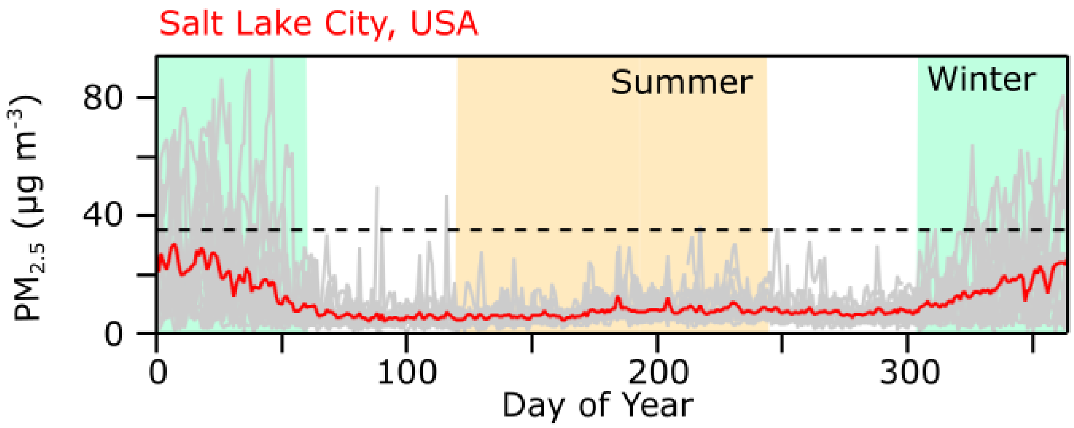
AQUARIUS Workshop // 26 September 2019

Wintertime $PM_{2.5}$ pollution persists in the US and elsewhere

Salt Lake Valley (SLV)
Cache Valley
Utah Valley

San Joaquin Valley (SJV)
South Coast Basin

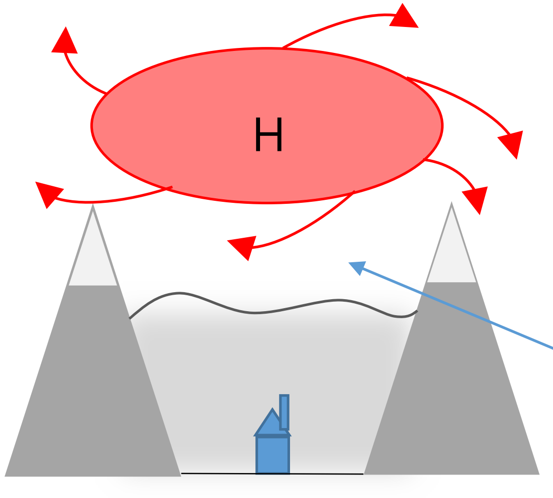




Salt Lake Valley pollution episodes occur during persistent cold air pools (PCAPs)

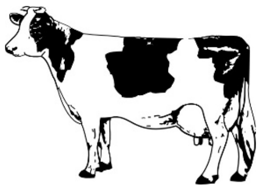
Typically more sensitive to these reductions

HNO_3 (g) + NH_3 (g) ↔ NH_4NO_3 (aq)



Warmer air

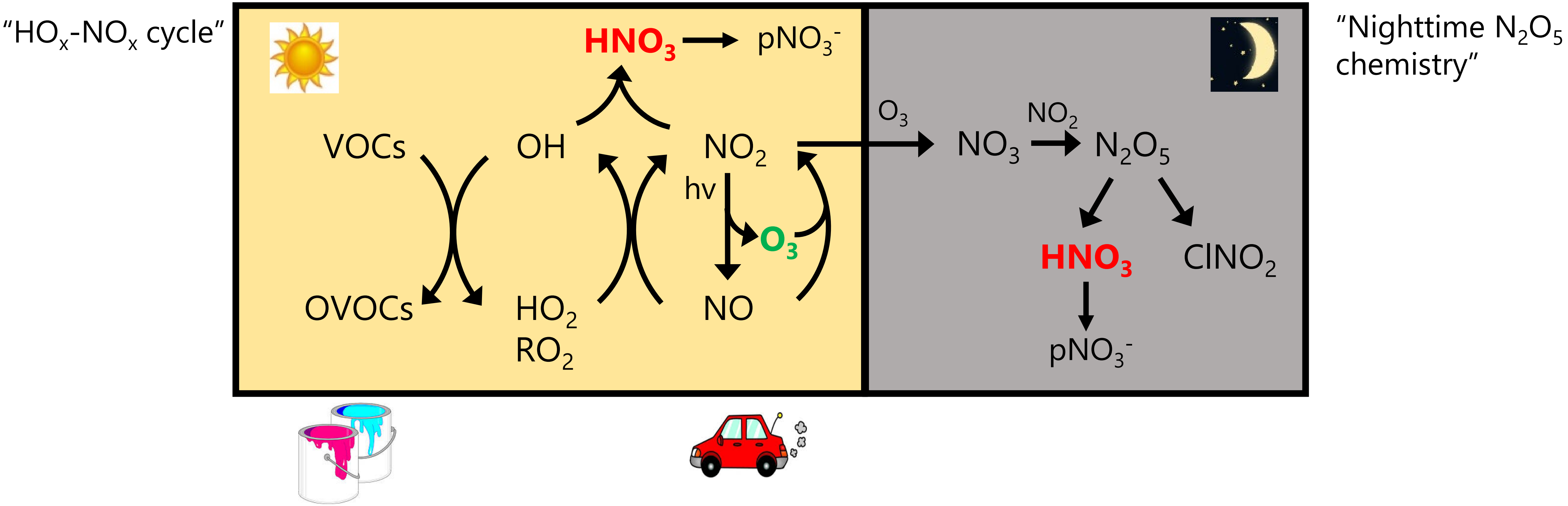
NO_x oxidation



In the SLV: $PM_{2.5}$ = Wintertime $PM_{2.5}$ ≈ Ammonium nitrate aerosol = HNO_3(g)

Some of the questions driving 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?



Traditional

$O_x = O_3 + NO_2$

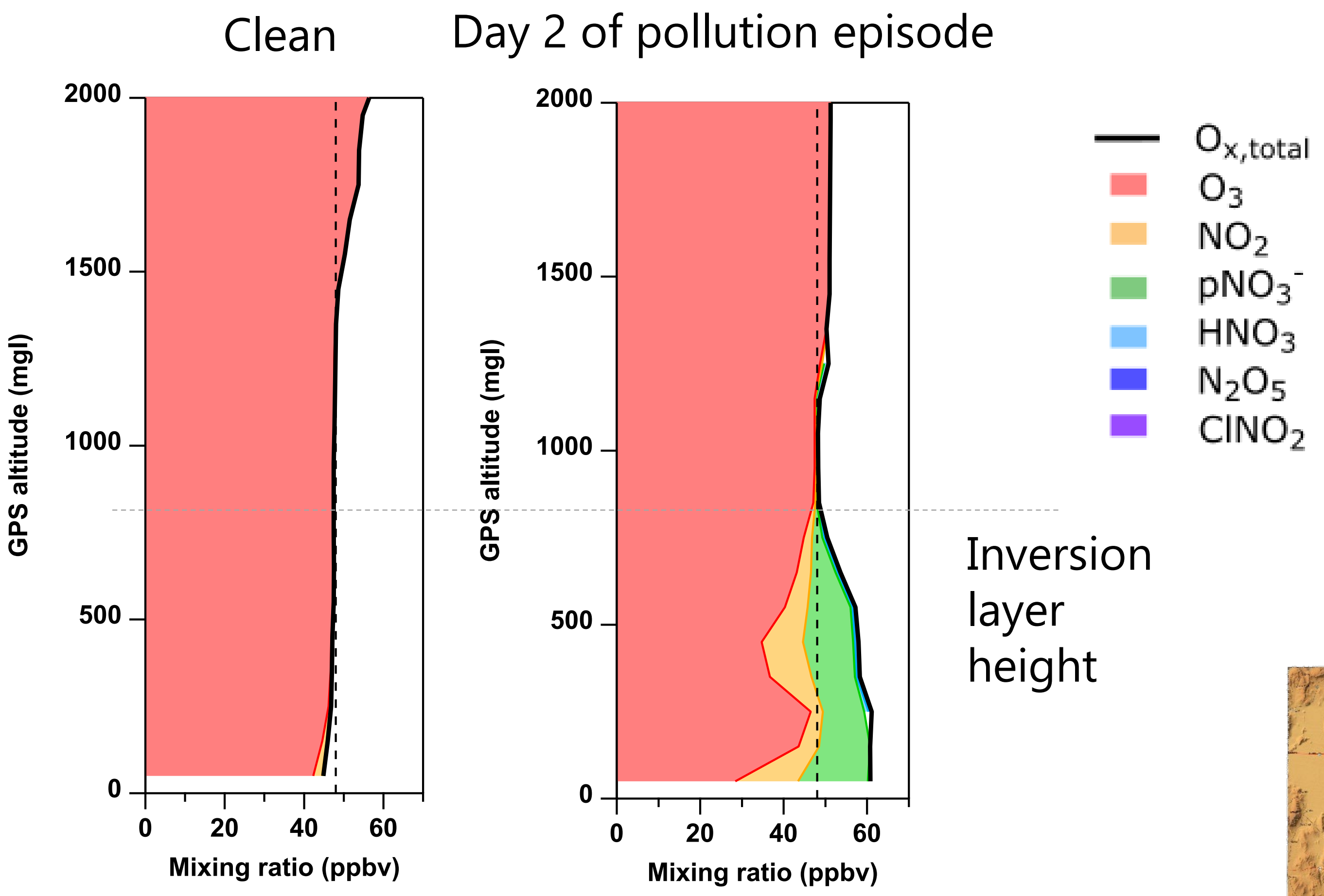
Parameter for daytime photochemical **O_3** production

More general term

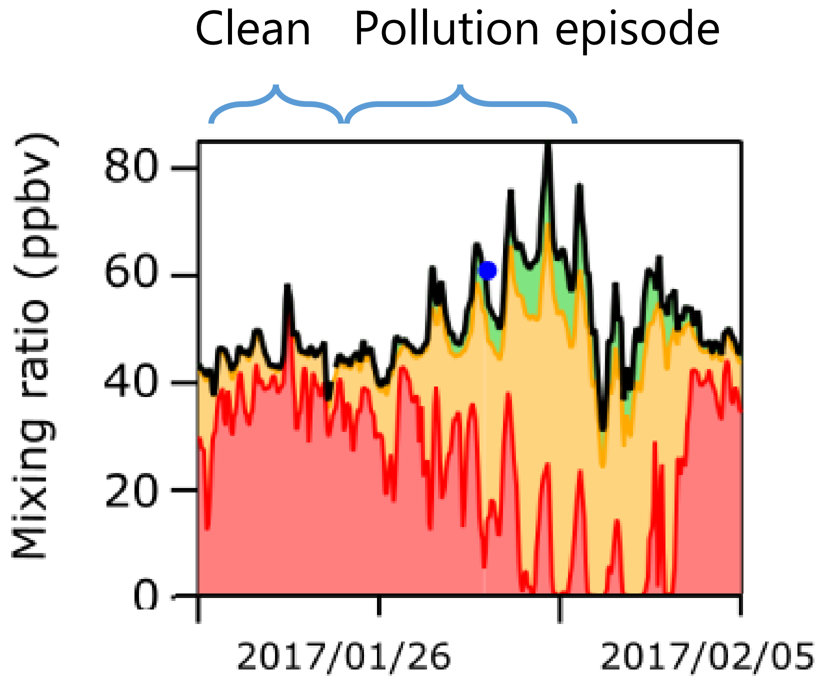
$O_{x,total} = O_3 + NO_2 + 2*NO_3 + 3*N_2O_5 + ClNO_2 + 1.5*(HNO_3 + pNO_3^-)$
$+ PANs + ANs + OH + ...$

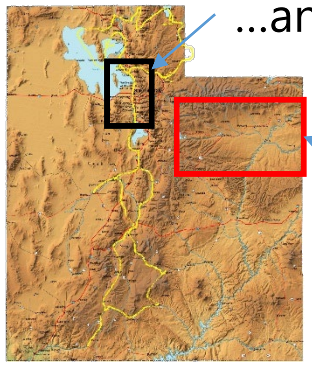
Parameter for either photochemical **O_3** or **HNO_3** production

During UWFPS we observed $O_{x,total}$ growth during the PCAPs – an indicator of photochemical activity



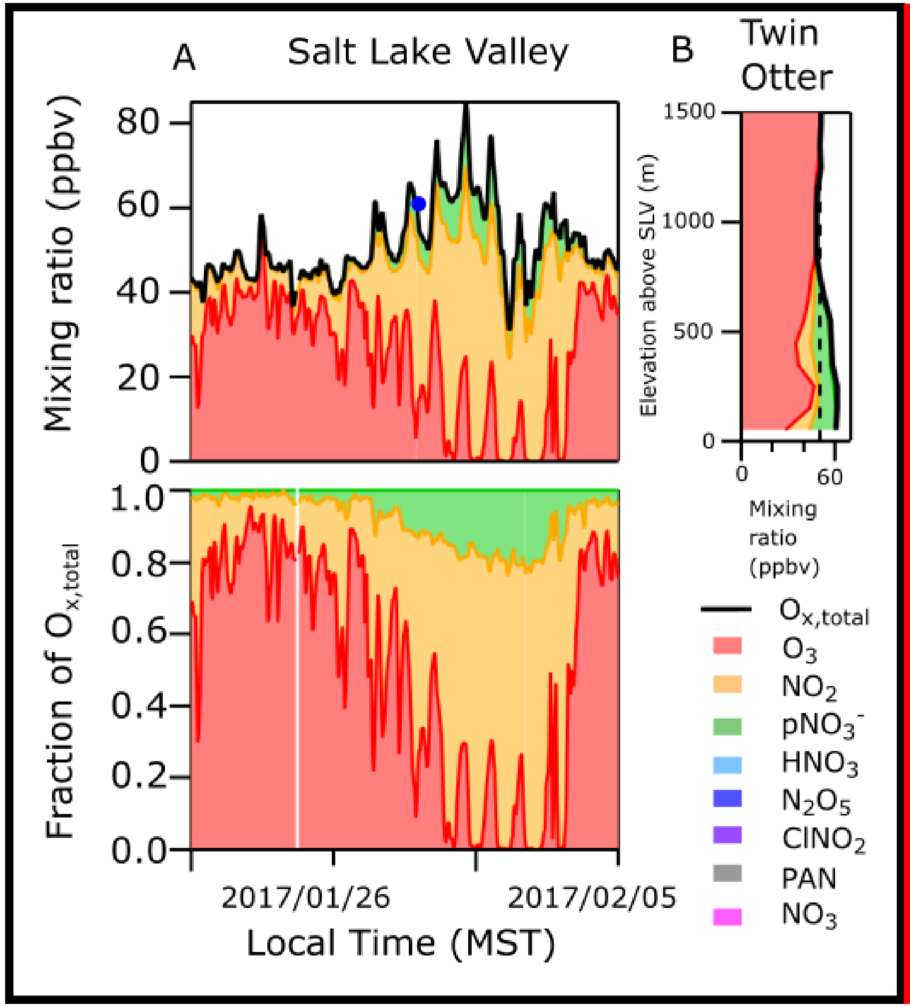
Inversion layer height

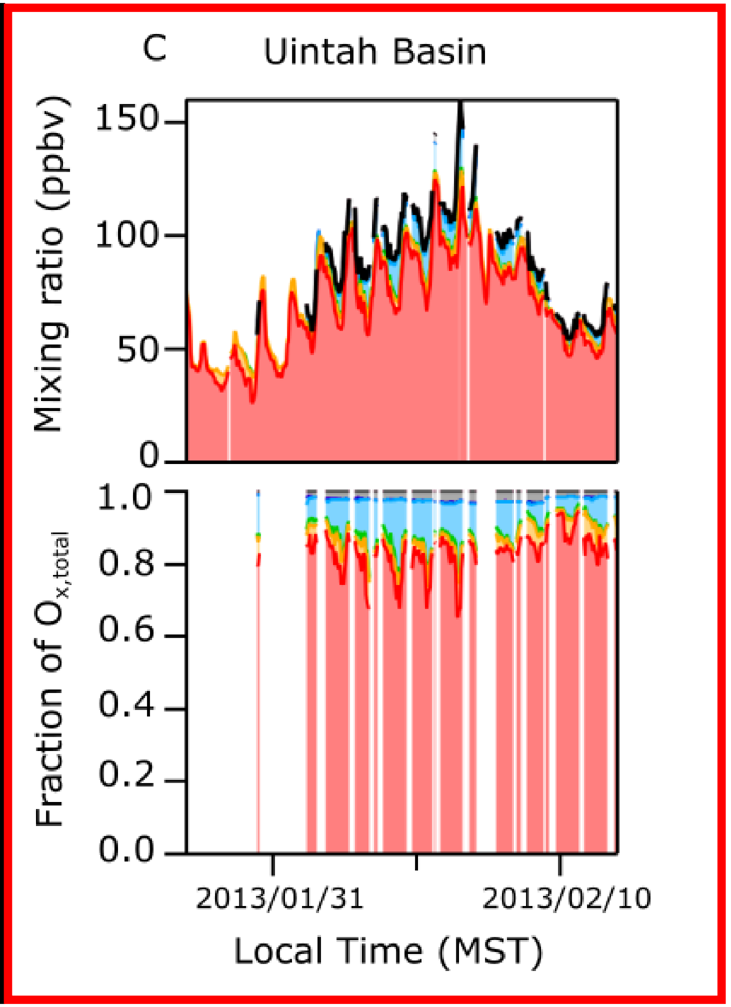




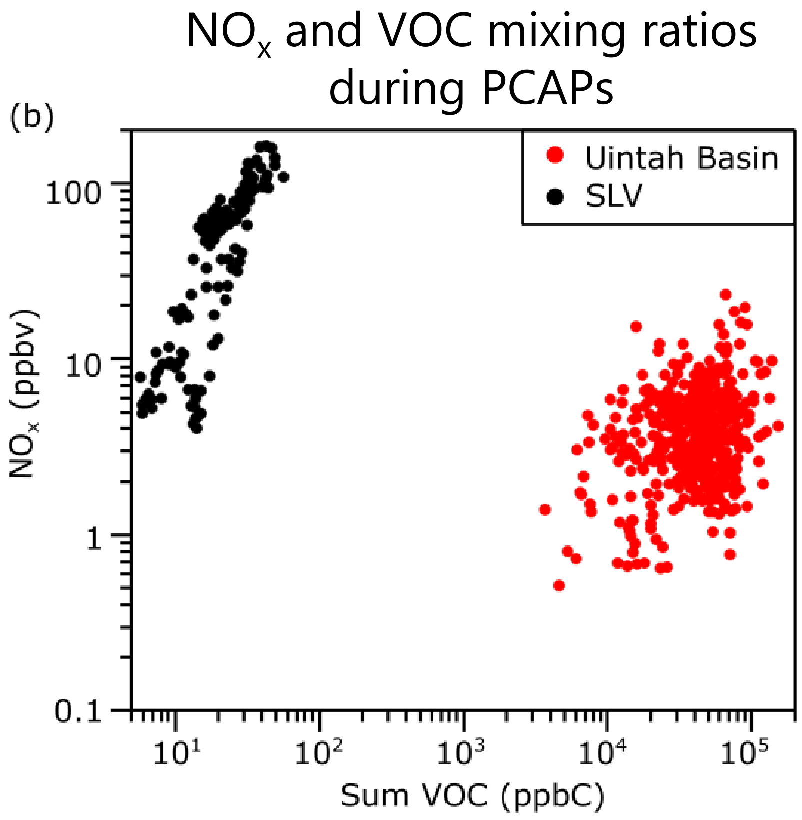
...and here?

Photochemistry important here during UBWOS

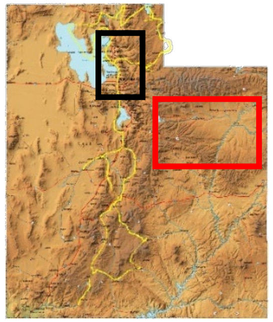




1) Photochemistry is important even in the winter.
2) $O_{x,total}$ describes both O_3 (Uintah) and pNO_3^- (SLV) pollution

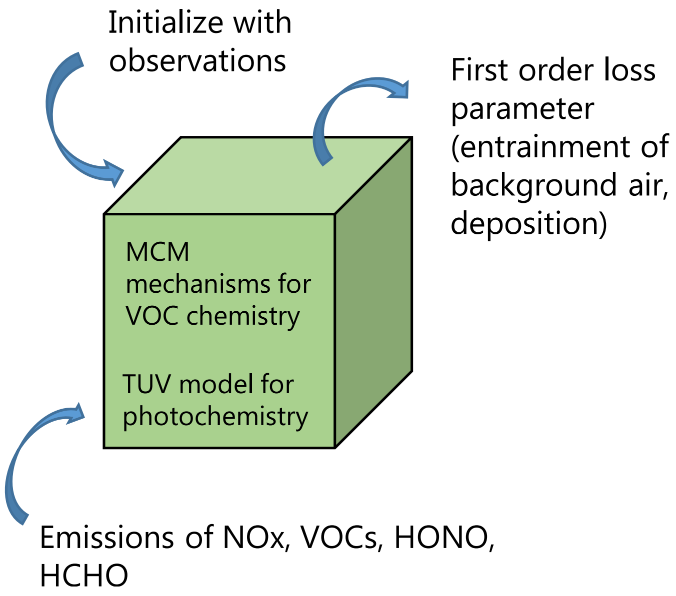


Salt Lake Valley
Population: ~1,000,000 (~800 people/km^2)
Oil & natural gas wells: 0

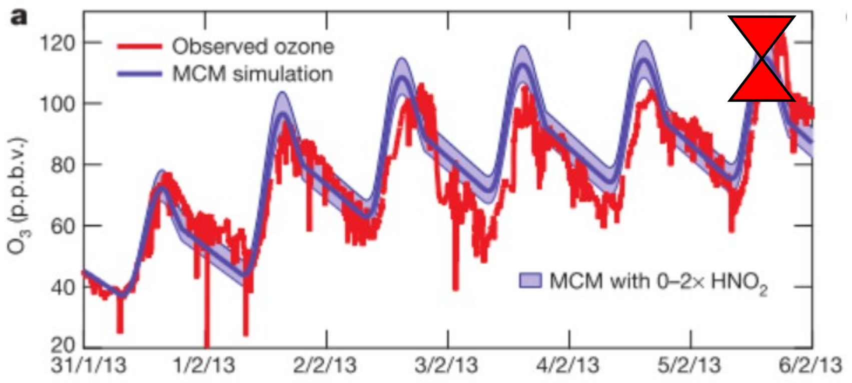


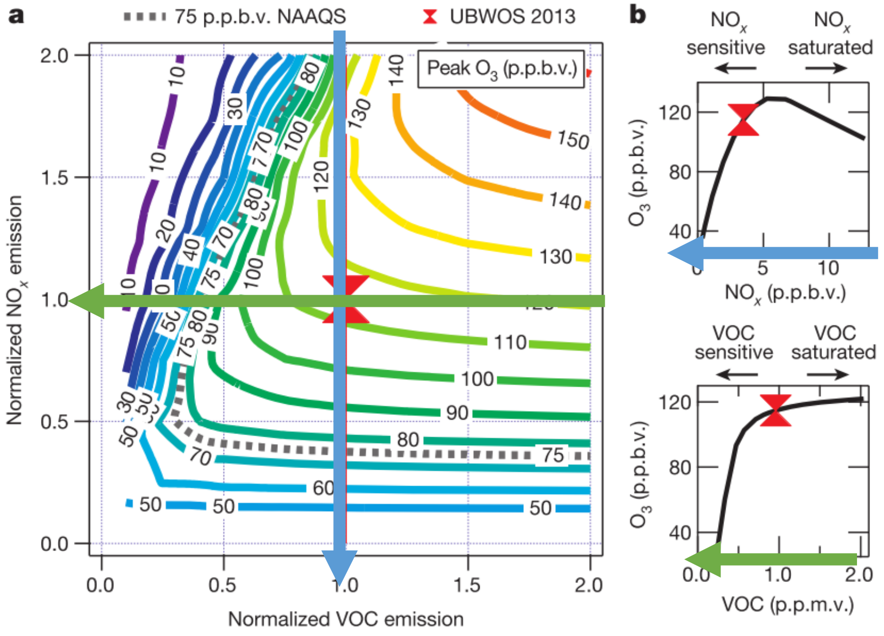
Uintah Basin
Population: ~50,000 (~2 people/km^2)
Oil & natural gas wells: ~10,000

DSMACC modeled the O_3 growth in Uintah basin – can a similar model described $O_{x,total}$ in the SLV?



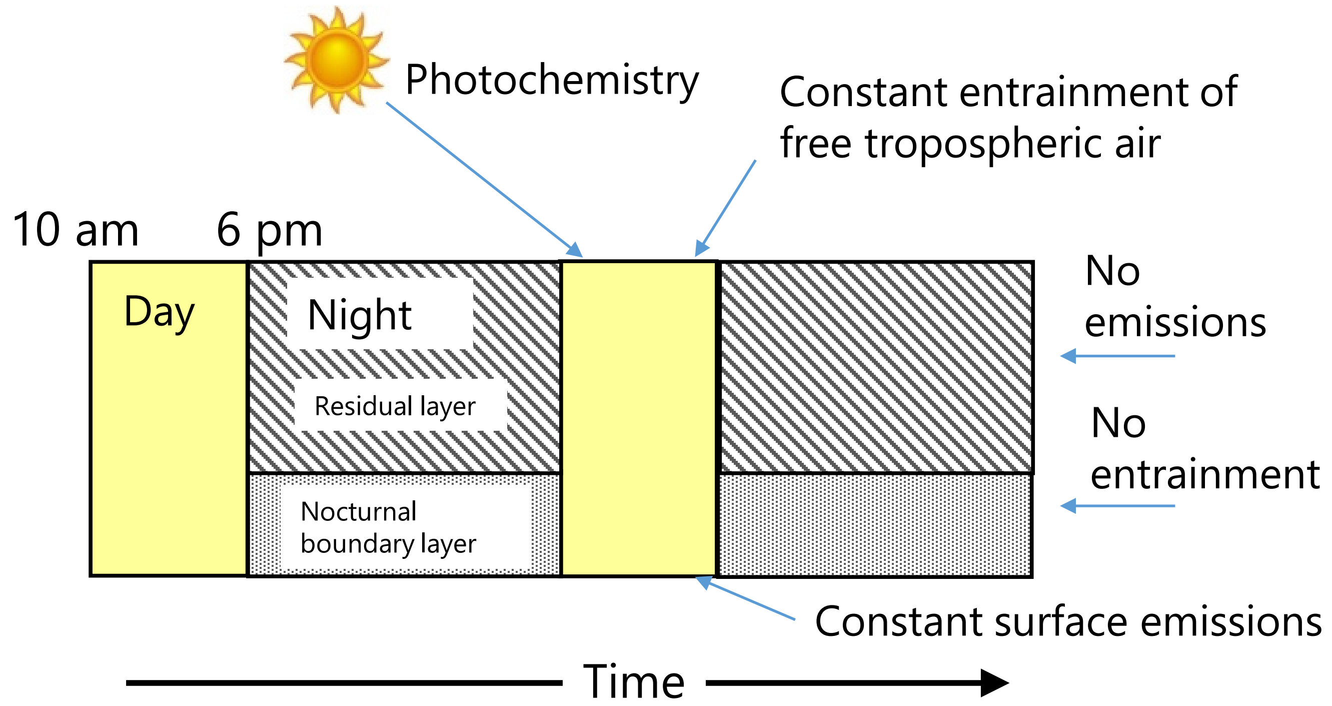
Dynamically Simple Model of Atmospheric Chemical Complexity



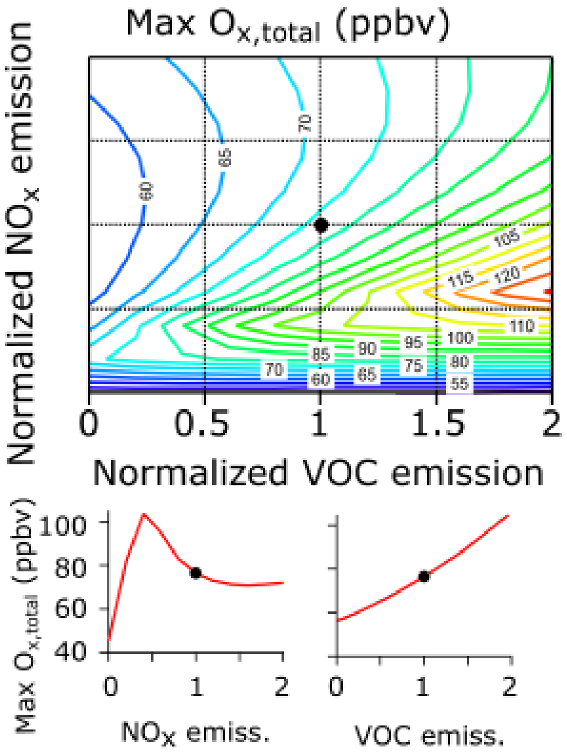


Edwards et at, *Nature* (2014)

Using a “split” DSMACC box model accounts for chemistry occurring in the residual layer at night



An $O_{x,total}$ isopleth shows the NO_x-VOC sensitivity of the SLV

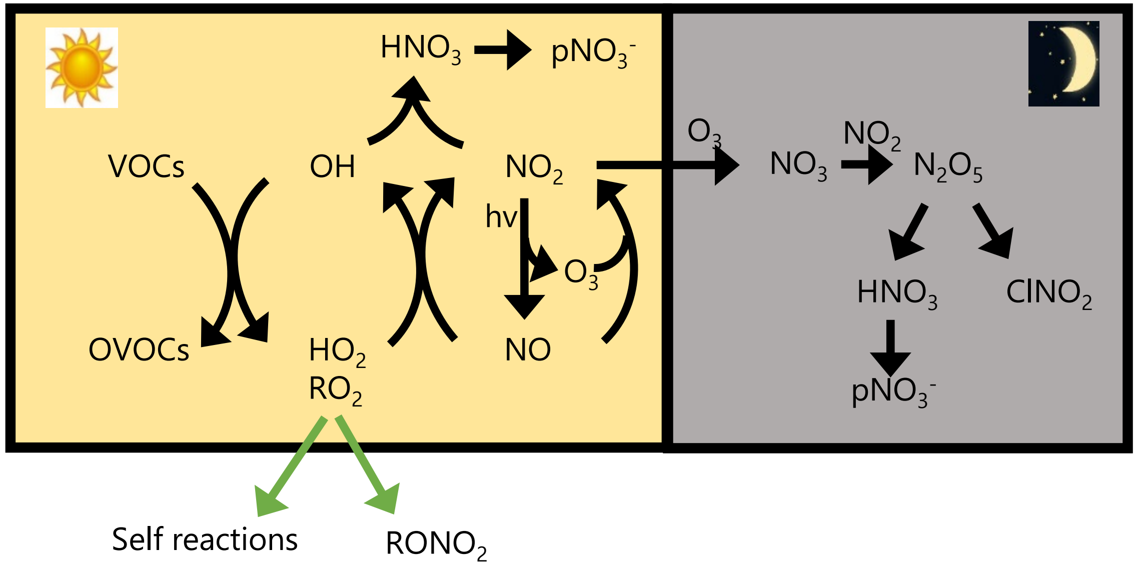


1) $O_{x,total}$ production in the SLV is NO_x-saturated and VOC-limited

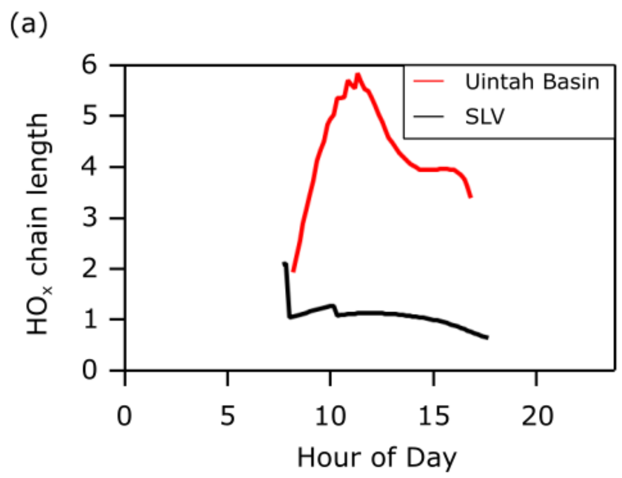
2) NO_x reductions, in the absence of concurrent VOC reductions, *will initially increase $O_{x,total}$* in the form of pNO_3^- and O_3.

Womack et al., *GRL*, **46**, 4971 (2019)

O_3 in Uintah and pNO_3^- in SLV can be explained by the HO_x chain length



$$HO_x \text{ chain length} = \frac{\Sigma \text{ Propagation reactions}}{\Sigma \text{ Termination reactions}}$$



Uintah: High VOC/NO_x propagates cycle, making O_3.

SLV: Low VOC/NO_x quenches cycle, terminating in HNO_3.

What we wish we had…

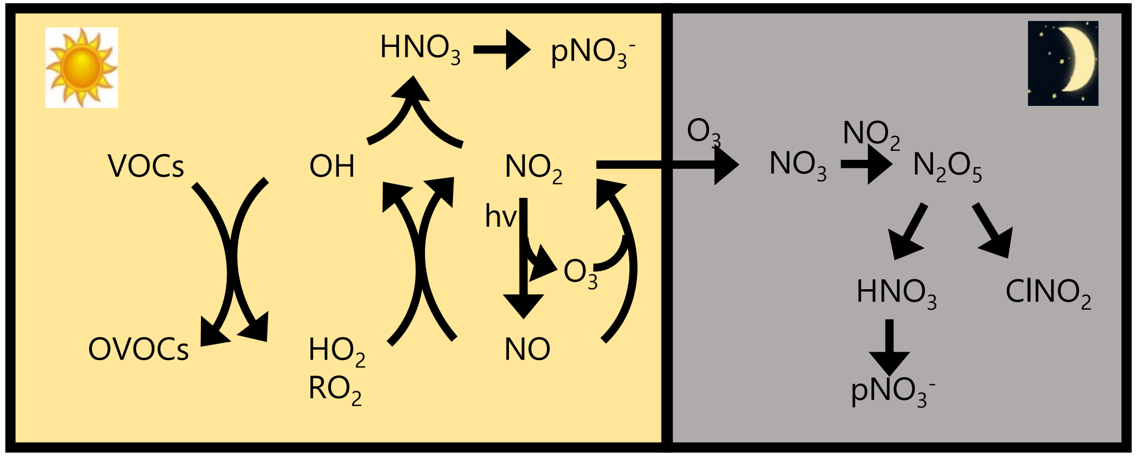
- More complete observations
  - Oxidized VOCs
  - Short lived radicals (HO_x, NO_3, etc.)
- More complete meteorology
  - Solar radiation and photolysis rates
  - Vertical measurements of the boundary layer dynamics

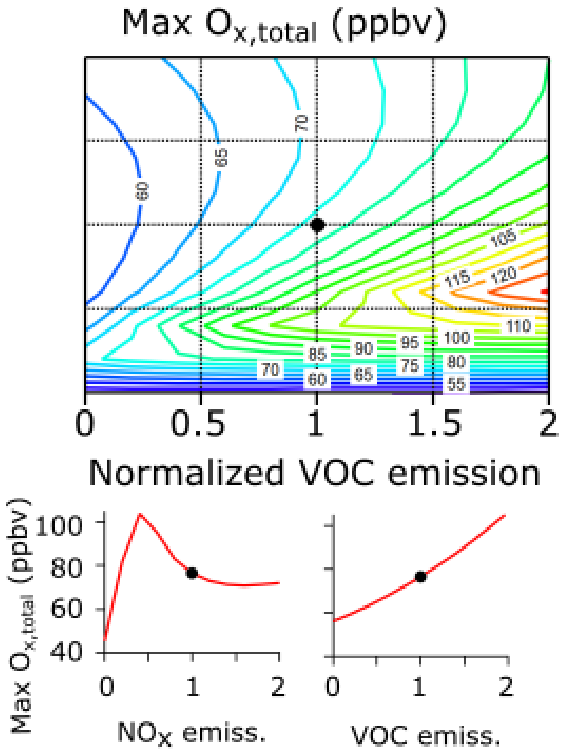
Unanswered questions

- Does VOC-limitation hold throughout PCAP?
- Is VOC-limitation valid throughout the winter season?
- Where else is this framework relevant?

Summary

- $O_{x,total}$ 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.

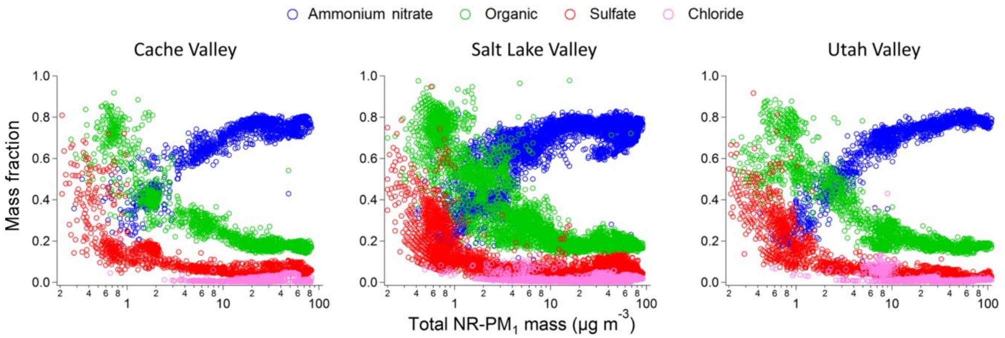




Extra slides

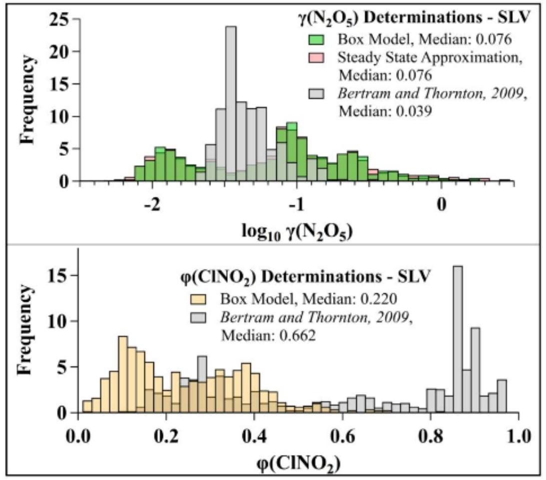
Ale Franchin et al.
ACP, **18**, 17259 (2018)

Airborne and ground-based observations of ammonium-nitrate-dominated aerosols in a shallow boundary layer during intense winter pollution episodes in northern Utah



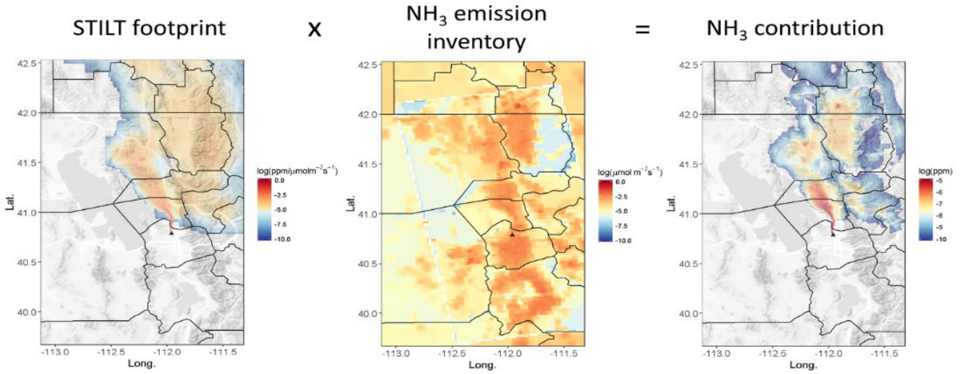
Erin McDuffie et al.
ACP Discussions, in review (2019)

On the contribution of **nocturnal heterogeneous reactive nitrogen chemistry** to particulate matter formation during wintertime pollution events in Northern Utah



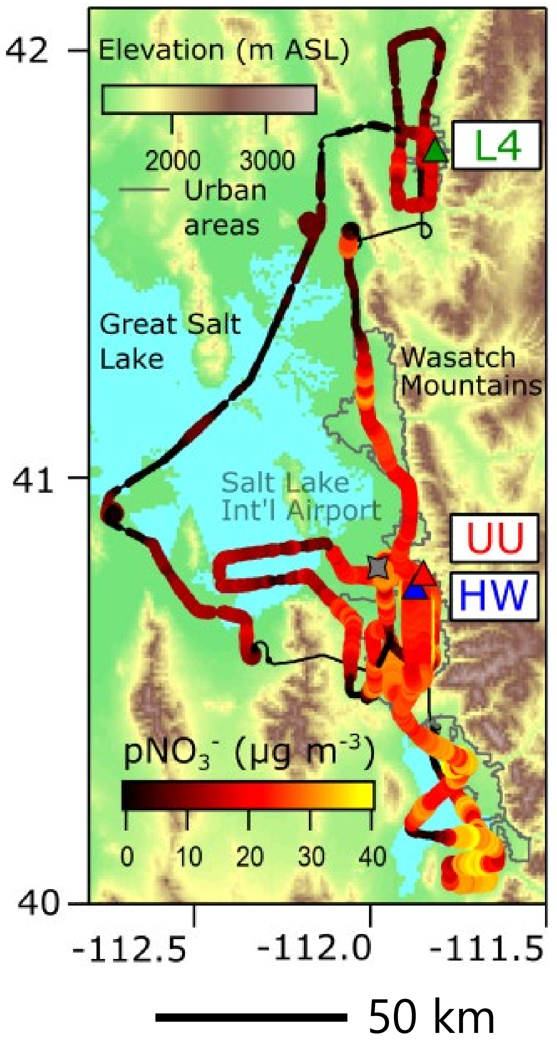
Alex Moravek et al:
ACP Discussions, in review (2019)

Wintertime **Spatial Distribution of Ammonia** and its Emission Sources in the Great Salt Lake Region



Utah Winter Fine Particulate Study (UWFPS)

January 16 – February 13, 2017



Cache Valley

Salt Lake Valley

Utah Valley

Logan (L4)

- NO_x, O_3, $PM_{2.5}$, NH_3, CH_4, CO_2
- I- CIMS (HONO, HNO_3, $ClNO_2$, N_2O_5)
- AMS (pNO_3)

Twin Otter (TO)

- NO_x, O_3, NH_3
- I- CIMS (HONO, HNO_3, $ClNO_2$, N_2O_5)
- AMS (pNO_3)

University of Utah (UU) and Hawthorne (HW)

- NO_x, O_3, CO, $PM_{2.5}$
- PTR-MS (aromatics, aldehydes)

Two major PCAPs observed.
Ammonium nitrate dominated $PM_{2.5}$.
Ammonia was usually in excess.
2017 was a typical winter.