CU MAX-DOAS, Observations of Halogen Emissions at The Great Salt Lake

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Overview

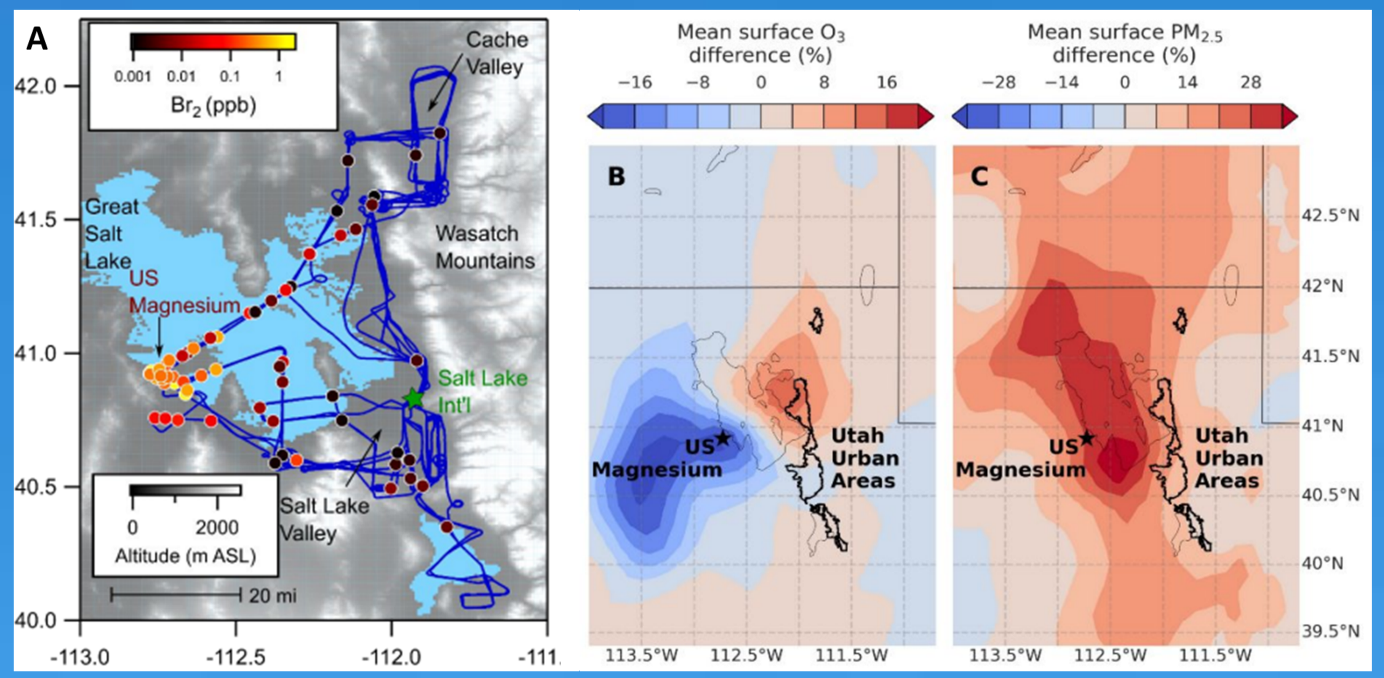
U.S. Magnesium is the largest emitter of halogens (Cl_2, Br_2, BrCl) in the United States. The plant is located in Salt Lake City, where halogen radical chemistry affects air quality. A plant shutdown provides an opportunity to study air quality impacts in the absence and presence of halogen emissions.

The goal is:

- Measure NO_2, HCHO, and BrO before, during and after the plant comes online.
- Assess the effect of industrial halogen emissions on BrO radical abundances.

The initial motivation stems from the Utah Winter Fine Particulate Study, an 2017 aircraft campaign where data showed:

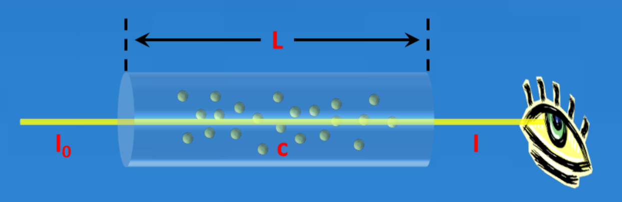
- Increases levels of bromine products (Br_2, BrCl, BrO) in plumes contributed by the US Magnesium Plant
- Increased levels of Ozone in plumes over urban regions of the Great Salt Lake Basin (GSLB)



(Figure A) The National Oceanic and Atmospheric Association's (NOAA) Twin Otter Aircraft flight track during UWFPS. High levels of Bromine are found in plumes above the magnesium plant. (Figures B and C) Increased levels of PM 2.5 and ozone are modeled due to halogen emissions from the magnesium plant. (Womack et al. 2023)

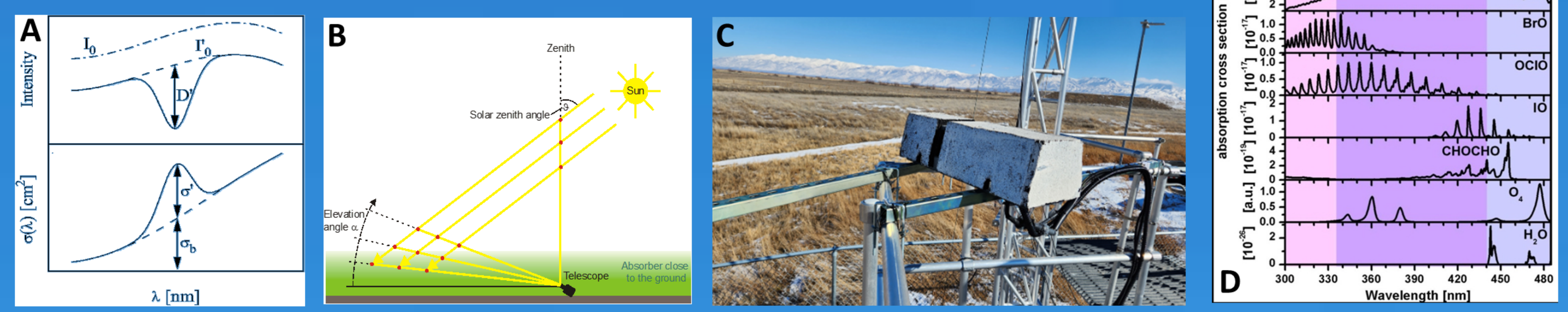
Differential Optical Absorption Spectroscopy (DOAS)

- Selectively and quantitatively with high sensitivity detect gases using their characteristic absorption cross section
- Simultaneously record many wavelengths intervals, and thus multiple gasses
- Use differences of intensities, rather than absolute intensities
- High pass-filter spectra to remove continuum
- Fit reference spectra to make use of all spectral information

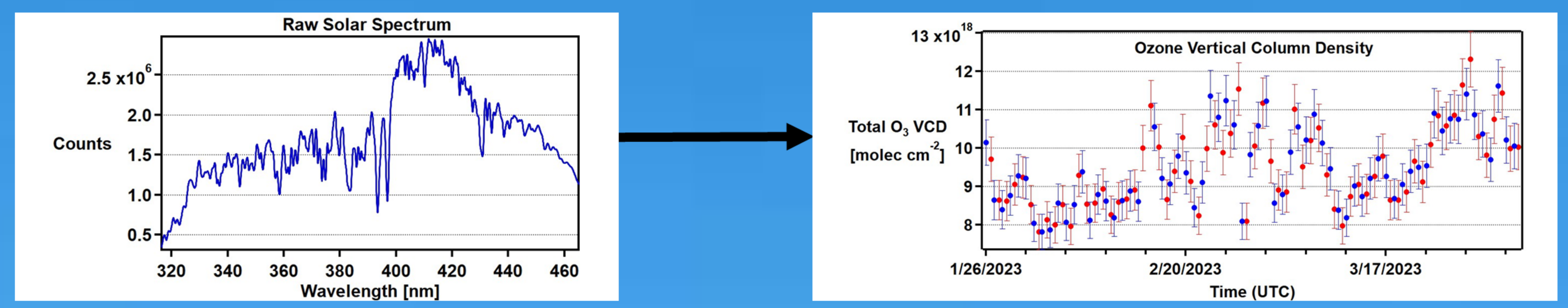


Lamber-Beer's Law: $\mathbf{I = I_0\, e^{-\sigma c L}}$

- σ absorption cross section
- c concentration of absorber
- L light path through absorber



(Figure A) Differential reduction in intensity D' due to differential absorption cross-section σ' of an atmospheric trace gas. (Figure B) Solar stray light MAX-DOAS measures the slant column density (SCD), the concentration integral along light path, which can be inverted to derive aerosol properties (optical and microphysical) and vertical profiles using Optimal Estimation.(Figure C) Absorption cross sections of selected atmospheric absorbers. (Figure D) University of Colorado's MAX-DOAS dual-axis telescope allows for different elevation angles.



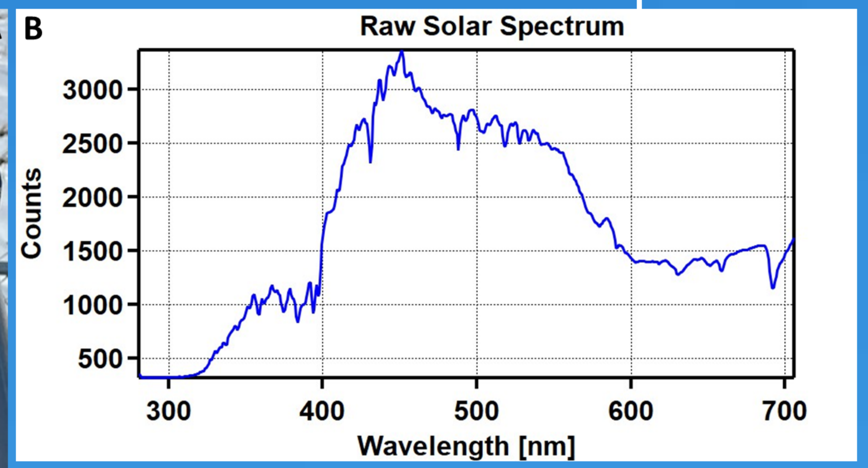
Diode Array Spectral Radiometer Instrument

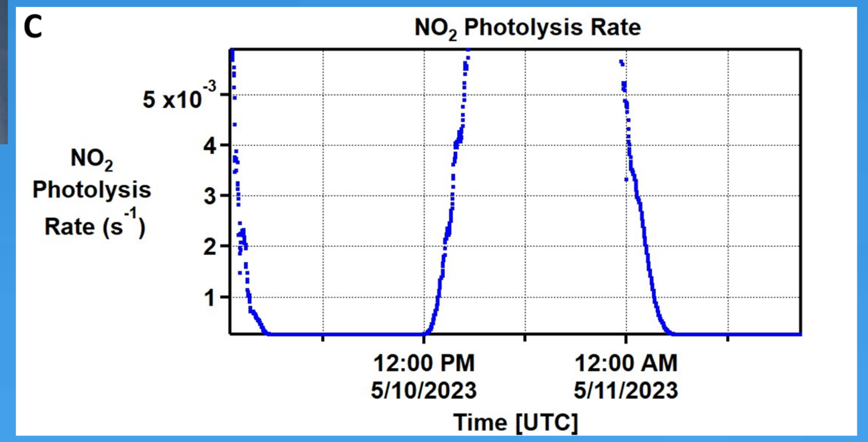
The Diode Array Spectral Radiometer is a light measurement tool that measures raw counts at each diode due to photons absorbed in that particular wavelength range. From these raw counts a photolysis rate for various species of known absorption cross sections can be calculated.

Those Species include:

- H_2O_2
- HCHO (High and Low Temperatures)
- HONO
- NO_2
- NO_3 (High and Low Temperatures)
- $O(^1D)$

These photolysis rates will be used to constrain halogen formation rates, specifically BrO, And better understand the ozone formation in GSLB.





(Figure A) Diode array Spectroradiometer clamped to a railing on the roof of the Salt Lake City UDAQ Inland Prison Site. (Figure B) Raw Solar Spectrum, counts versus wavelength of a solar spectrum (Figure C) Time series of NO_2 photolysis rate

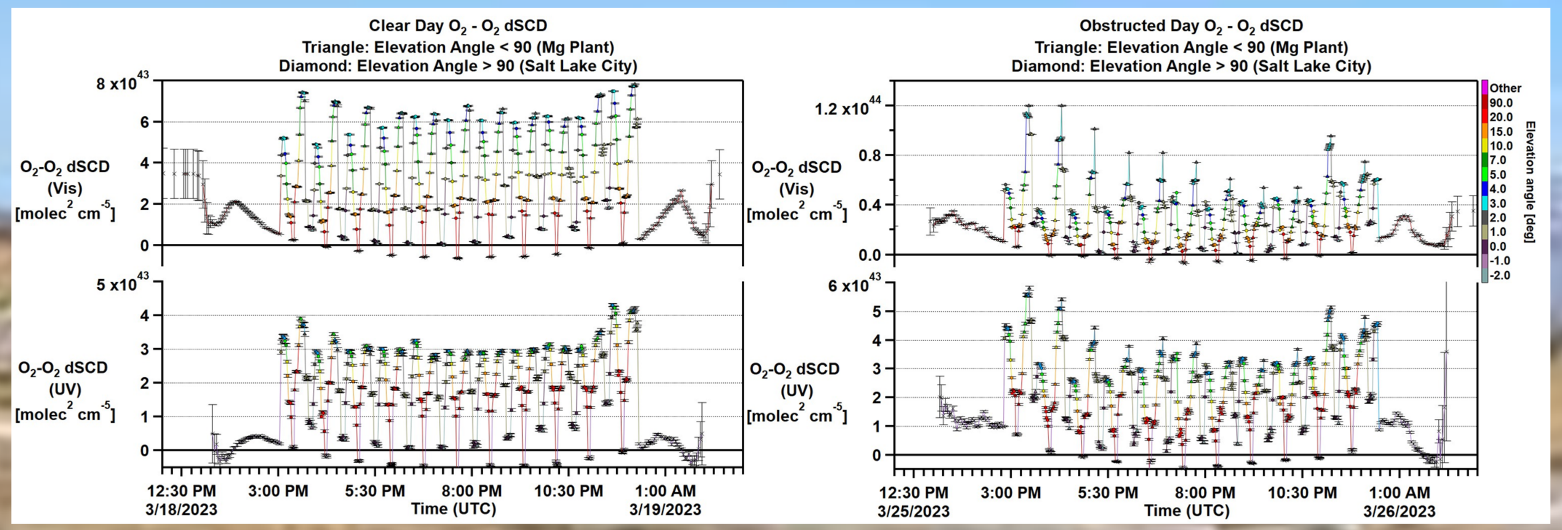
O_2-O_2 Differential Slant Column Densities (dSCD's)

O_2-O_2 is a calibration gas and aerosol proxy that helps constrain the photon path distribution

O_2-O_2 is therefore useful to help constrain radiative transfer models that allow us to better understand tropospheric vertical columns (VCDs)

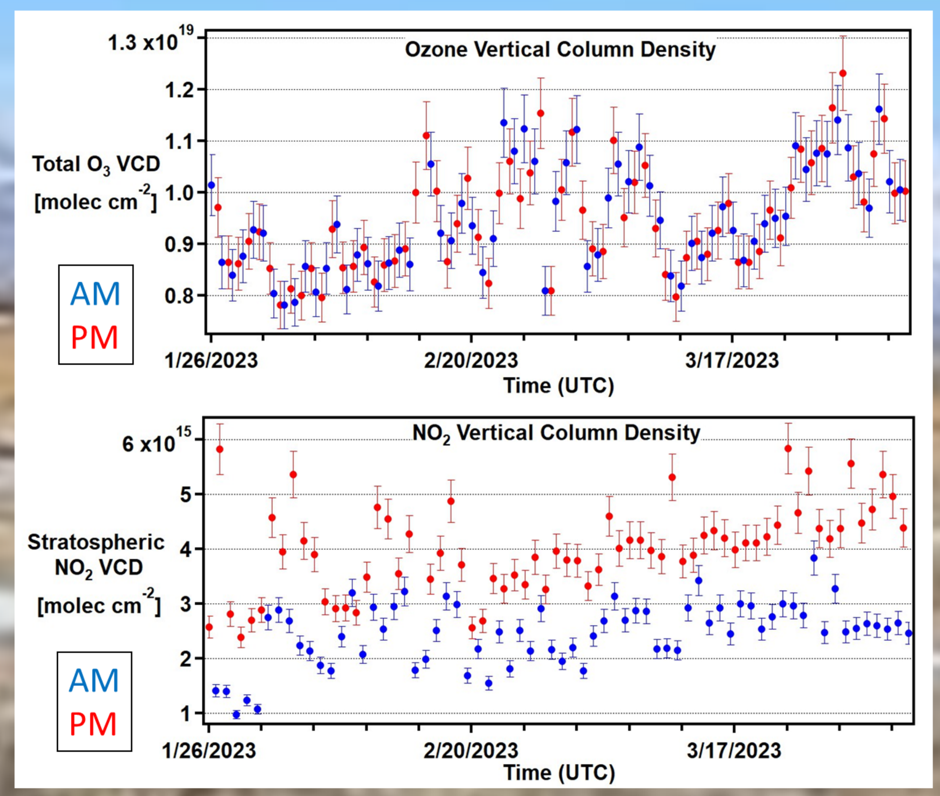
O_2-O_2 is well-mixed in the atmosphere. We observe larger of O_2-O_2 dSCD's over an urban city (diamonds) which demonstrates aerosol presence while in the magnesium plant/Salt Lake direction (triangles) slightly lower O_2-O_2 dSCD's are observed due to lower aerosols concentrations.

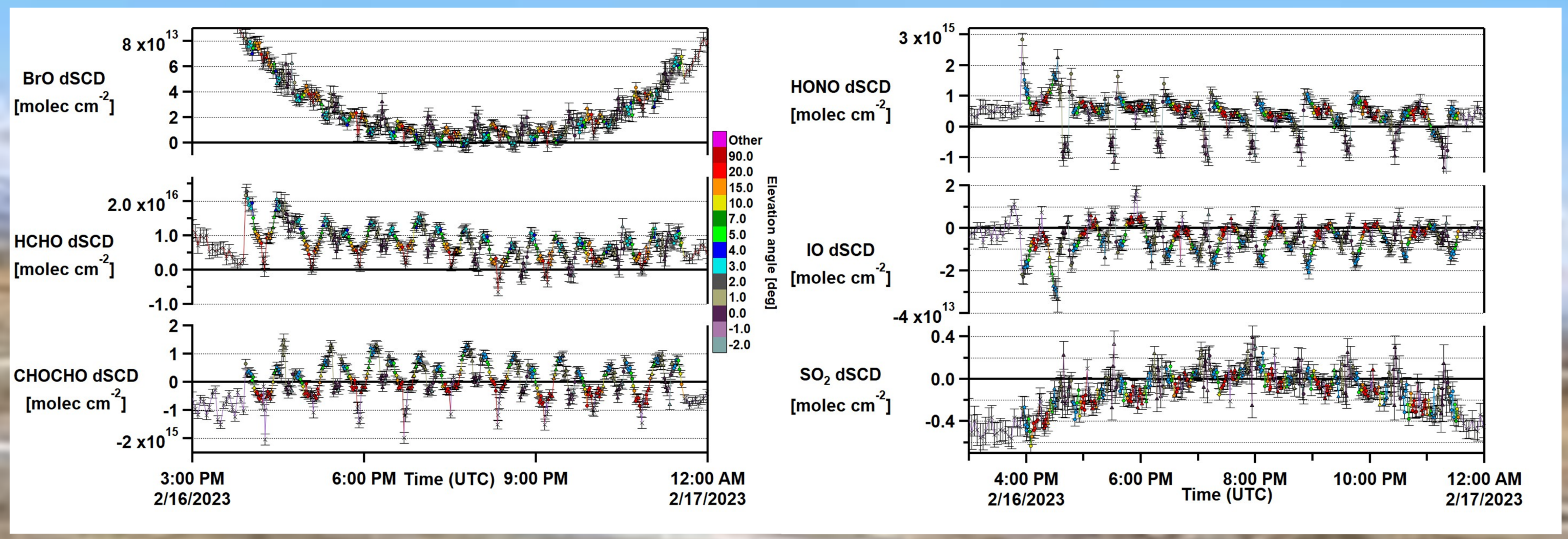
O_4 (O_2-O_2) dSCD's are used to identify clear days. A clear day would represent a day whose data is unobstructed by clouds. There are obstructions on the urban facing elevation angles (diamonds) below approximately 3 degrees above horizontal.



Important Species: dSCD's and Vertical Column Densities (VCD's)

Species Being Measured	Fit Window (nm)	Why species is being measured?
Nitrogen Dioxide (NO_2)	425 – 290	Criteria air pollutant (monitored by EPA); Tropospheric NO_2 contributes to O_3 formation; Stratospheric NO_2 is a tracer for jet stream location
Ozone (O_3)	450 – 550	Ground level criteria air pollutant; Stratospheric ozone protects humans from harmful UV radiation; Tracer for location of jet stream
Water Vapor (H_2O)	425 – 490	Tracer for atmospheric dynamics (weather fronts, etc.)
Bromine Oxide (BrO)	328.5 – 359	Tracer for bromine emitted by the magnesium plant
Formaldehyde (HCHO)	328.5 – 359	Carcinogen; Radical precursor; Formaldehyde to NO_2 ratio (FNR) helps constrain VOC versus NOx control on ozone production rate
Glyoxal (CHOCHO)	434 – 460	Radical and aerosol precursor; Glyoxal to Formaldehyde ratio (GFR) helps constrain VOC speciation
Sulfur Dioxide (SO_2)	323 – 335	Criteria air pollutant; Precursor for sulfate aerosol
Iodine Monoxide (IO)	417.5 – 438	Destroys tropospheric ozone and participates in new particle formation (PM 2.5)
Nitrous Acid (HONO)	335 – 373	Helps drives hydroxyl radical regeneration → net ozone production





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