

# Halogen-induced ozone depletions over the Great Salt Lake

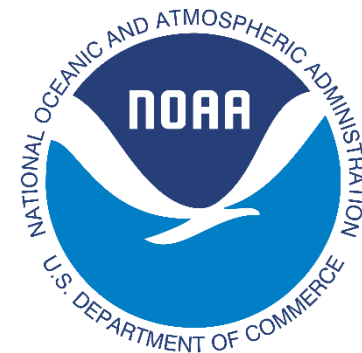
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NOAA Chemical Sciences Laboratory

Science for Solutions 5

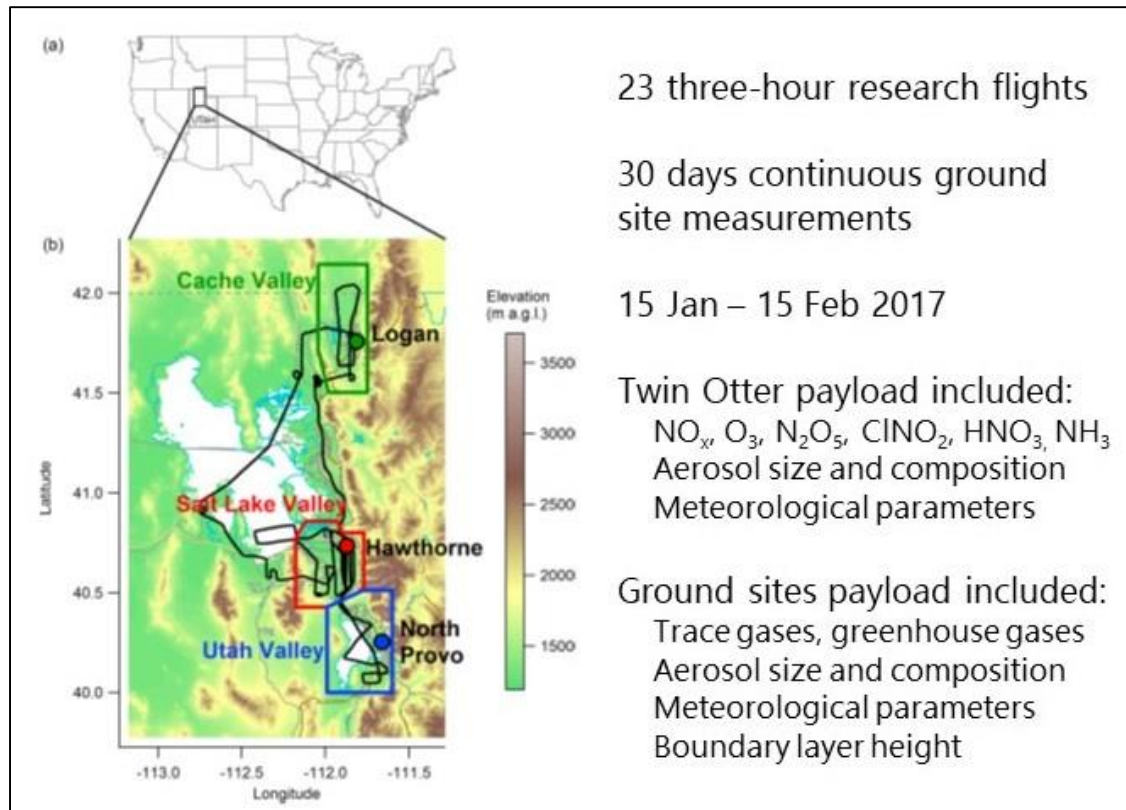
March 25, 2021



# UWFPS 2017 targeted PM<sub>2.5</sub> production – but also found large halogen emissions

## Utah Winter Fine Particulate Study:

Primary motivation: Study PM<sub>2.5</sub> pollution episodes...

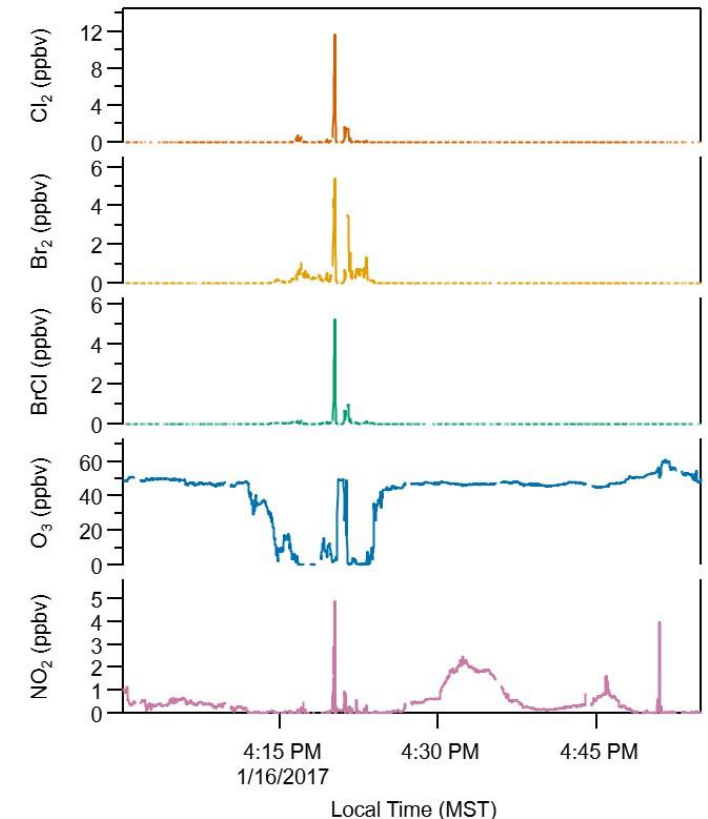
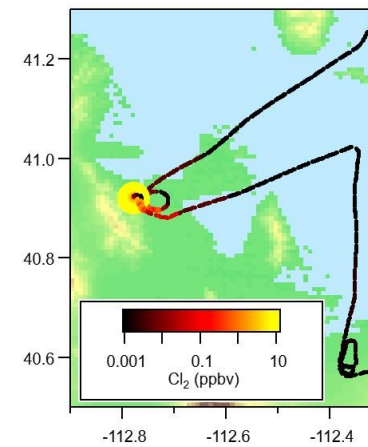
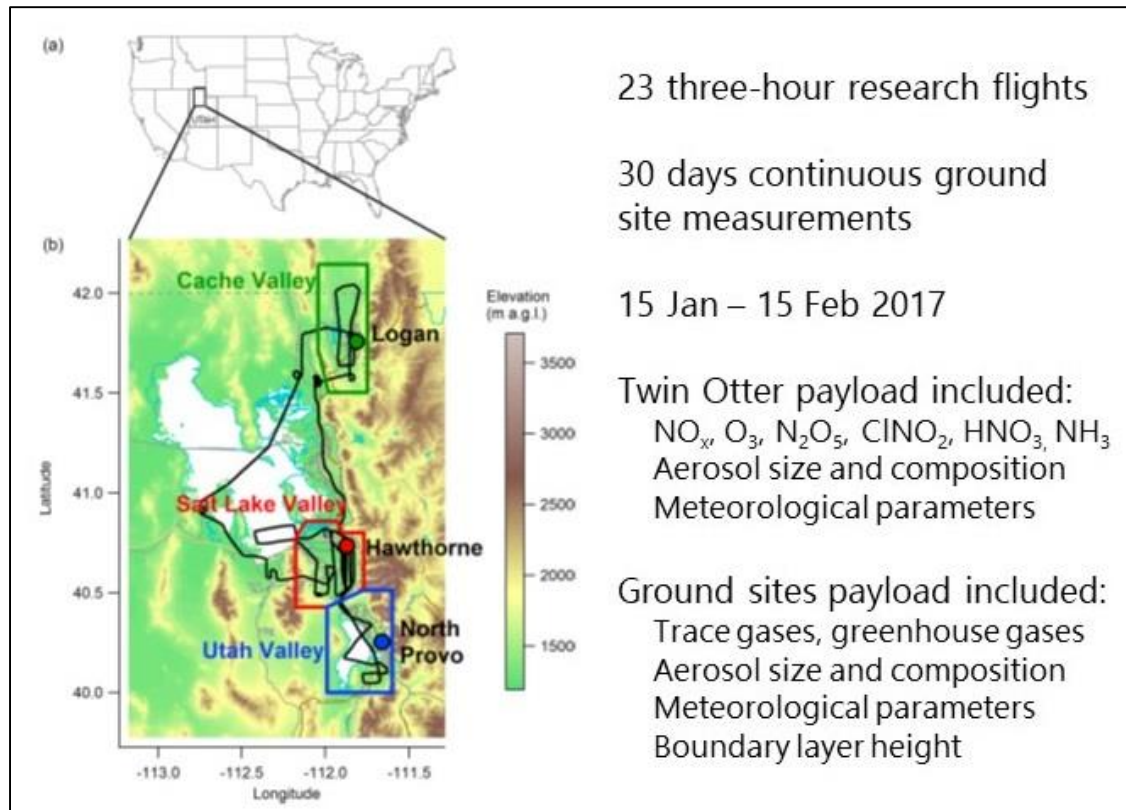


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Utah Winter Fine Particulate Study:

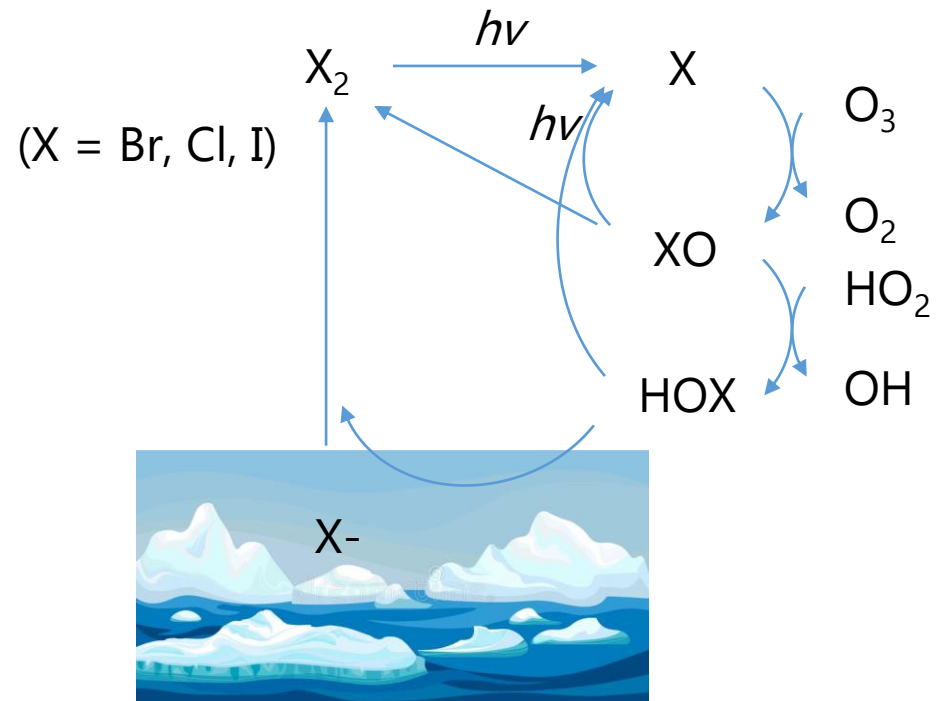
Primary motivation: Study PM<sub>2.5</sub> pollution episodes...

...but on Flight #1, we flew over an industrial area on the west side of the lake with high halogens emissions, and **complete ozone depletion**.



# Halogen-induced ozone depletion is usually a polar phenomenon

Arctic "bromine explosion" simplified mechanism:

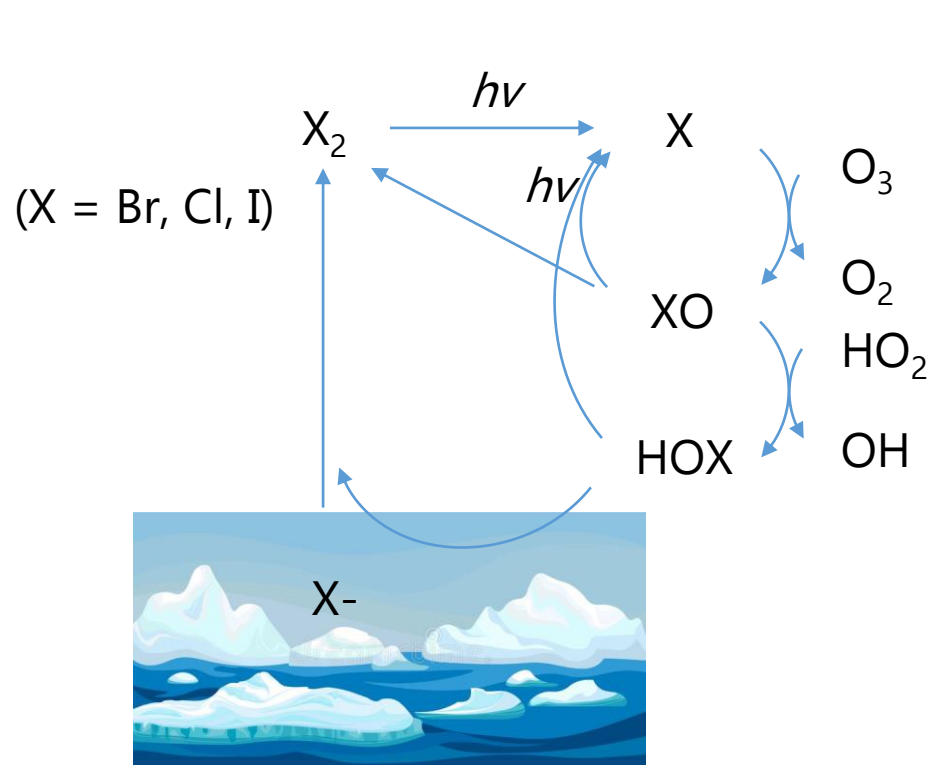


Pristine atmosphere

Typical halogen concentrations: **a few pptv**

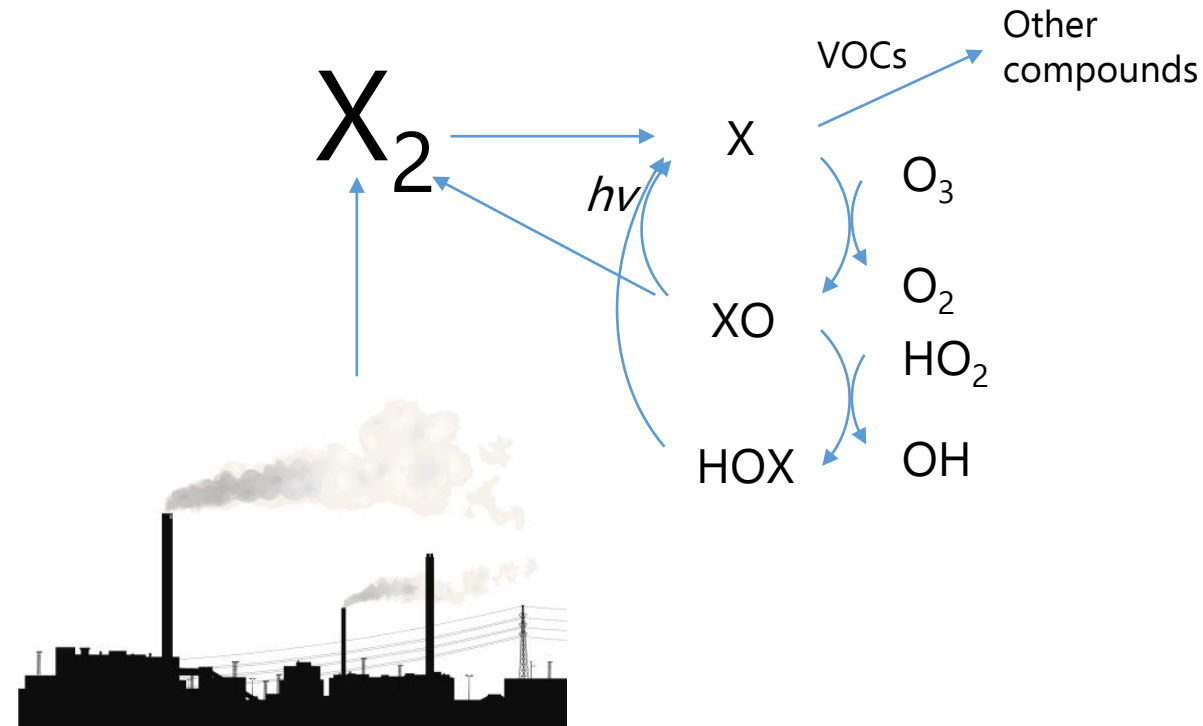
# Halogen-induced ozone depletion is usually a polar phenomenon

Arctic "bromine explosion" simplified mechanism:



Pristine atmosphere  
 Typical halogen concentrations: **a few pptv**

Great Salt Lake industrial point source:



Typical halogen concentrations: **5 – 500 ppbv!!**  
 Rarely seen in the midlatitudes

1. What is the extent of the influence of these halogen emissions?
  - Use Twin Otter observations and STILT modeling to trace air masses
2. What is the emission flux from this industrial point source?
  - Use nighttime observations and a mass-balance technique
3. What happens downwind?
  - Use a photochemical 0D box model

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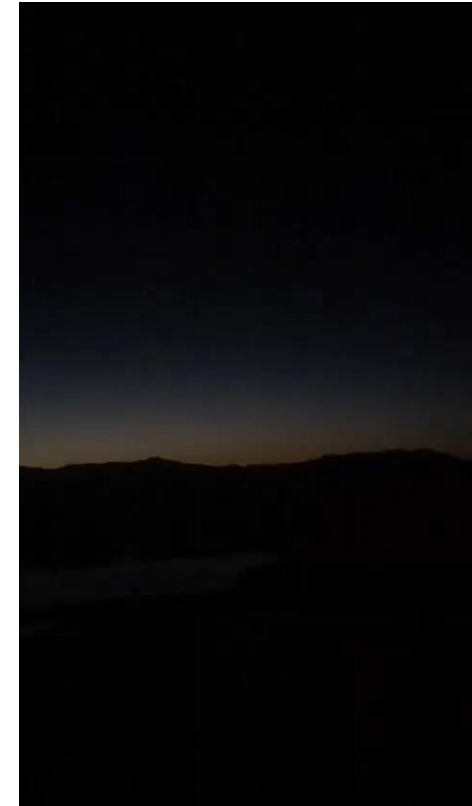
# Halogens were observed on the NOAA Twin Otter aircraft by mass spectrometry

University of Washington iodide chemical ionization mass spectrometer (I- CIMS)



Photo credit: Thornton Lab

- Calibrated for  $\text{Cl}_2$ ,  $\text{Br}_2$ ,  $\text{BrCl}$ ,  $\text{HCl}$ ,  $\text{HONO}$ ,  $\text{HNO}_3$ ,  $\text{HOCl}$ ,  $\text{HOBr}$ ,  $\text{ClNO}_2$ ,  $\text{BrNO}_2$ .
- Uncalibrated for  $\text{ClO}$ ,  $\text{BrO}$  and some others
- Some instrument interferences must be accounted for
- ~185 distinct halogen peaks were found, spanning 19 of the 23 Twin Otter flights
- **Are we sure the industrial area is the source?**



Video credit:  
L. Goldberger

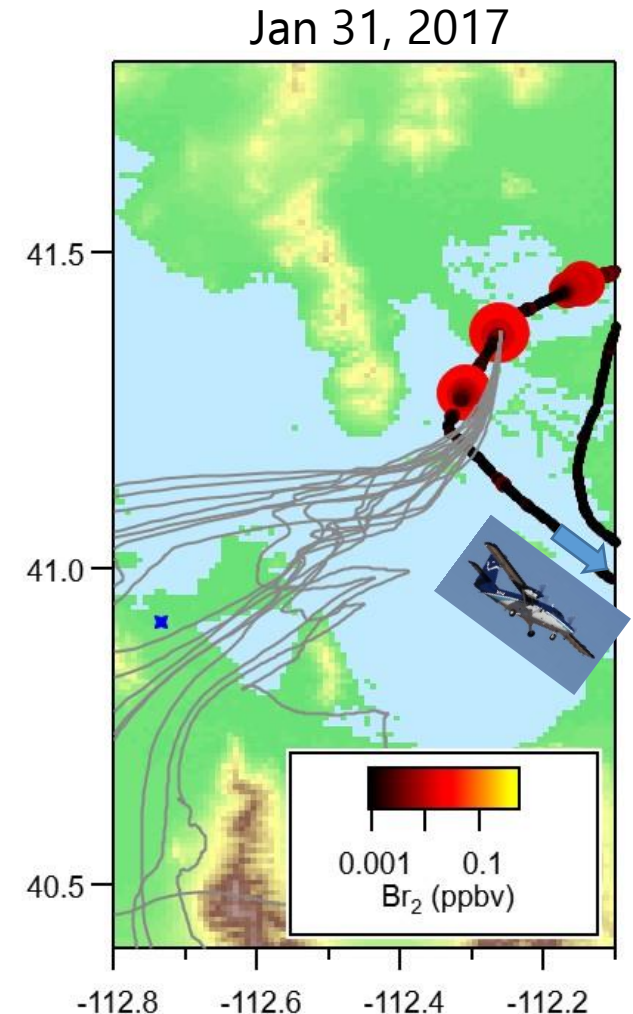
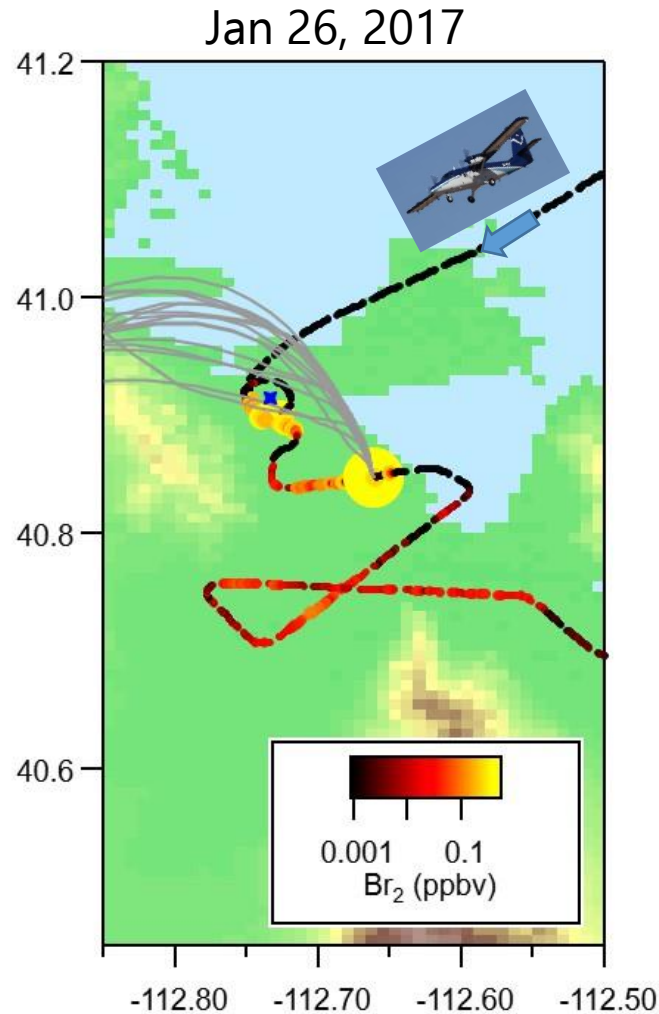
Video and plume location confirm **industrial source**, not GSL source



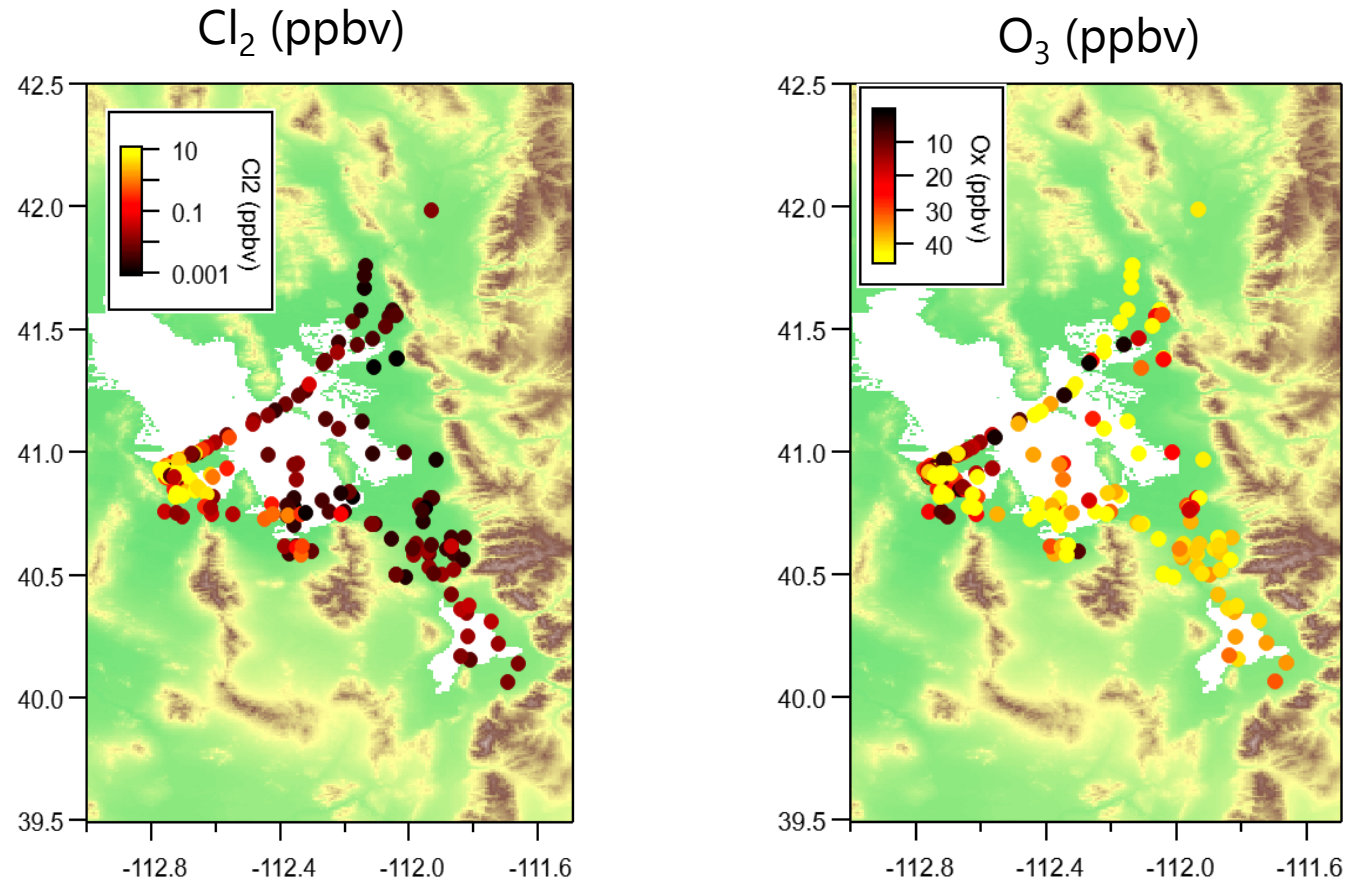
# Back trajectories can link observations to sources

The Stochastic Time-Inverted Lagrangian Transport (STILT) model

- Determines where an air parcel may have come from
- Prof. John Lin (U. Utah) ran this model every 1-2 minutes for the Twin Otter observations
- 200 “particles” followed back in time for 24 hours



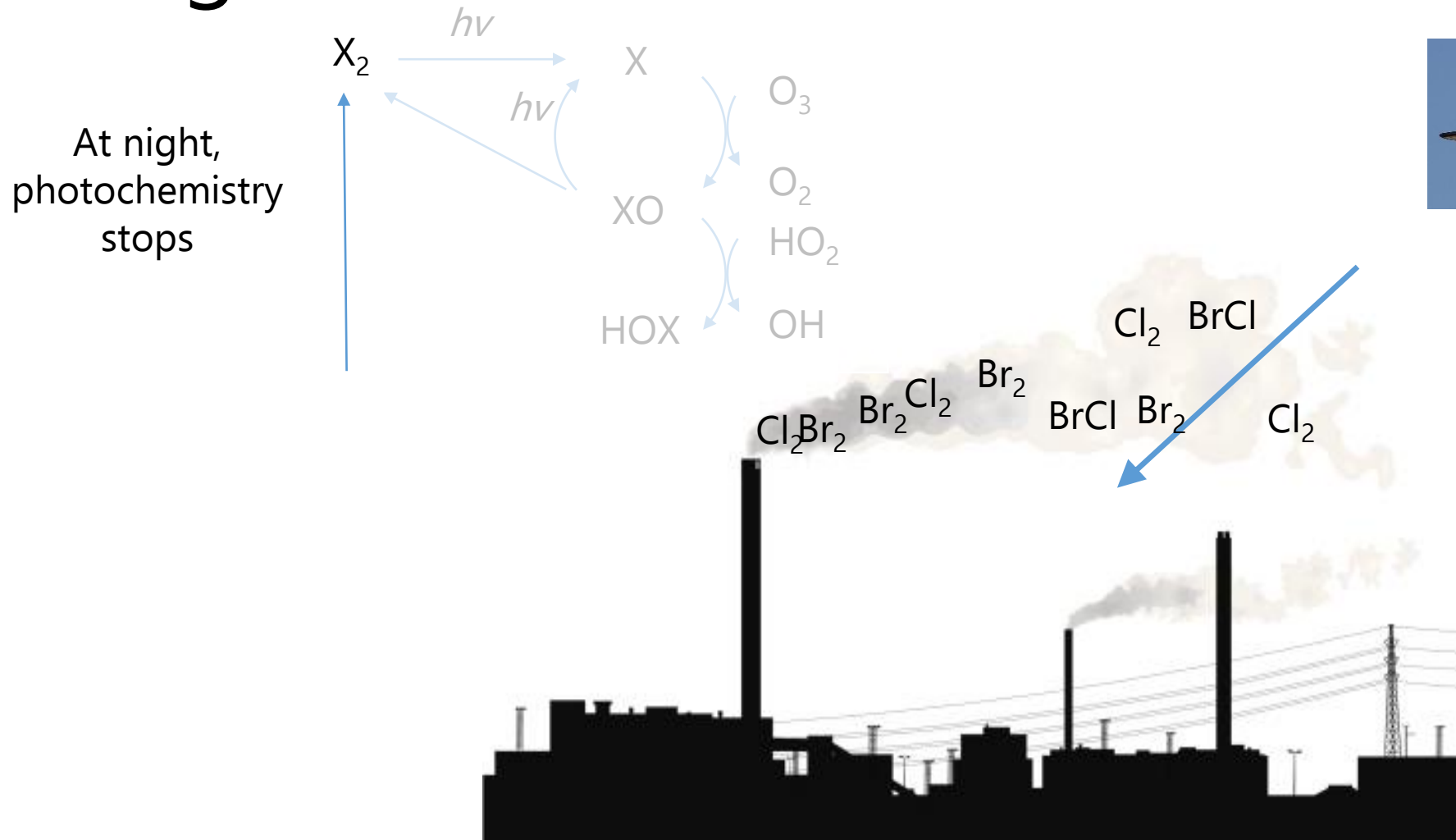
# There is evidence of halogen-induced ozone-depletion throughout the area



Each plot shows an individual detection of "influenced" air detected on the Twin Otter. Most of the effects are on the west side of the lake, with **some influence on populated areas.**

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# Emission flux can be estimated from nighttime Twin Otter observations



Integrate across plume, weight by wind speed, to get emission flux

There were 3 night flights with well-defined wind

Total of 21 plume crossing

# Our measurements of halogen emission fluxes are in agreement with self-reported figures

- In 2015, the point source reported HAPs (hazardous air pollutants)
  - 1880 tons/year Cl<sub>2</sub>
  - 1550 tons/year HCl

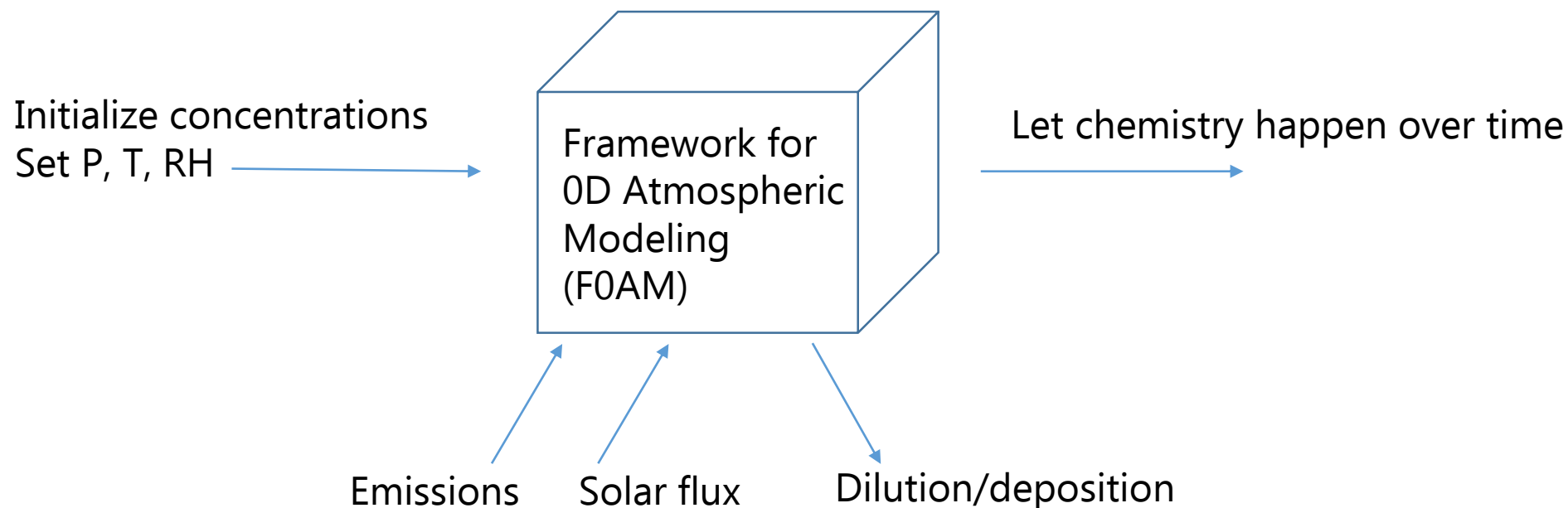
\*Numbers are preliminary. Please don't cite at this time\*

Species	Measured Emission Flux (g/sec)	Self-reported emission flux (g/sec)
Cl <sub>2</sub>	61 (ranges 0 – 350)	54.1
HCl	41 (ranges 0 – 150)	43.1
Br <sub>2</sub>	12 (ranges 0 – 190)	Not reported
BrCl	32 (ranges 0 – 290)	Not reported

- However, Br<sub>2</sub> and BrCl are not on the EPA HAP list
- If we scale these emissions, this would be equivalent to **370 tons/year Br<sub>2</sub>, 990 tons/year BrCl**

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# Zero-dimensional box modeling



## Pros

- Simple, easy to run, very fast
- Explicit chemical detail
- Useful way to understand plume chemistry

## Cons

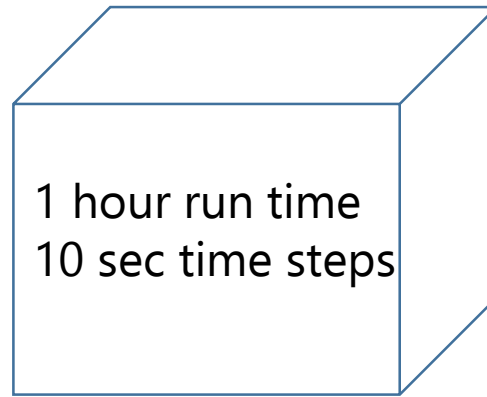
- Doesn't include plume dynamics
- Sometimes oversimplified

# As an example, we look at the effect of adding bromine

$\text{Cl}_2 = 100 \text{ ppbv}$   
 $\text{HCl} = 50 \text{ ppbv}$   
( $\text{BrCl} = 20 \text{ ppbv}$ )  
( $\text{Br}_2 = 2 \text{ ppbv}$ )

Profile of  
background VOCs

$P = 850 \text{ mbar}$   
 $T = 0 \text{ deg C}$   
 $\text{RH} = 72\%$   
Midday sun

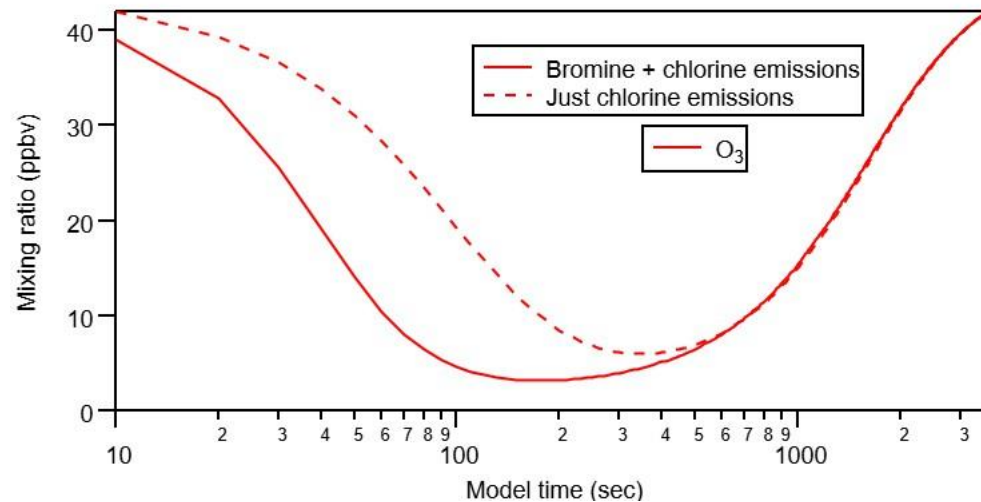
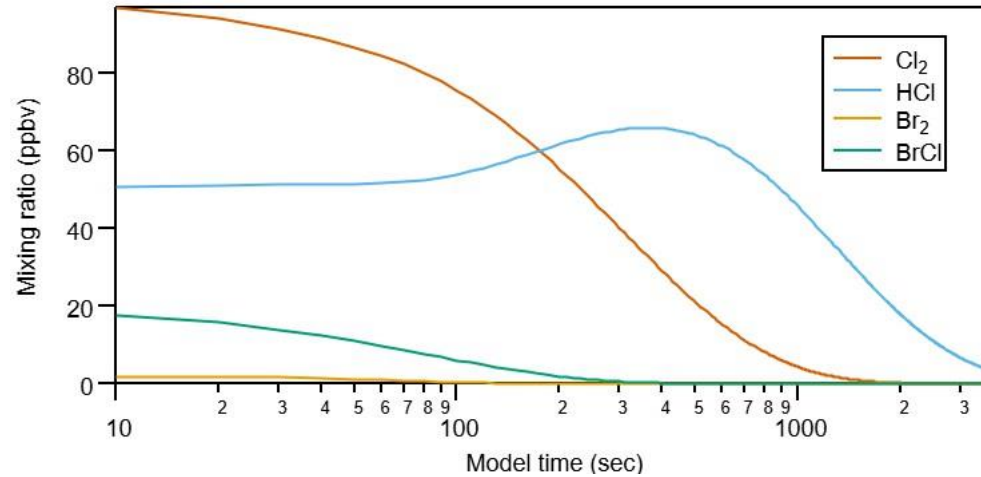


1<sup>st</sup> order general dilution constant

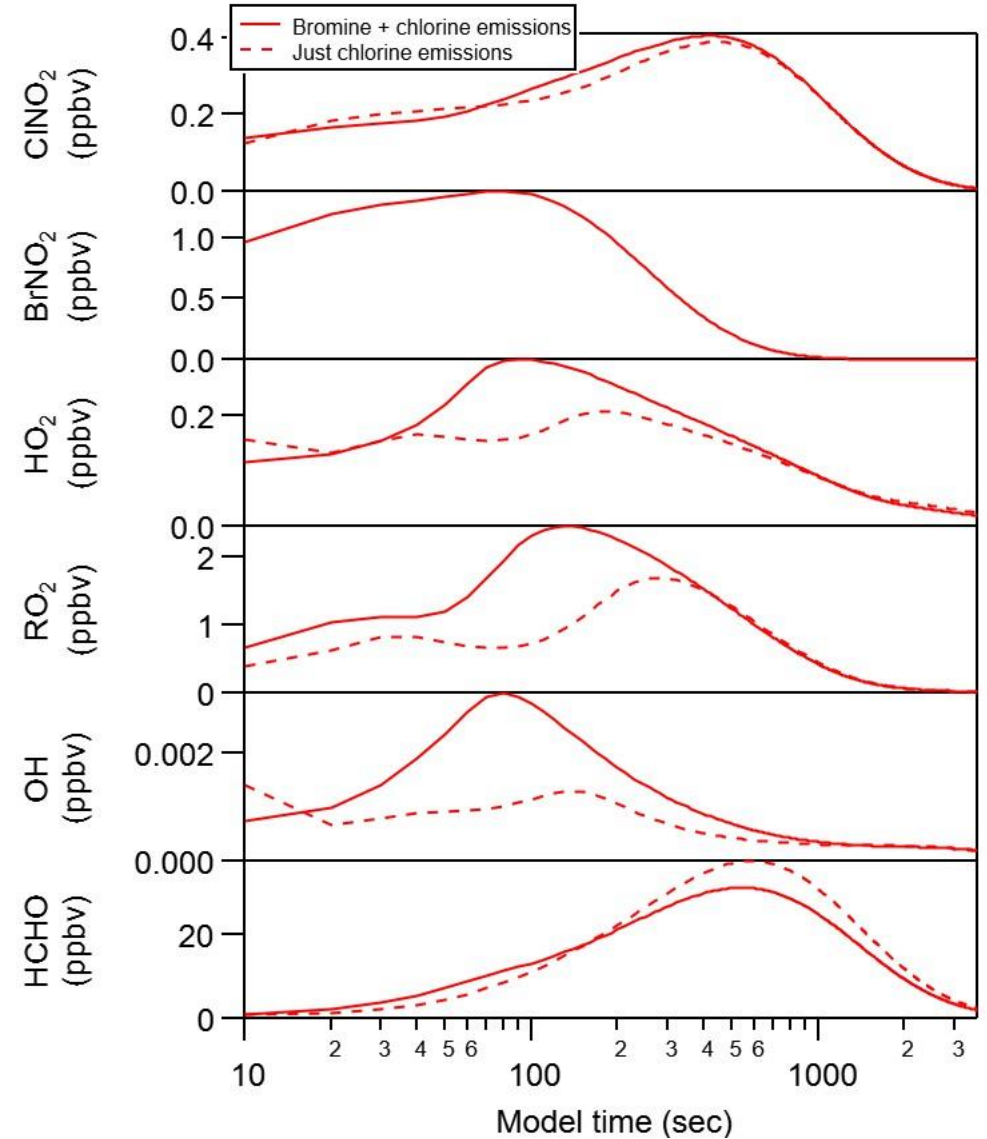
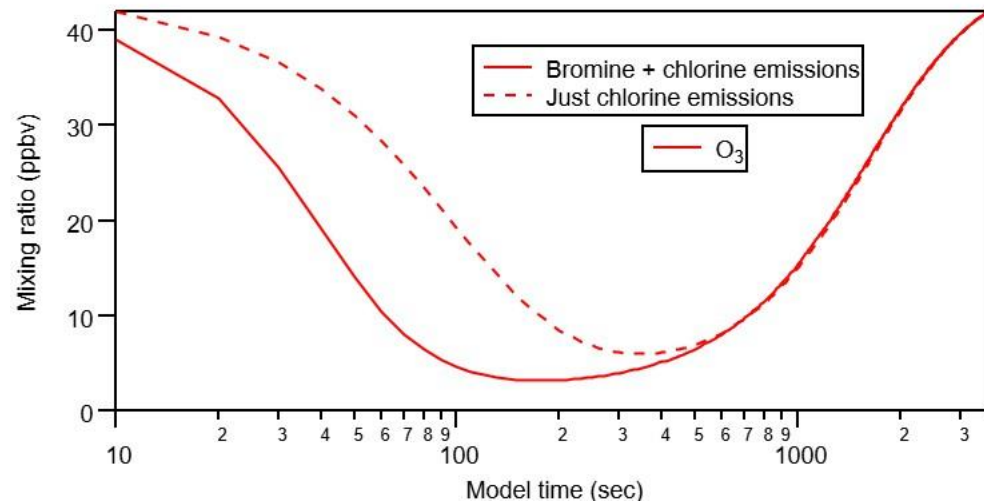
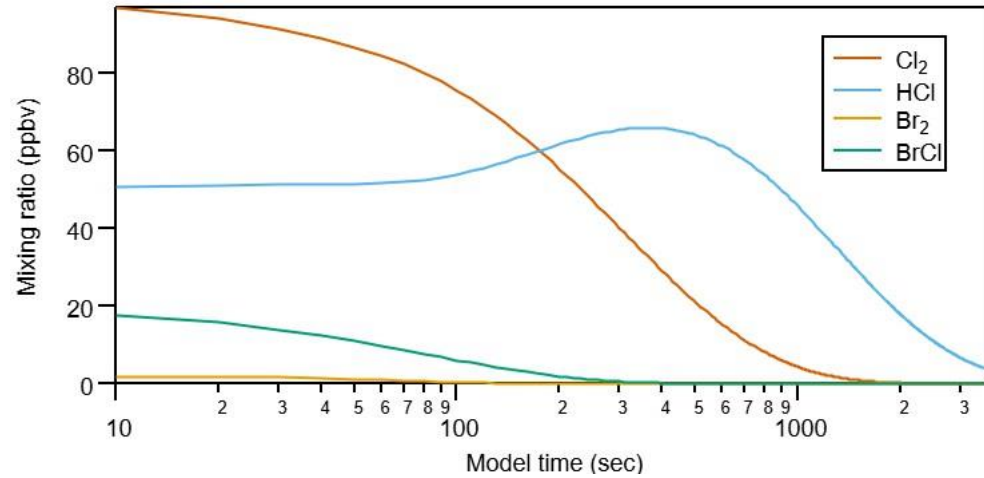
What happens to halogens?  
What happens to ozone?  
What are the other products?  
What is the effect of bromine?



# The introduction of bromine changes the chemistry



# The introduction of bromine changes the chemistry



1. What is the extent of the influence of these halogen emissions?

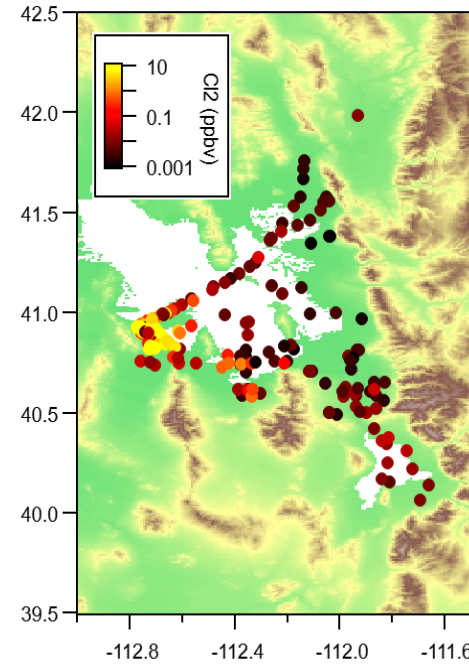
Possibly widespread

2. What is the emission flux from this industrial point source?

Both chlorine and bromine are emitted. Final emission estimates forthcoming.

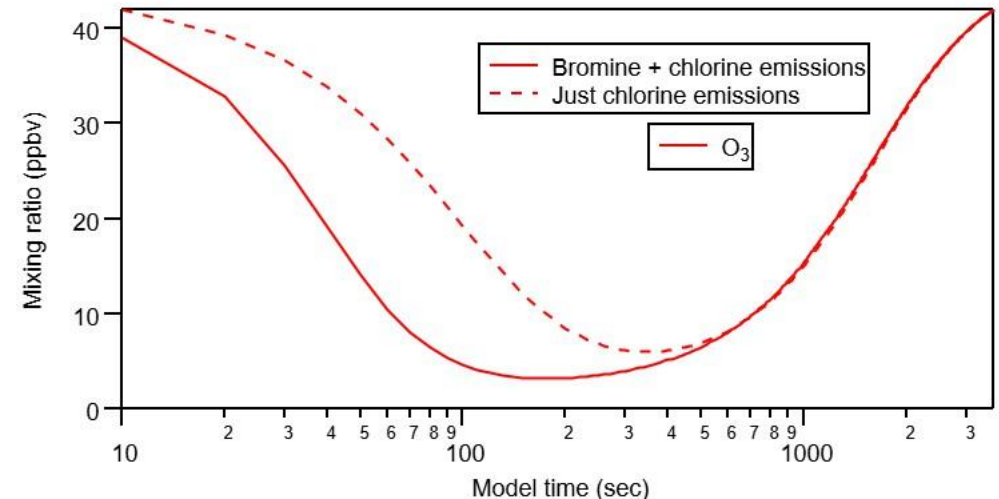
3. What happens downwind?

Pending further modeling, but interesting chemistry nevertheless.



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## NOAA Aircraft Operations Center

Rob Mitchell, JC Clarke

... **And the rest of the UWFPS team**