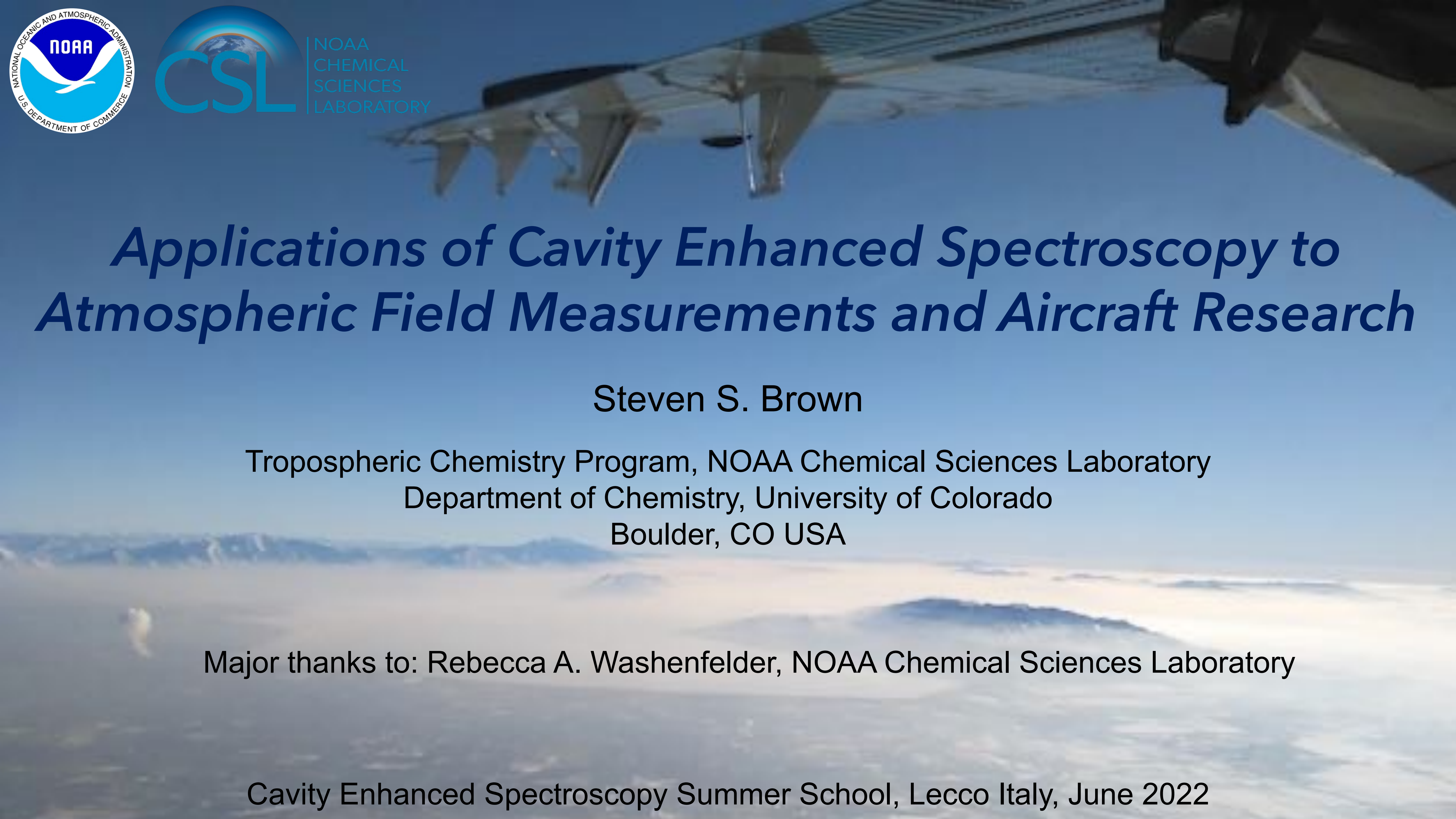

Applications of Cavity Enhanced Spectroscopy to Atmospheric Field Measurements and Aircraft Research

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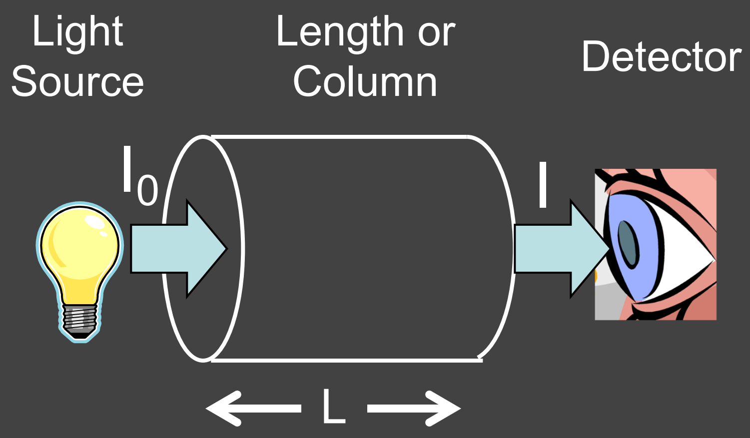
Major thanks to: Rebecca A. Washenfelder, NOAA Chemical Sciences Laboratory

Cavity Enhanced Spectroscopy Summer School, Lecco Italy, June 2022

Atmospheric Science and Spectroscopy

- Numerous *very* high sensitivity analytical methods in atmospheric science …. Mass spectrometry, fluorescence luminescence, chromatography, etc.
- Major advantage to spectroscopic methods (at least via Beer-Lambert extinction) is that they are ***absolute***
- *But* … generally ***insensitive*** compared to other methods


Light Source

Length or Column

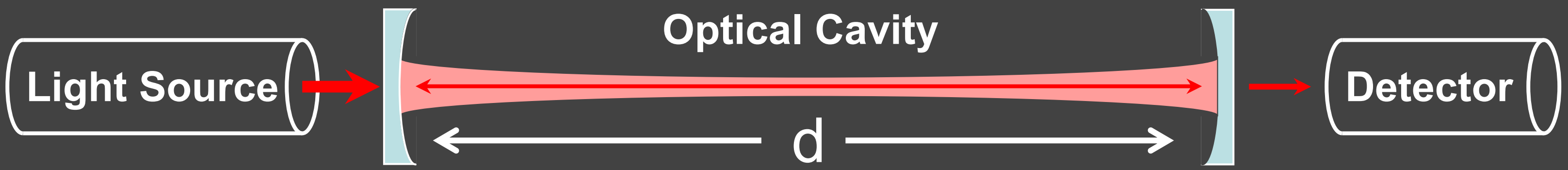
Detector

I_0

I

← L →

Cavity Enhanced Spectroscopy


Optical Cavity

Light Source

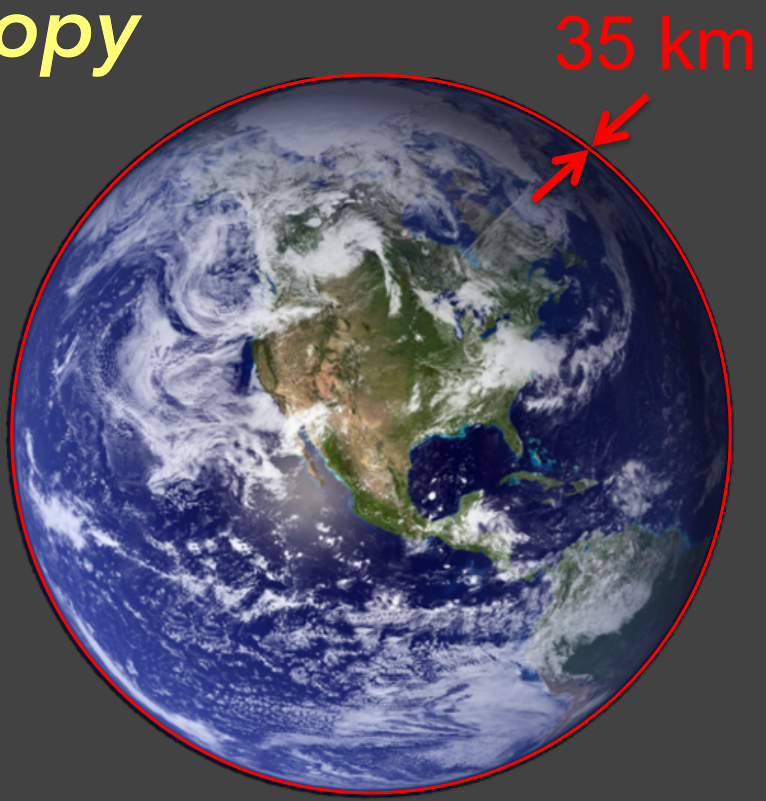
Detector

d

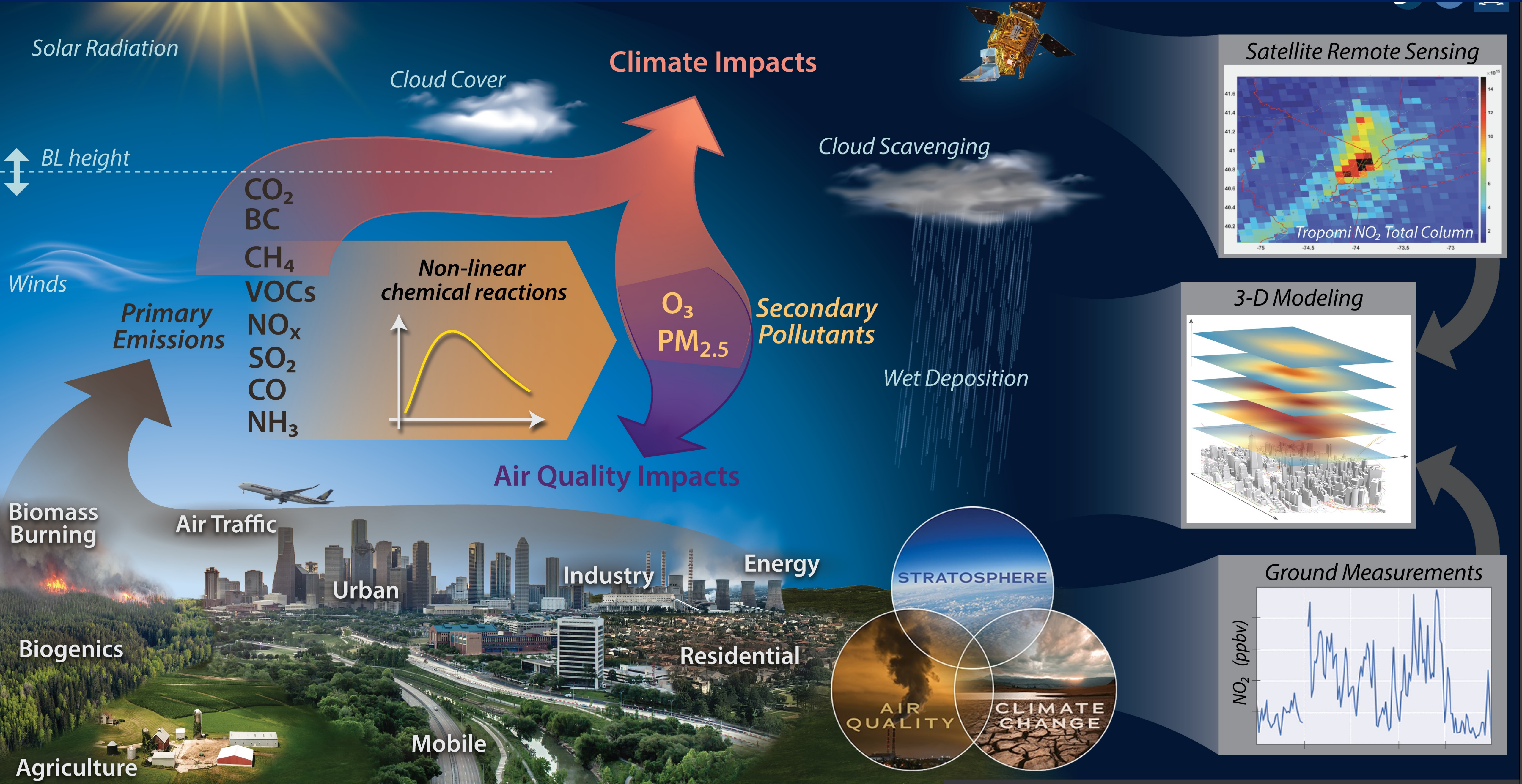
$$L_{eff} = \frac{d}{(1-R)}$$

For R ≈ 0.9999 (or $1\text{-}R \approx 10^{-4}$) and d = 1 m

Effective path length is comparable to the depth of the atmosphere



Scientific Questions in Atmospheric Chemistry & Composition



Solar Radiation

Cloud Cover

Climate Impacts

BL height

Winds

Primary Emissions

CO_2
BC
CH_4
VOCs
NO_x
SO_2
CO
NH_3

Non-linear chemical reactions

O_3
$PM_{2.5}$

Secondary Pollutants

Air Quality Impacts

Cloud Scavenging

Wet Deposition

Biomass Burning
Air Traffic
Urban
Industry
Energy
Biogenics
Residential
Agriculture
Mobile

STRATOSPHERE
AIR QUALITY
CLIMATE CHANGE

Satellite Remote Sensing

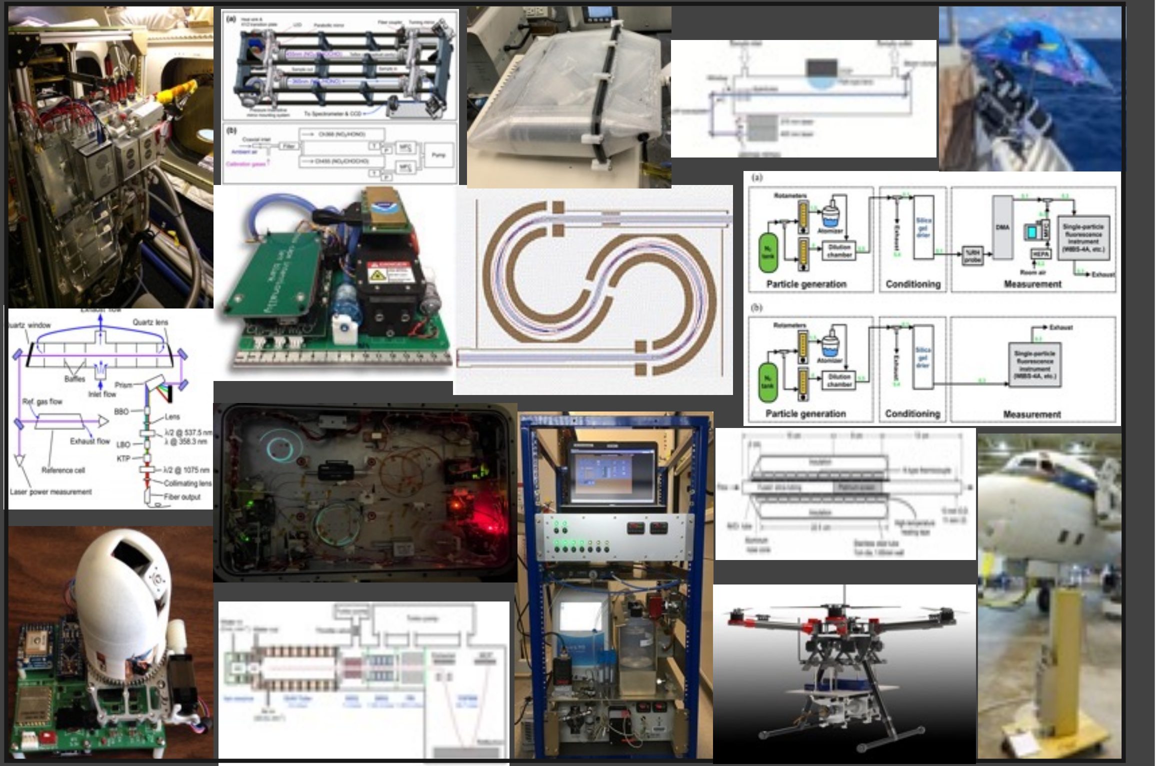
Tropomi NO_2 Total Column

3-D Modeling

Ground Measurements

INSTRUMENT DEVELOPMENT & FIELD CAMPAIGNS

Significant focus on development of atmospheric measurement technology

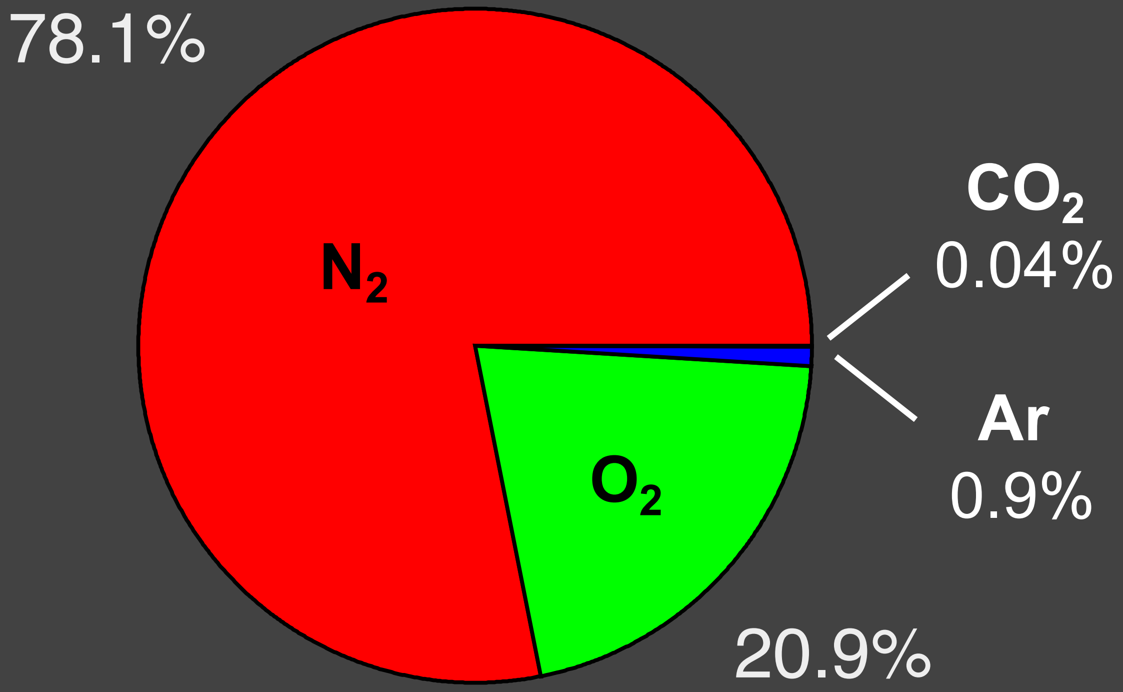


e.g. PALMS sTOF, Nitric Oxide Laser Induced Fluorescence (NO-LIF), Micro Doppler Lidar (MICRO DOP), Miniature Sun Photometer

Tropospheric Chemistry Focus on Mass Spectrometery and Optical Spectroscopy

Deployment of custom instruments on fixed and mobile platforms

Atmospheric Composition



The remaining 0.03% represents most of the interesting atmospheric chemistry

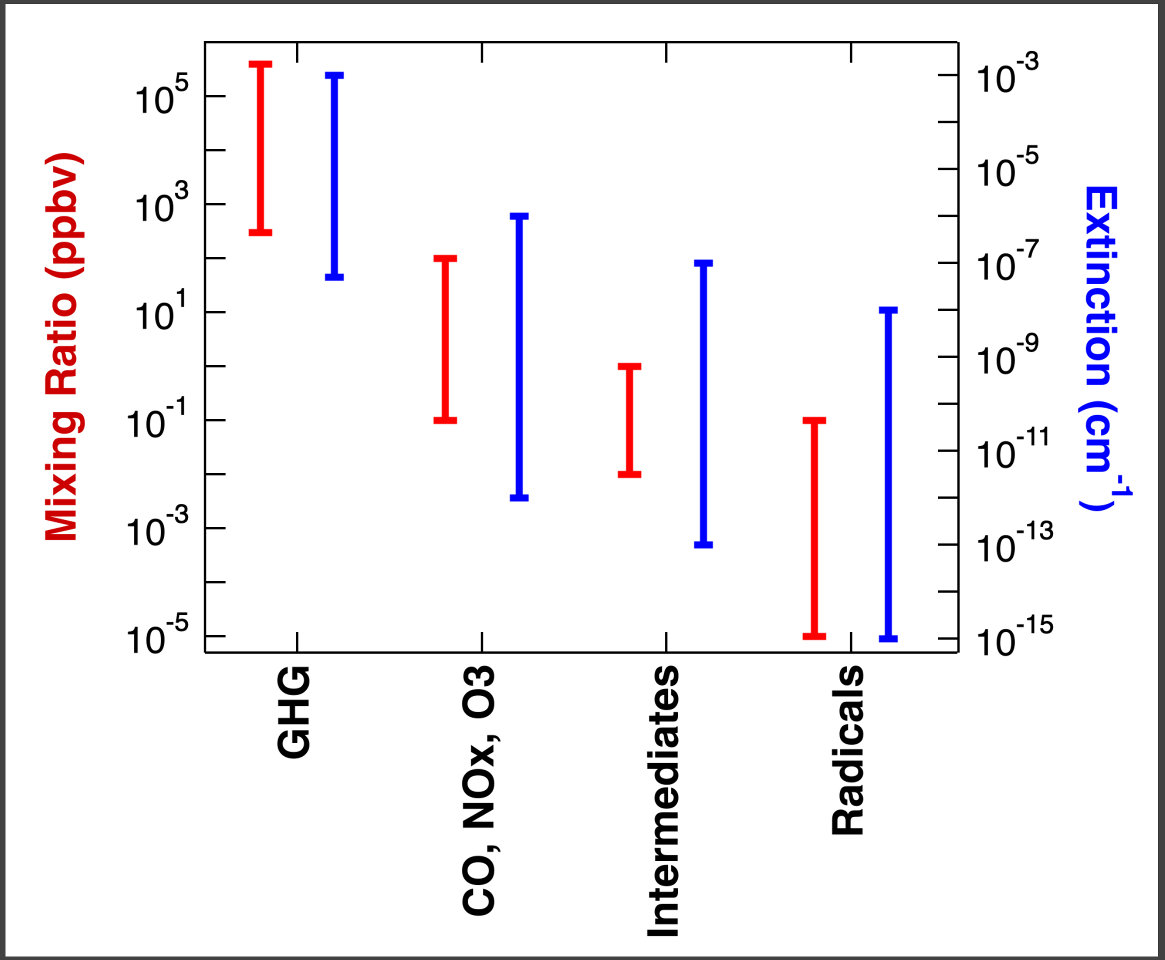
But … Optical extinction (α) of atmospheric trace gases can be ***very*** small

Optical Extinction

$$\alpha\ (\mathrm{cm^{-1}}) = N\ (\mathrm{molec\ cm^{-3}})\ \sigma\ (\mathrm{cm^{2}\ molec^{-1}})$$

Abs. cross section range in the atmosphere

$$\sigma \approx 10^{-21} - 10^{-17}\ \mathrm{cm^{2}\ molecule^{-1}}$$



And Then There are Particles !

Particulate matter with diameter less than 2.5 microns & 10 microns are regulated pollutants

Optical extinction range: 10^{-9} - 10^{-4} cm^{-1}

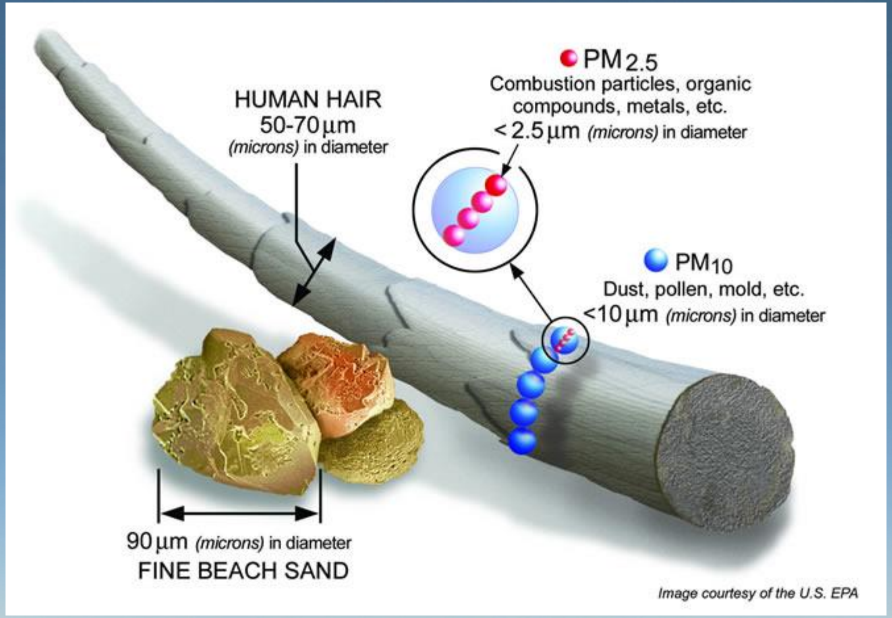
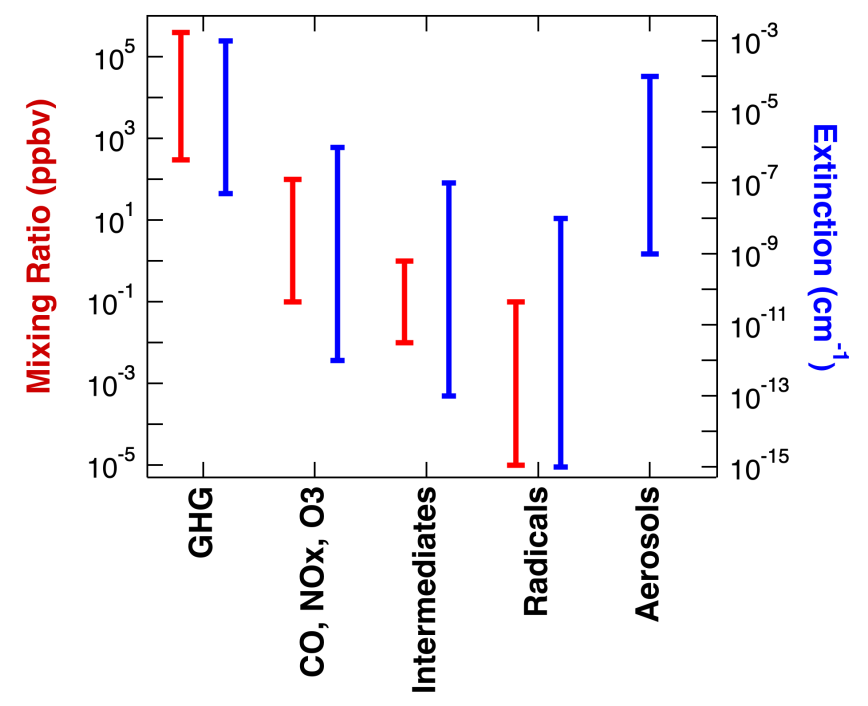


Image courtesy of the U.S. EPA

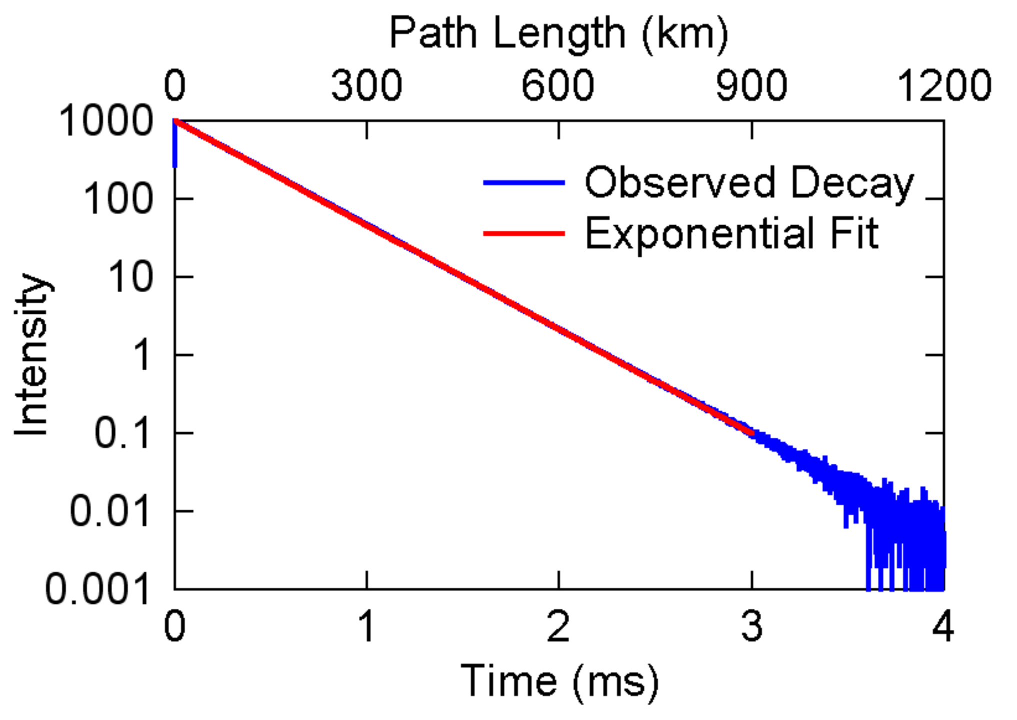


Cavity Enhanced Path Length

- Example @ 662 nm: Reflectivity = 99.999 – 99.9995% ($1-R = 5\text{-}10 \times 10^{-6}$)

- Ring down time constant $\tau > 300\ \mu s$
  Effective path length $L_{eff} > 100$ km

- Sensitivity $\leq 10^{-10}\ cm^{-1}\ Hz^{-1/2}$



But … What actually limits this path length in an atmospheric sample ?

$$L_{eff} = c\tau_0 = L_{base}\left[(1-R) + L_{base}\left(\alpha_{Rayleigh} + \alpha_{Mie} + \sum_i \alpha_i\right)\right]^{-1}$$

Per Pass Losses
100 cm
Cavity

Mirror Reflectivity
≥ 5 ppm

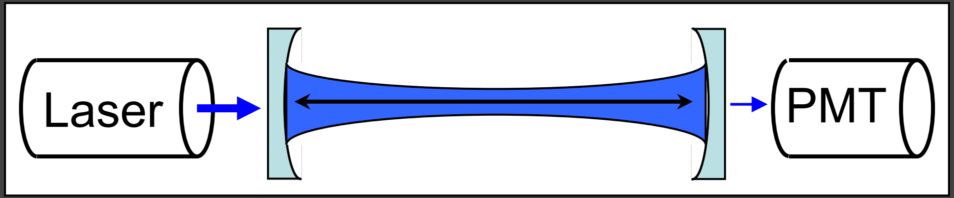
Rayleigh Scattering
1.5 - 40 ppm
across visible

Mie Scattering
<1 - 100 ppm
but variable !

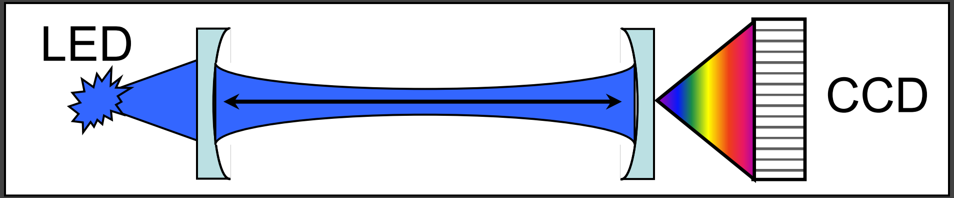
Trace gas
absorption
≤ 10 ppm
Variable !

Cavity Enhanced Spectroscopy Techniques

Time



Intensity



$$\frac{dI_{in}(\lambda)}{dt} = c\left(-\frac{(1-R(\lambda))}{d} - \sum \alpha_i(\lambda)\right) I_{in}(\lambda) + ck_s I_s(\lambda)$$

R = Reflectivity
α = Extinction coefficient
d = Cavity length
c = Speed of light

- Narrowband laser sources
- Shut off I_S instantaneously
- Integrate dI/dt

$$I(t) = \exp\left[-\left(c\sum_i \alpha_i + 1/\tau_0\right)t\right]$$

$$\sum_i \alpha_i = \frac{1}{c}\left(\frac{1}{\tau} - \frac{1}{\tau_0}\right)$$

Absolute measurement of α (λ) as long as scheme exists for determining τ_0 independently of τ

- Laser or broadband source
- Continuous, Constant I_S
- Let dI/dt = 0 (steady state)

Define $I_0(\lambda)$, $I(\lambda)$ as cavity with, without absorbers

$$\sum \alpha_i(\lambda) = \left(\frac{1-R(\lambda)}{d} + \alpha_{Ray}\right)\left(\frac{I_0(\lambda) - I(\lambda)}{I(\lambda)}\right)$$

Even if scheme exists to separate I(λ), $I_0(\lambda)$, ***still*** must determine 1-R(λ)/d ***and*** know α_{Ray} - Requires Calibration !

Considerations for a Field Instrument

Field instruments are about more than just about the optics !

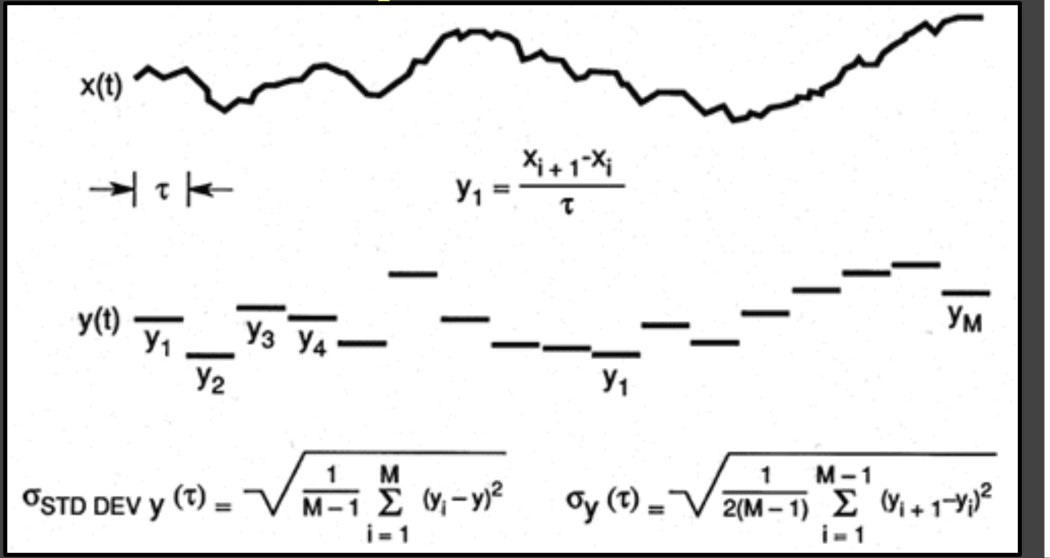
- Sampling time
- Precision and detection limit

Closely related

- Method for determining and acquiring zeros (I_0)
- Method for calibration or validation
- Materials for sample handling
- Optical stability and mirror cleanliness
- Engineering requirements: Size, weight, and portability
- Automation and ease of use

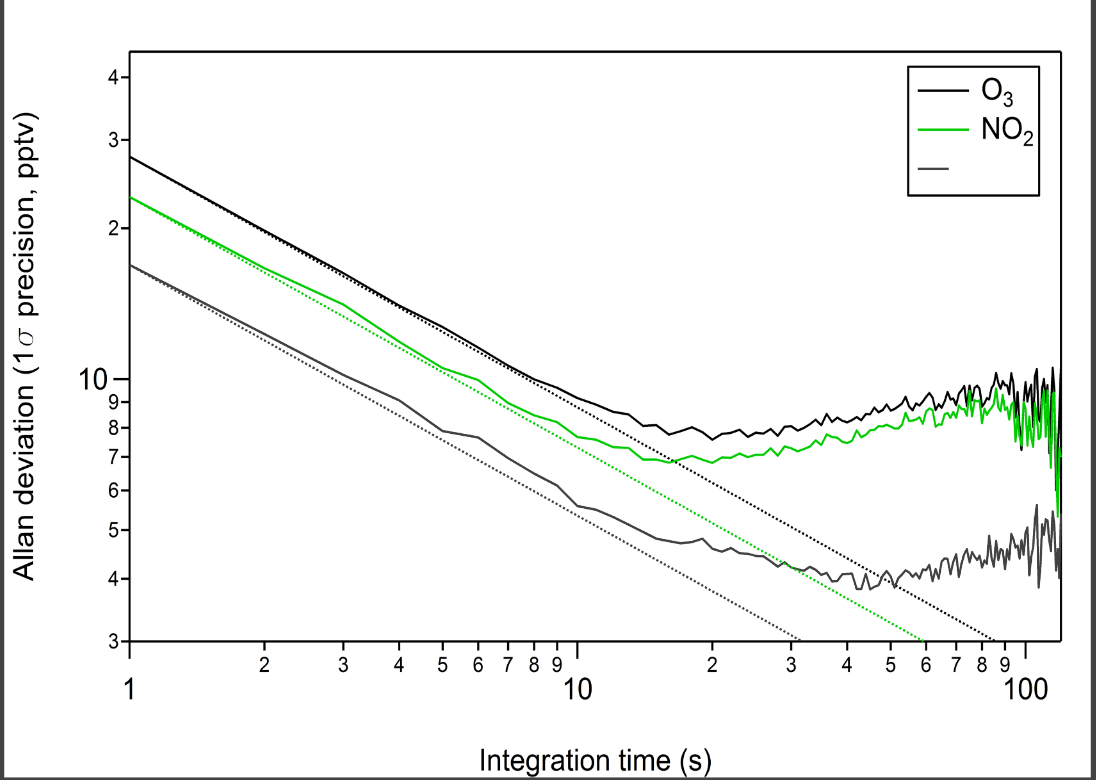
Detection Limit, Precision and Time Response

Allan-Werle Deviation



$$y_1 = \frac{x_{i+1} - x_i}{\tau}$$

$$\sigma_{\mathrm{STD\,DEV}\,y}(\tau) = \sqrt{\frac{1}{M-1}\sum_{i=1}^{M}(y_i - \bar{y})^2} \qquad \sigma_y(\tau) = \sqrt{\frac{1}{2(M-1)}\sum_{i=1}^{M-1}(y_{i+1} - y_i)^2}$$



Precision requirement is a function of the measurement platform

Aircraft

Cruising speed ≈ 100 m s-1

Spatial resolution @ 1 s = 100 m

1 Hz (or sub 1Hz) time resolution required

Ground Site

Data commonly reported at 1 min – 1 hour resolution

Daily / diel profiles often define the science

Flux Measurement

Dependence of mixing ratio with vertical wind

Variability on 10 Hz time scale

Mirror Cleanliness and Optical Stability

The atmosphere is a dirty place !

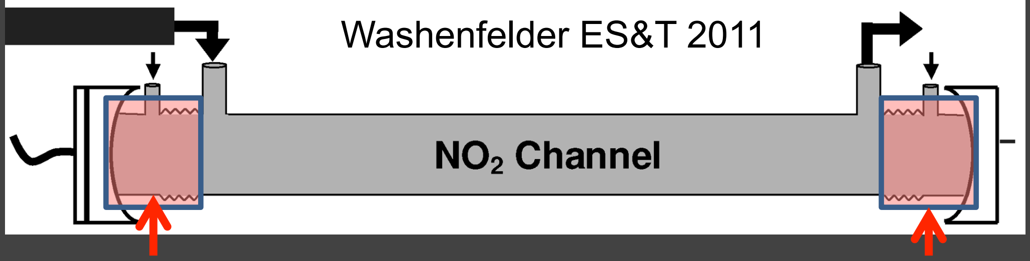
Severe urban air pollution

Wildfires and agricultural burning

High relative humidity

Approaches

- Purge volumes



Washenfelder ES&T 2011

Purge volumes with flows ~1% of sample flow

- Operation at reduced P and / or increased T
- Inlet filtration to remove particulates

Measurement platforms may be harsh

Photo: J. Gilman

P-3: Four engine turboprop aircraft that flies hurricanes

Research Vessels: e.g. 8 m swells in the North Atlantic

Approaches

- Isolation

- Many optical cavity based instruments are remarkably robust against shock and vibration
- Actually superior to other alignments ... e.g. Herriot Cells

Engineering: Size, Weight, Power, Automation

All field measurement platforms, but especially aircraft, benefit from reductions in size, weight and power

Power consumption costs twice:
- Limitation in power availability
- Dissipation of heat load

CES instruments actually have an inherent benefit in this regard due to:

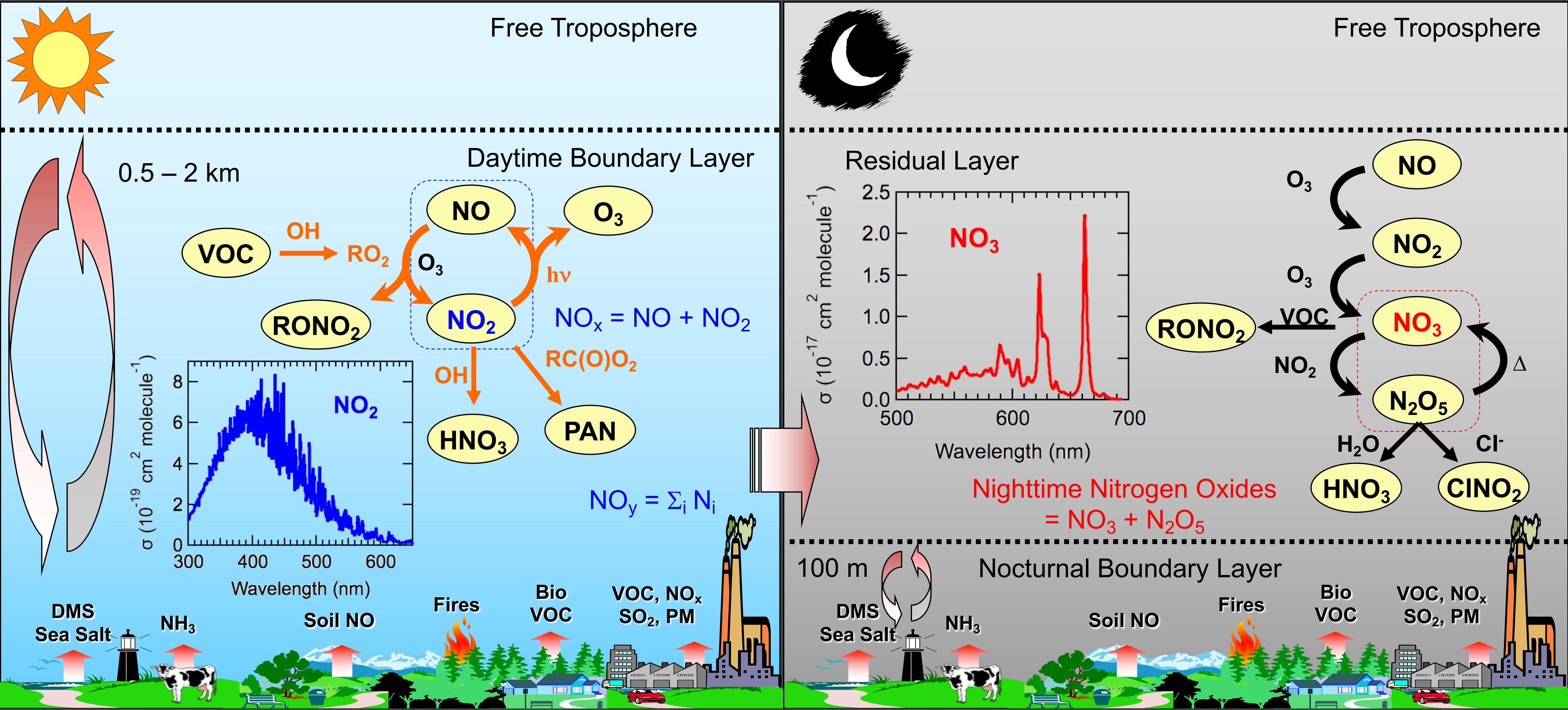
- Miniature opto-electronics components
- Not just small, but also low power
- Reduced requirements for vacuum

Automation: You don’t always get to fly with your instrument!

Example: NASA ER2 & WB57, single pilot, high altitude

NOAA Twin Otter, Inside and Outside, 2017

Example 1: Nitrogen Oxide and Ozone Cycles

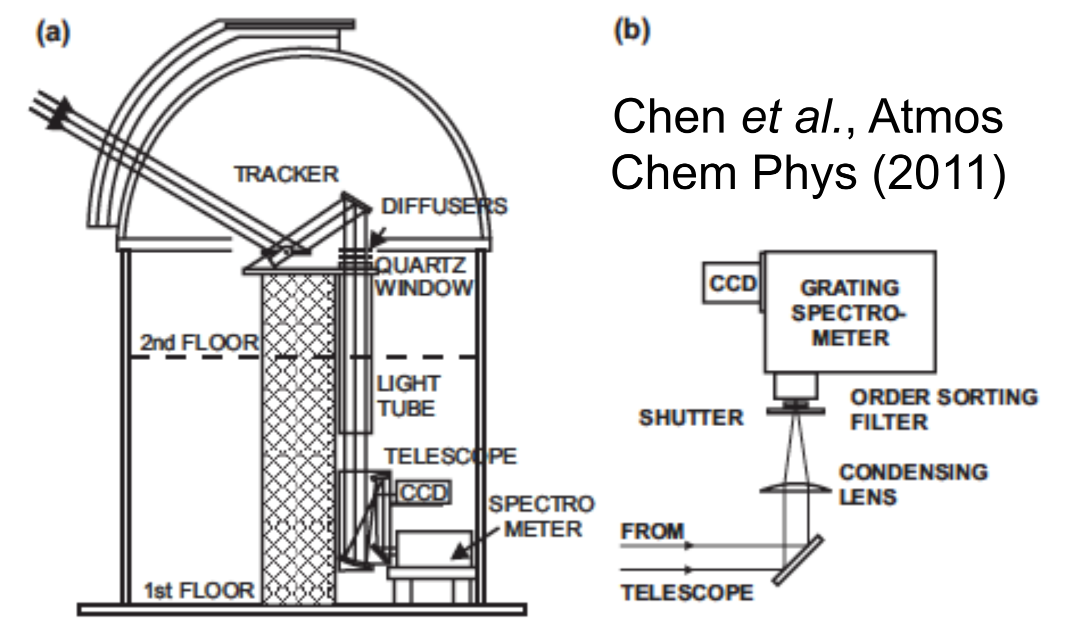


Photochemical O_3, rapid NO_x & VOC oxidation

O_3 consumption, dark NO_x oxidation, radical reservoirs, stratification

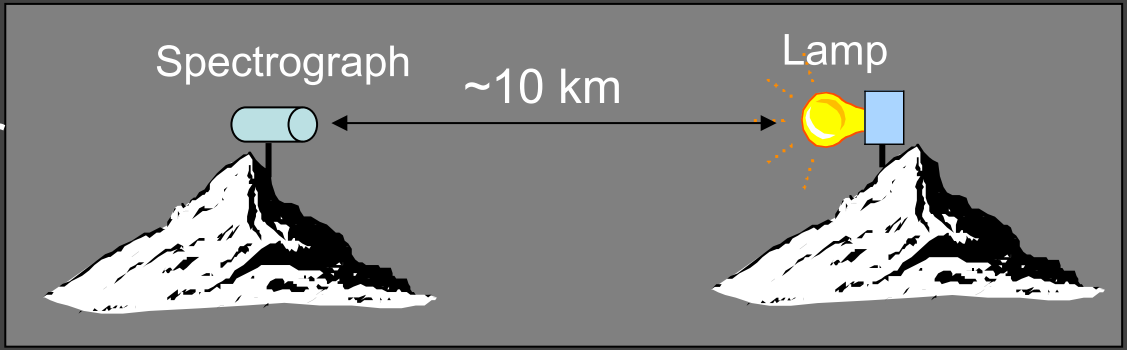
Nitrate Radical (NO_3) Atmospheric Spectroscopy

Passive – e.g., lunar light source



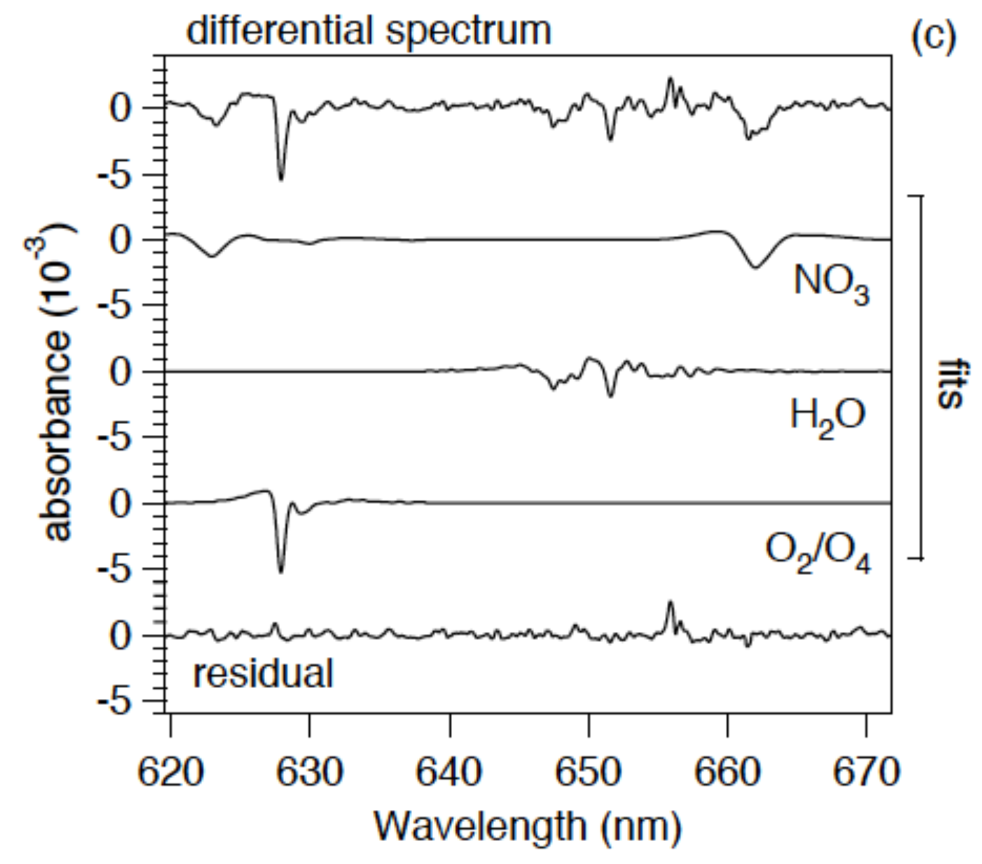
Chen *et al.*, Atmos Chem Phys (2011)

Active – Xe Arc Lamp or LED on long path

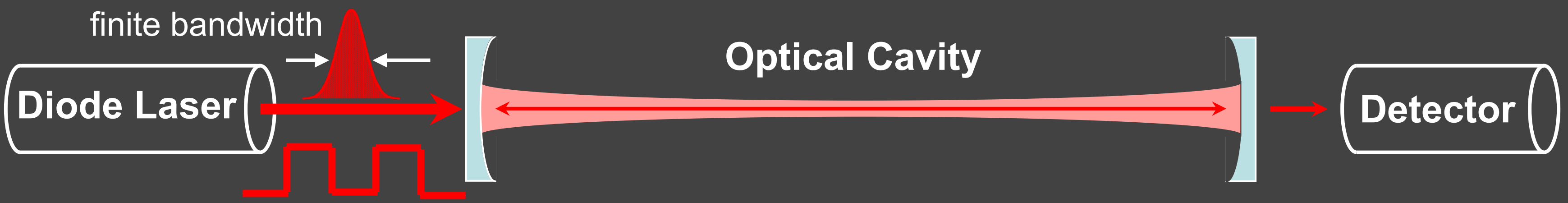


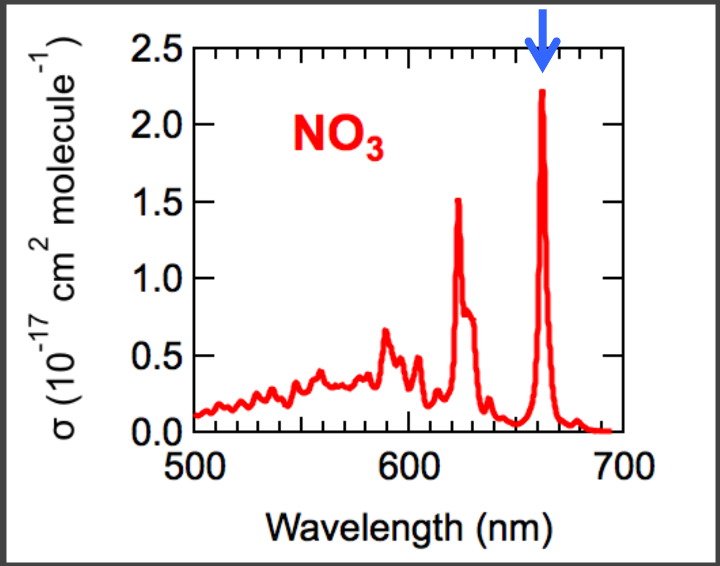
Platt, U., *et al.*, Geophys. Res. Lett., 1980.
Noxon, J. F., *et. al.*, 1980.

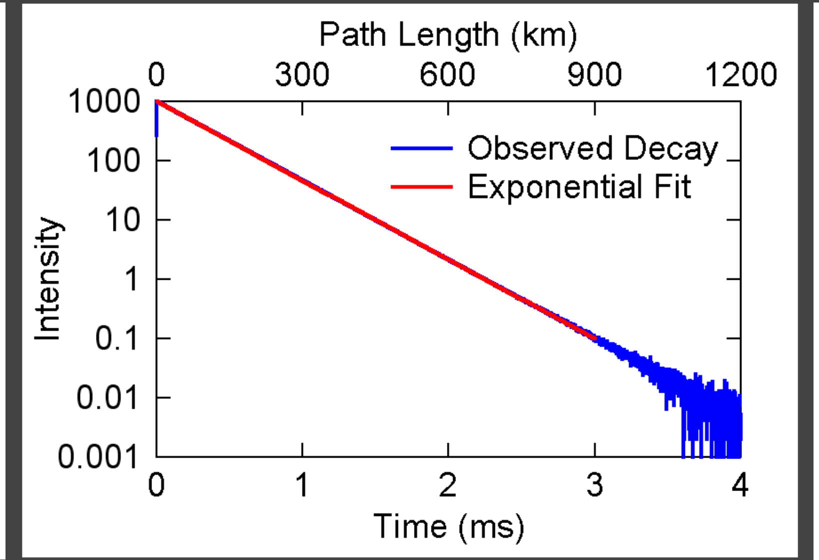
Differential Optical Absorption Spectroscopy (DOAS)

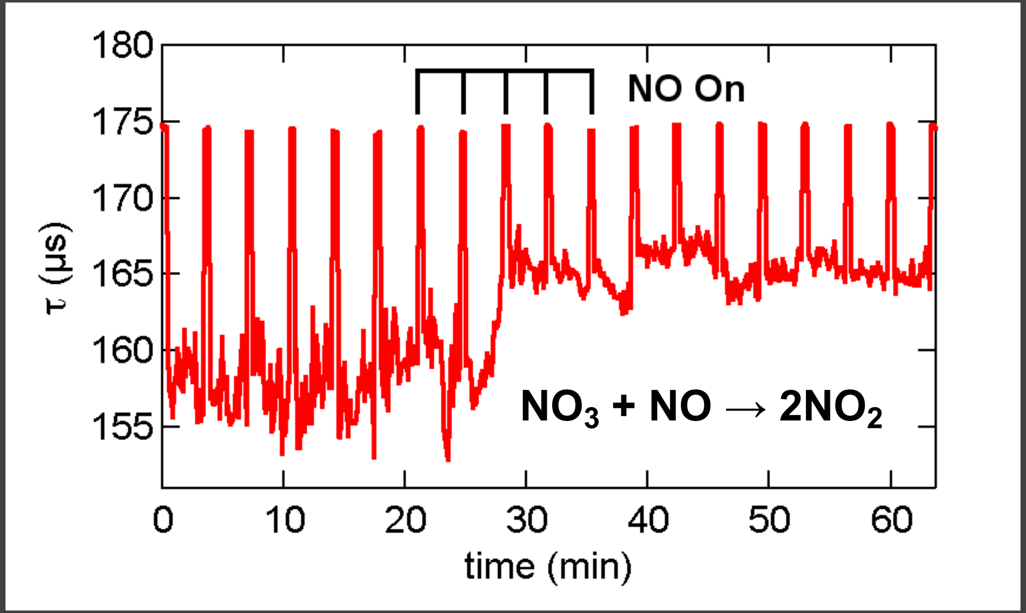


NO_3 Cavity Ring-Down Spectroscopy





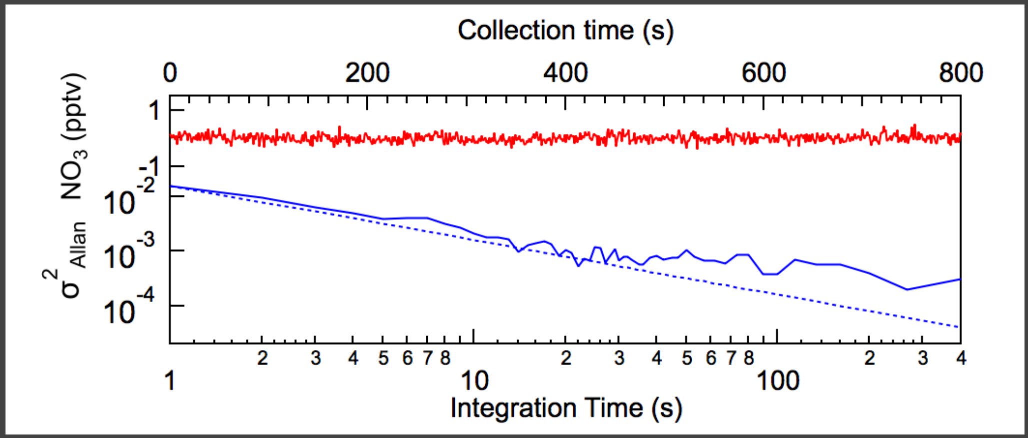




Fix laser at 662 nm

Modulate NO_3 via: $NO_3 + NO \rightarrow 2NO_2$

Reaction is rapid and specific to NO_3

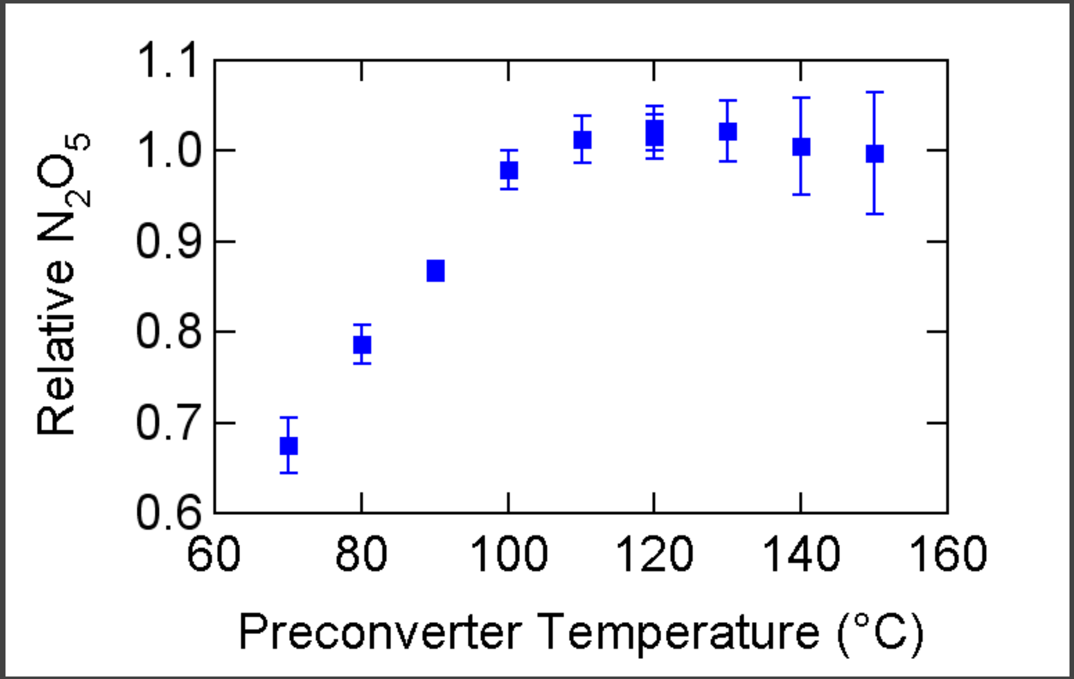


662 nm absorption + NO titration = highly specific NO_3 detection
Sensitivity as good at 0.2 pptv @ 1 Hz

Simultaneous Detection of N_2O_5

$$NO_2 \xrightarrow[k]{O_3} NO_3 \underset{K_{eq}}{\overset{NO_2}{\rightleftharpoons}} N_2O_5$$

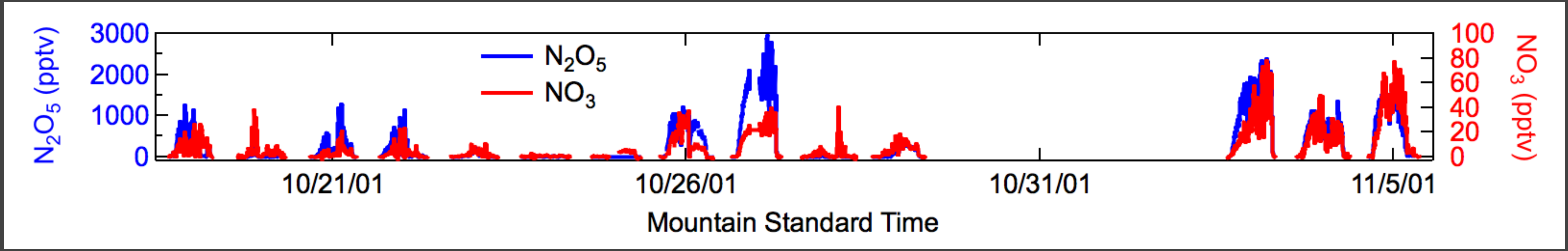
Exploit thermal equilibrium between
NO_3 and N_2O_5



- Thermal conversion of $N_2O_5 \rightarrow NO_3$ in a heated inlet

$$\boxed{N_2O_5 \xrightarrow{\Delta} NO_3 + NO_2}$$

- Measure sum of NO_3 and N_2O_5; N_2O_5 = heated - ambient signal



NO_2 Measurement at 405 nm

- 405 nm very near the O_3 minimum @ 385 nm

  50 ppbv O_3 = 1 pptv NO_2

- No significant H_2O or O_4 (O_2-O_2) absorption bands

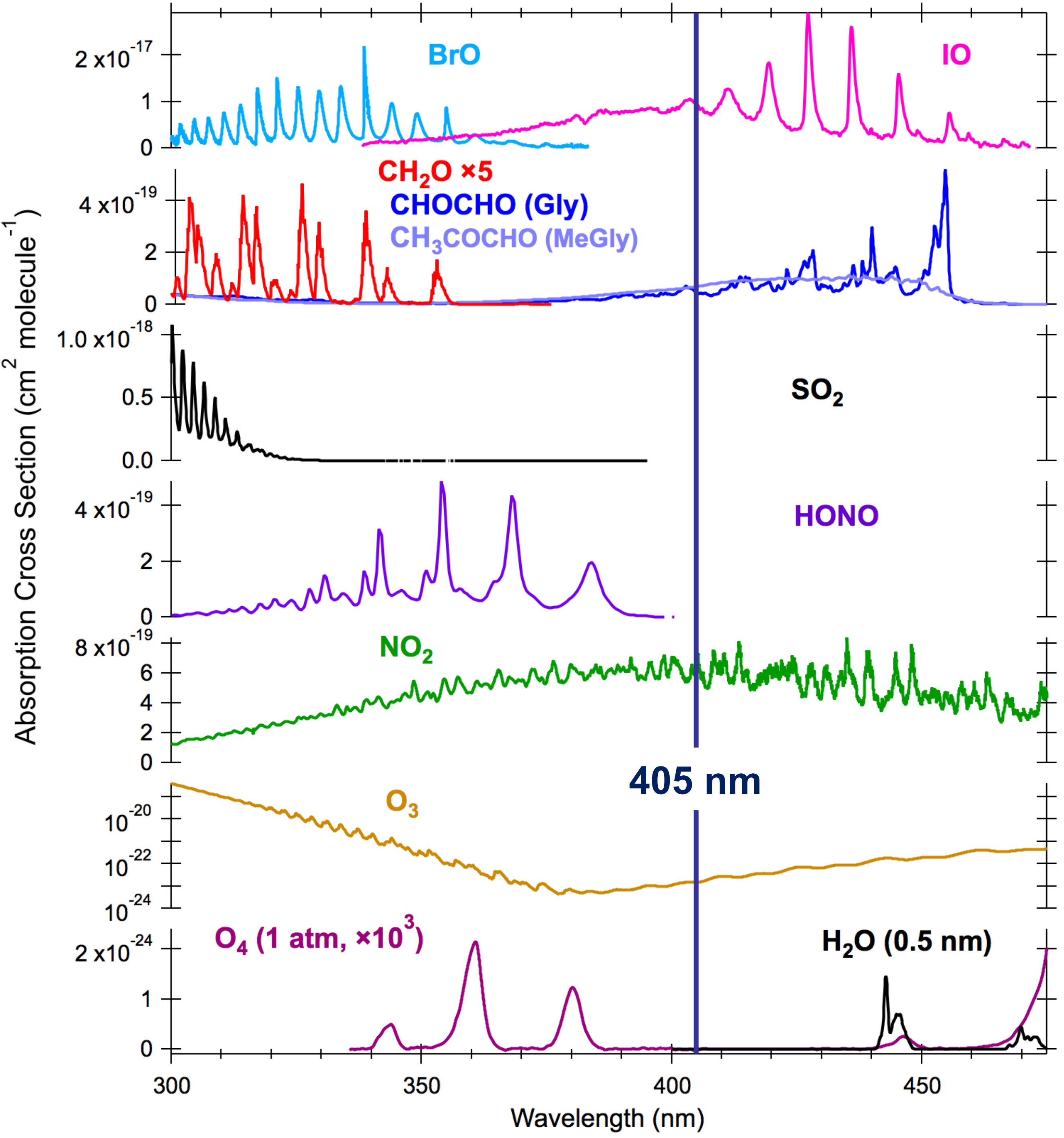
- Glyoxal / Methylglyoxal *can* present an interference

  200 pptv Glyoxal ≈ 20 pptv NO_2

- IO also potential interference

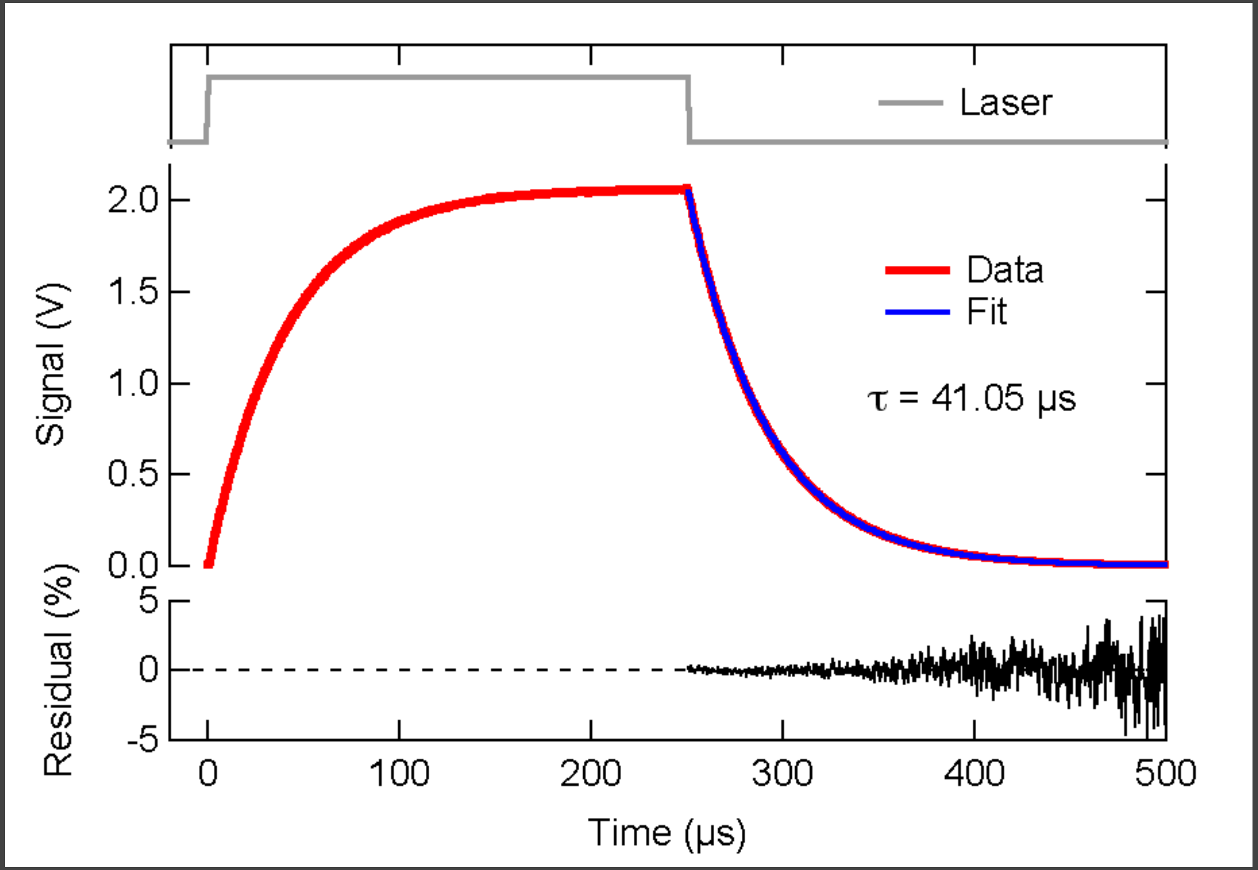
  1 pptv IO ≈ 15 pptv NO_2

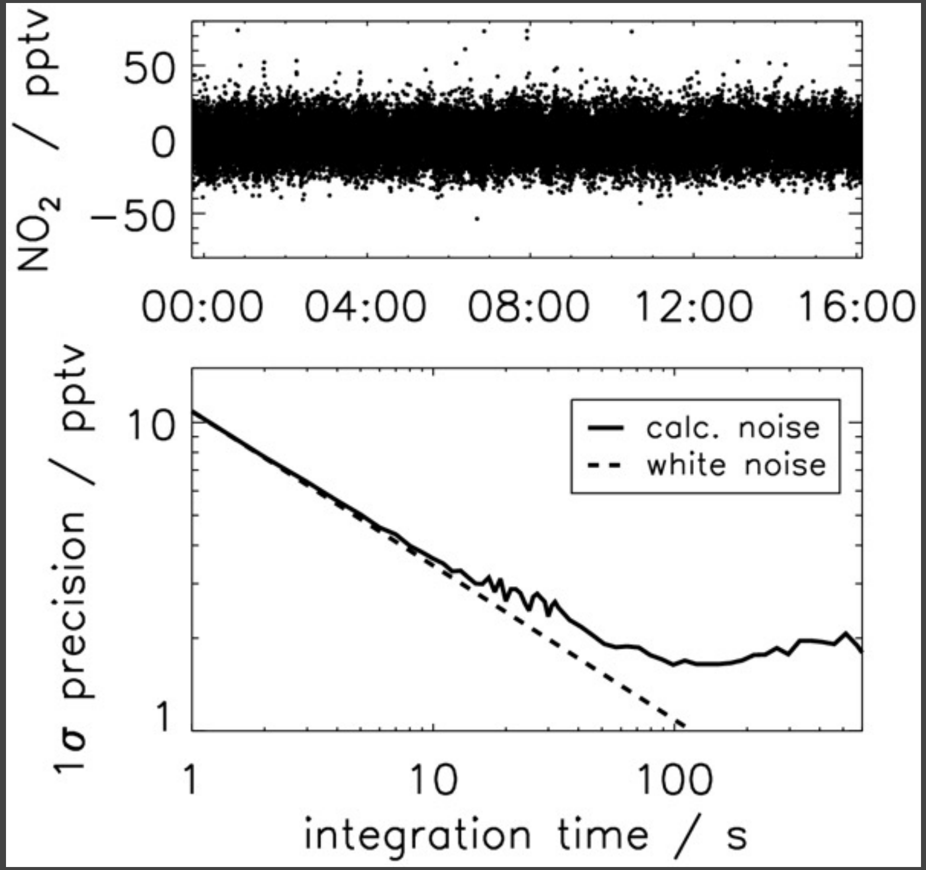
Total gas phase optical extinction @ 405 nm is a nearly interference-free measure of NO_2



NO_2 Cavity Ring Down Spectroscopy

Fuchs, Environ. Sci. & Tech. 2009





- 405 nm diode laser modulated at 2 KHz
- R(405 nm) ~99.995, L_{eff} ~ 8.5 km

Allan-Werle deviation

$\alpha = 2 \times 10^{-10}$ cm^{-1} Hz$^{-1/2}$

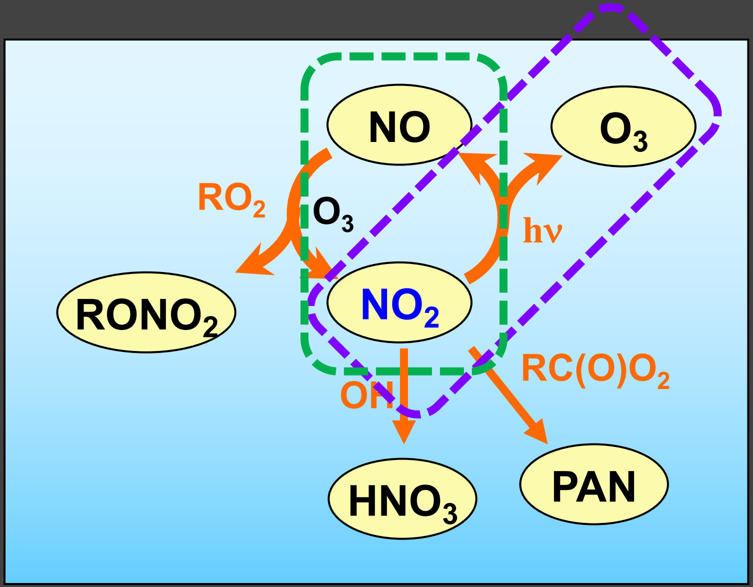
Precision = 22 pptv / 1 Hz / 2σ

5 pptv / 1 minute / 2σ

Accuracy = 3%

Conversion of NO and O_3 to NO_2

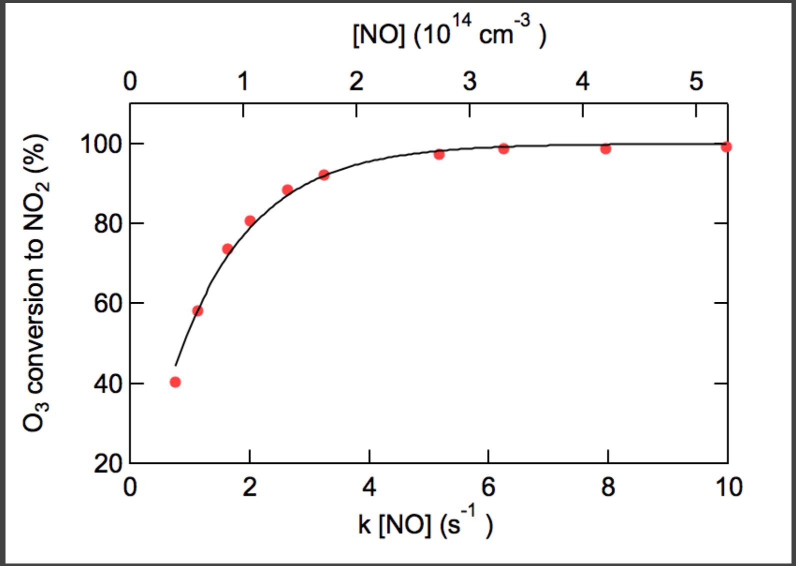
Photochemical Nitrogen Oxide Cycle



NO_x and O_x are conserved quantities useful for definition of photochemical nitrogen and ozone cycles

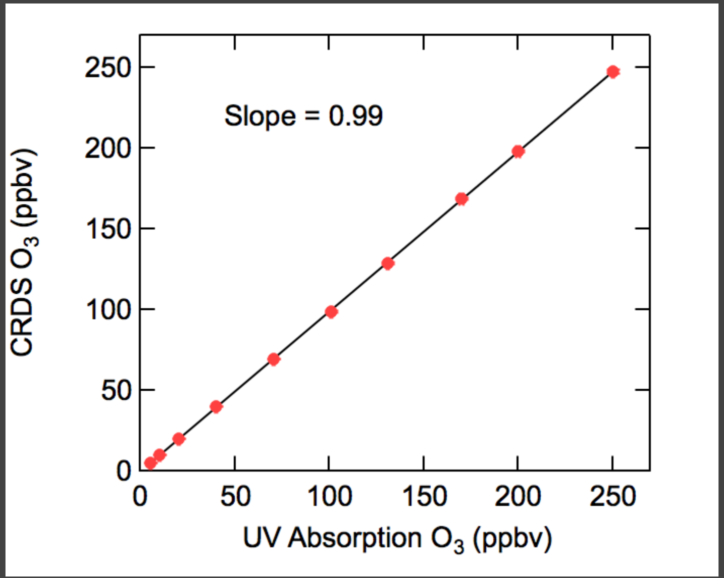
$NO_x = NO + NO_2$

- $NO + O_3 \rightarrow NO_2 + O_2$
- 18 ppmv O_3 (O_2 or air + Hg lamp) yields > 99% conversion in 0.5 s
- Small (<2%) correction for oxidation of NO_2 to N_2O_5, small optical extinction due to excess O_3

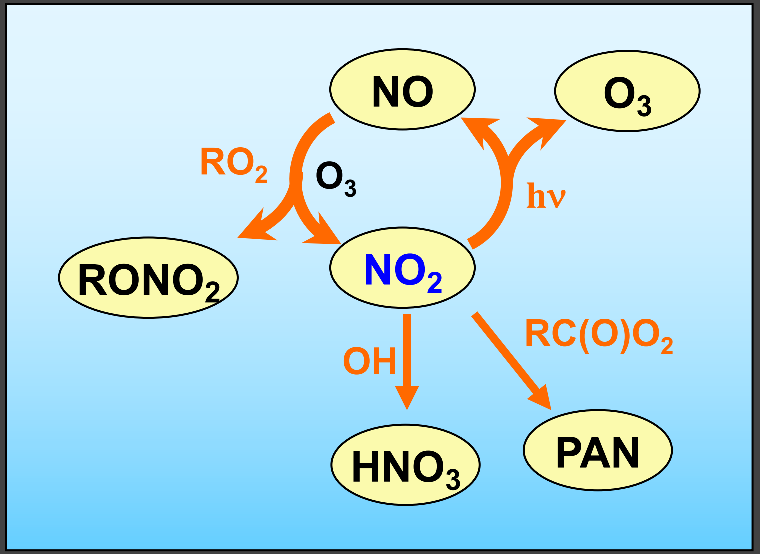


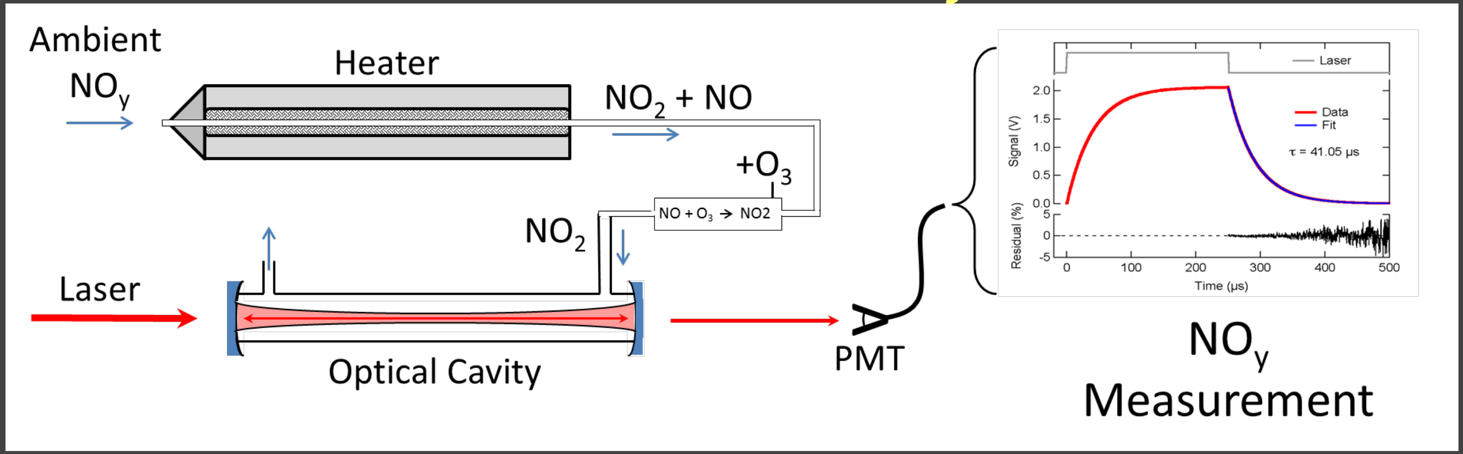
$O_x = O_3 + NO_2$

- $O_3 + NO \rightarrow NO_2 + O_2$
- Same rate, different excess reagent
- No extinction from background O_3, but ... NO_2 background (~ 0.2%) present in the added NO

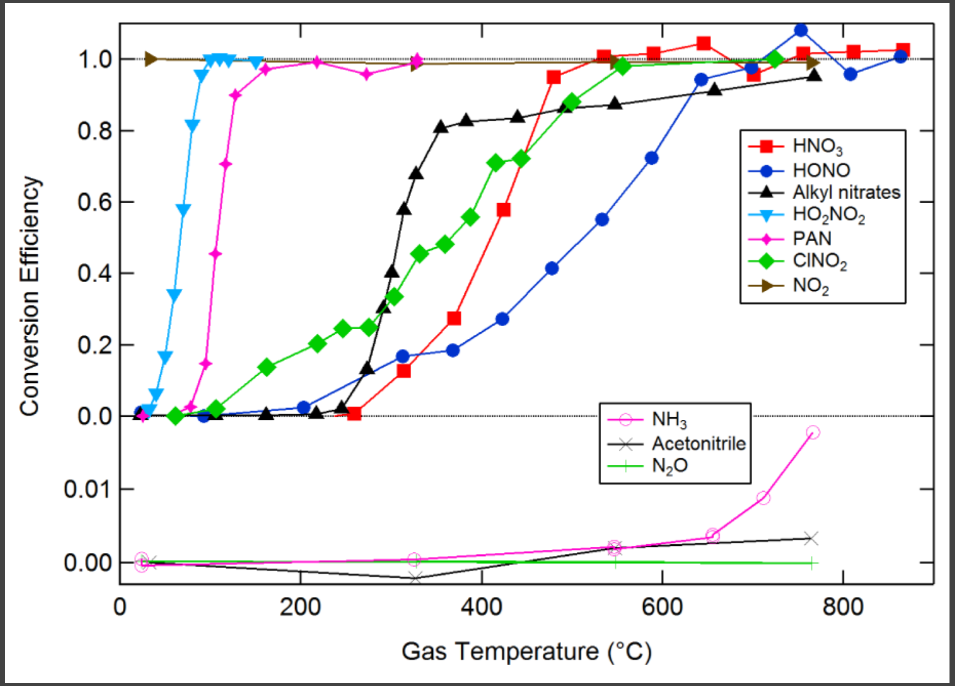


Conversion of NO_y to NO_2





$NO_y = \Sigma_i N_i$



Wild *et al.*, ES&T (2014)
Womack *et al.*, AMT (2017)

1. Convert most $NO_y \rightarrow NO_2$ in 650 C quartz oven

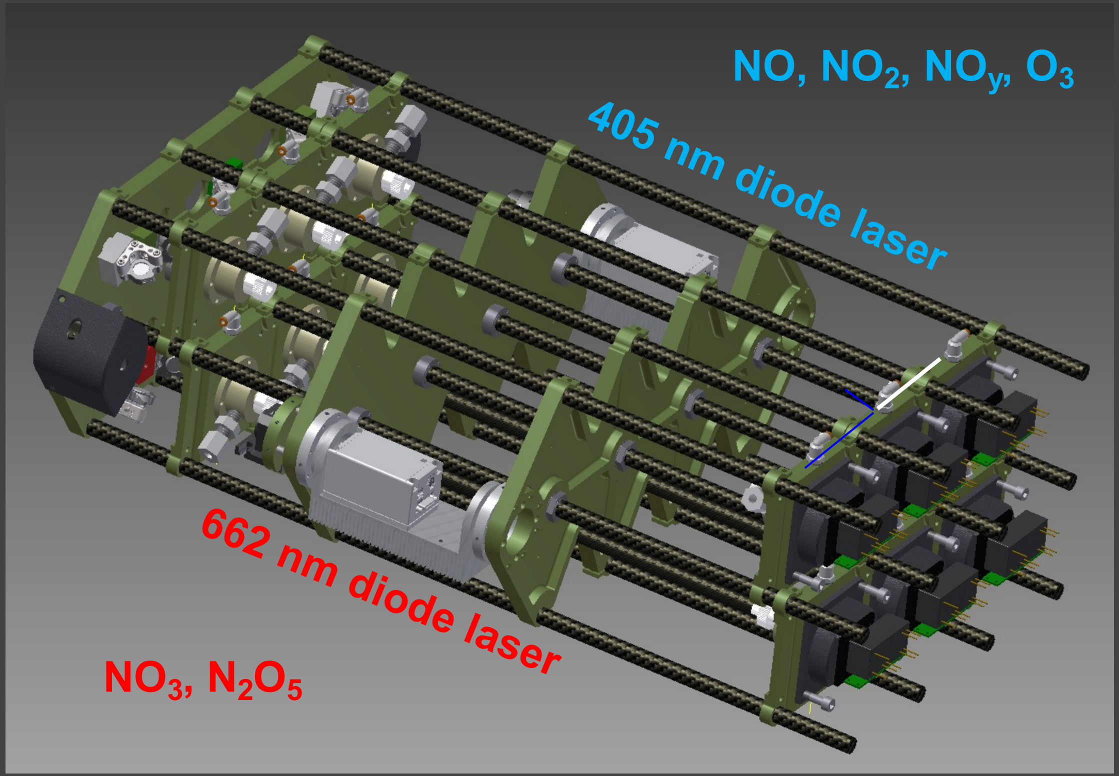
$$NO_y + \Delta(650\ ^\circ C) \rightarrow NO_2$$

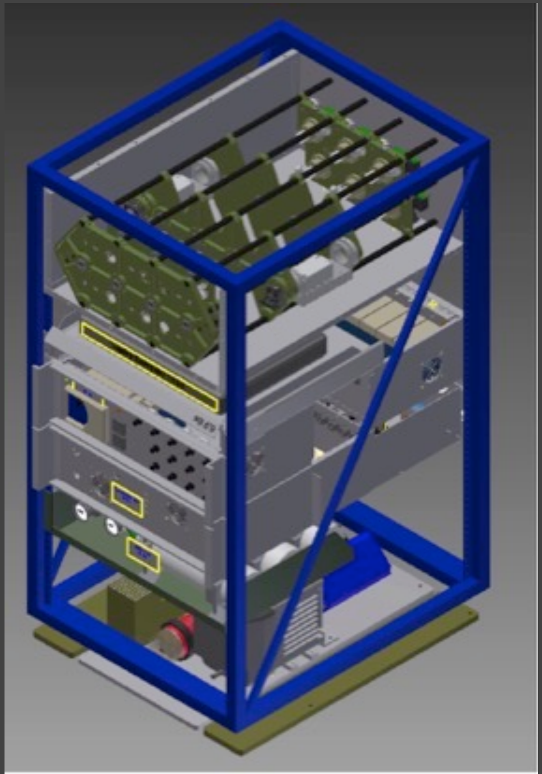
2. Convert $NO \rightarrow NO_2$ in excess O_3 (same as NO_x channel)

$$NO + O_3\ (\text{excess}) \rightarrow NO_2$$

Accuracy = 12 %, based on in-field comparison to other NO_y instruments

6-Channel Nitrogen Oxide Cavity Ring-Down Spectrometer





NOAA
NATIONAL OCEANIC AND ATMOSPHERIC ADMINISTRATION
U.S. DEPARTMENT OF COMMERCE

Bill Dubé

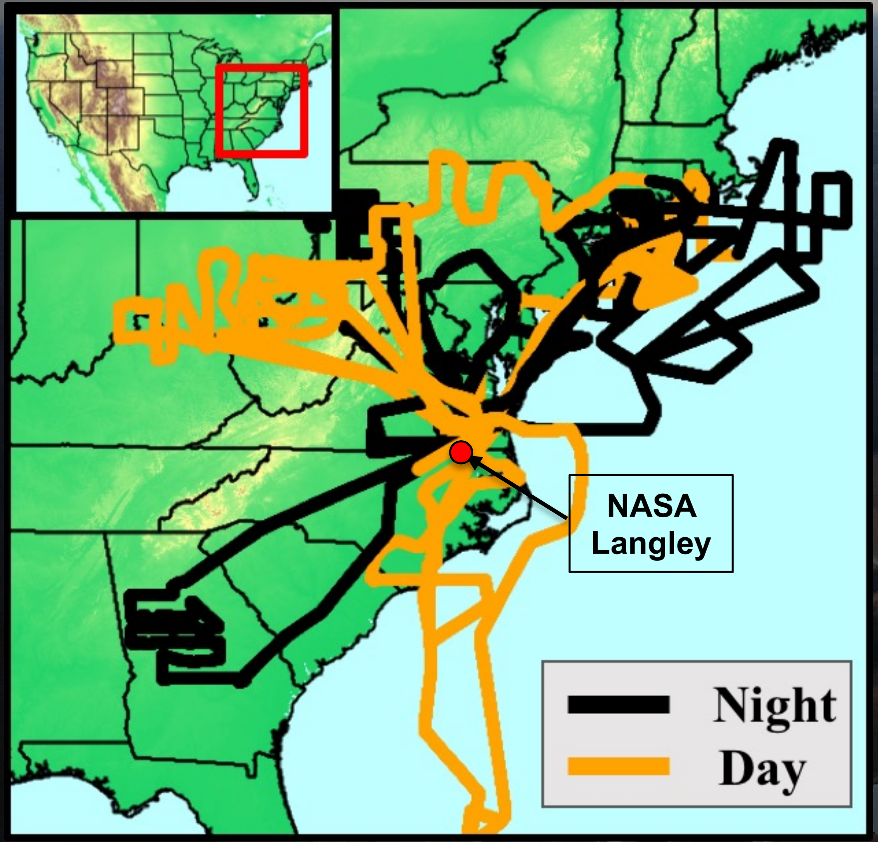
405 nm: Detect NO_2 directly
Convert NO, O_3 to NO_2 via:
$NO + O_3 \rightarrow NO_2$
Convert NO_y to NO_2 via:
$NO_y + \text{heat} + O_3 \rightarrow NO_2$
NO_y = total reactive nitrogen
L.O.D. = 20-50 pptv (2σ, 1Hz), 3-12% Accuracy

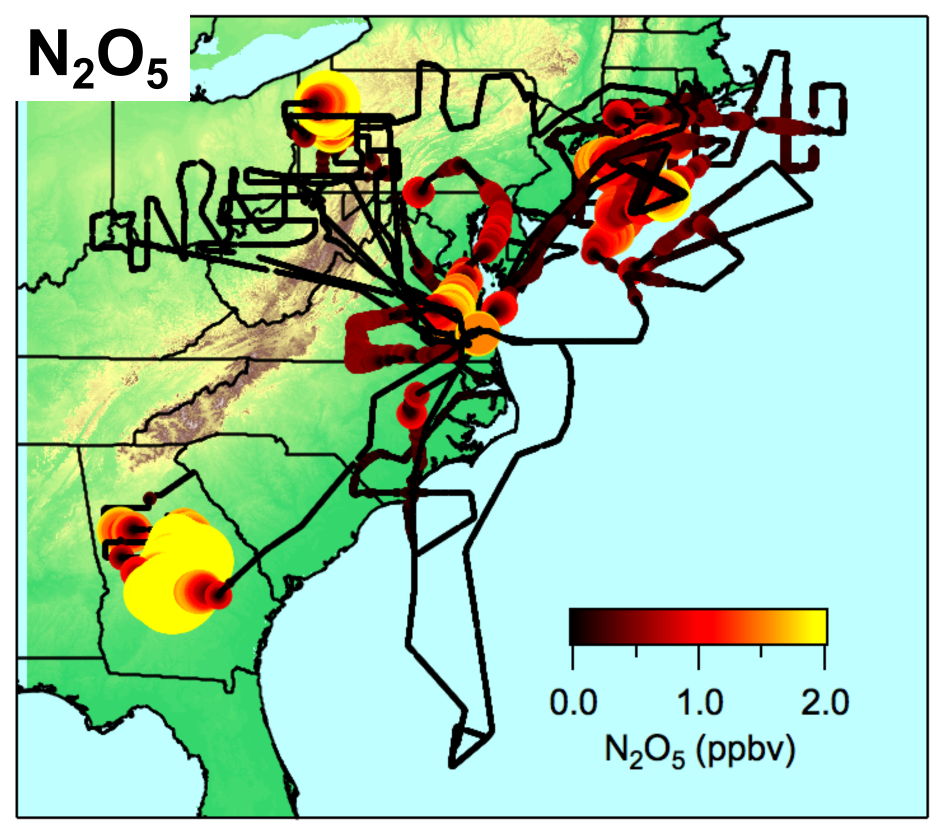
662 nm: Detect NO_3 directly
Convert N_2O_5 to NO_3 via:
$N_2O_5 + \text{heat} \rightarrow NO_3 + NO_2$
L.O.D = 0.2 - 3 pptv, 10-20% Accuracy

High precision, fast response NO, NO_2, NO_y, O_3, NO_3, N_2O_5 with single calibration standard

Wintertime INvestigation of Transport, Emissions and Reactivity (WINTER)

NSF / NCAR C-130 Aircraft February 1 – March 15, 2015, United States East Coast

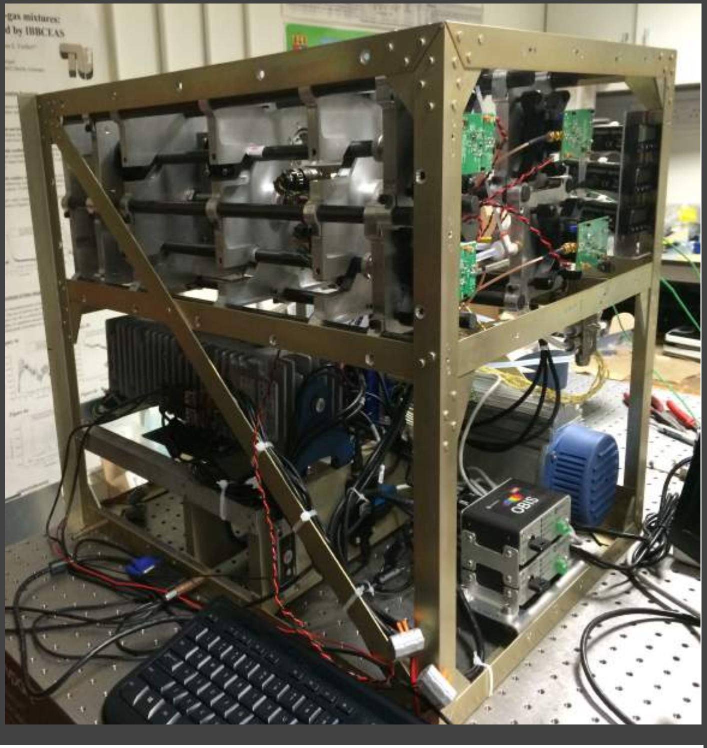




NO_3, N_2O_5, NO, NO_2, O_3 and NO_y in urban outflow from the U.S. East coast during winter

Data used to constrain (among other results) the rates and mechanism for N_2O_5 uptake

CARIBIC Autonomous Ring-Down Instrument for Nitrogen Oxides (CARDINO)



Four Cavity Ring Down Spectroscopy (CRDS) channels:

662 nm: NO_3, N_2O_5

405 nm: NO_2, O_3

45 x 50 x 59 cm^3, 55 kg

Scientific goals:

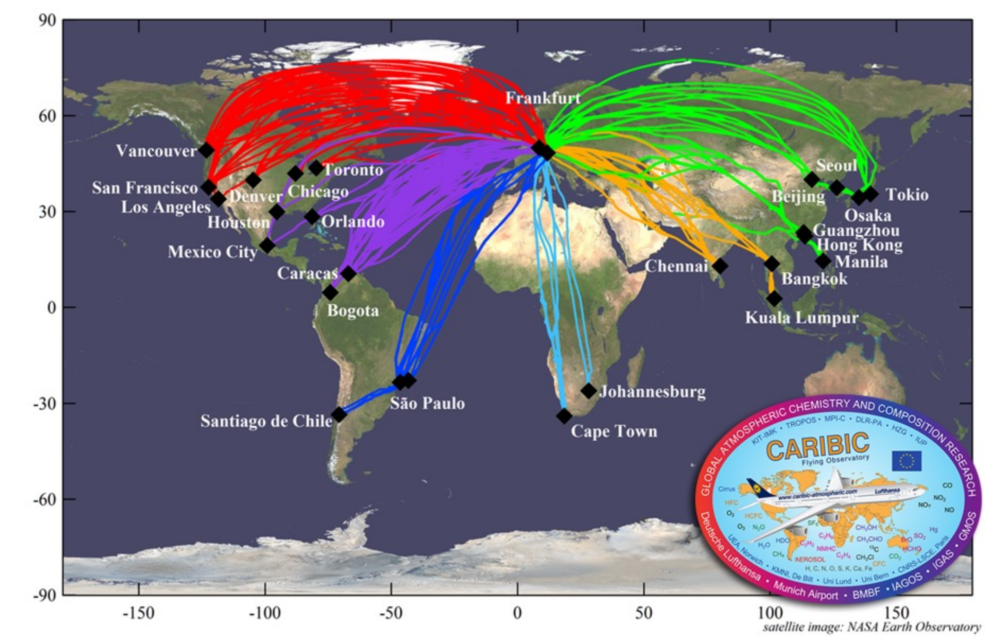
- *In-situ* NO_3, N_2O_5 in the UT / LS with global coverage
- Fast response CRDS NO_2, O_3 on CARIBIC

Andy Ruth

University College Cork, Ireland

Andreas Zahn

Karlsruhe Institute of Technology, Germany



ucc
Coláiste na hOllscoile Corcaigh, Éire
University College Cork, Ireland

KIT
Karlsruher Institut für Technologie

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NATIONAL OCEANIC AND ATMOSPHERIC ADMINISTRATION
U.S. DEPARTMENT OF COMMERCE

Example 2: UV & Visible Atmospheric Trace Gases

- Single wavelength CRDS @ 405 nm shown to be specific to NO_2 for urban impacted environments

- Broadband light sources + optical cavities (broadband CES) useful for other trace gases

- NO_2, Glyoxal, Methylglyoxal
  LED @ 455 nm (438 – 468 nm)

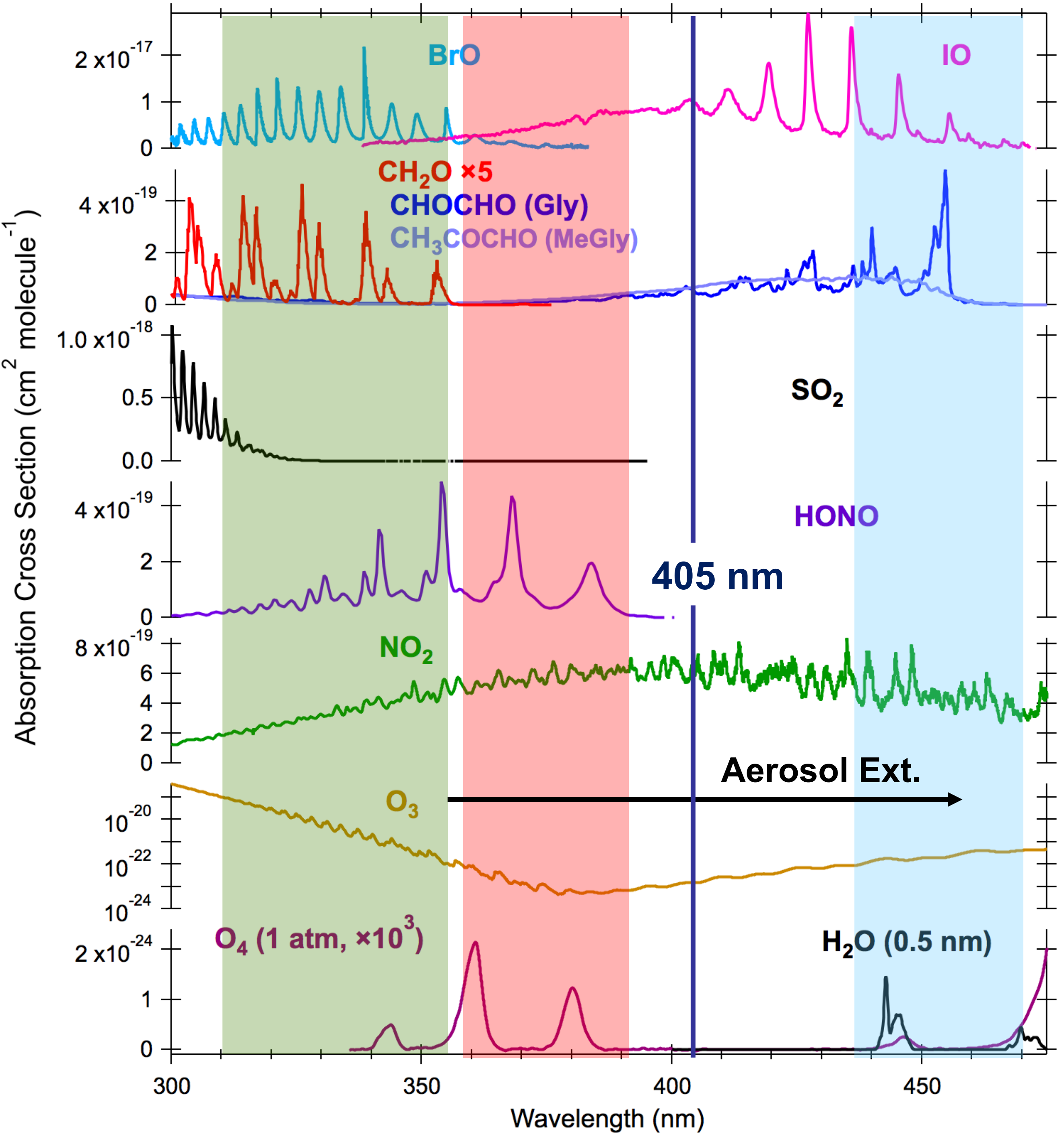
- NO_2, HONO
  LED @ 365 nm (360 – 390 nm)

Min *et al.*, AMT 2016

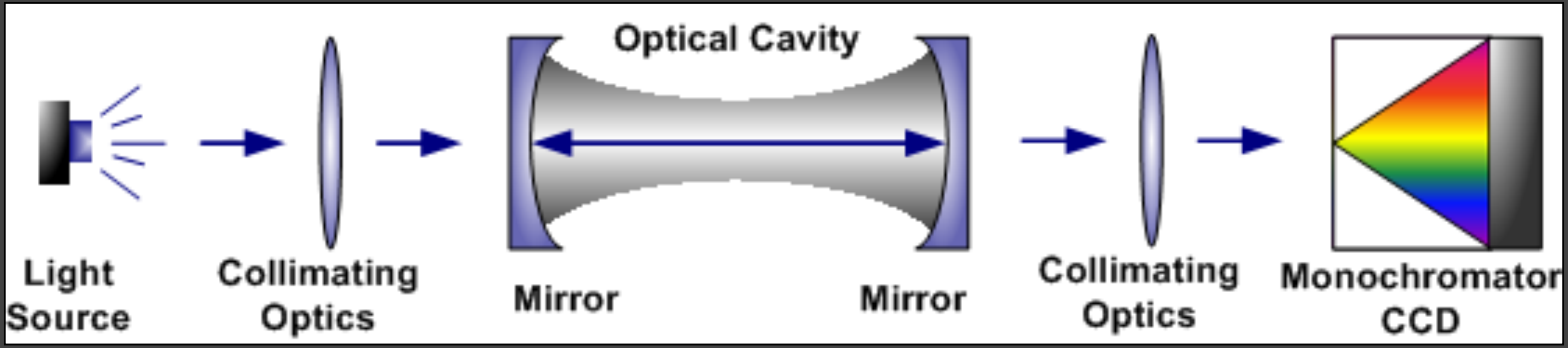
- CH_2O, broadband aerosol extinction using laser driven light source

Washenfelder AMT 2013, 2016
Womack ACP 2021

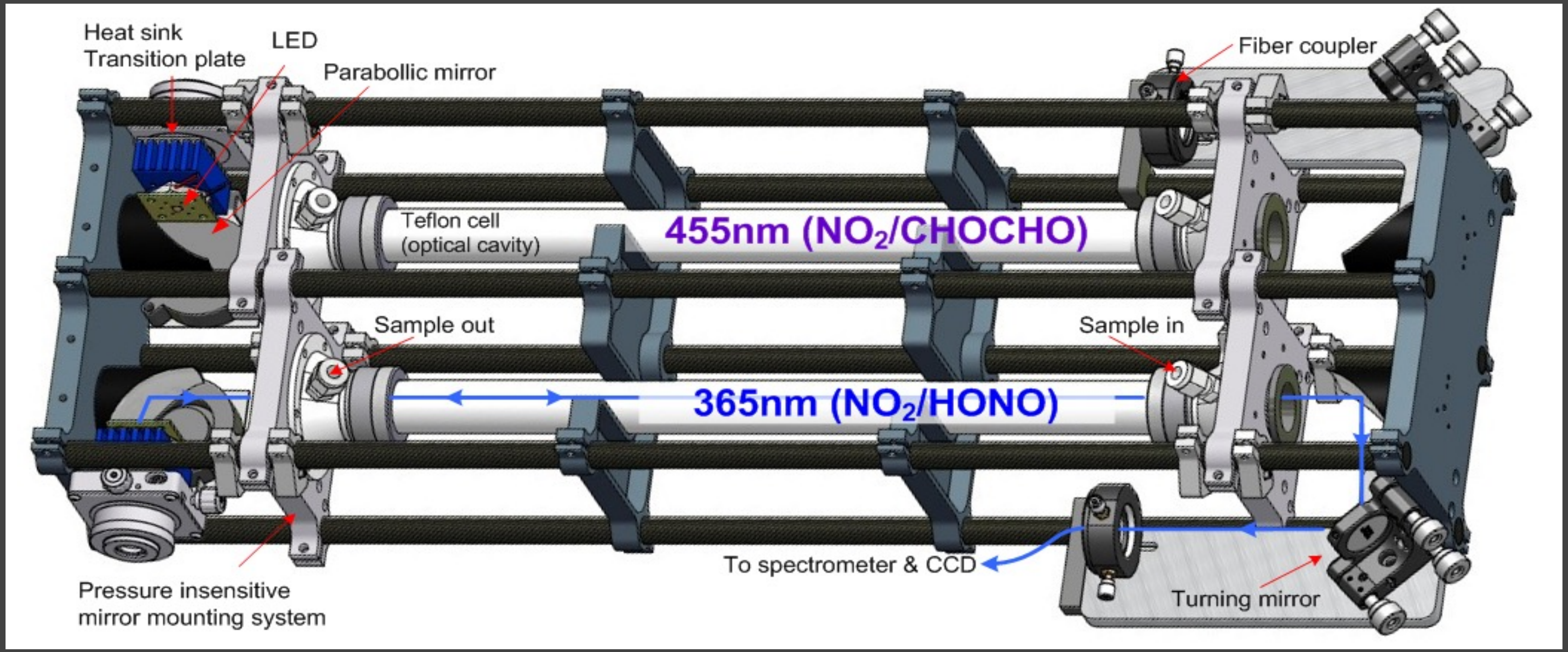
- Future: IO, BrO, SO_2



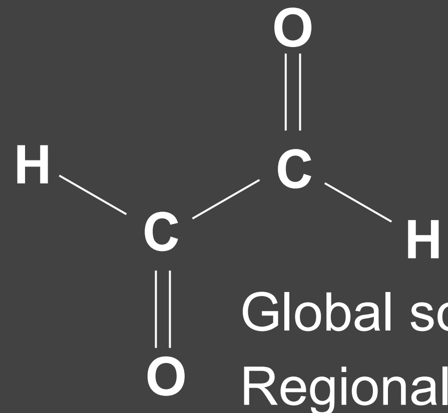
The Airborne Cavity Enhanced Spectrometer (ACES)

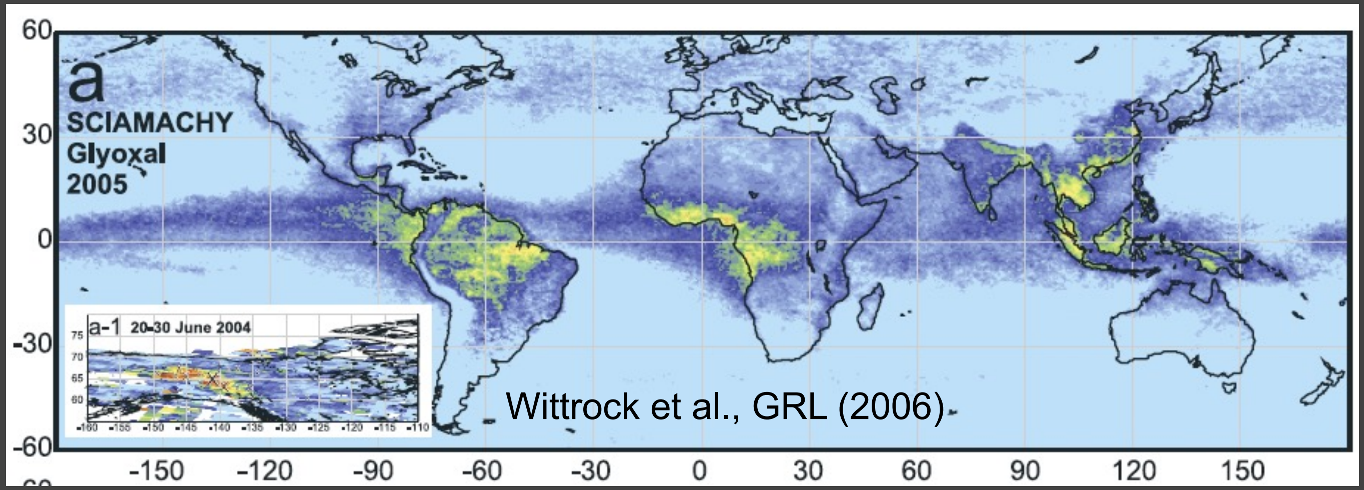


Kyung-Eun Min, Kyle Zarzana, Rebecca Washenfelder, Carrie Womack

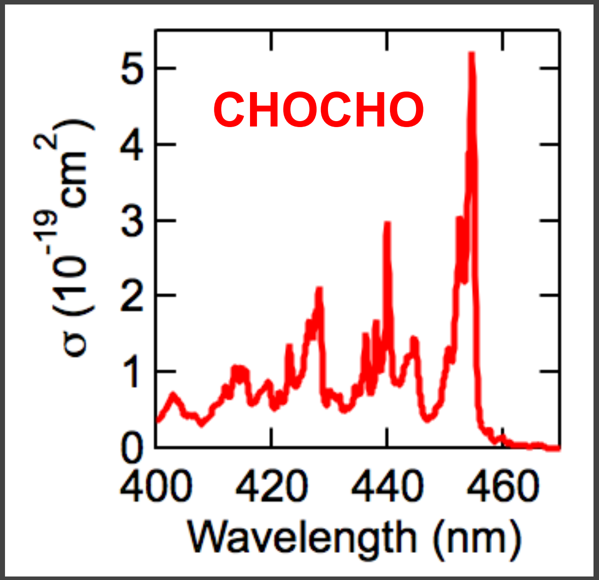


Glyoxal (CHOCHO)





Wittrock et al., GRL (2006)



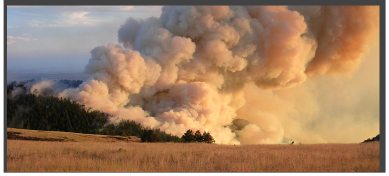
Global source: Isoprene oxidation, fires

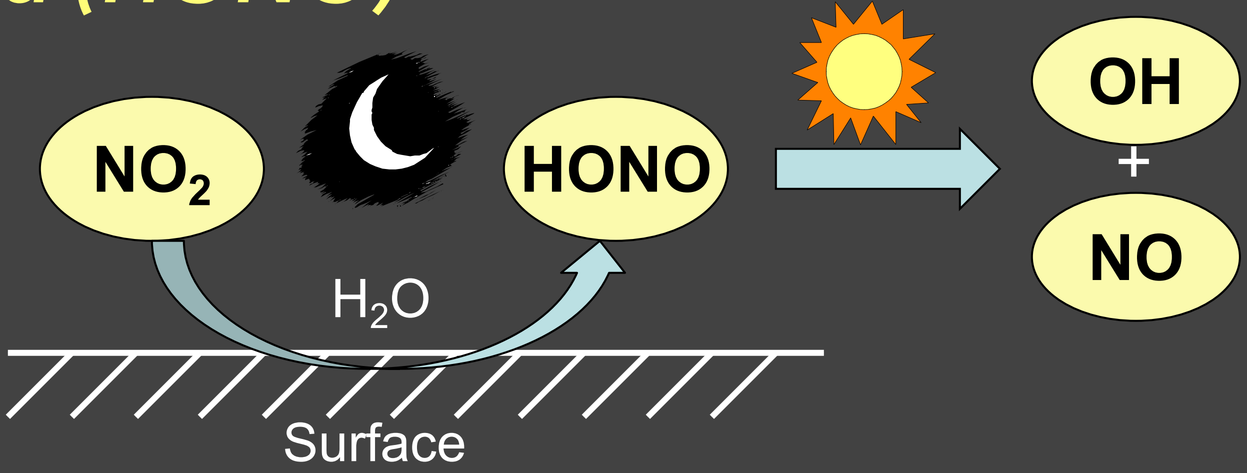
Regional / Urban source: Aromatic, acetylene oxidation

Oligomerization thought to be an important route to organic aerosol

Nitrous Acid (HONO)

Both of these species are emitted in large quantities by fires





NO_2

HONO

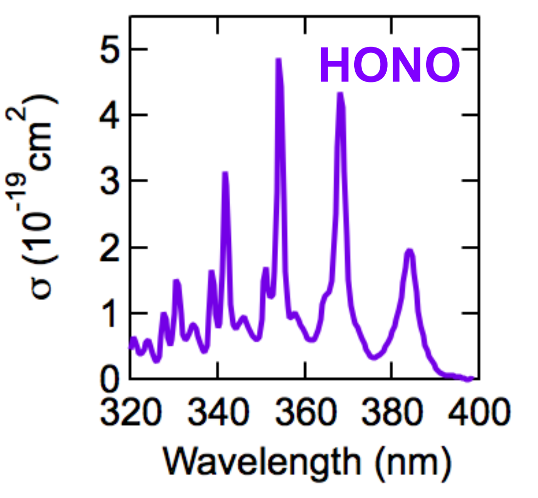
H_2O

Surface

OH

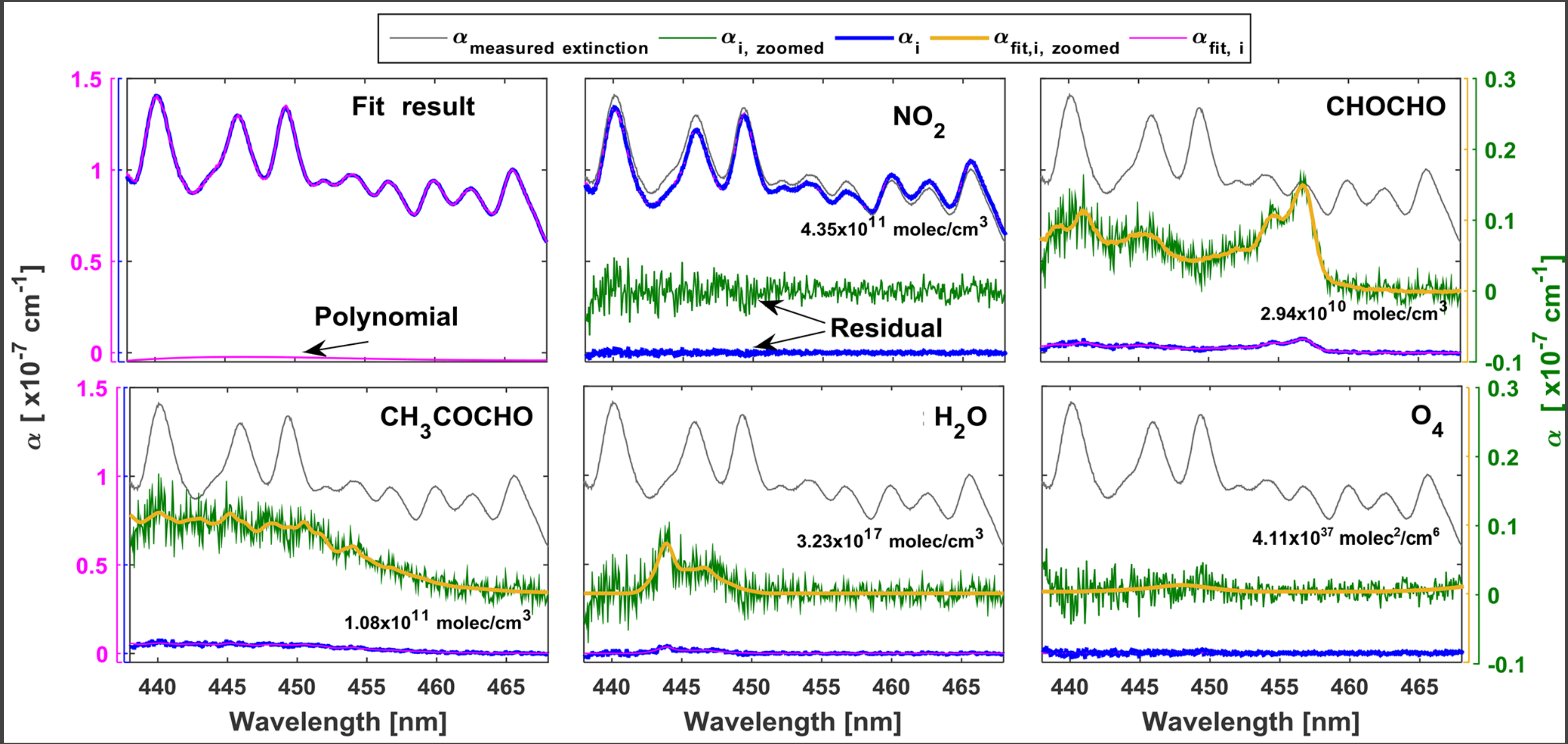
+

NO



Important source of photochemical radicals in polluted environments

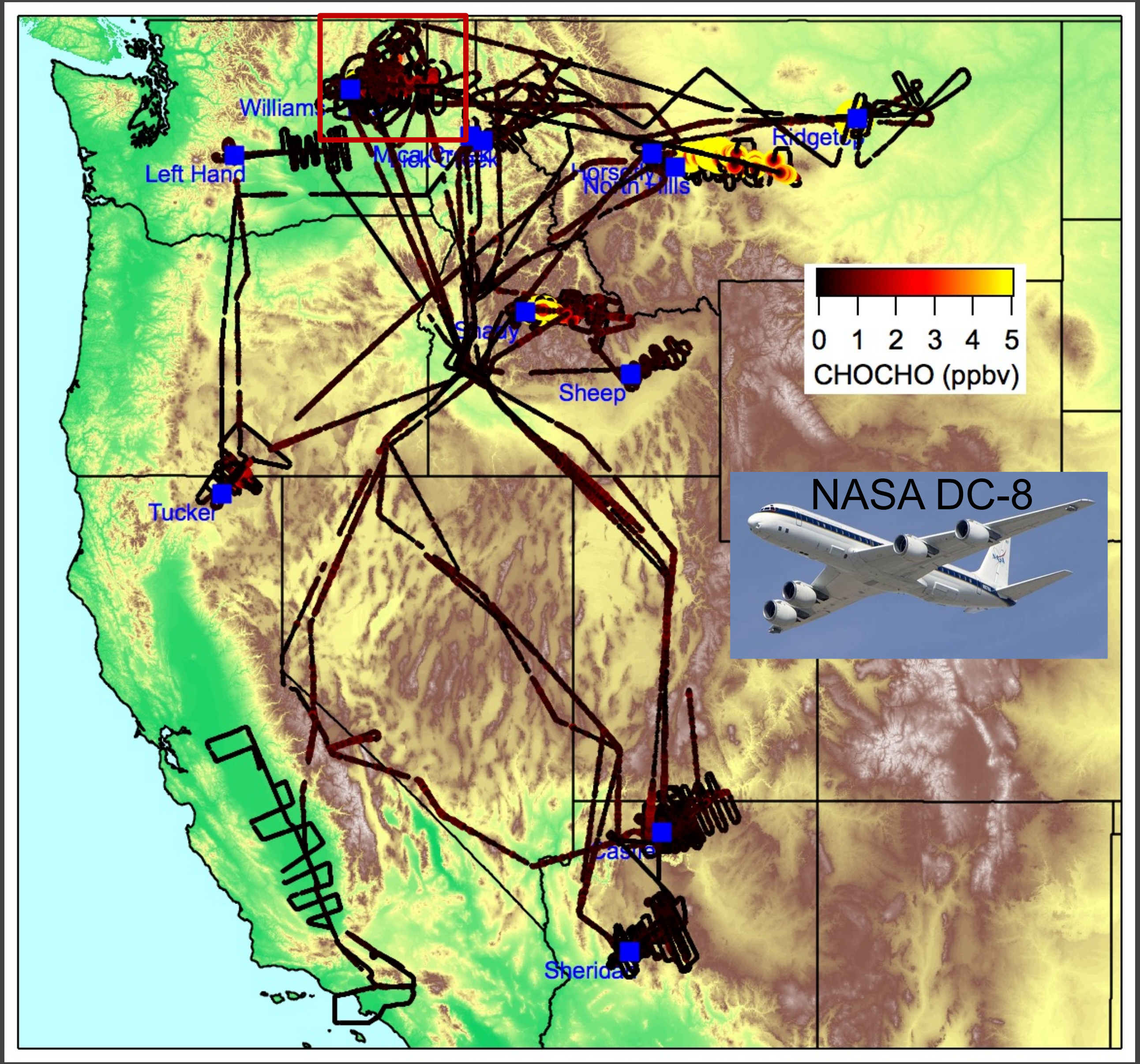
Spectral Fitting

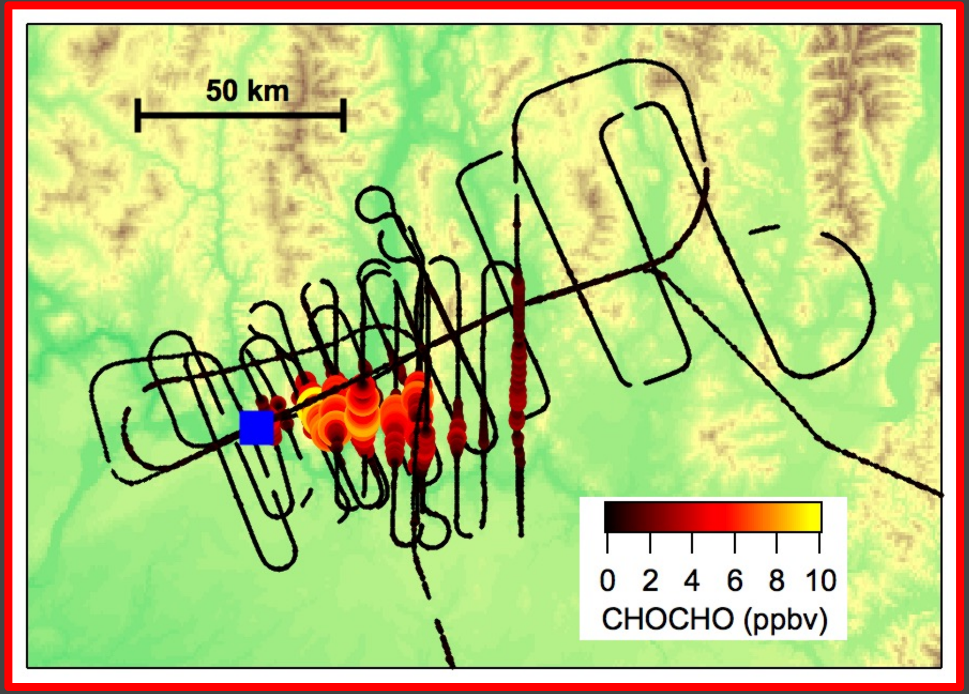


2013: Differential Optical Absorption Spectroscopy Intelligent Systems (DOASIS)

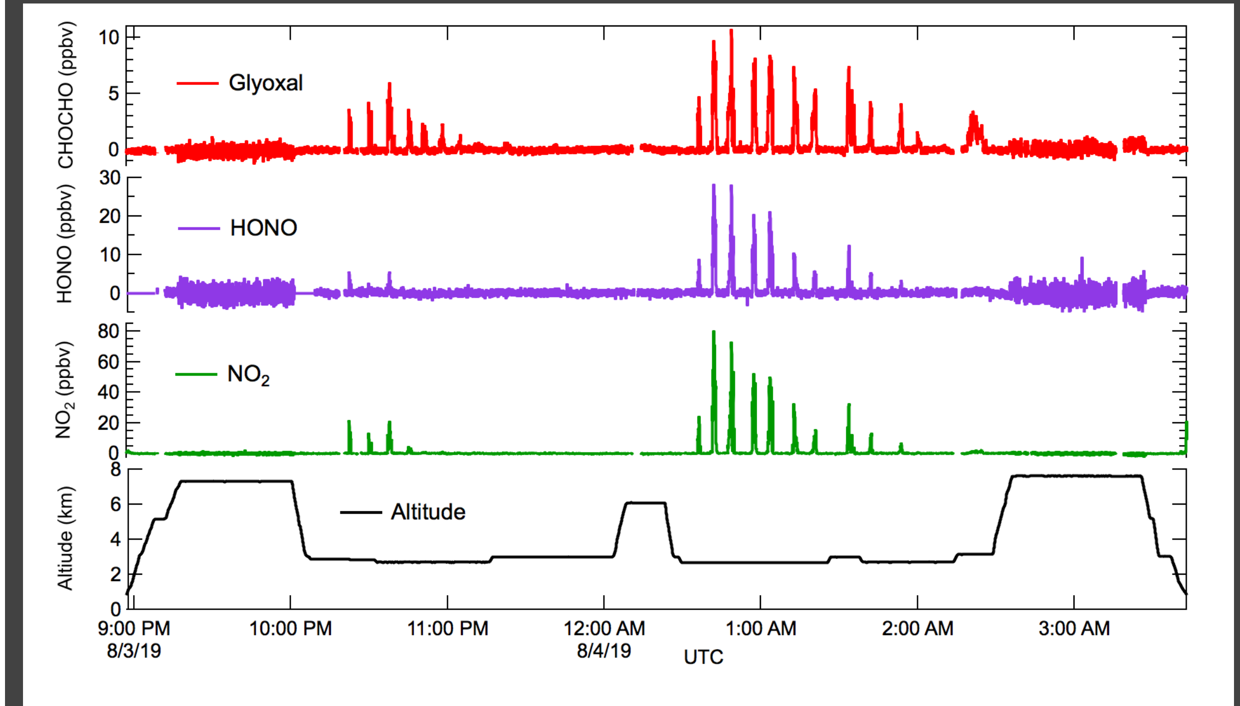
2022: Custom fitting software written in Igor Pro by from Carrie Womack, to be released publicly

Airborne CHOCHO, NO_2, HONO
FIREX-AQ 2019

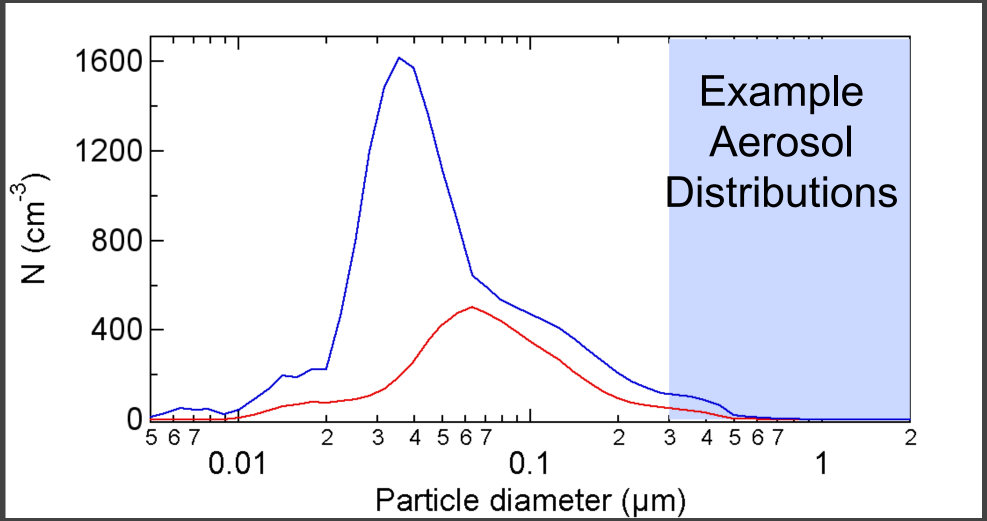


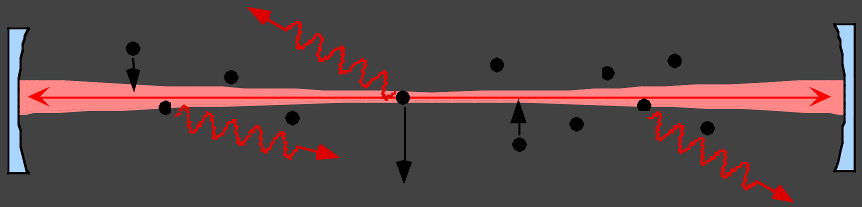


Carrie Womack



Example 3: Aerosol Extinction

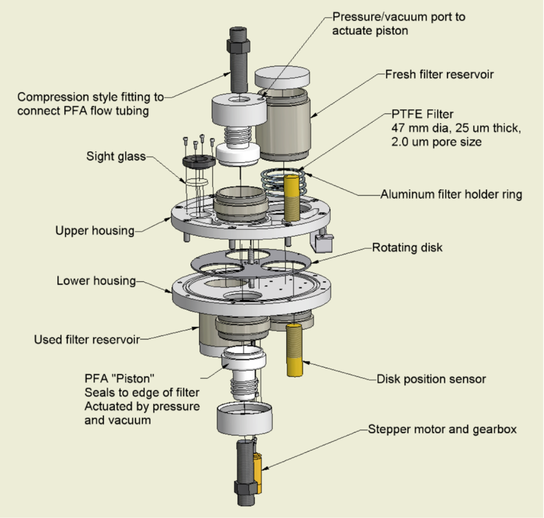




For $\alpha_{\min} \leq 10^{-10}$ cm^{-1}, detect single particles with $d \geq 0.3$ μm

Statistically noisy signal that interferes with trace gas absorption

Gas phase instruments typically use filters to eliminate influence of aerosol extinction

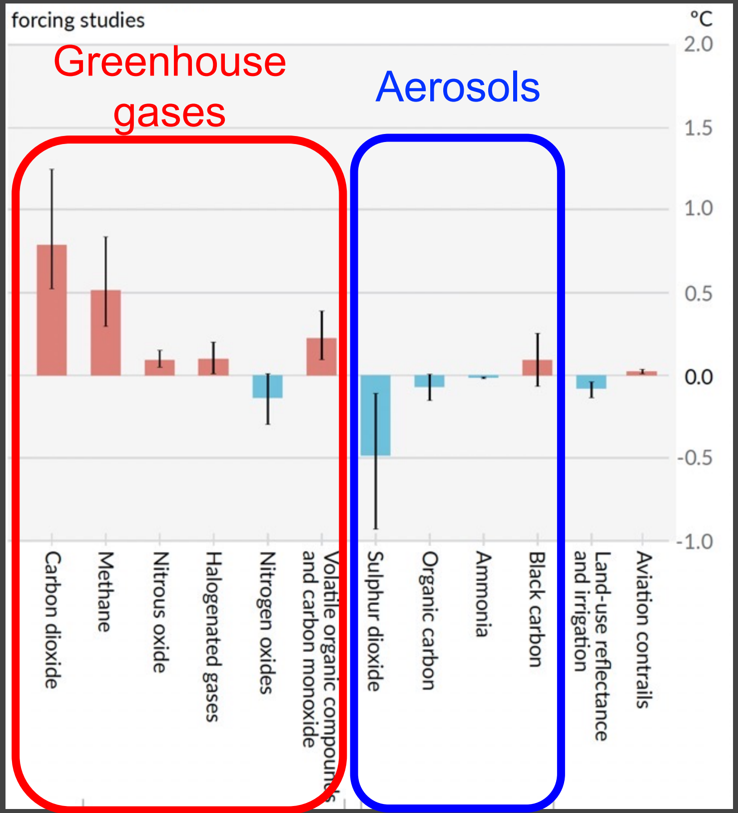


Automated filter changer for autonomous operation
Dubé et al., Rev. Sci. Instr. 2006

Aerosols are a significant contribution to global radiative forcing due in part to their extinction

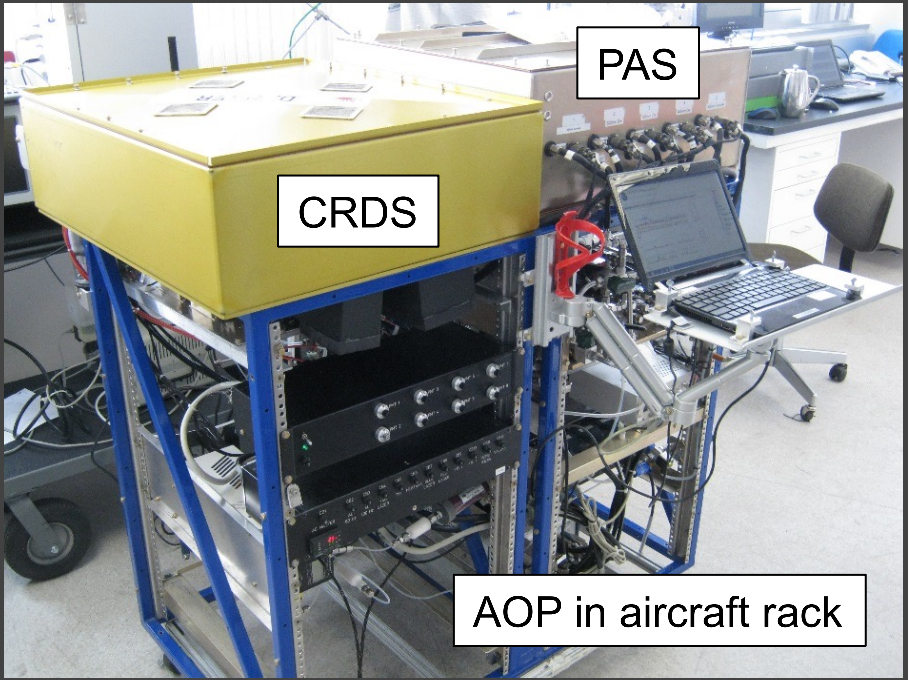
Highly uncertain effect

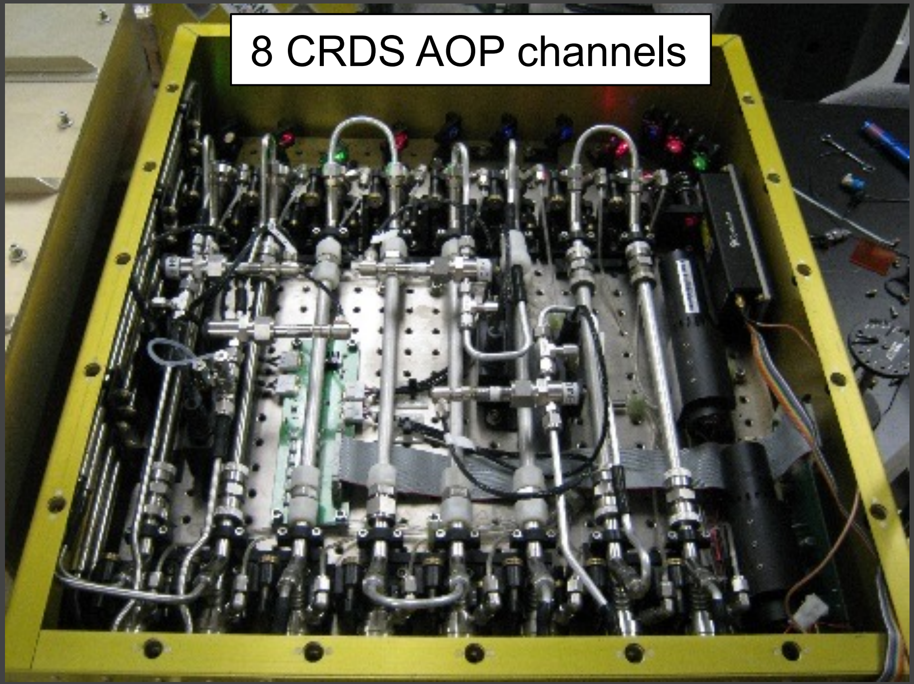
IPCC 2021



NOAA Aircraft Aerosol Optical Properties (AOP) Instrument

3 wavelength aerosol extinction (CRDS) and absorption (PAS) @ 405, 532 and 660 nm





PI: Dan Murphy, Cloud & Aerosol Processes Group

3 humidified channels
1 denuded channel to remove volatile species

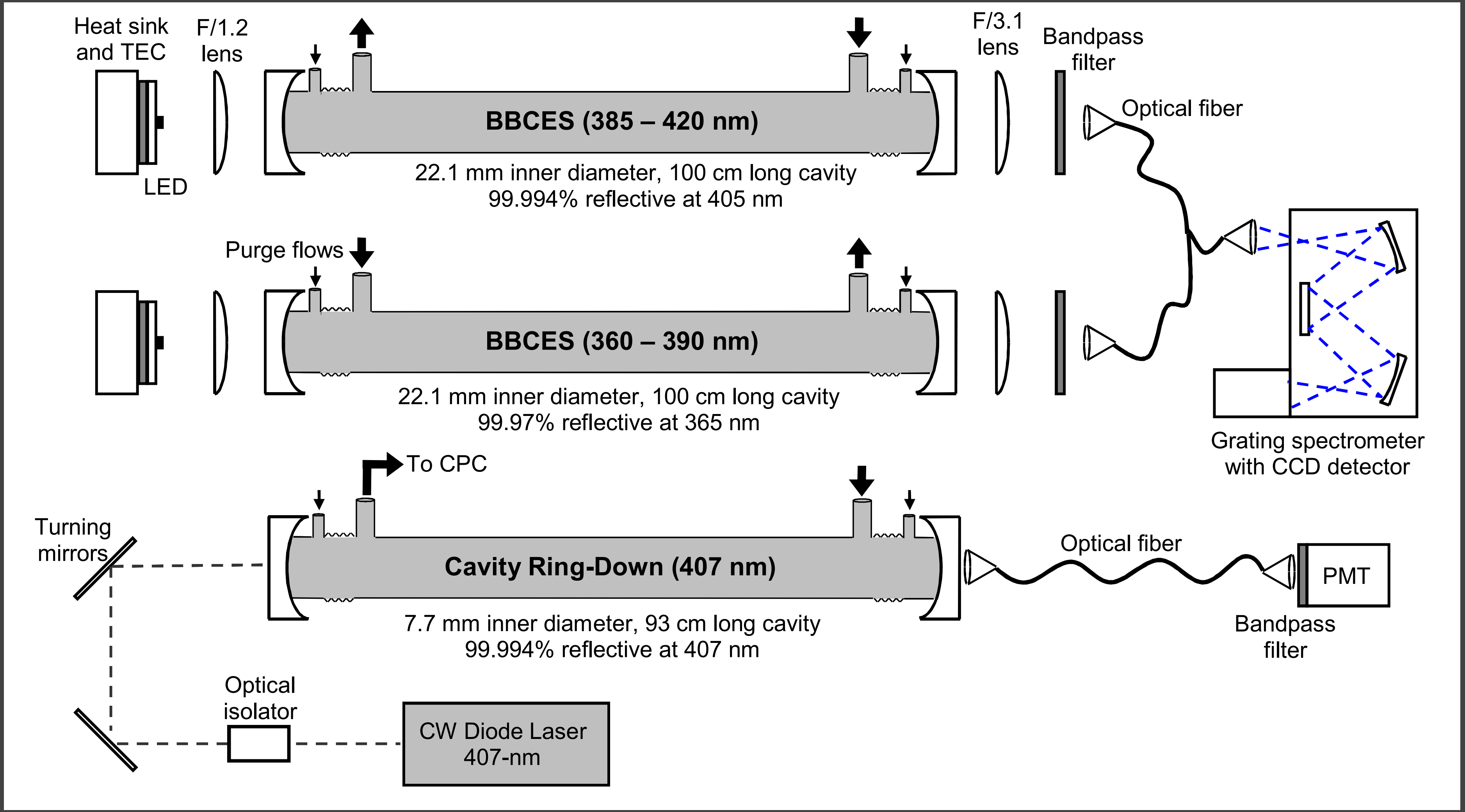
NO_2 and O_3 (which absorb at 405 and 532 nm) are removed using activated charcoal

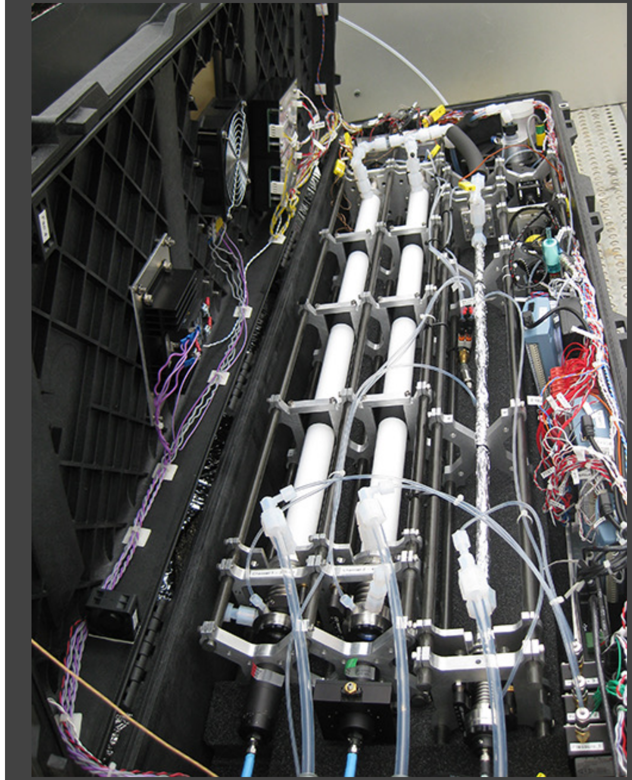
Sensitivity:	0.1 $Mm^{-1} = 10^{-9}$ cm^{-1} in 1 second
Method for acquiring zeros:	Filtration of air sample
Method for validation:	Comparison with scattering instrument
Materials:	Metal cells with conductive tubing
Engineering:	~1.2 m x 0.05 x 0.05 m; 90 kg; Fully automated

Aerosol extinction is a strong function of both wavelength and relative humidity due to particle growth

Langridge et al., Aerosol Sci. Tech. 2011

Broadband Cavity Enhanced Aerosol Spectrometer



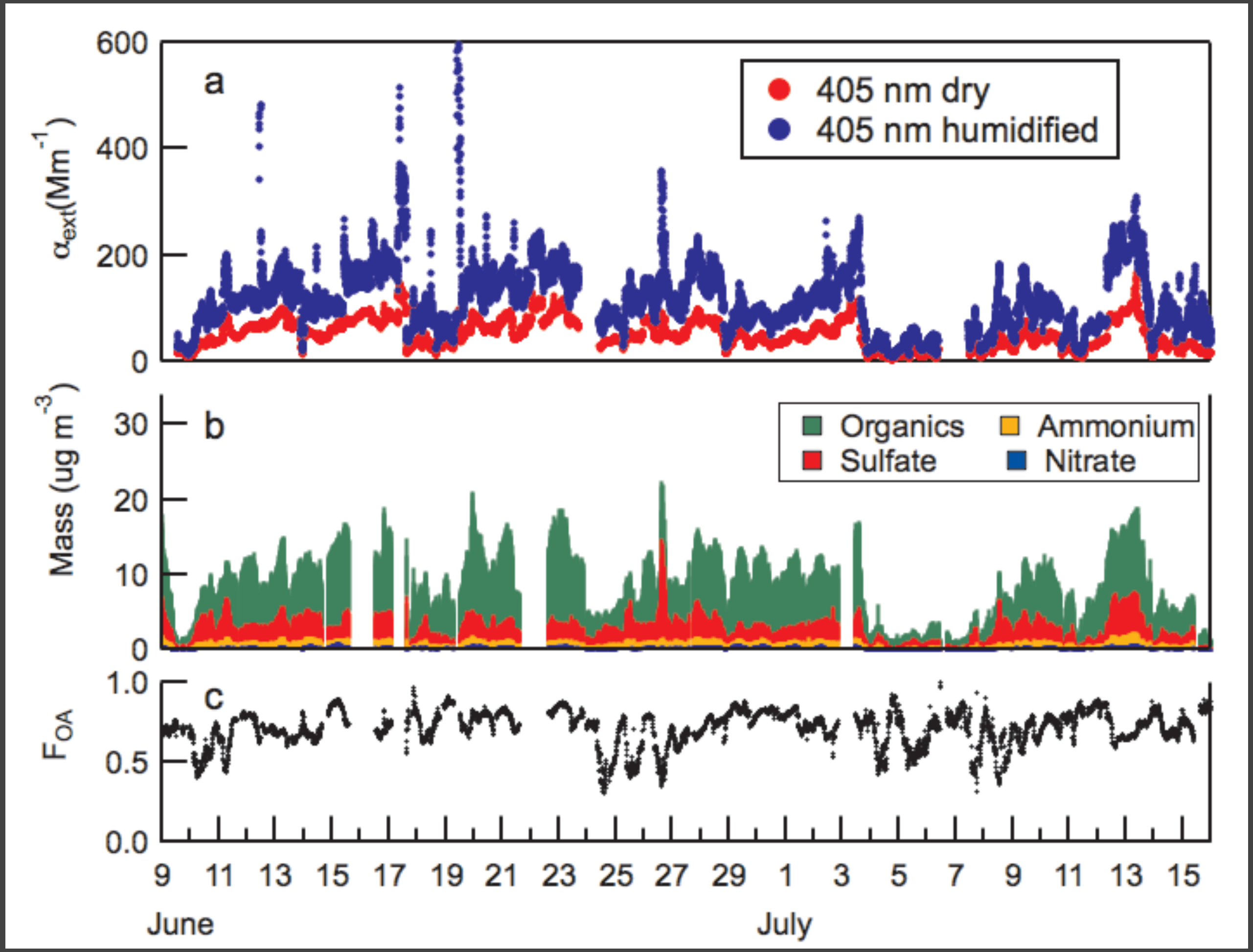


LED light sources, grating spectrometer CCD, two broadband and one single wavelength channel

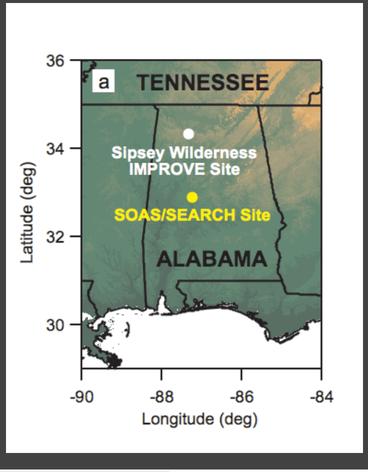
Washenfelder et al., Atmos. Chem. Phys, 2013

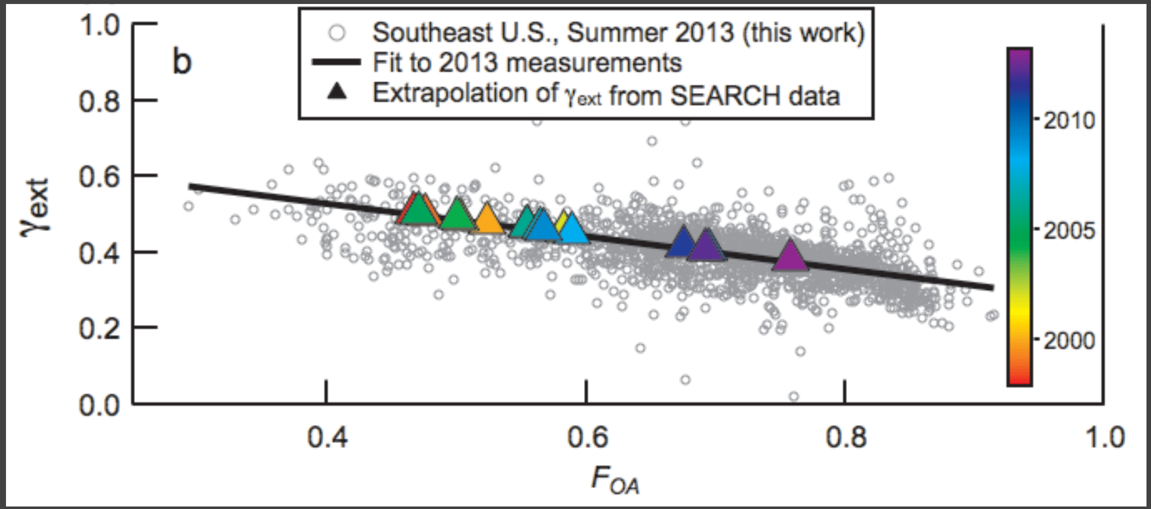
Aerosol Extinction, Relative Humidity & Composition

Relative humidity dependence of extinction F(RH) depends on aerosol organic content, $F_{OA} = \frac{\text{OA Mass}}{\text{Total Mass}}$




Talladega National Forest, AL
June 1 – July 15 2013



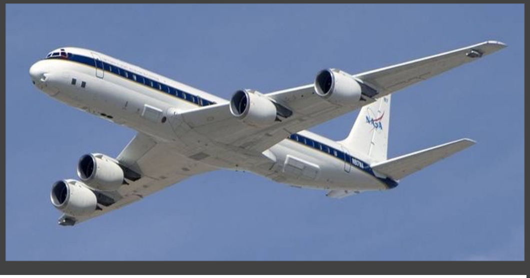


1990 – 2018 emissions reductions in aerosol precursors: SO_2 90%, NO_x 60%
Reduction in *both* aerosol mass and F(RH) leads to strong trends in extinction

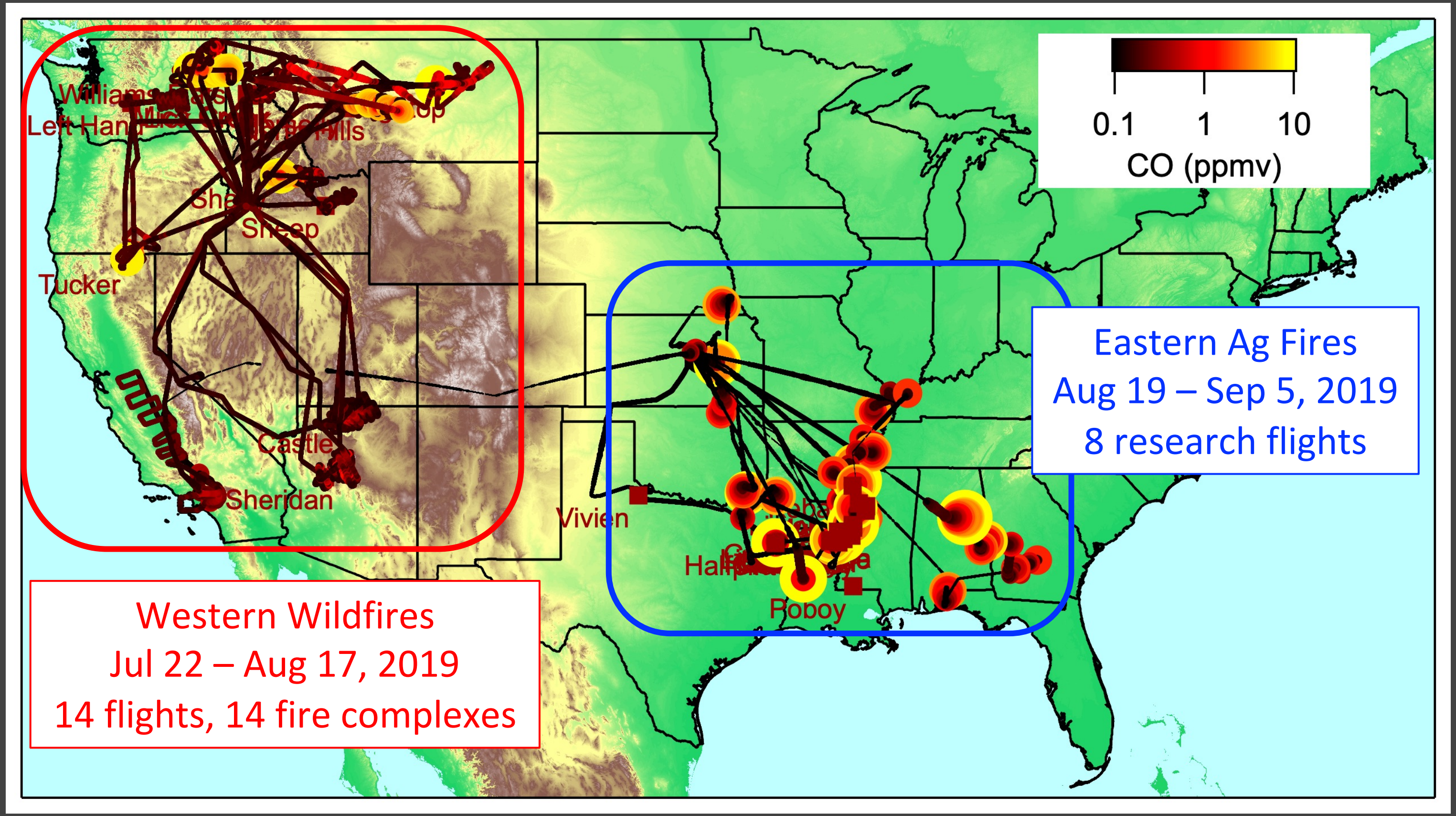
Attwood et al., Geophys. Res. Lett. 2014

Example 4: Fire Research and Instrument Comparisons

NASA DC-8: Western wildfires and eastern agricultural fires, focus on emissions and photochemistry



NOAA Twin Otter: Western wildfires, emissions, photochemistry and nighttime chemistry



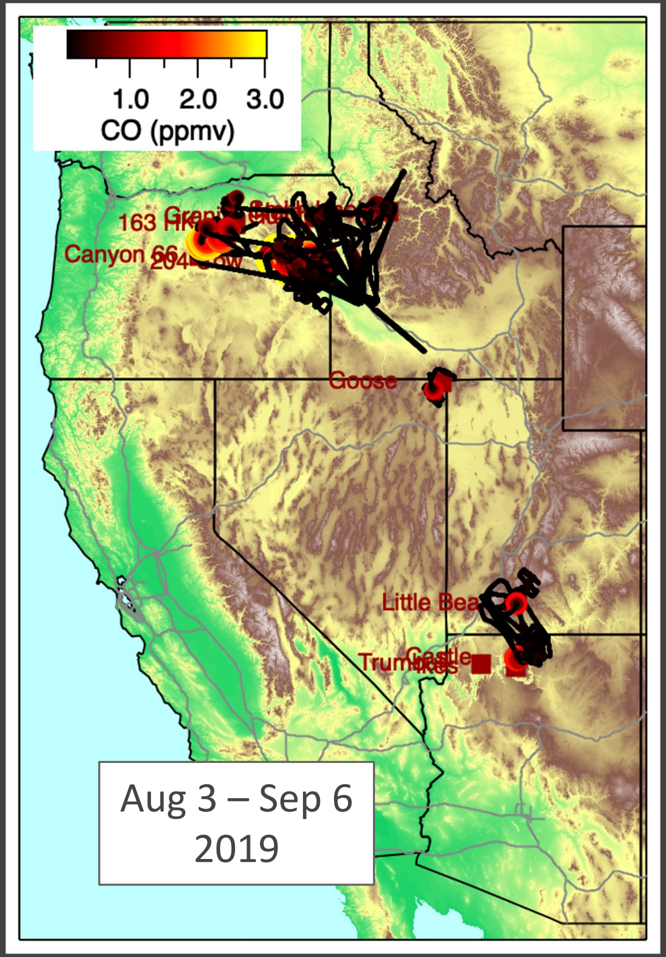
Western Wildfires
Jul 22 – Aug 17, 2019
14 flights, 14 fire complexes

Eastern Ag Fires
Aug 19 – Sep 5, 2019
8 research flights

16 flight days

39 research flights

10 fires or complexes



Aug 3 – Sep 6
2019

Carbon Monoxide (CO) from commercial ICOS (LGR, NASA DC-8) and CRDS (Picarro, NOAA Twin Otter) Instruments

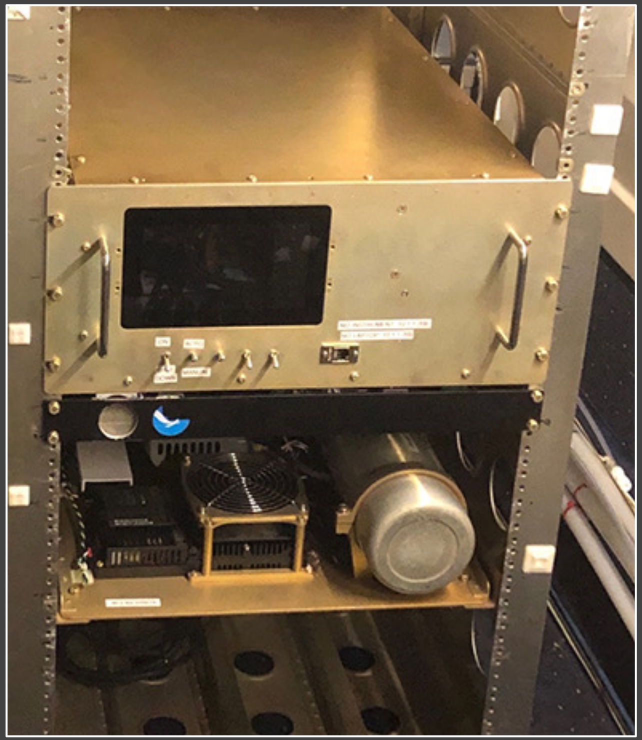
DC-8 Aircraft Instruments

Chemiluminescence (CL)

Measure NO directly

NO_2, NO_y, O_3 via inlet conversions (e.g., NO_2 + hν → NO @390 nm LED)

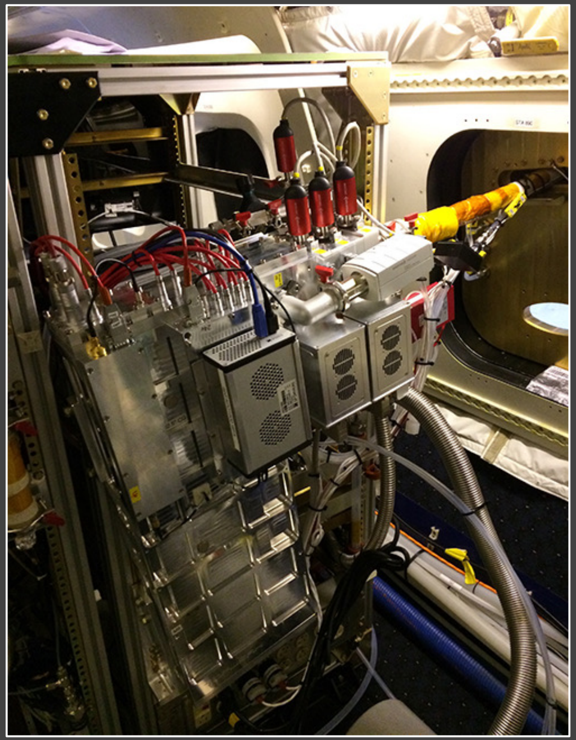
Laser Induced Fluorescence (LIF)



NOAA NO LIF instrument shown

Not shown: NO_2 LIF instrument (NASA)

Chemical Ionization Mass Spectrometer (CIMS)



>300 masses with high sensitivity

Calibration challenging !
Few masses quantified

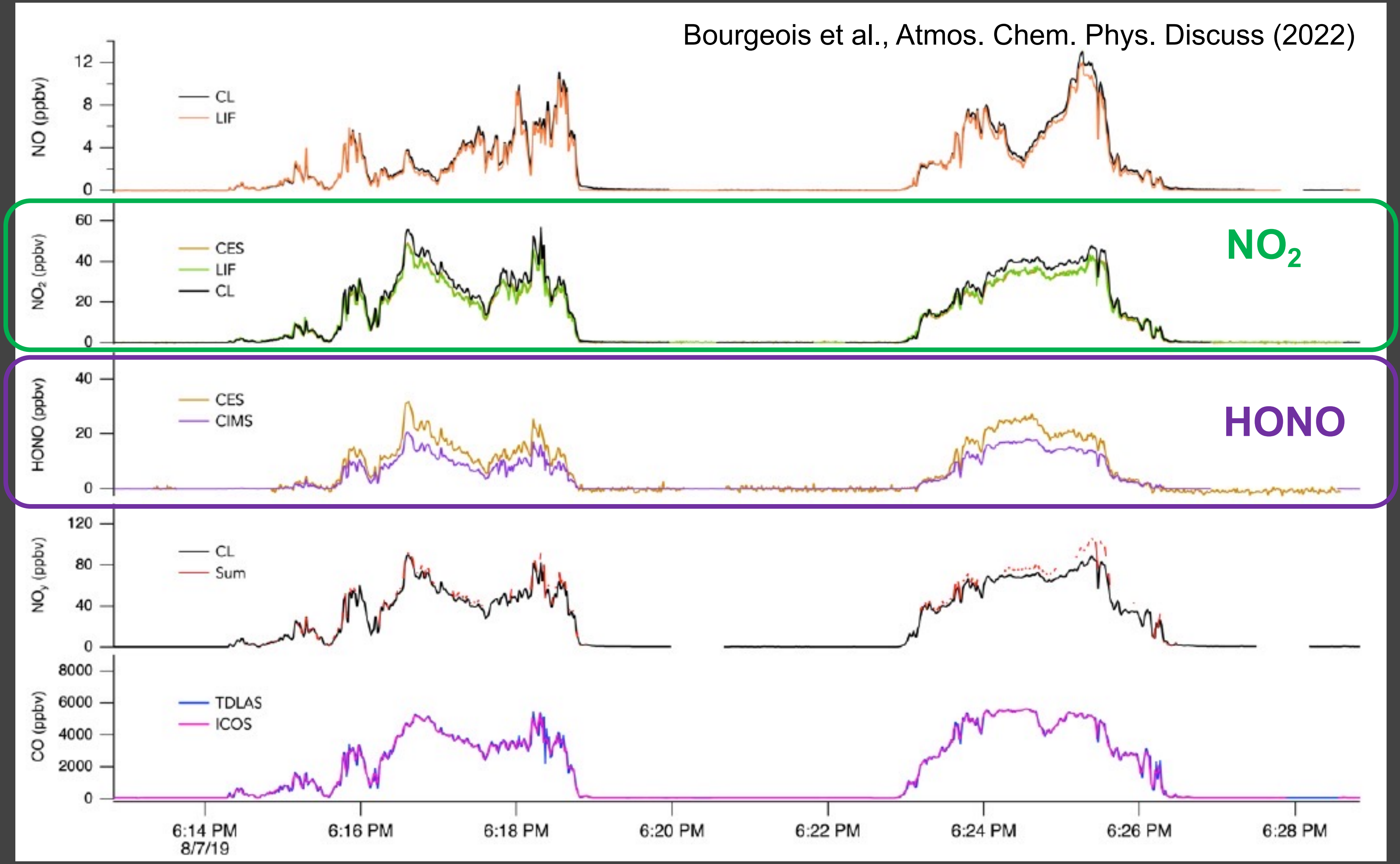
Airborne Cavity Enhanced Spectrometer (ACES)

455 nm: NO_2, CHOCHO, CH_3CHO

365 nm: HONO (NO_2)

Instrument Comparisons to Broadband CES

Two passes of a large wildfire plume, Williams Flats, August 2019


Bourgeois et al., Atmos. Chem. Phys. Discuss (2022)

ToF CIMS = Time of Flight Chemical Ionization Mass Spectrometry; LIF = Laser Induced Fluorescence

Redundancy in measurements essential to assess accuracy

NO_2: Chemiluminescence (CL) with photolytic conversion of $NO_2 \rightarrow NO$ has been a standard

- Both CES (direct, absolute) and LIF (direct, calibrated) are lower but agree with each other

HONO: CIMS is high precision but CES more accurate

Instrument Comparisons to ACES

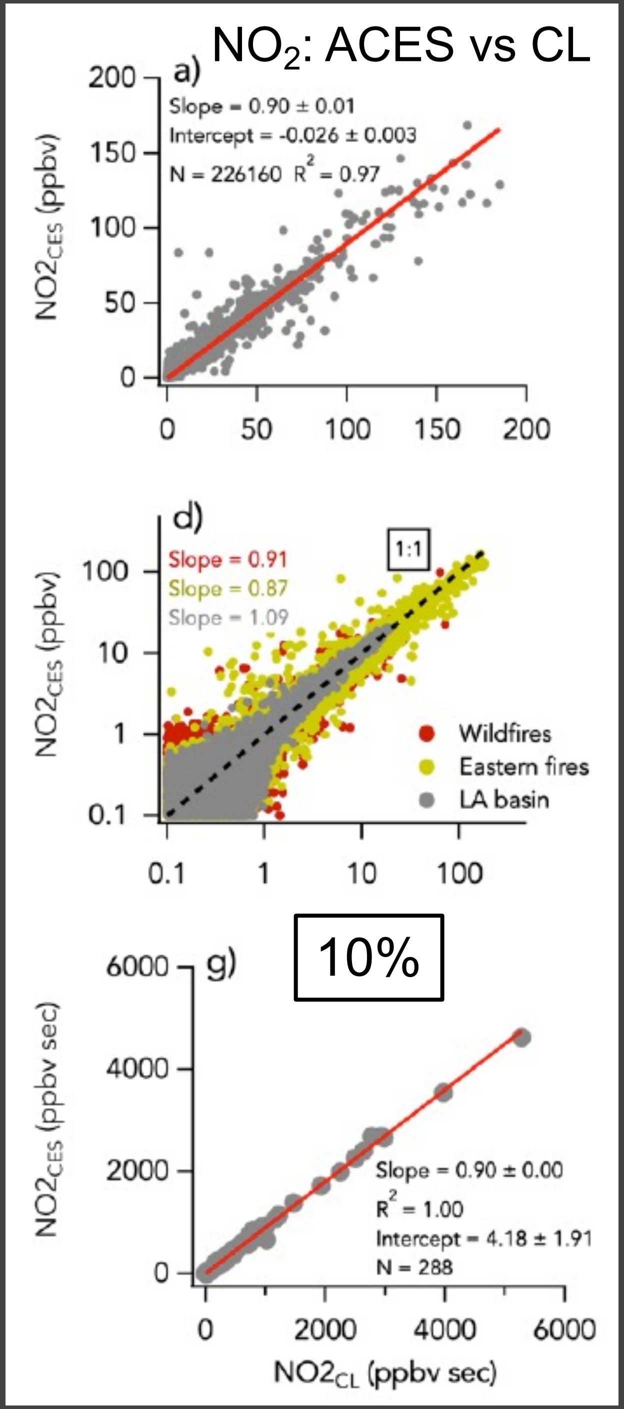
1 Hz data, linear scale, all flights

N = 226,000 – 310,000 !

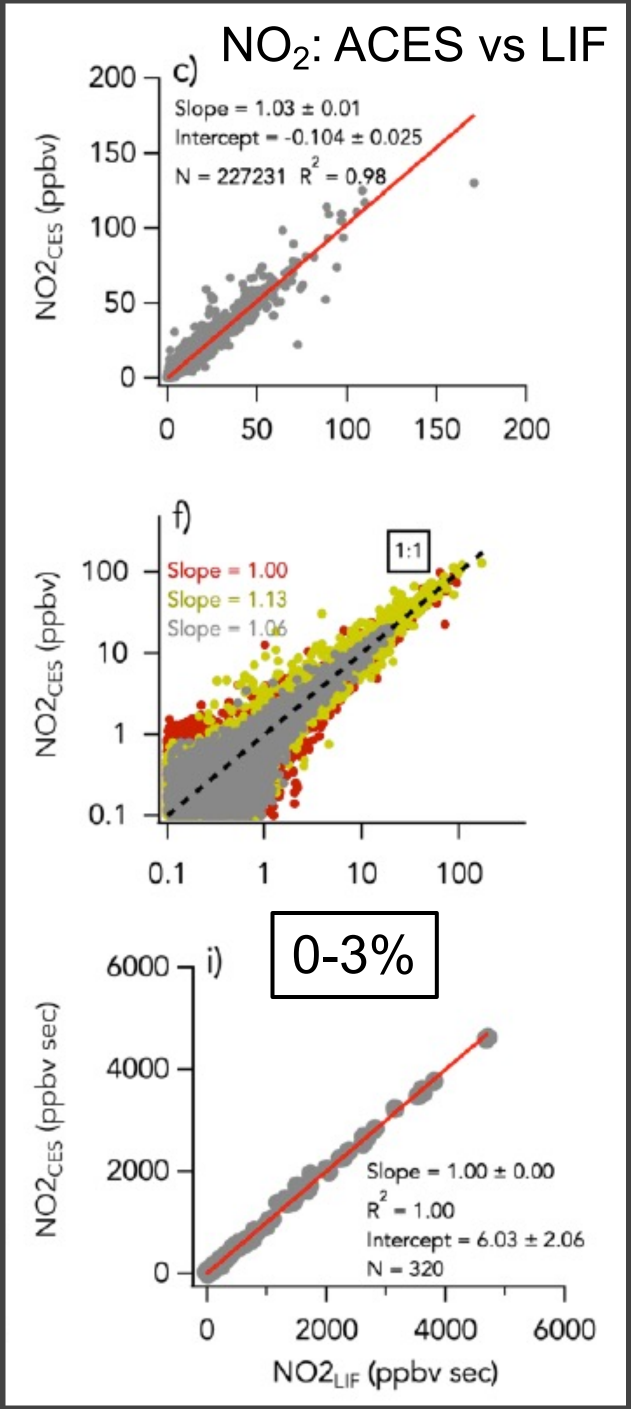
1 Hz data, log scale, categorized by wildfires, agricultural fires, and urban flights

Integrals for transects of wildfire plumes

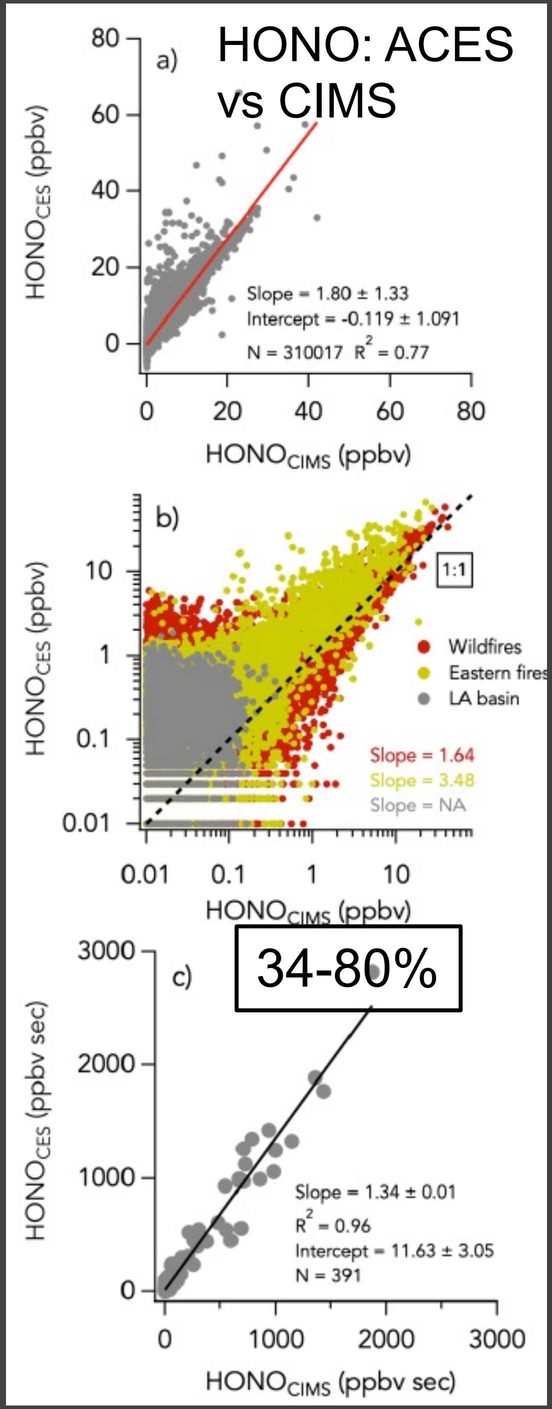
Bourgeois et al., Atmos. Meas. Tech. Discuss. 2022


NO_2: ACES vs CL

10%

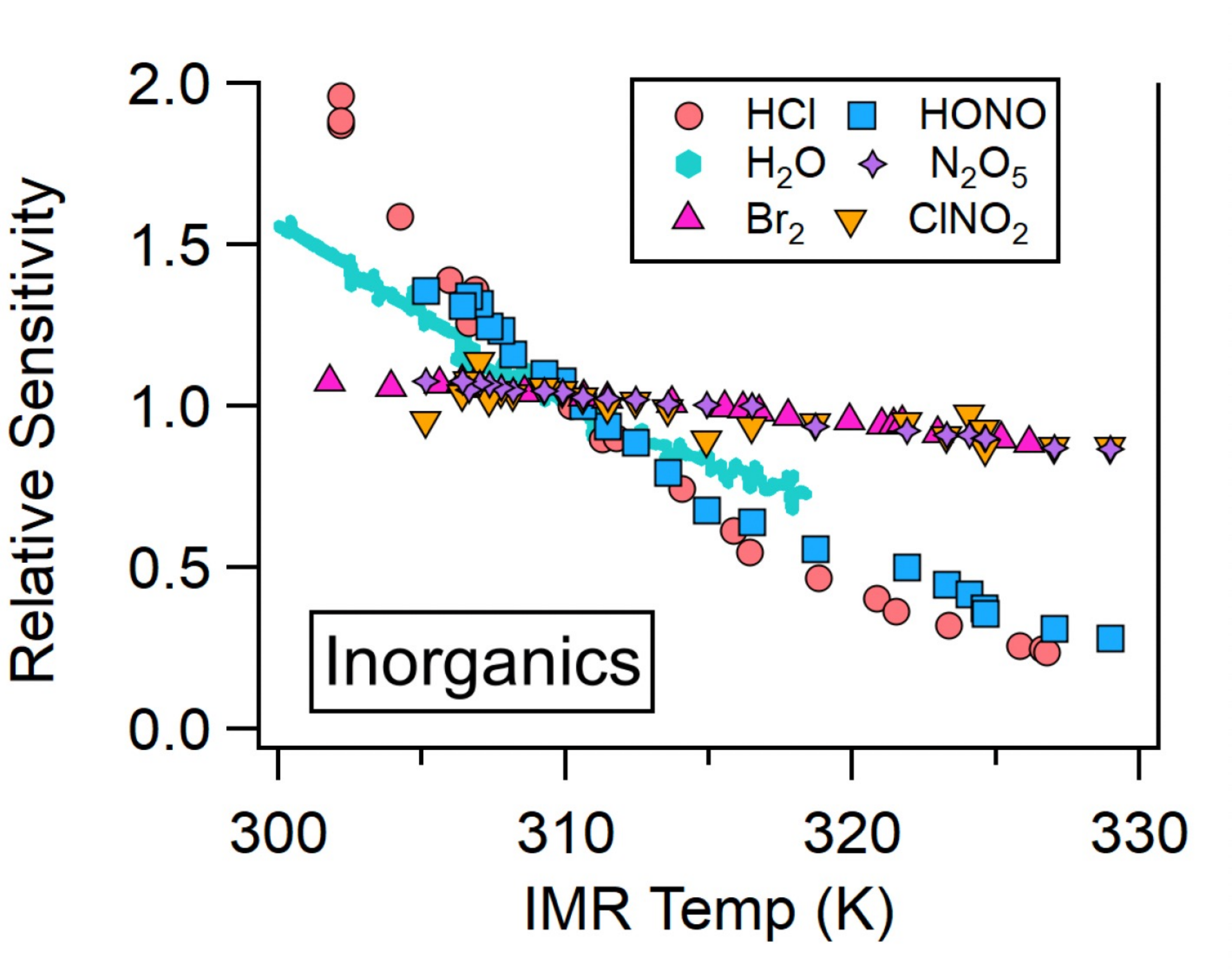

NO_2: ACES vs LIF

0-3%


HONO: ACES vs CIMS

34-80%

CIMS HONO Calibration

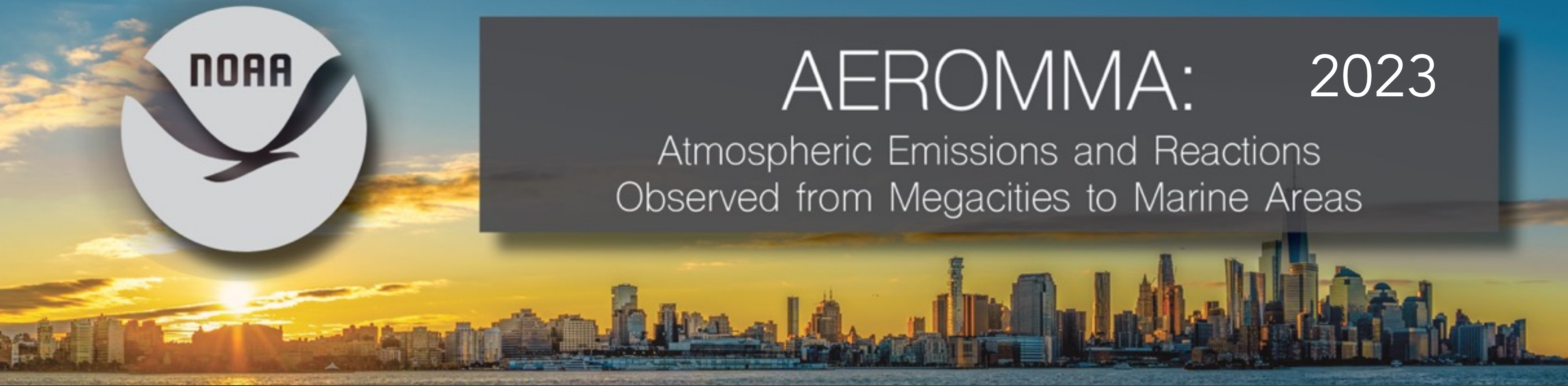


Robinson et al., Atmos. Meas. Tech. Discuss. 2022

Recent work from our group shows the variability in sensitivity of CIMS instruments – factor of 4 over 25 C T range

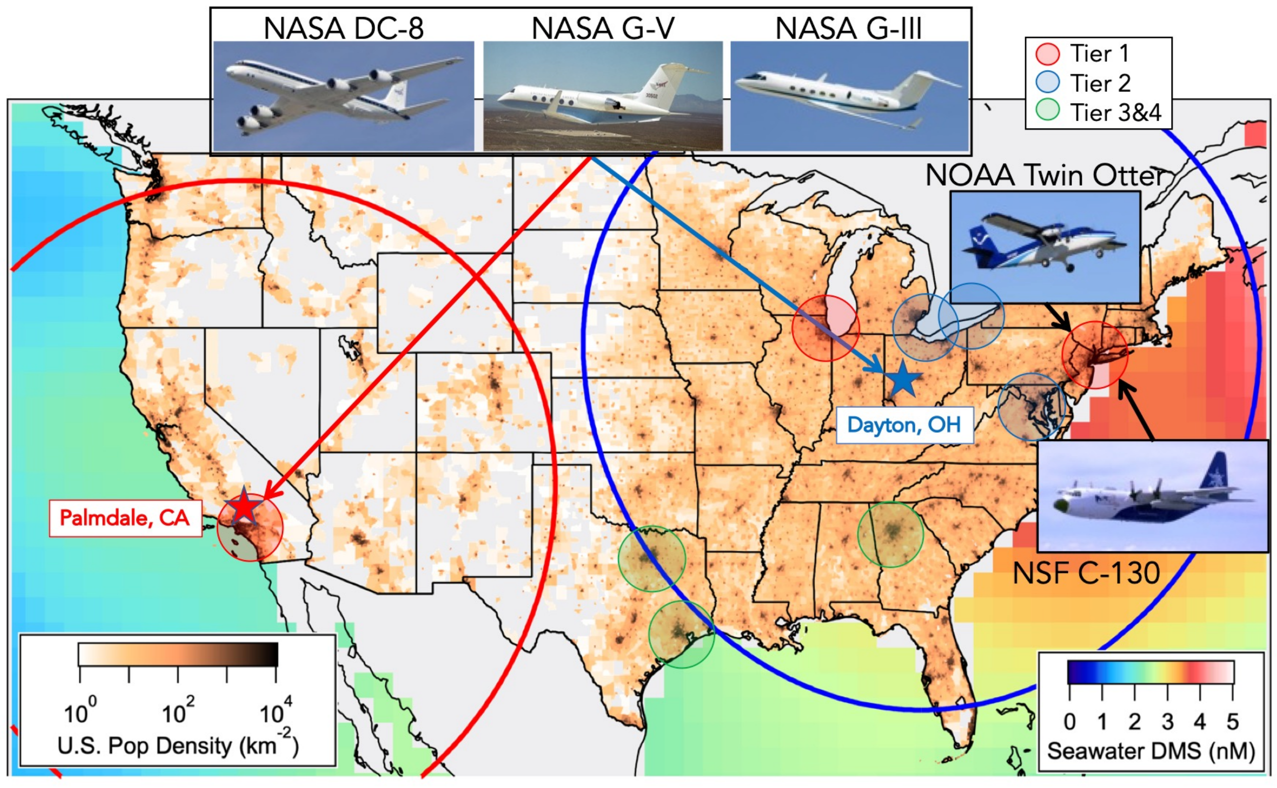
Flight to flight differences in HONO calibrations and overall difference between CES and CIMS attributable to T dependent calibration

ACES (600 pptv) is a *lower precision* instrument than CIMS (2 pptv) but in this case a *more accurate* one

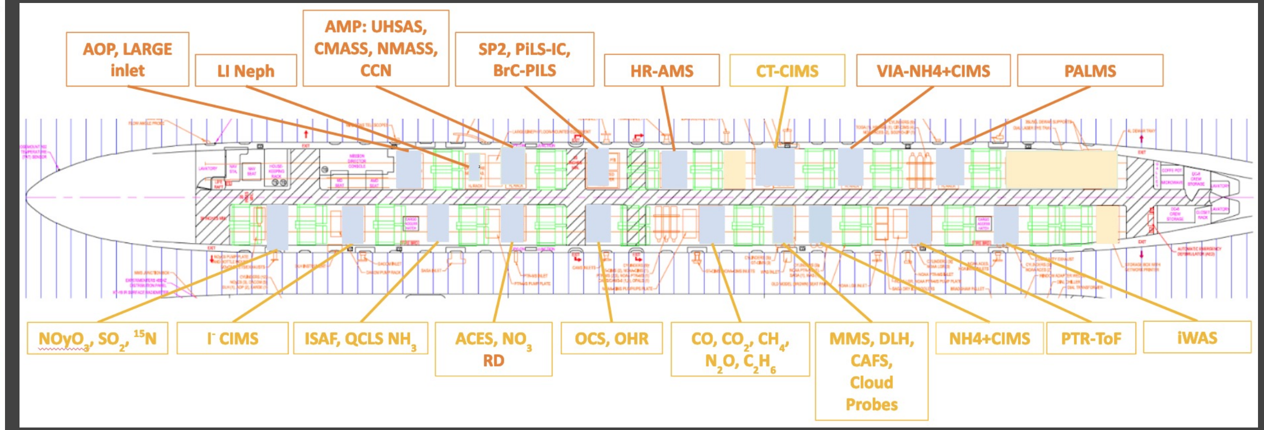


AEROMMA: 2023

Atmospheric Emissions and Reactions Observed from Megacities to Marine Areas



DC-8 Instrument Layout



CES instruments from this talk: ACES, NO_3 & NO_2 CRDS, Aerosol Optical Properties, Commercial CO and Greenhouse Gases

CES for Field Measurements and Aircraft Research

Advantages

- Absolute analytical method
- Compact, low power designs
- Robust in harsh environments

Disadvantages

- Low sensitivity relative to fluorescence, mass spectrometry

Applications

- Trace gas measurements relevant to air quality and climate
- Aerosol extinction – visibility and climate
- Standard for greenhouse gases