# *Atmospheric Instrumentation:*

## *Airborne measurements of chemical composition*

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# *Outline*

- Measurement fundamentals
  - Calibration, quality control, and intercomparison
- Research from airborne platforms
  - Examples of research aircraft
- Instrumentation for chemical composition
  - Gas phase
  - Aerosol phase
  - Remote vs. in-situ
- Examples of research missions
- Group design of mission plans

# *Challenges*

- The atmosphere has a complex chemical composition with large variability
  - Potentially large range of concentrations
    - Sufficient sensitivity for ambient conditions
    - Sufficient linearity to cover range
  - Variability over space and time
    - Appropriate time resolution of measurements
    - Sufficient precision to identify relevant variability
  - Need selective techniques to identify and quantify
    - Potential for interferences and artifacts
    - Stable, well characterized standard scales
    - Ability to compare and combine data

# *Challenges*

- Understanding complex chemical processes requires complementary measurements of excellent quality
- Measurement precision, accuracy, and limitations needs to be clearly communicated to users.

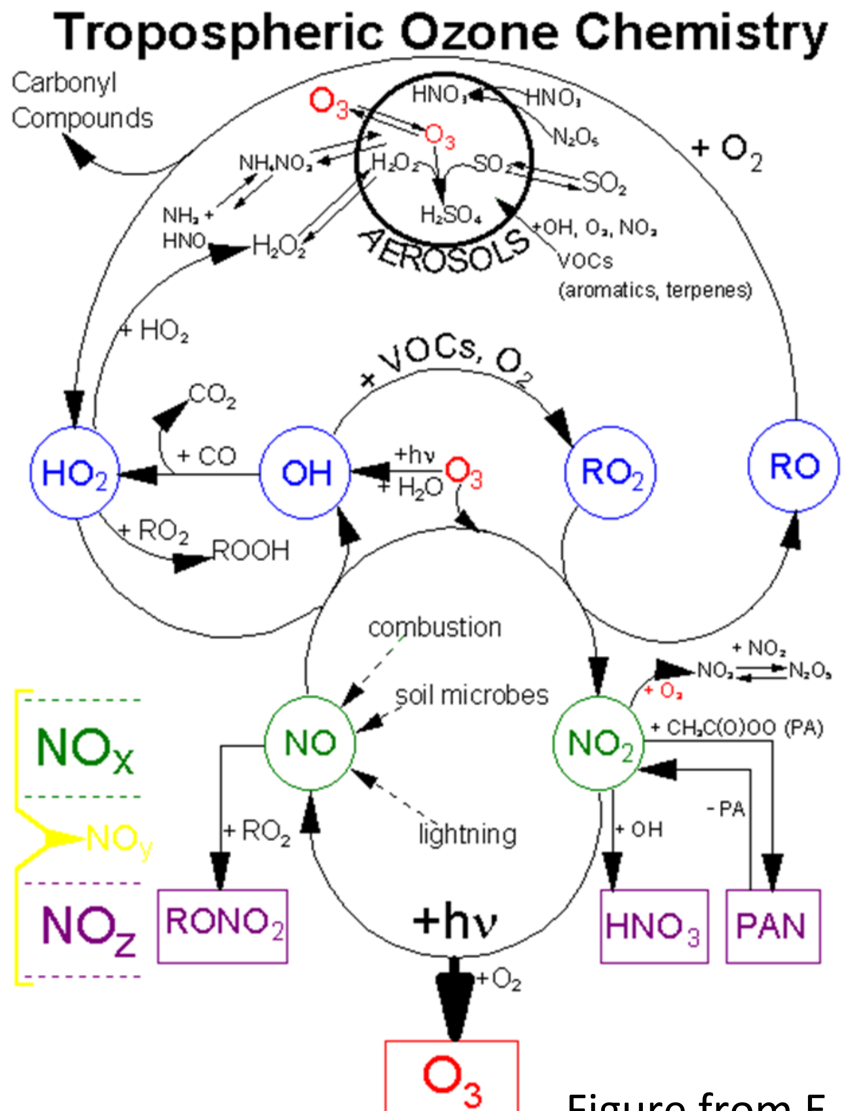
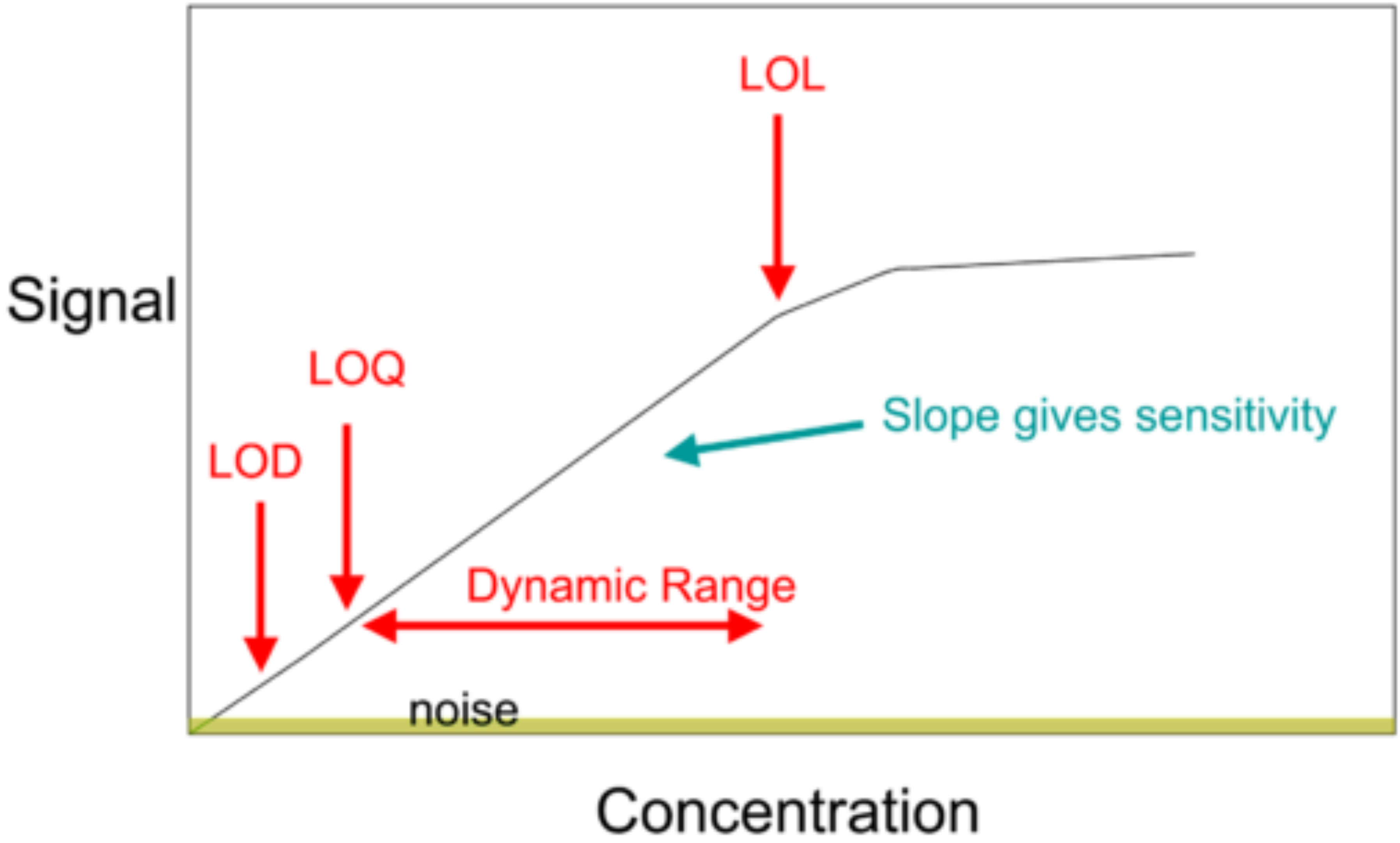



Figure from E. Apel

# *Measurements - Basics*

- Specificity
- Linearity
- Range
- Limit of Detection
- Limit of Quantitation
- Precision
- Accuracy

# *Measurements - Basics*



# *Limits of detection and quantitation*

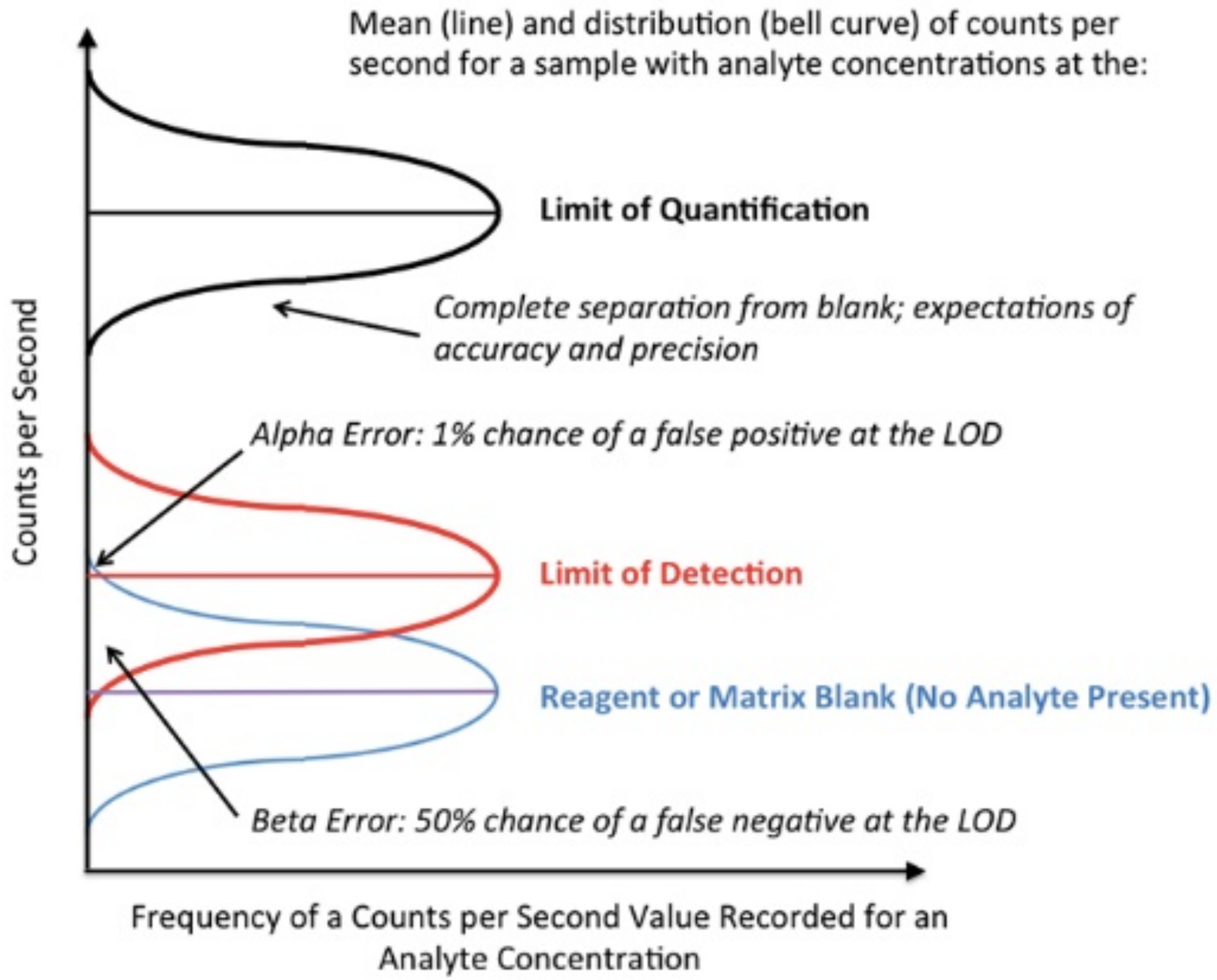
**LOD**

- ✓ Lowest amount of analyte in a sample that can be detected but not necessarily quantitated.
- ✓ Estimated by Signal to Noise Ratio of 3:1.

**LOQ**

- ✓ Lowest amount of analyte in a sample that can be quantified with suitable accuracy and precision.
- ✓ Estimated by Signal to Noise Ratio of 10:1.

# *Limits of detection and quantitation*



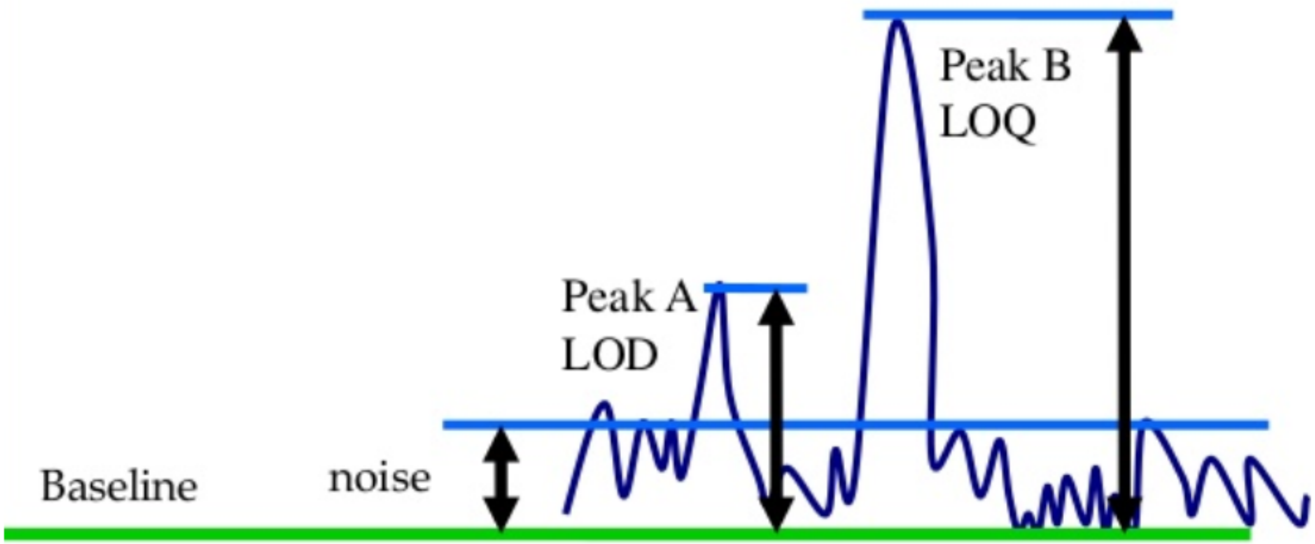
# *Limits of detection and quantitation*

## LOQ, LOD and SNR

Limit of Quantitation

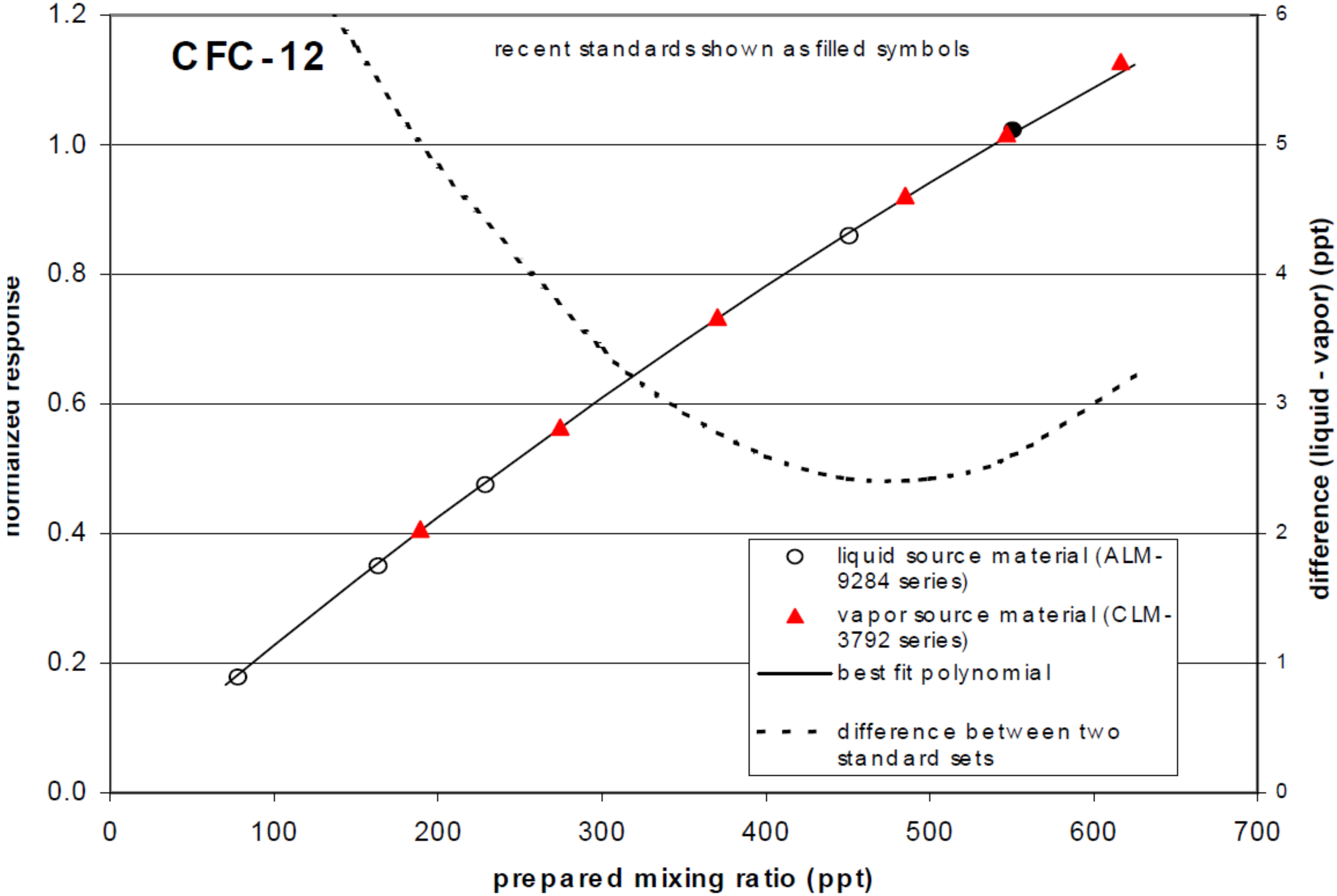
Limit of Detection

Signal to Noise Ratio



# Calibration

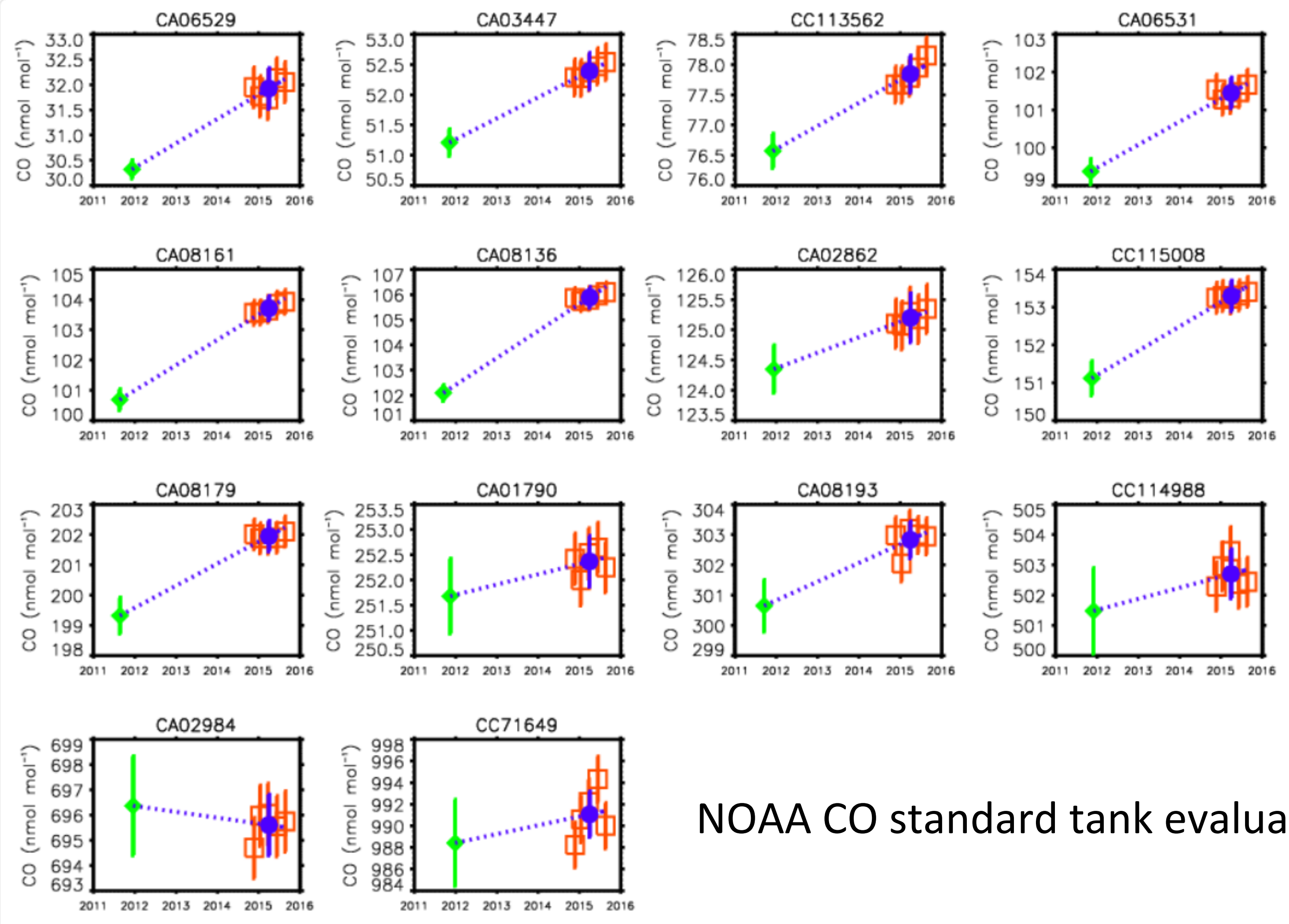
From B. Hall



# Calibration – Standard scales

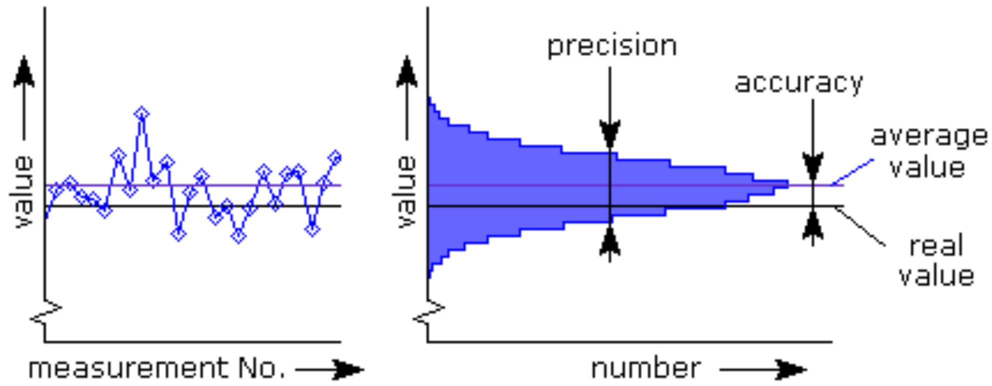
| Species | Previous Scale | Current Scale | Note | N | Range |
|---|---|---|---|---|---|
| CFC-12 | 2001 | 2008 | 1 | 15 | 150-650 ppt |
| CFC-11 | 1992 | 2016 | | 5 | 100-260 ppt |
| CFC-113 | 2003 | no change | | 10 | 20-110 ppt |
| CH3CCl3 | 2003 | no change | | 10 | 10-180 ppt |
| CCl4 | 1996 | 2008 | 2 | 7 | 25-150 ppt |
| halon 1211 | 1996 | 2006 | 3 | 5 | 3-7 ppt |
| halon 1301 | 1990 | 2006 | 4 | 6 | 2-5 ppt |
| HCFC-22 | 1992 | 2006 | 5 | 9 | 75-200 ppt |
| HCFC-141b | 1994 | no change | | 3 | 5-50 ppt |
| HCFC-142b | 1994 | no change | | 3 | 5-50 ppt |
| HFC-134a | 1995 | no change | | 2 | 5-10 ppt |

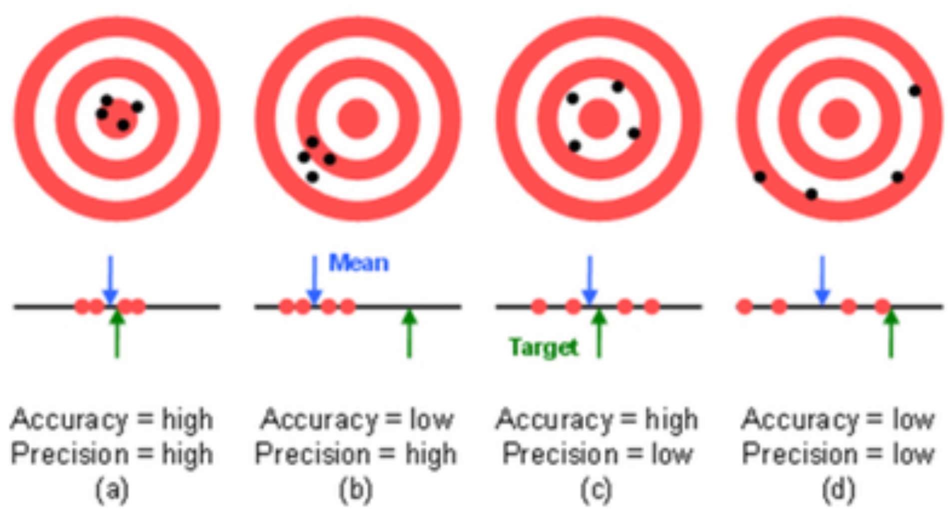
# *Calibration – Standard drift*




NOAA CO standard tank evaluation

# Measurements – Precision/ Accuracy



# Measurements - Comparisons

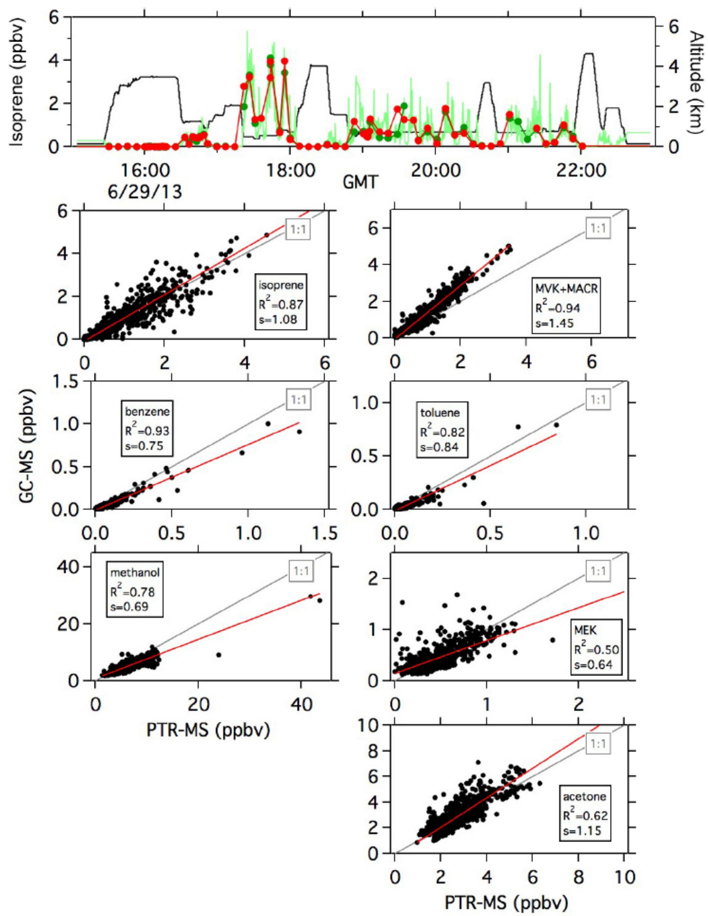



**Figure 4.** Inter-comparison between PTR-MS and iWAS/GCMS.

From Warneke et al., AMT, 2016

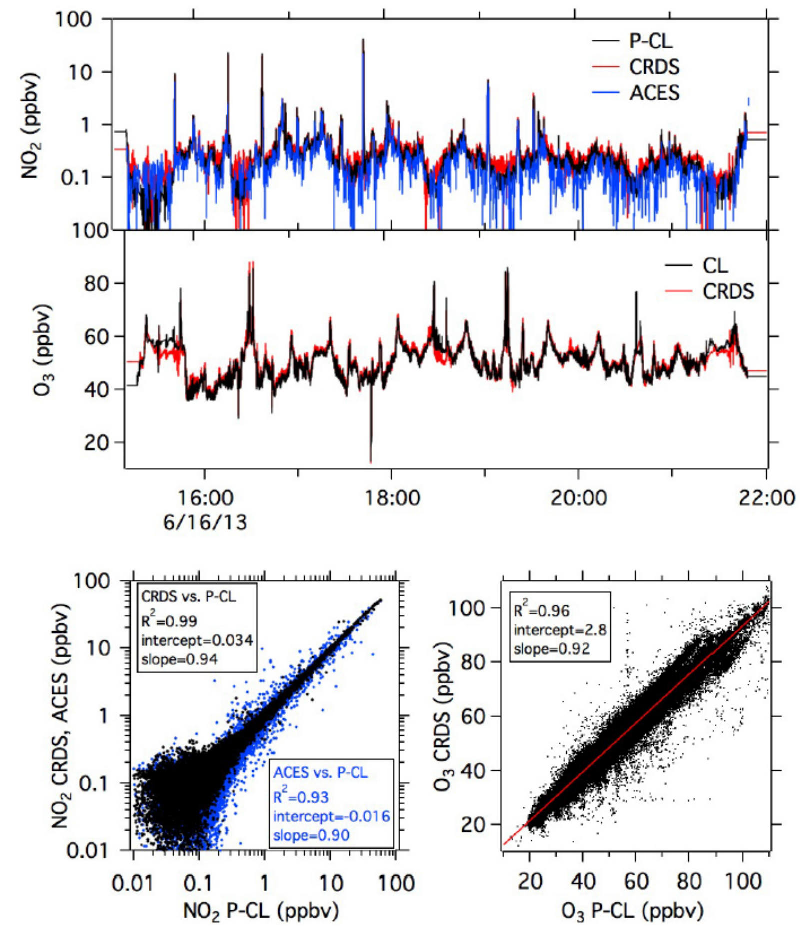
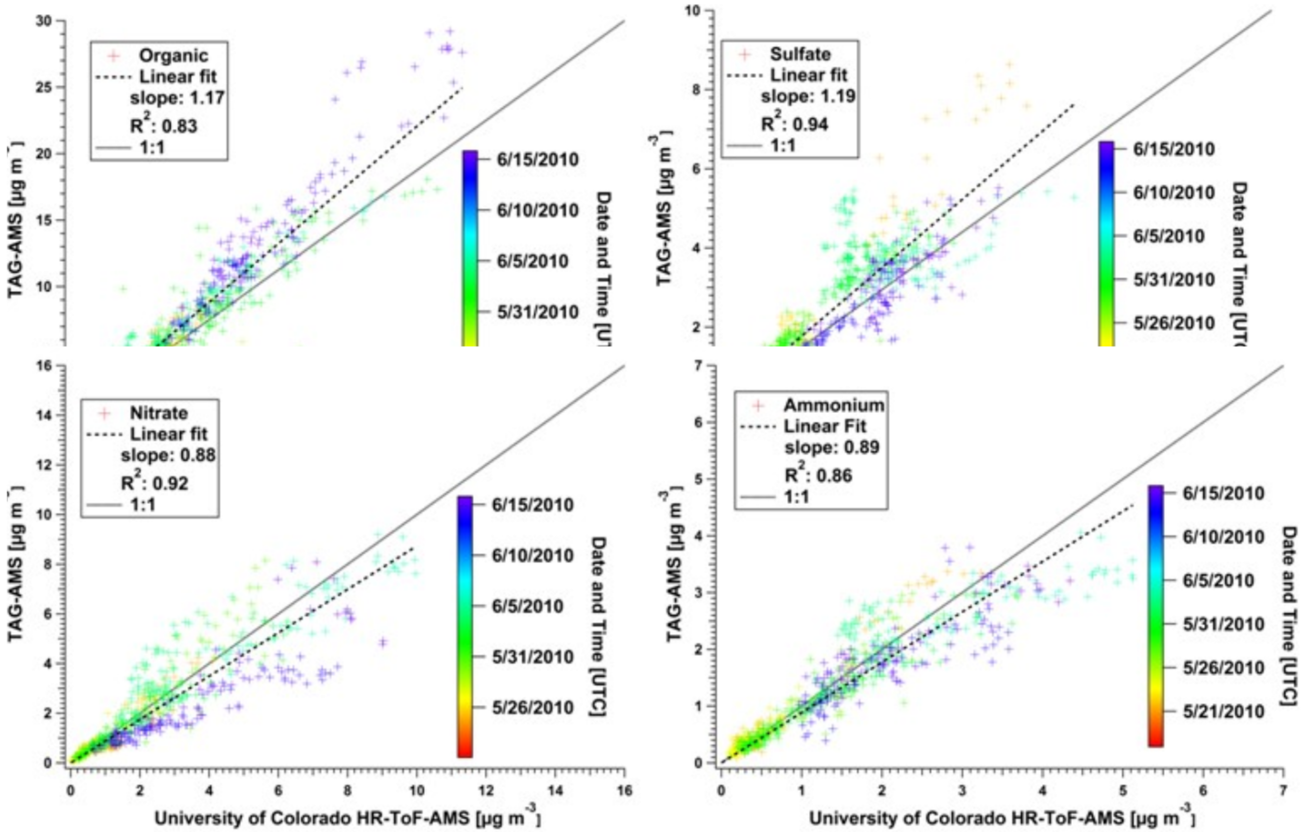



**Figure 3.** $NO_2$ inter-comparison between P-CL, CRDS and ACES instruments and ozone inter-comparison between P-CL and CRDS.

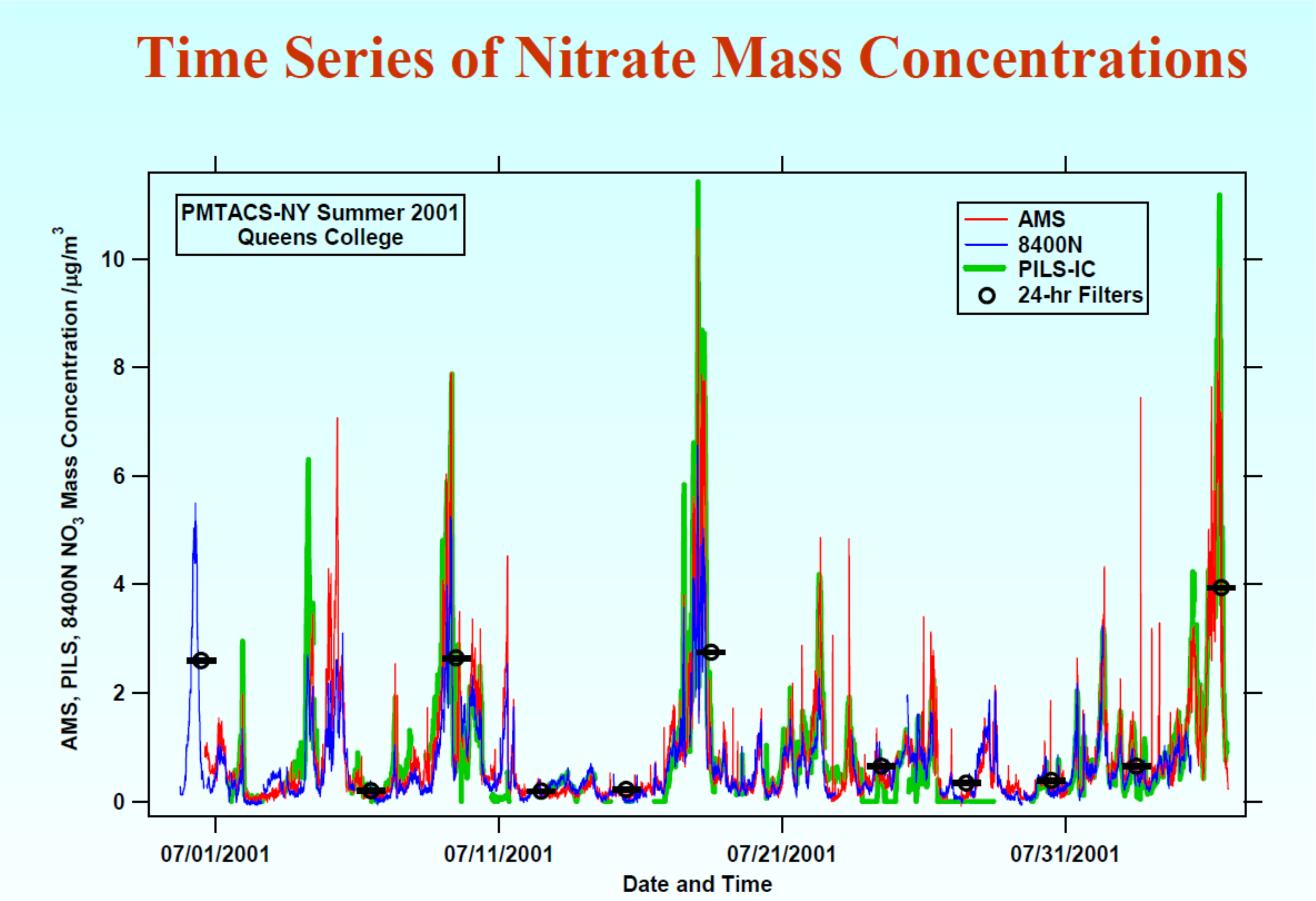
# *Measurements - Comparisons*

# Measurements - Comparisons

## HR-ToF-AMS comparison

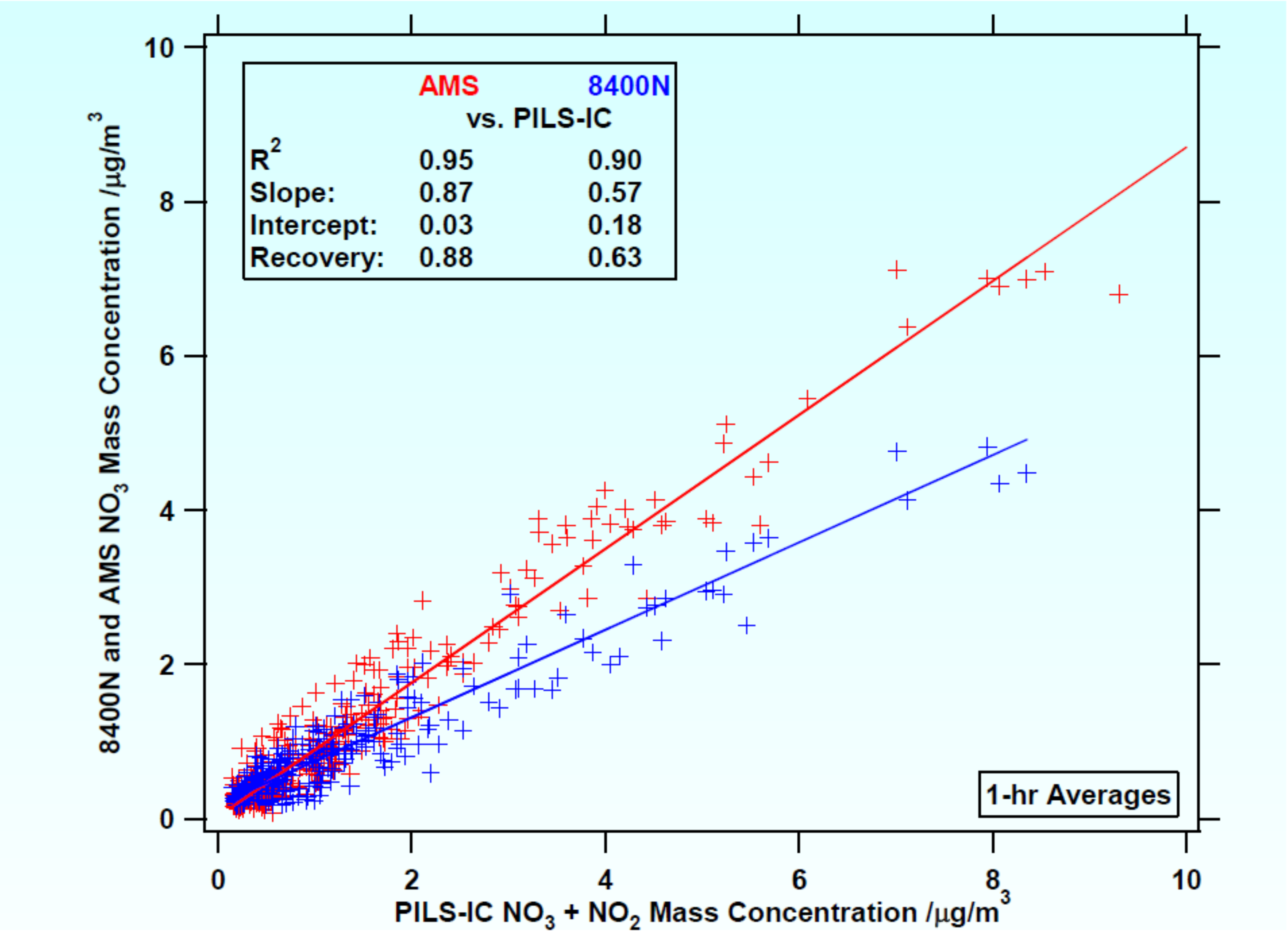


# Measurements - Comparisons



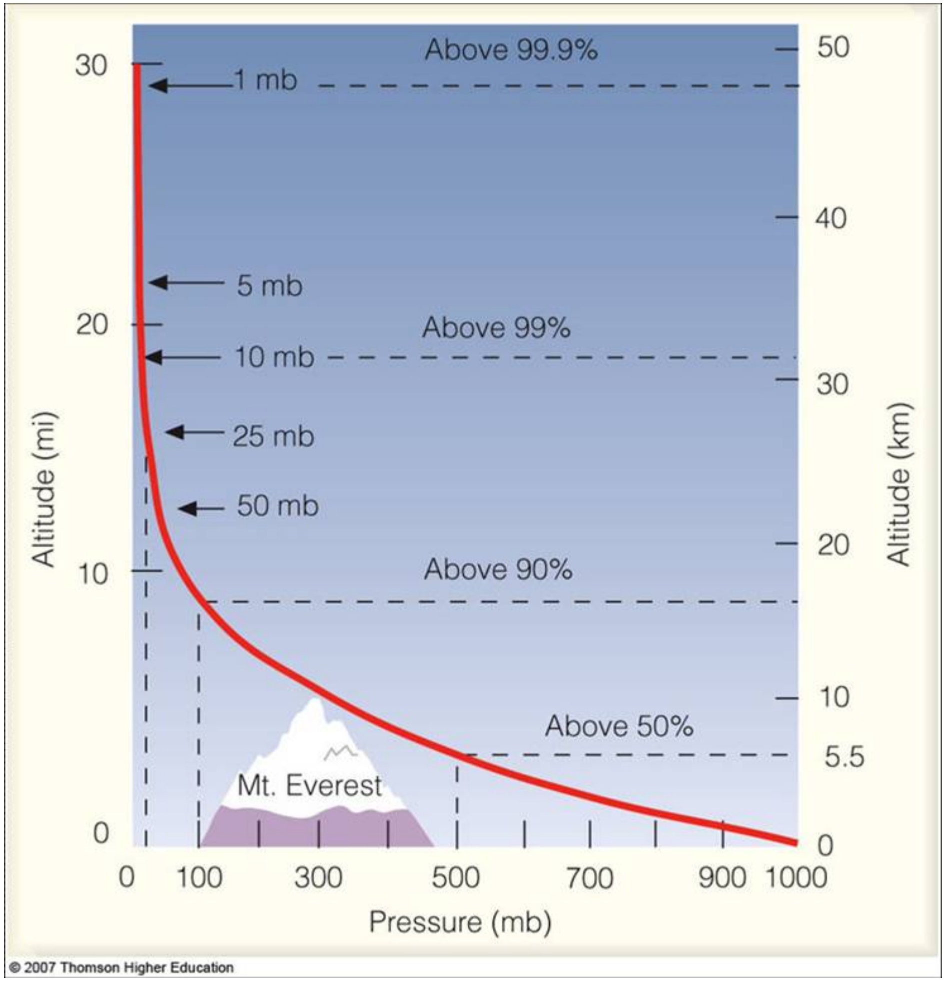

From Hofgre et al., AAAR

# *Measurements - Comparisons*



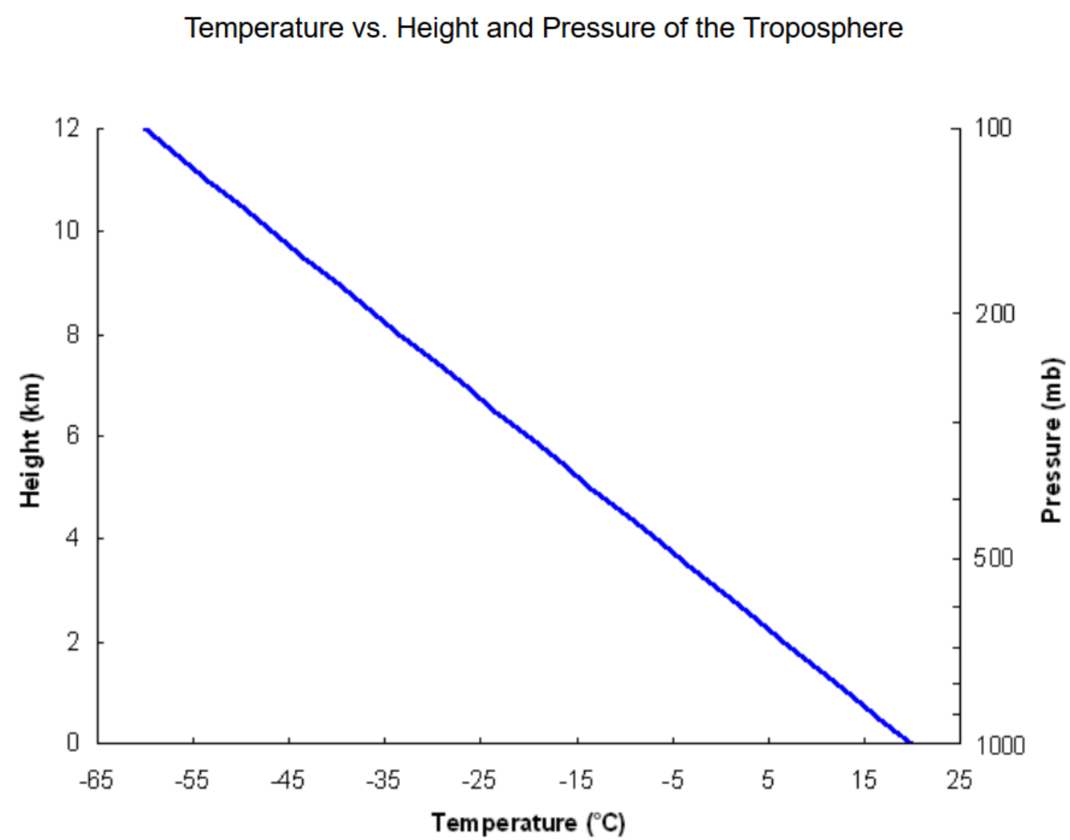
# *Measurements from aircraft*

- Pressure variation
  - 1000 -70 hPa



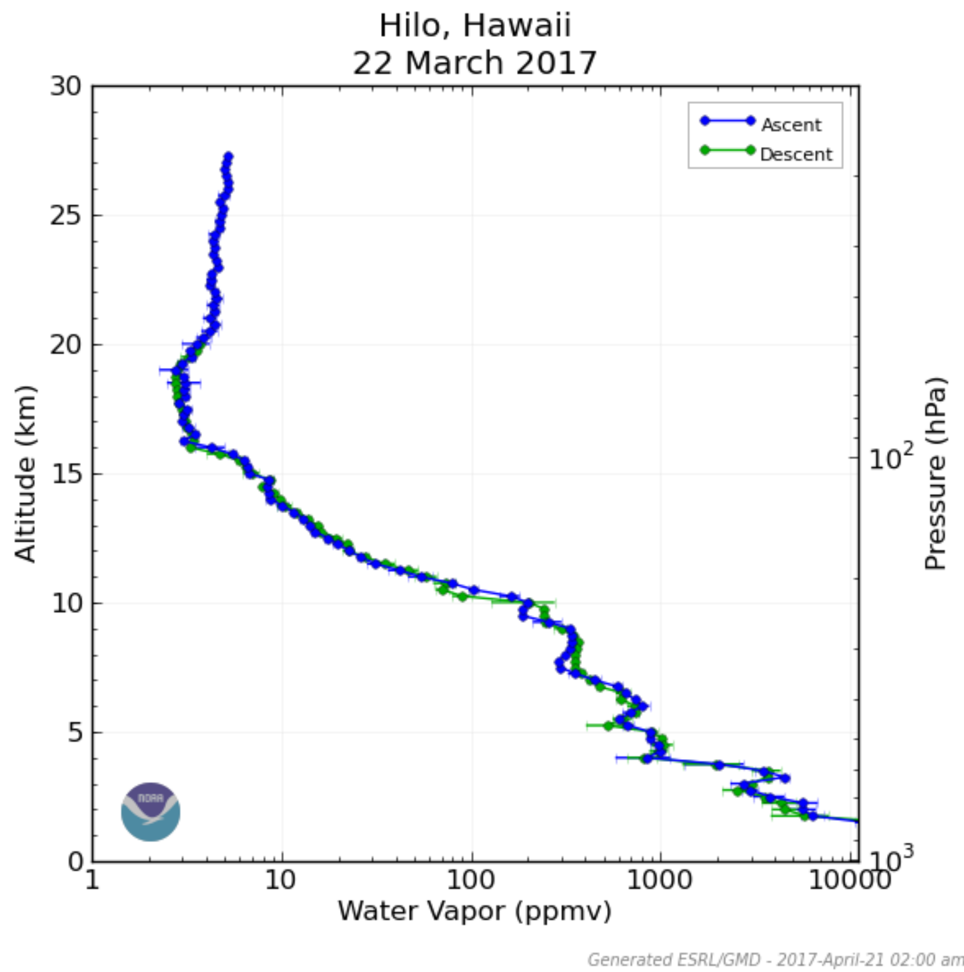
# *Measurements from aircraft*

- Pressure variation
  - 1000 -70 hPa
- Temperature
  - <-70 °C - >30 °C



# *Measurements from aircraft*

- Pressure variation
  - 1000 -70 hPa
- Temperature
  - <-70 °C - >30 °C
- Water vapor
  - <2 ppm - >3%
  - 4 orders of magnitude

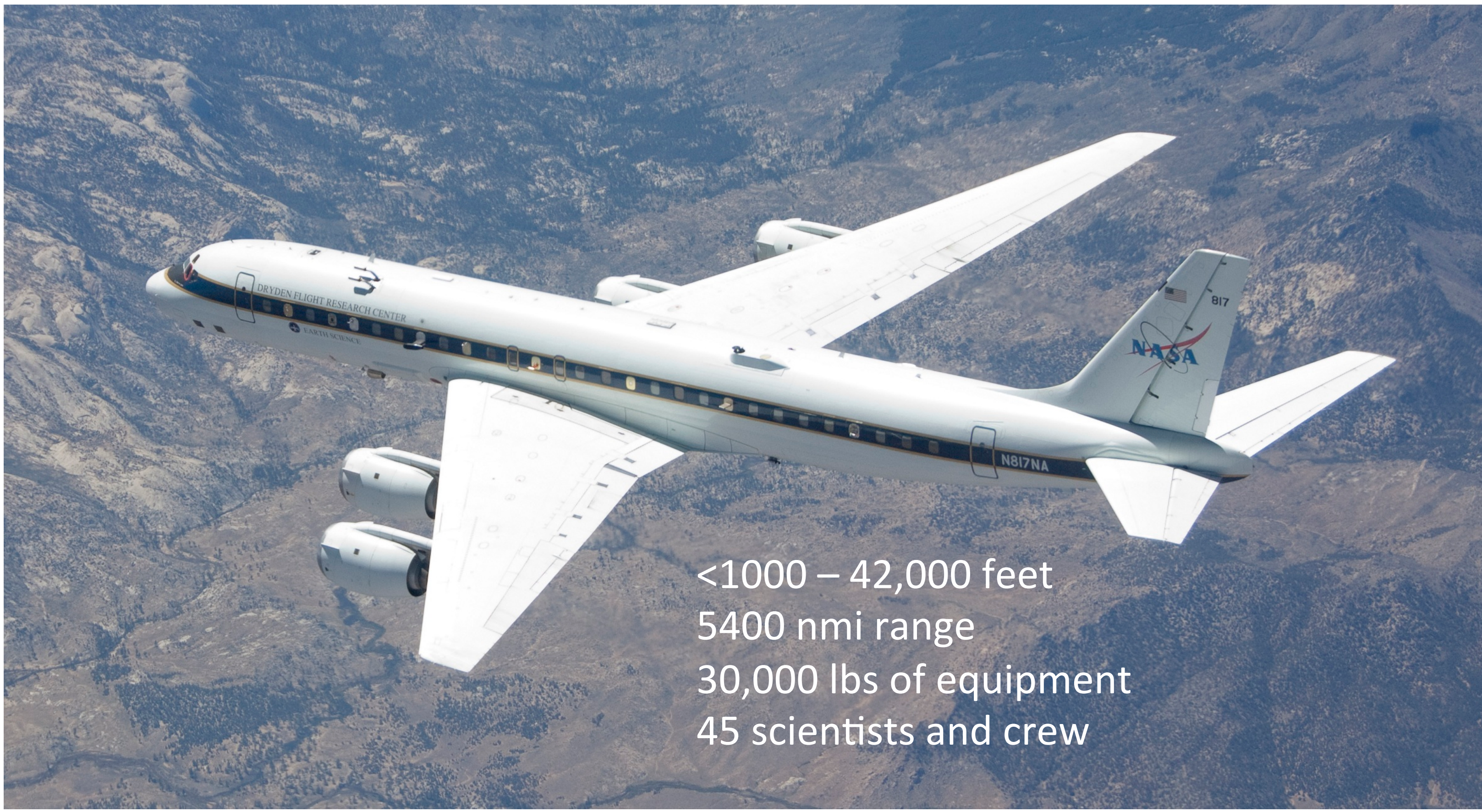


# *Measurements from aircraft*

- Motion!
  - Air speeds
    - 170 – 240 m/sec
  - 5 sec = 1 km
  - 1 min = 12 km
  - 5 min = 60 km
- Vertical profiles
  - 500 m/min

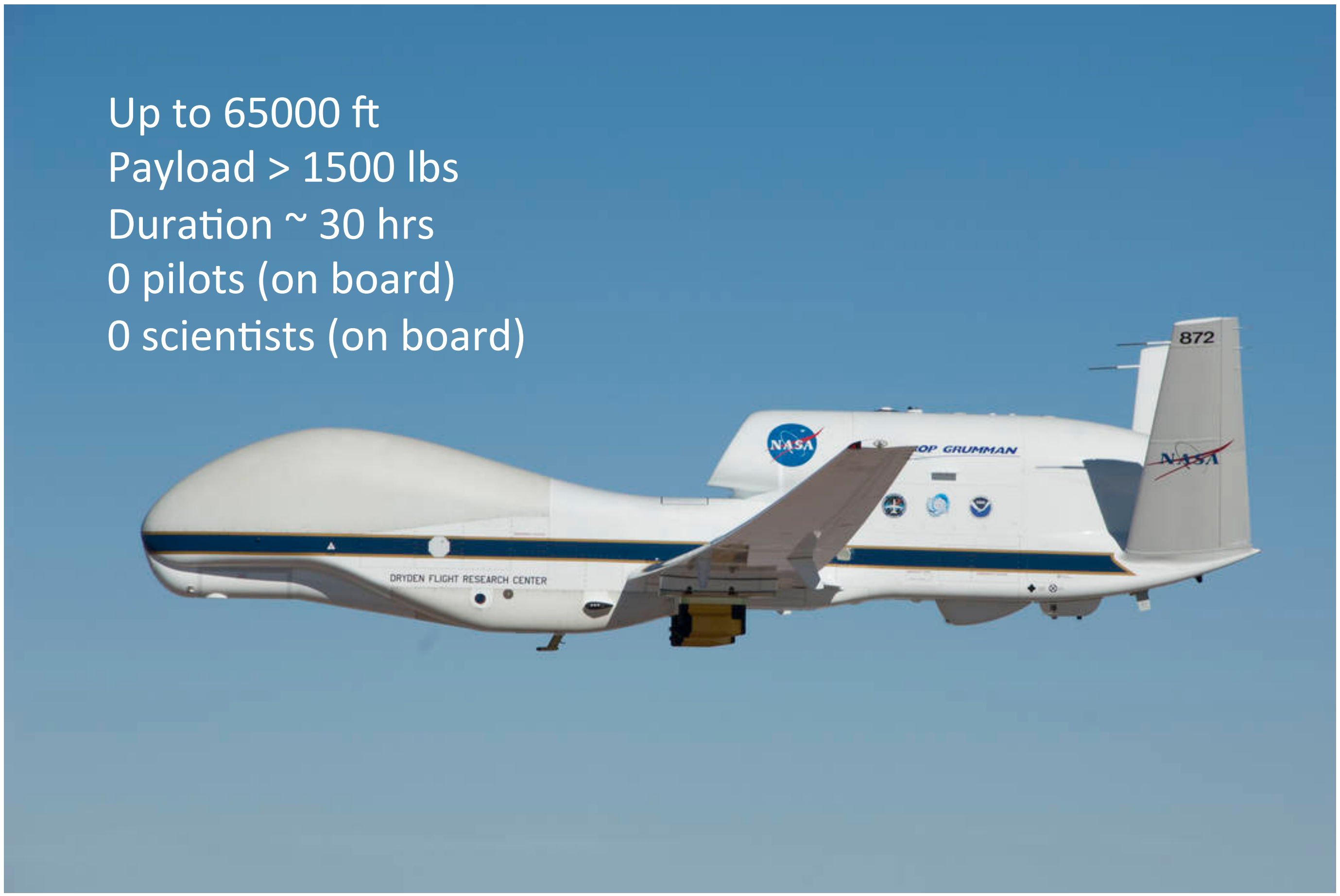
# *Measurements - Inlets*

# *Research Aircraft – NASA DC-8*

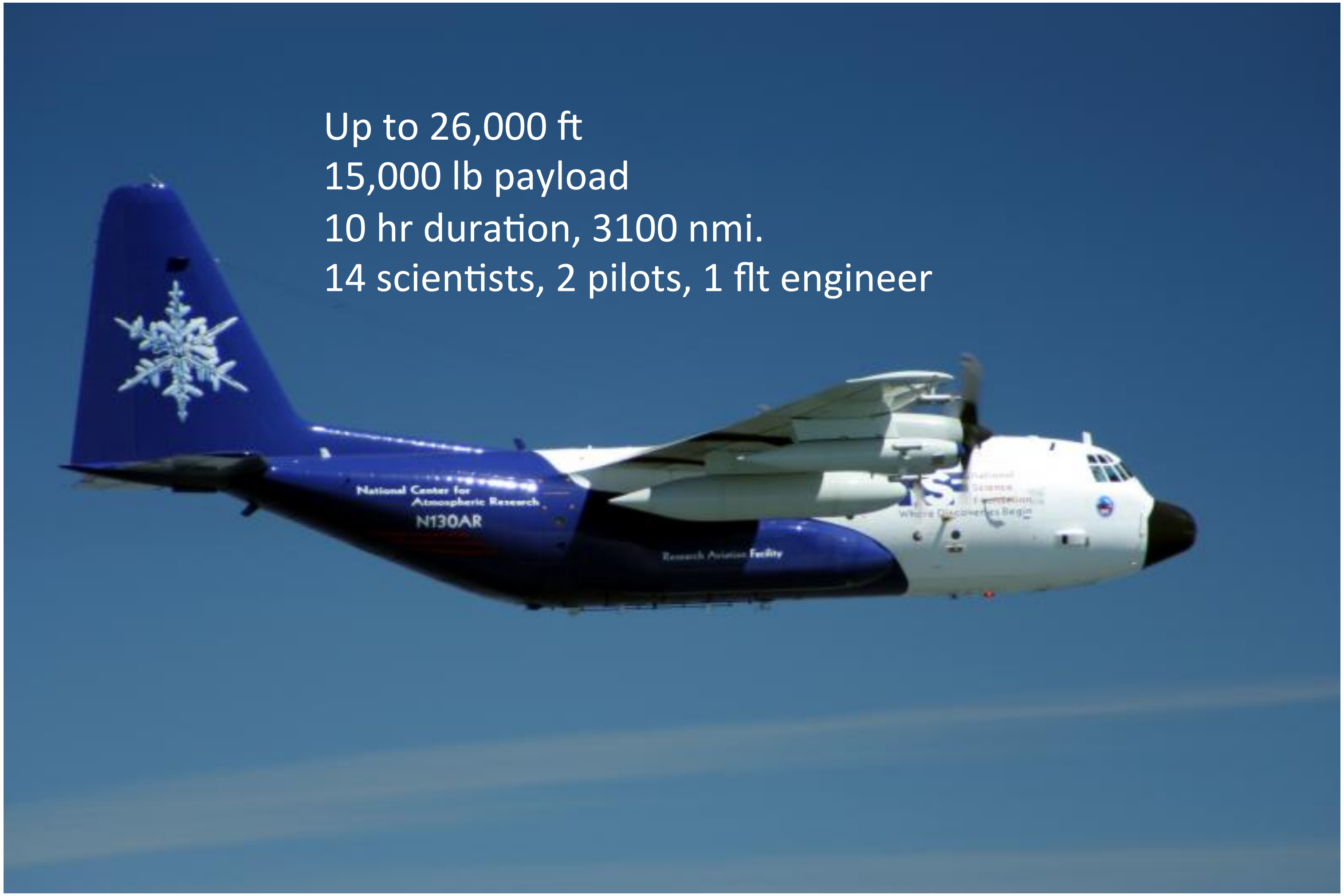


# Research Aircraft – NASA ER-2

# *Research Aircraft – NASA Global Hawk*



# *Research Aircraft – NSF/NCAR C-130*



# *Research Aircraft – NSF/NCAR GV*

**Up to ~50,000 ft**
**6000 lb payload**
**7000 mi. range**
**2 pilots, 1 engineer, 4 – 6 scientists**

# *Research Aircraft – NASA WB-57*

# *Preparing instruments : C-130*

# *Preparing instruments : DC8*

KORUS - AQ

# *Preparing instruments : GV*

# *Preparing instruments : WB-57*

# *Instrumentation for chemical composition measurements*

In-situ

Remote sensing

Gas phase

Aerosol phase

Lidars, DOAS

Stable

Reactive

Size differentiated

Single particle or bulk

# *Gas phase composition*

**Stable**

- Ozone
- $CO$, $CO_2$, $CH_4$
- $NO_x$, $NO_y$, PAN, $HNO_3$, …
- $NH_3$
- VOC
- $SO_2$
- $H_2O_2$, $CH_3OOH$
- $CH_2O$

**Reactive**

- $OH$, $HO_2$
- $RO_2$

# *In-situ techniques*

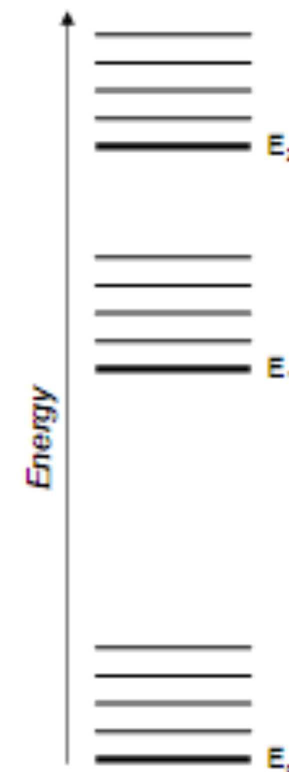
- IR Spectroscopy – Formaldehyde, CO, $CO_2$
- Chemiluminescence – $NO_{x,y}$, $O_3$
- Mass Spectrometry: e.g., OH – CIMS (chemical ionization mass spectrometry), PTR-MS, GC-MS
- Laser induced fluorescence – LIF: OH, $NO_2$, PANs
- Laser Absorption Spectroscopy – many
- Cavity Ring Down Spectroscopy - many

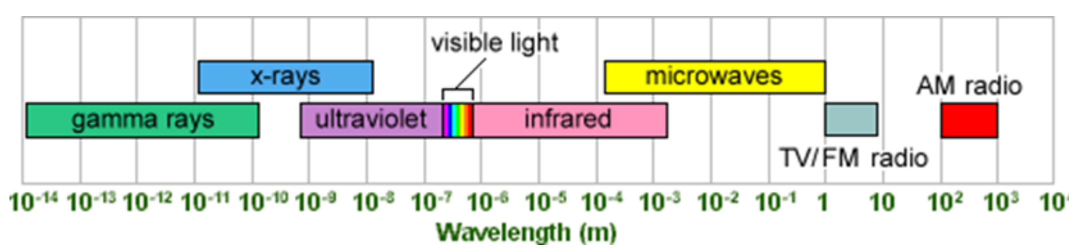
Slides from E. Apel, NCAR

Gas-phase

# Review of Spectroscopy

- Identify and quantify species based on their interactions with energy
  - Energy: **radiation**, acoustic waves, beams of particles such as ions and electrons
- The energy difference b/w states is unique for every species!
- Quantum theory:
  - Atoms, ions, and molecules exist in discrete states, characterized by definite amounts of **E**
  - When a species changes its state, it absorbs or emits an amount of energy *exactly* equal to the energy difference between states, $\mathbf{E = h\Delta v}$



# Review of spectroscopy

- **Absorbance**:
  - Select frequencies are removed from the incident light by absorption.
  - Absorption promotes molecules from ground state to an excited state.
  - Analytical techniques: IR and UV-VIS

- **Emission**:
  - Select frequencies are emitted when excited molecules return to ground state
  - Initial excitation occurs by irradiation or rxn
  - Analytical techniques: Fluorescence and Chemiluminescence

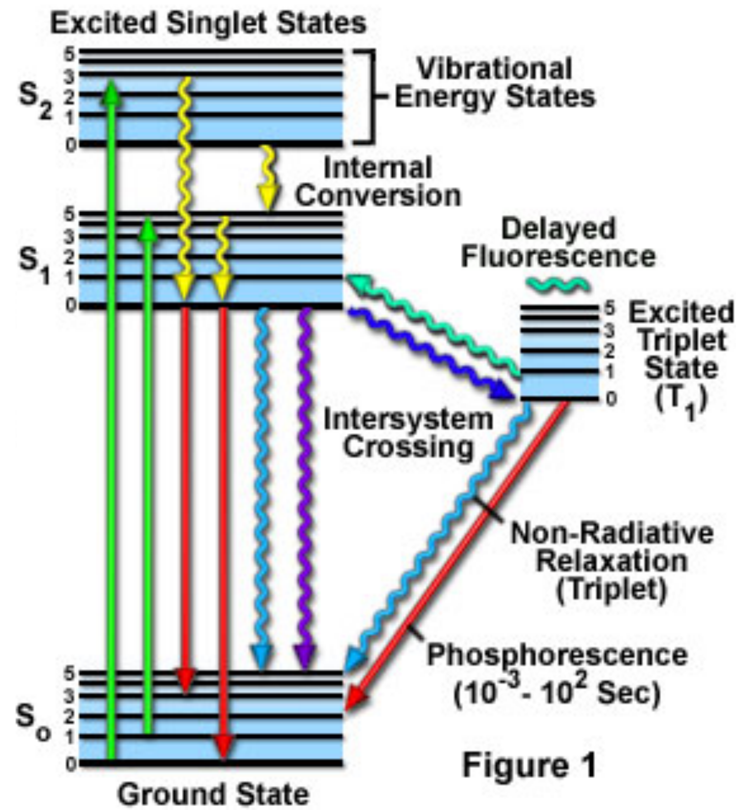
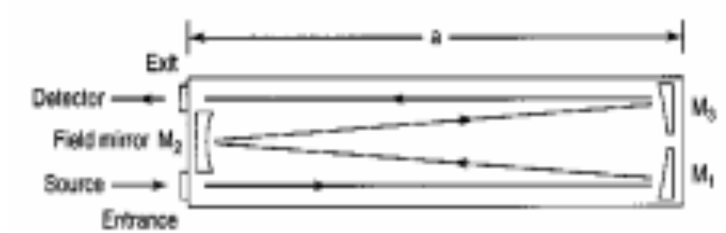


Figure 1

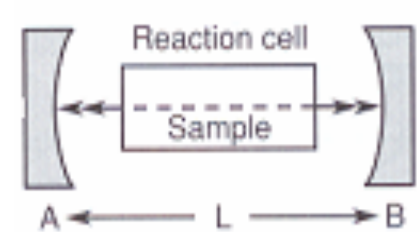
# Absorbance-Based Techniques

*Gas-phase*

- Direct absorption spectroscopy:
  - $A = \ln(I_o/I) = \sigma L N$
  - Longer pathlength ⇨ Higher sensitivity
    - Mulitpath cells:
      - Pathlength = 0.5 – 100 m
      - Lose power due to mirrors
    - Cavity based methods:
      - Pathlength = 1 – 10 km
      - Expensive mirrors and pulsed laser
    - Long distance measurements:
      - Pathlength = 100 m – 1 km
      - In situ measurements
      - Poor spatial resolution




Multipass White cell. *FP&P*




Cavity ring down cell. *FP&P*

# Emission-Based Techniques

*Gas-phase*

- **Chemiluminescence:** detect photons emitted by electronically excited products of a reaction

  $O_3 + NO \rightarrow NO_2^* + O_2$

  $NO_2^* \rightarrow NO_2 + h\nu$ (*hν* is detected)

  - For detection of NO, add excess $O_3$ to the air stream.
  - This reaction can be used to detect either $O_3$ or NO.

- **Fluorescence:** detect photons emitted by molecules excited with a laser or UV-lamp

  $SO_2 + h\nu \rightarrow SO_2^*$

  $SO_2^* \rightarrow SO_2 + h\nu'$ (*hν'* is detected, normally $h\nu' < h\nu$ )

  - NO, $SO_2$, $NO_2$ are some of the molecules that have large fluorescence quantum yields.

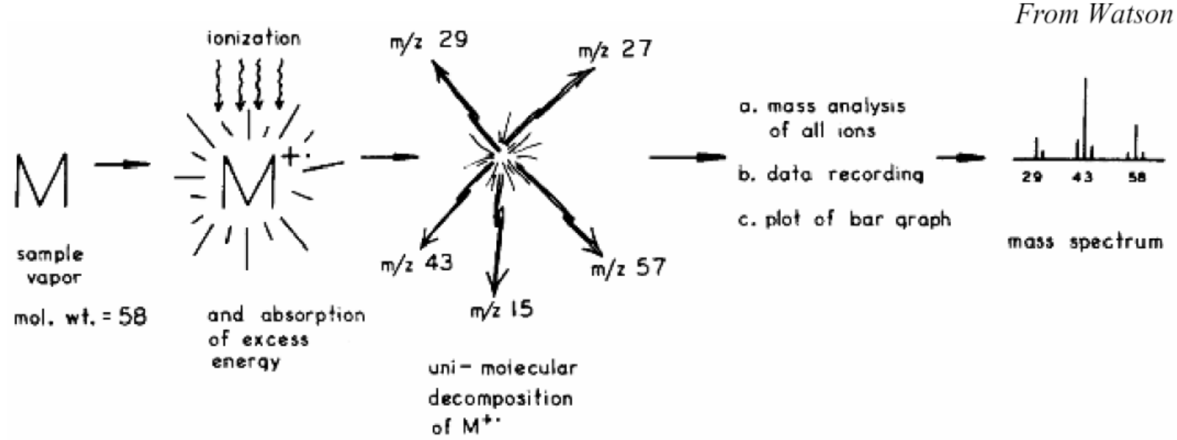
# *Mass Spectrometry*

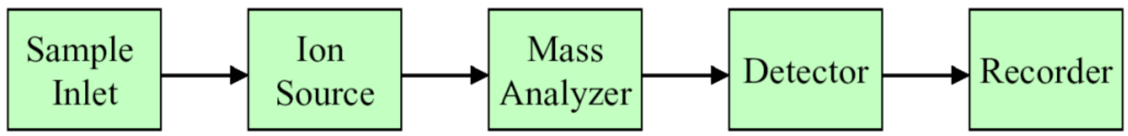
1. A small sample is ionized, usually to cations by loss of an electron. **The Ion Source**

2. The ions are sorted and separated according to their mass and charge. **The Mass Analyzer**

3. The separated ions are then measured, and the results displayed on a computer. **The Detector**

*From Watson*



# Electron impact ionization

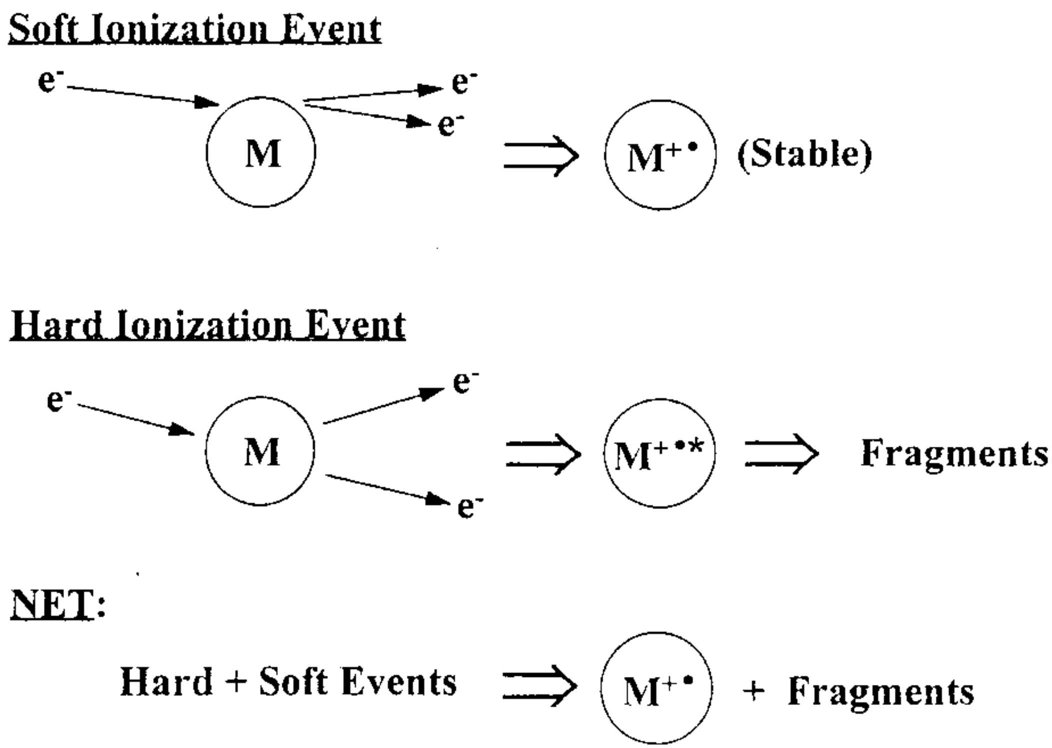
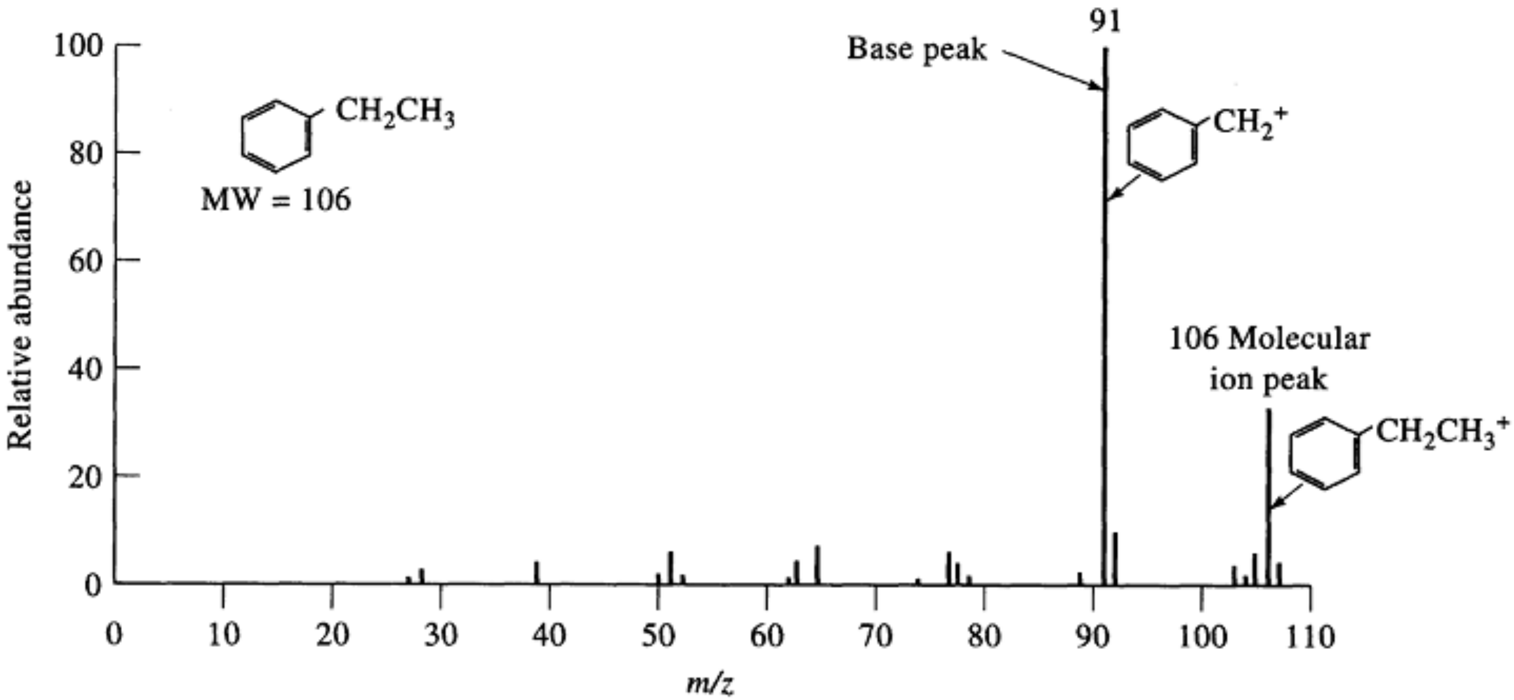



**Figure 13-3** Electron ionization accompanied by different degrees of excitation of the molecular ion. Soft ionizing events transfer little excess energy to the ionized molecule, which is observed intact. Harder collisions also occur and give rise to the fragment ions frequently seen in EI mass spectra.

# *Mass spectrum*

Graph of ion intensity versus mass-to-charge (m/z) ratio



# *Chemical Ionization MS (CIMS)*

- Gaseous atoms of the sample are ionized by collisions with ions produced by electron bombardment of an excess reagent gas – many uses exploited in recent times (acetate, $I^-$, $H_3O^+$, …)

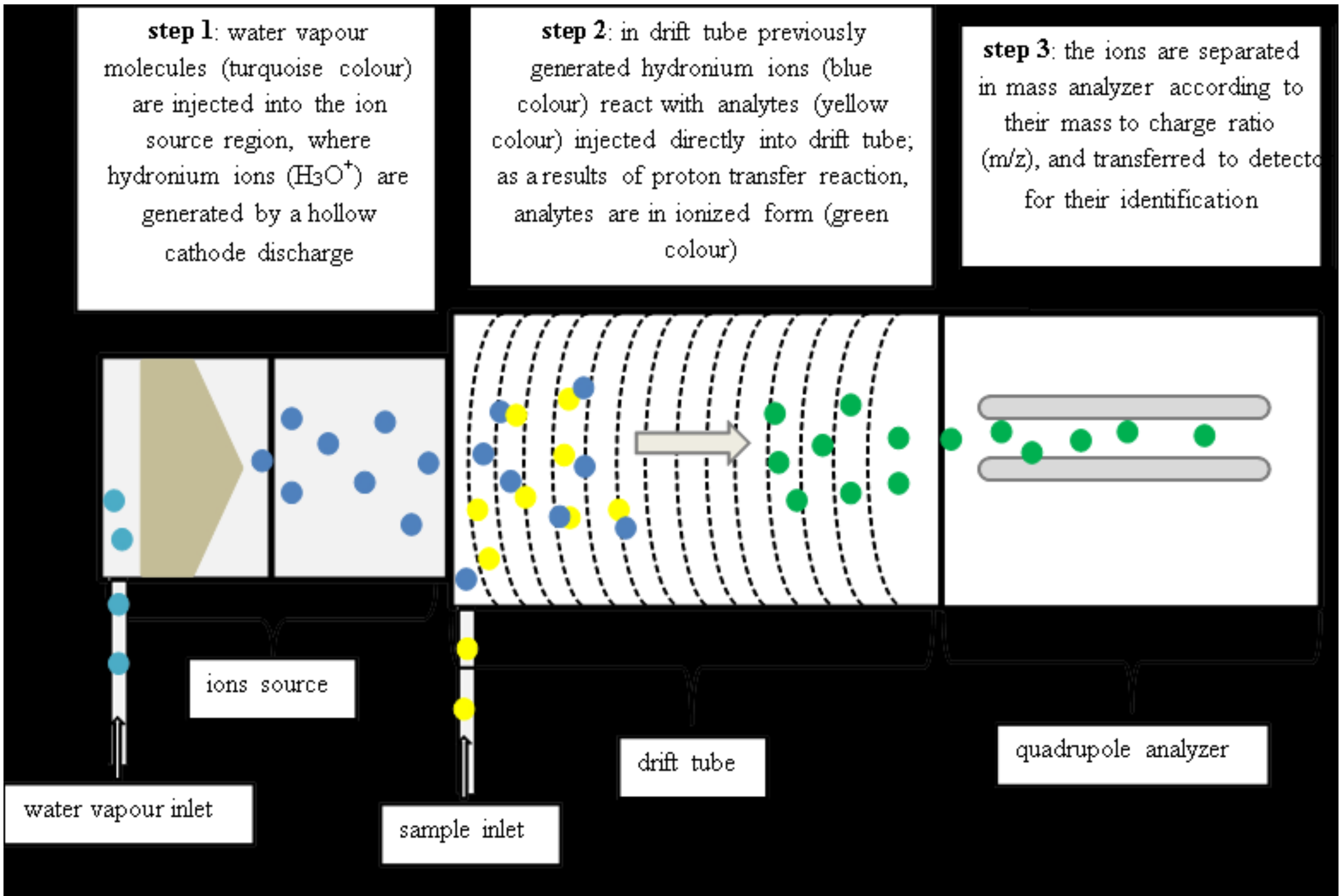
- Schemes developed for detection of PAN, OH, HO2, NH3, VOCs (PTR-MS)…..

- Most common – positive ions, but negative ions are used (e.g., PAN CIMS) with analytes containing very electronegative atoms

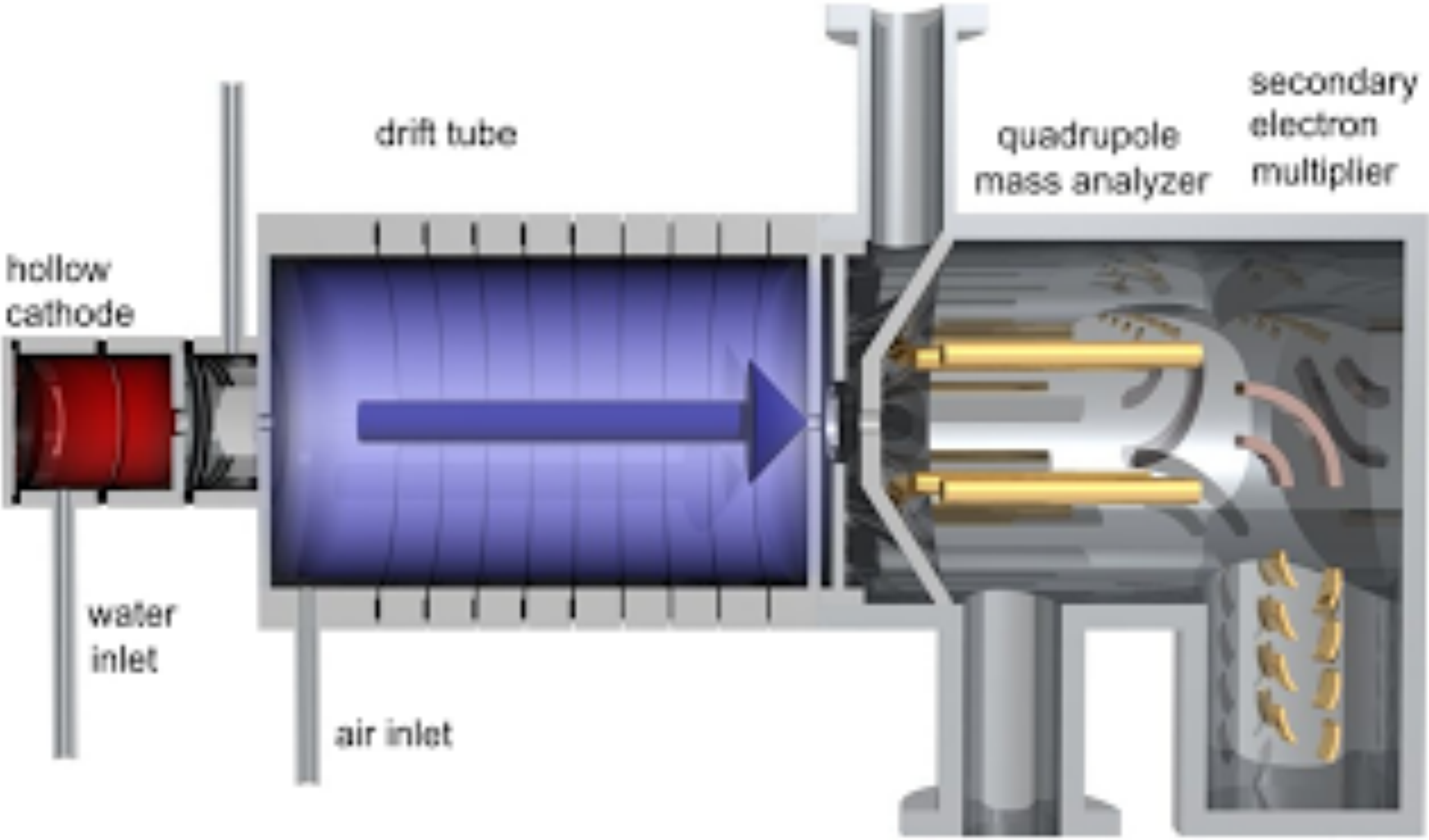
# *Proton Transfer Reaction (PTR)-MS for Fast Response VOC measurements*

- Alcohols: methanol
- Aldehydes: formaldehyde, acetaldehyde, pentanal, pentenal, 3-methyl butenal
- Ketones: acetone, methyl ethyl ketone, methyl vinyl ketone, methacrolein
- NMHCs: isoprene, benzene, toluene, C8-aromatics, C9-aromatics, C10-aromatics, terpenes
- Others: acetonitrile, DMS

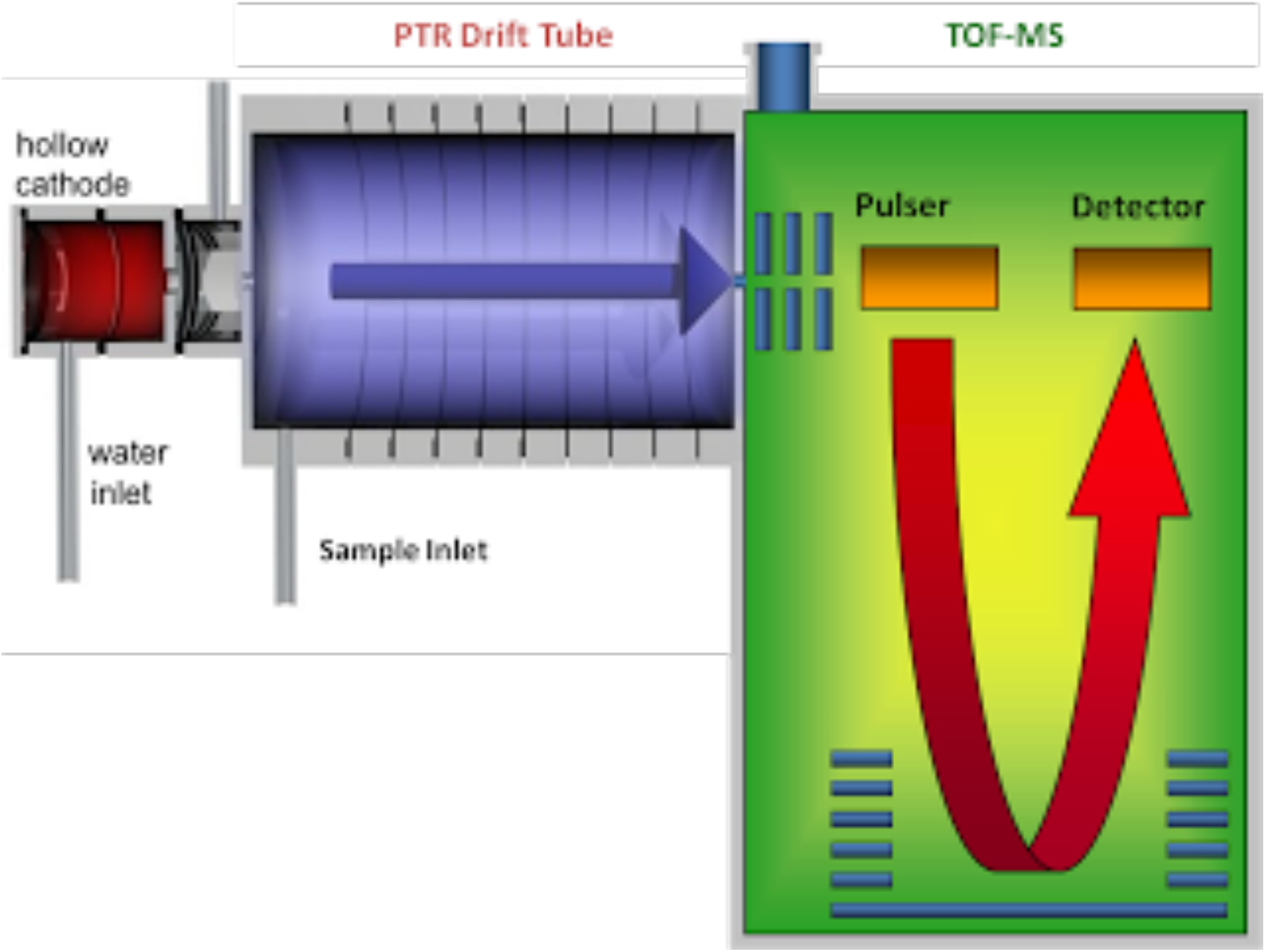
# Proton Transfer Mass Spectrometer (PTR-MS)



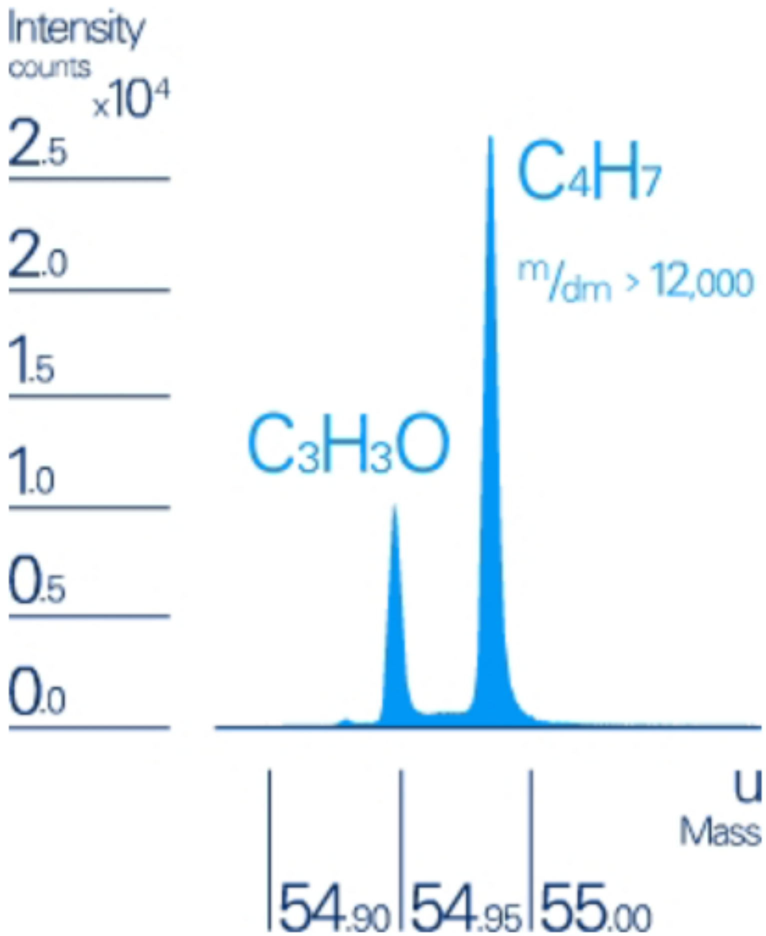
# *Proton Transfer Mass Spectrometer (PTR-MS)*



# *Proton Transfer Mass Spectrometer (PTR-TOF-MS)*

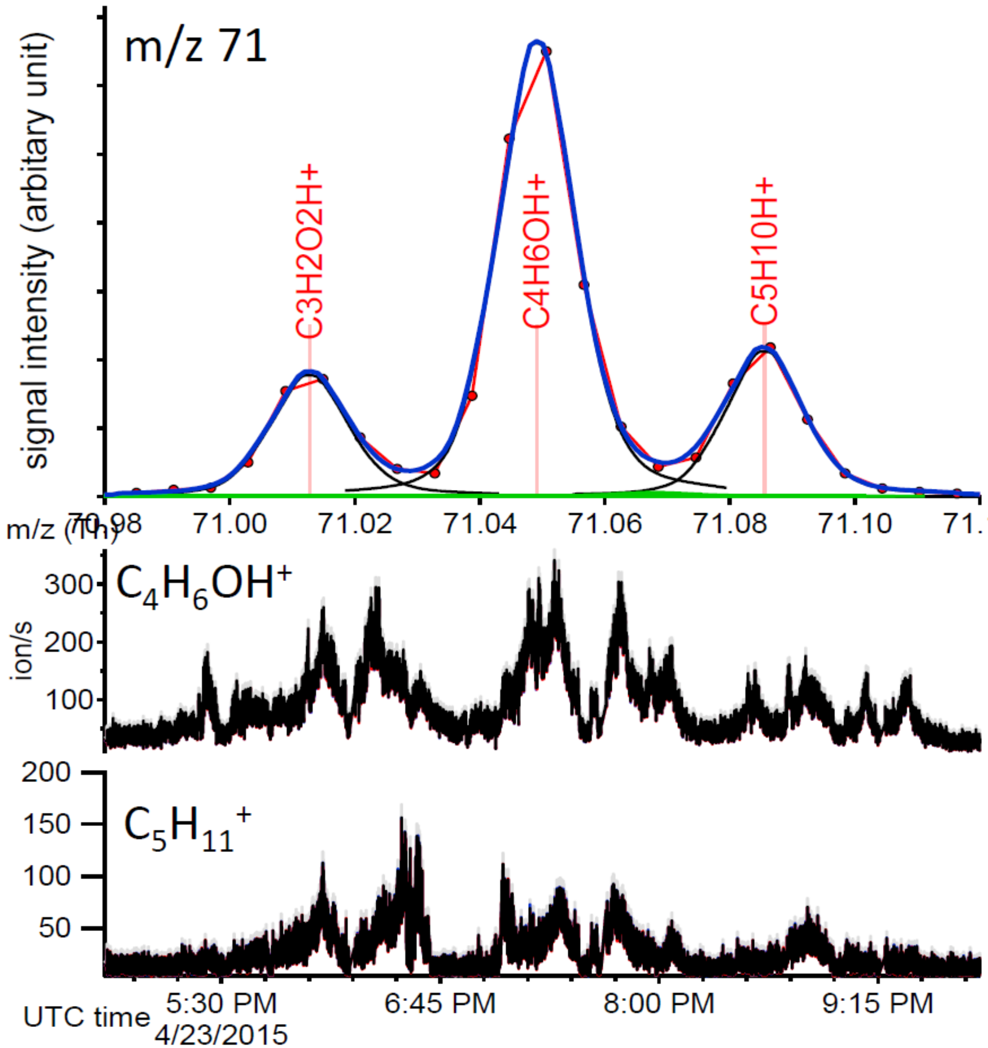


# High resolution (HR) mass spectrum




Both ions have nominal m/z of 55, but exact masses allow discrimination

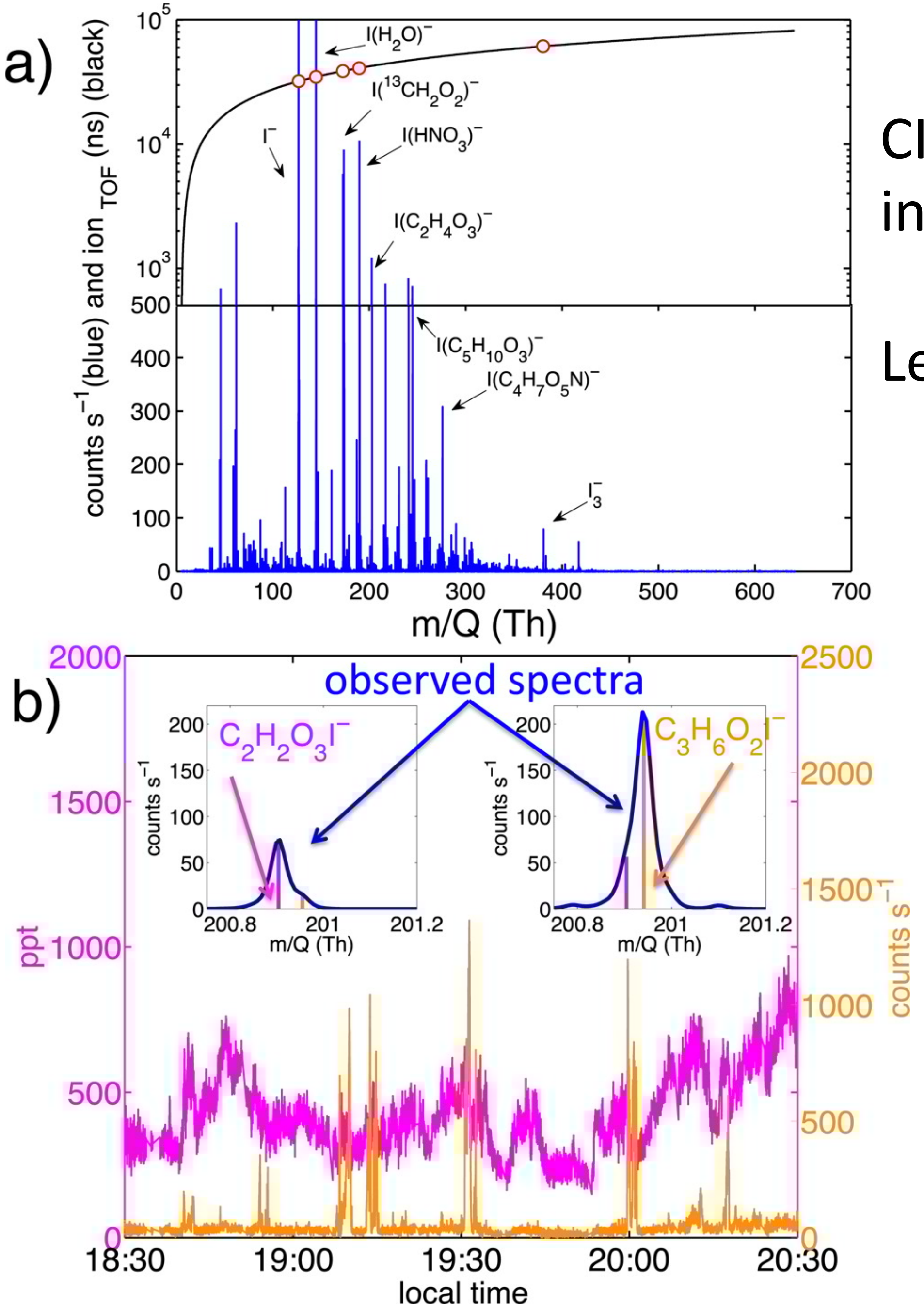
# *High resolution (HR) mass spectrum*




Ions have same nominal m/z of 71, but exact masses allow discrimination

Example of data

From Koss et al., AMTD, 2017




CIMS Iodide adduct measurements in SE US

Lee et al., 2014, ES&T

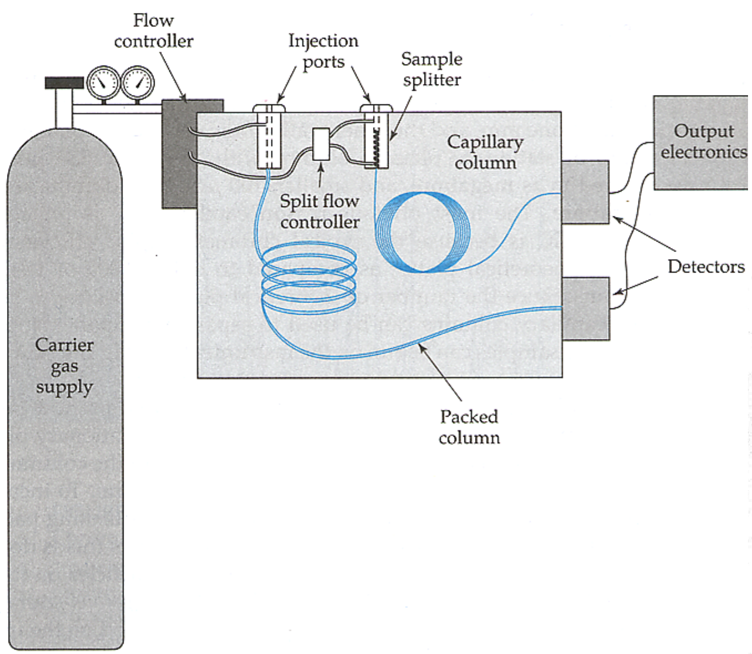
$C_2H_2O_3I^-$ = glyoxylic acid

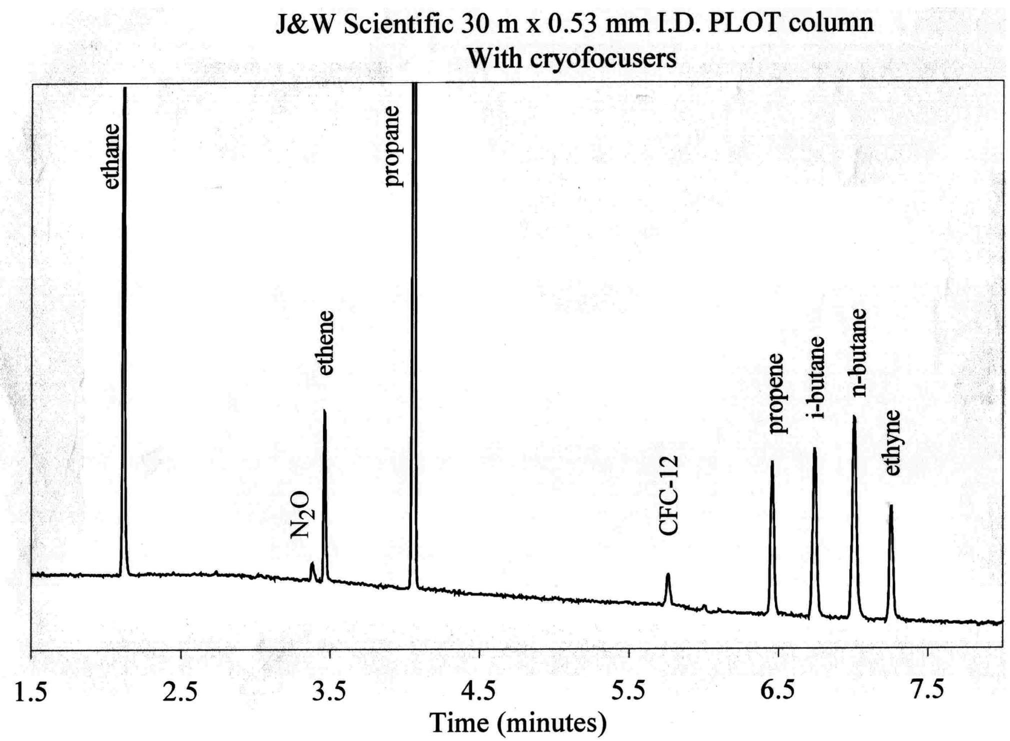
$C_3H_6O_2I^-$ = hydroxyacetone or Propionic acid

# Combination techniques – e.g., GC-FID, GC-MS

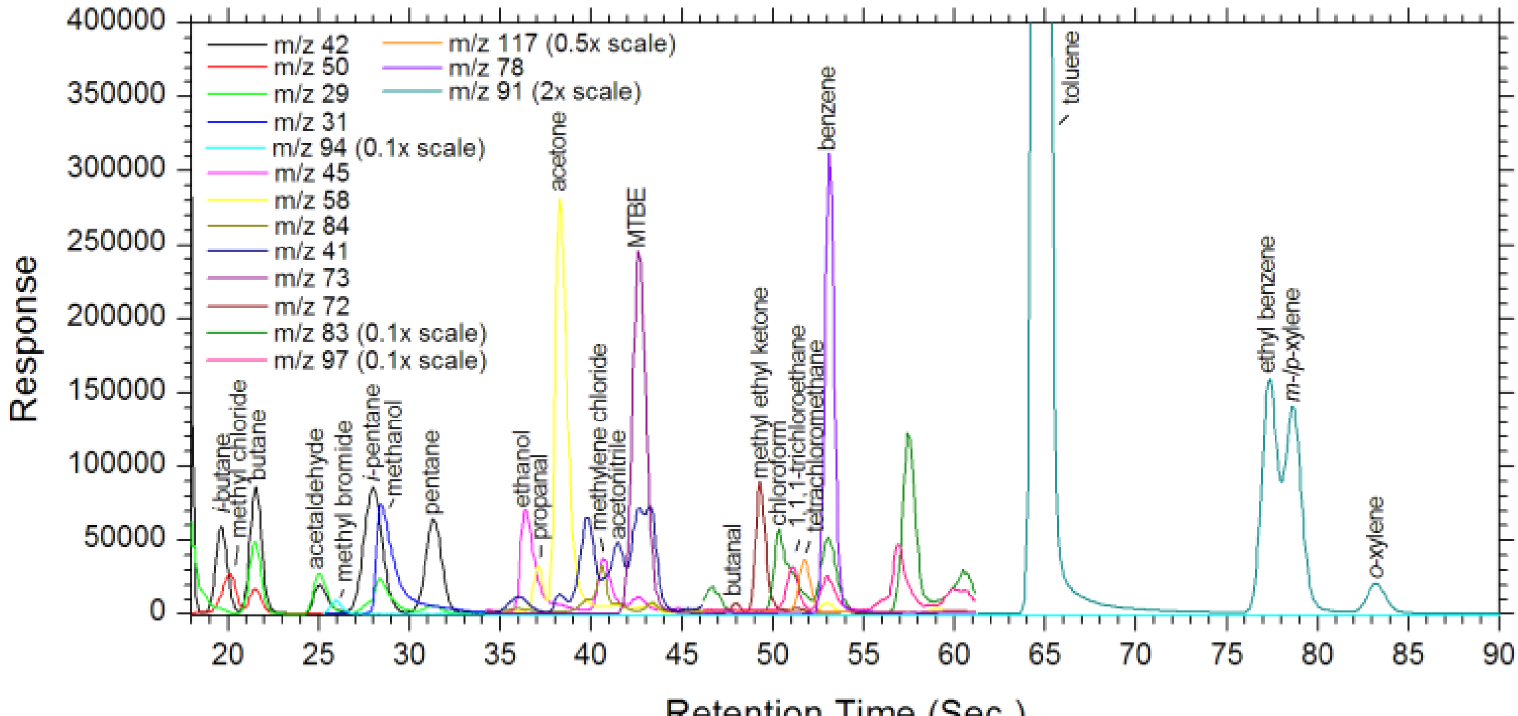
- Complex Matrix – or multiple species with similar characteristics

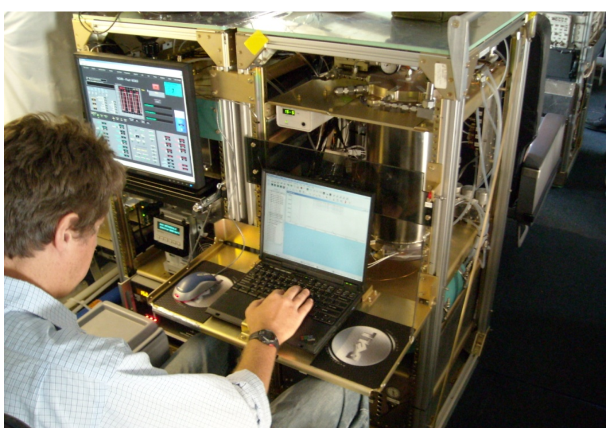
- Separate and then detect



# Trace Organic Gas Analyzer (TOGA)



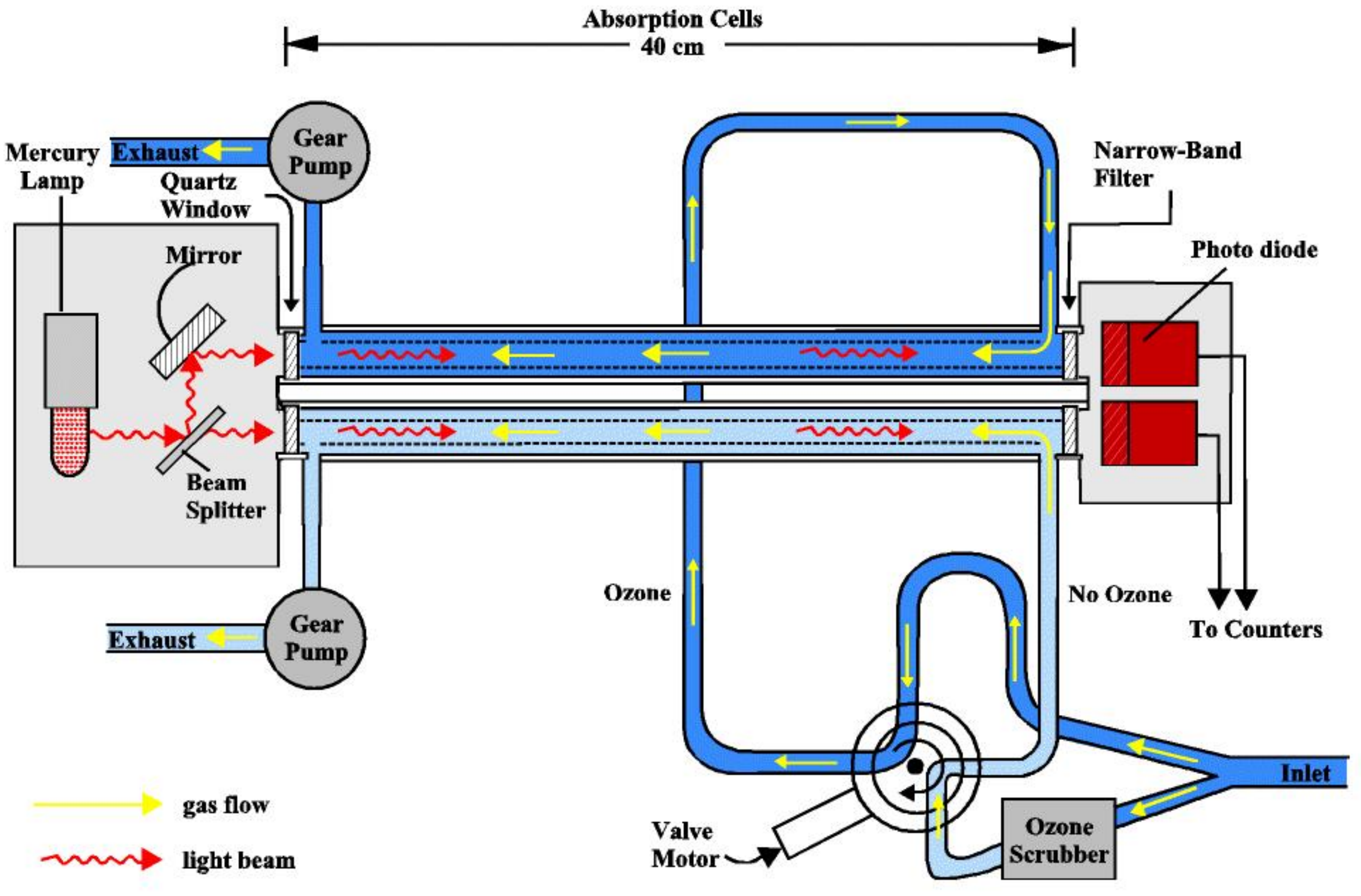



GC – MS selected ion chromatogram

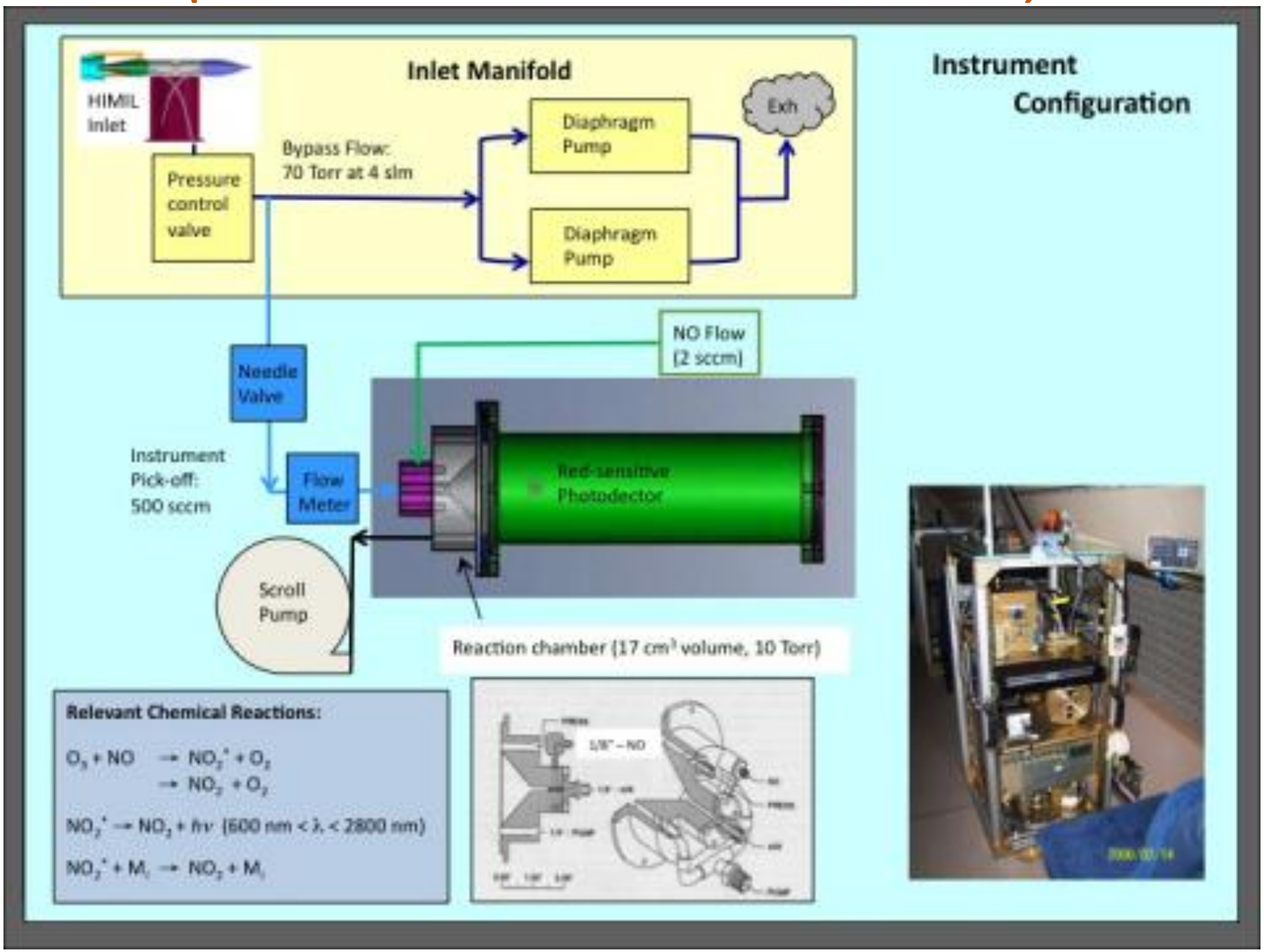
D. Riemer operating TOGA on GV aircraft

# *Examples of instruments*

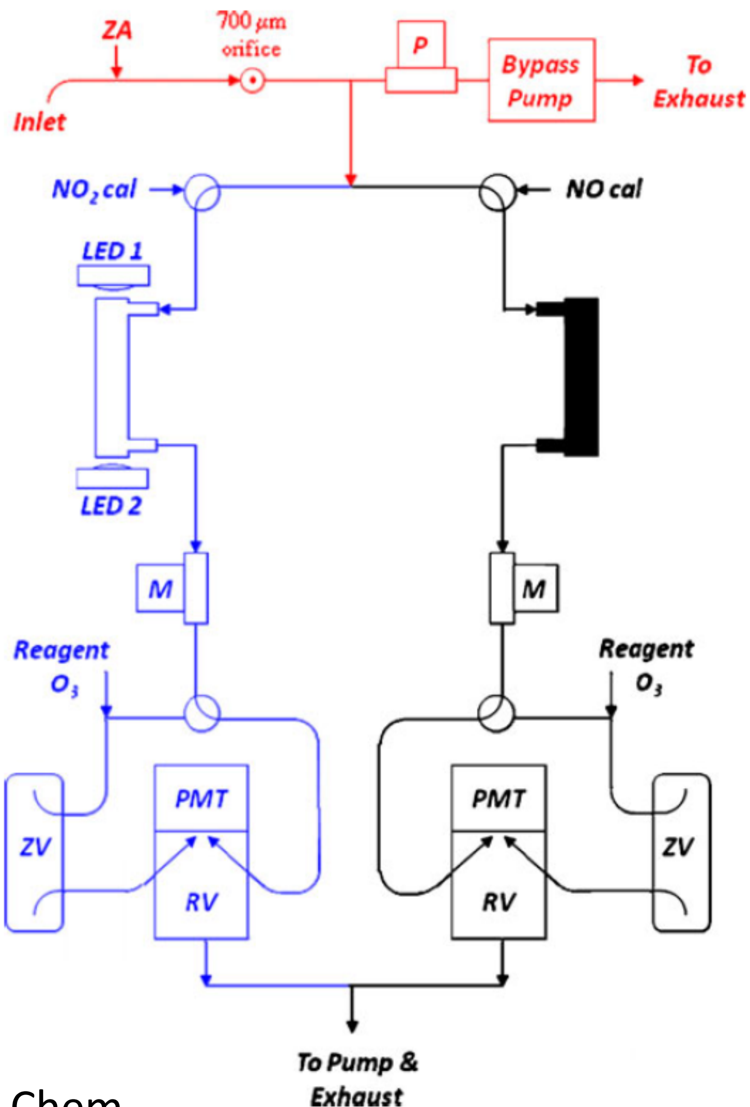
# NOAA Ozone Photometer



# NCAR Fast Ozone (Chemiluminescense)

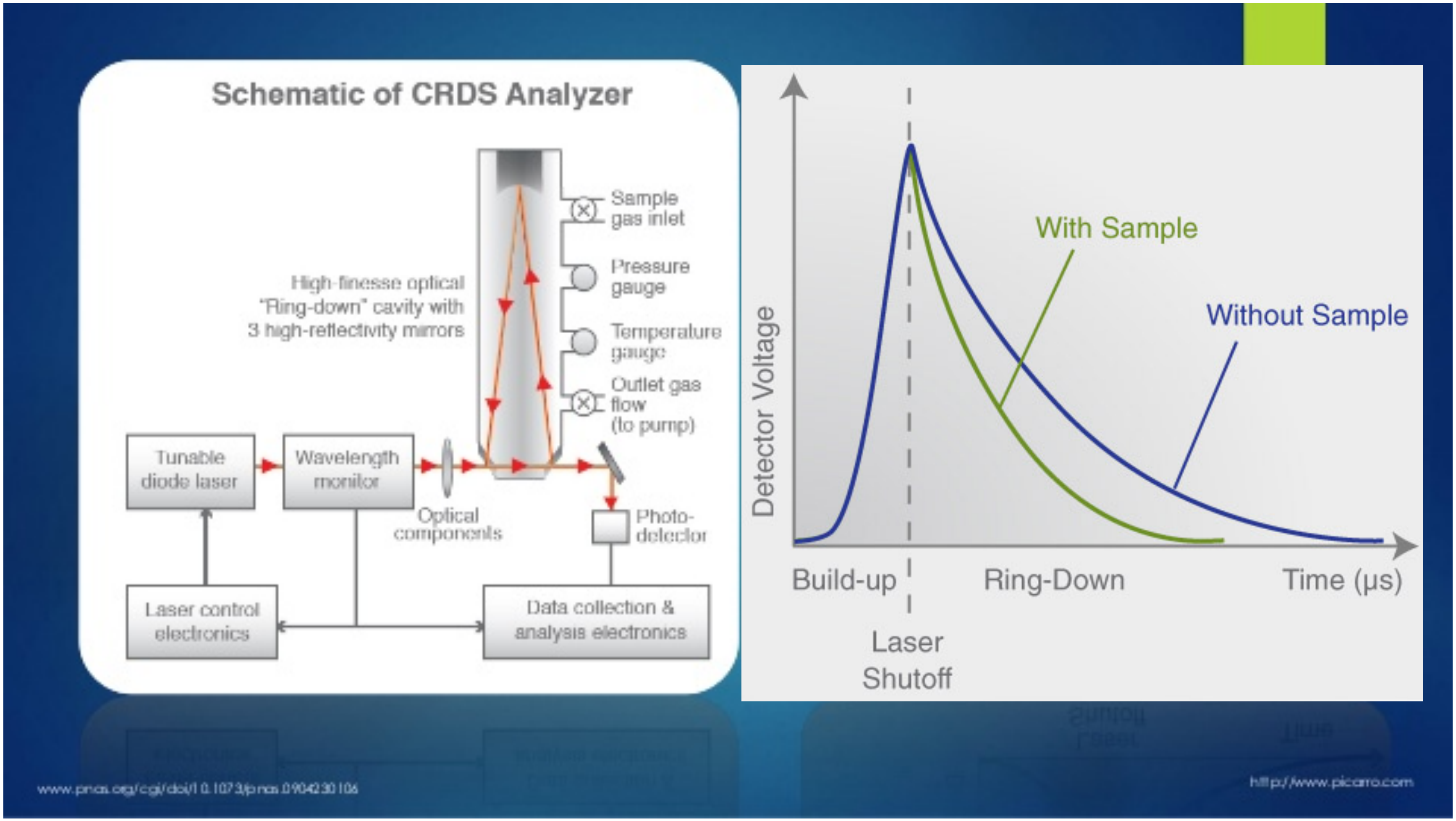


# $NO/NO_2$ measurement




Pollack et al., 2011, J.Atm.Chem.

# *Cavity Ring-Down Spectroscopy (CRDS)*
# *$CO$, $CO_2$, $CH_4$, $N_2O$, $H_2O$, isotopes*



# $NO_3$, $N_2O_5$...Cavity Ring-Down



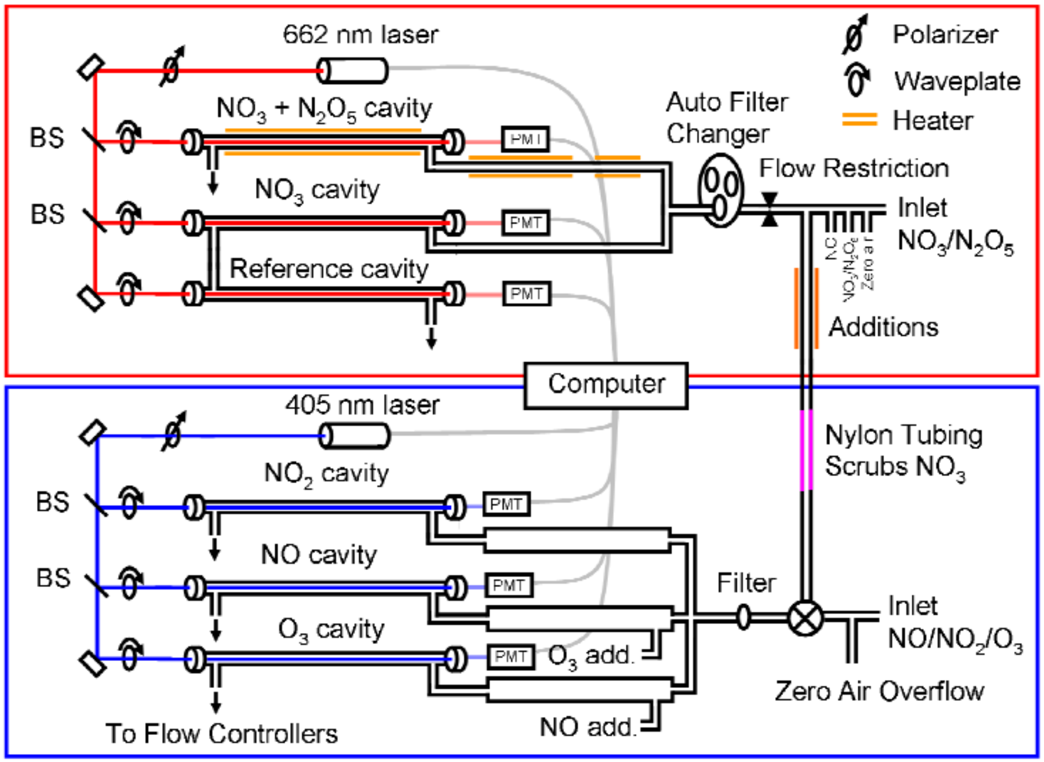
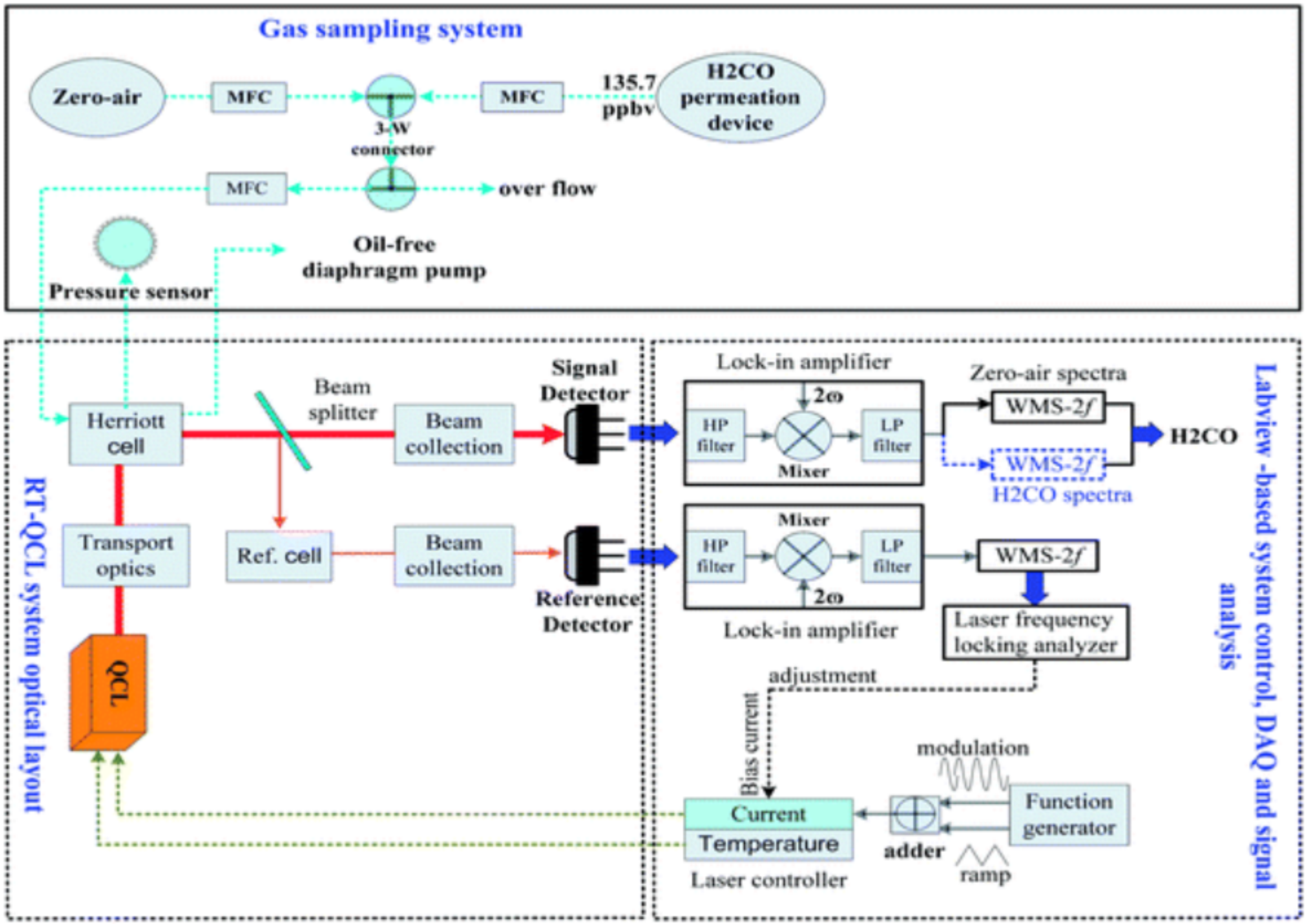


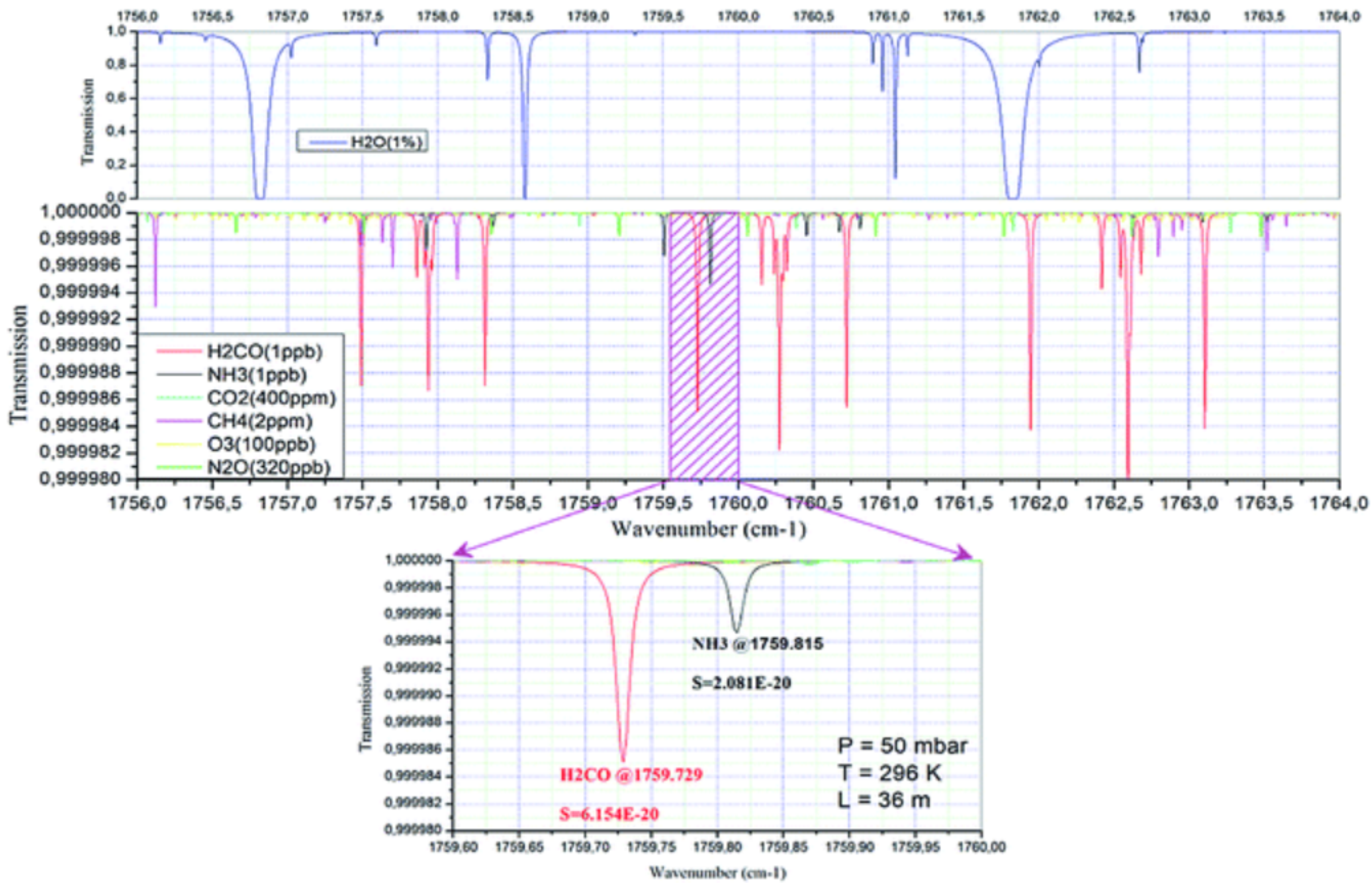

**Fig. 1.** Instrument schematic. The upper part framed in red shows the $NO_3$ and $N_2O_5$ measurement. The lower part framed in blue shows the NO, $NO_2$ and $O_3$ measurement. BS denotes a beamsplitter. A photo of the optical bench instrument is shown on the right.

# Diode Laser (QCL) Formaldehyde




Li et al., RSC, 2014

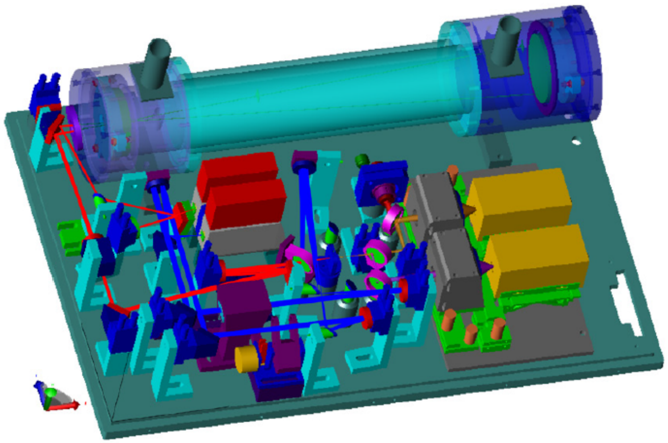
# *Diode Laser (QCL) Formaldehyde*



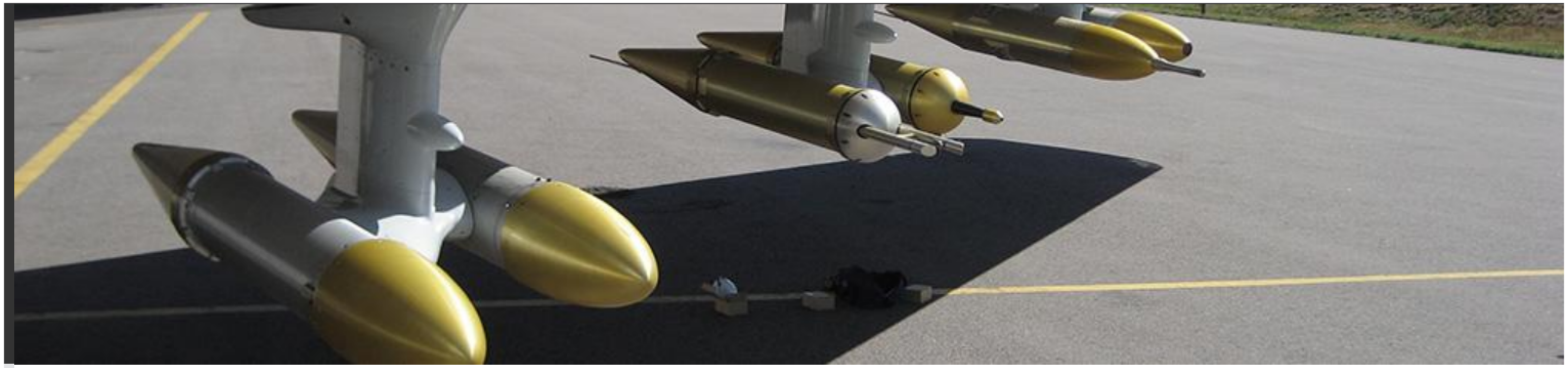

Li et al., RSC, 2014

# *Other laser based measurement*

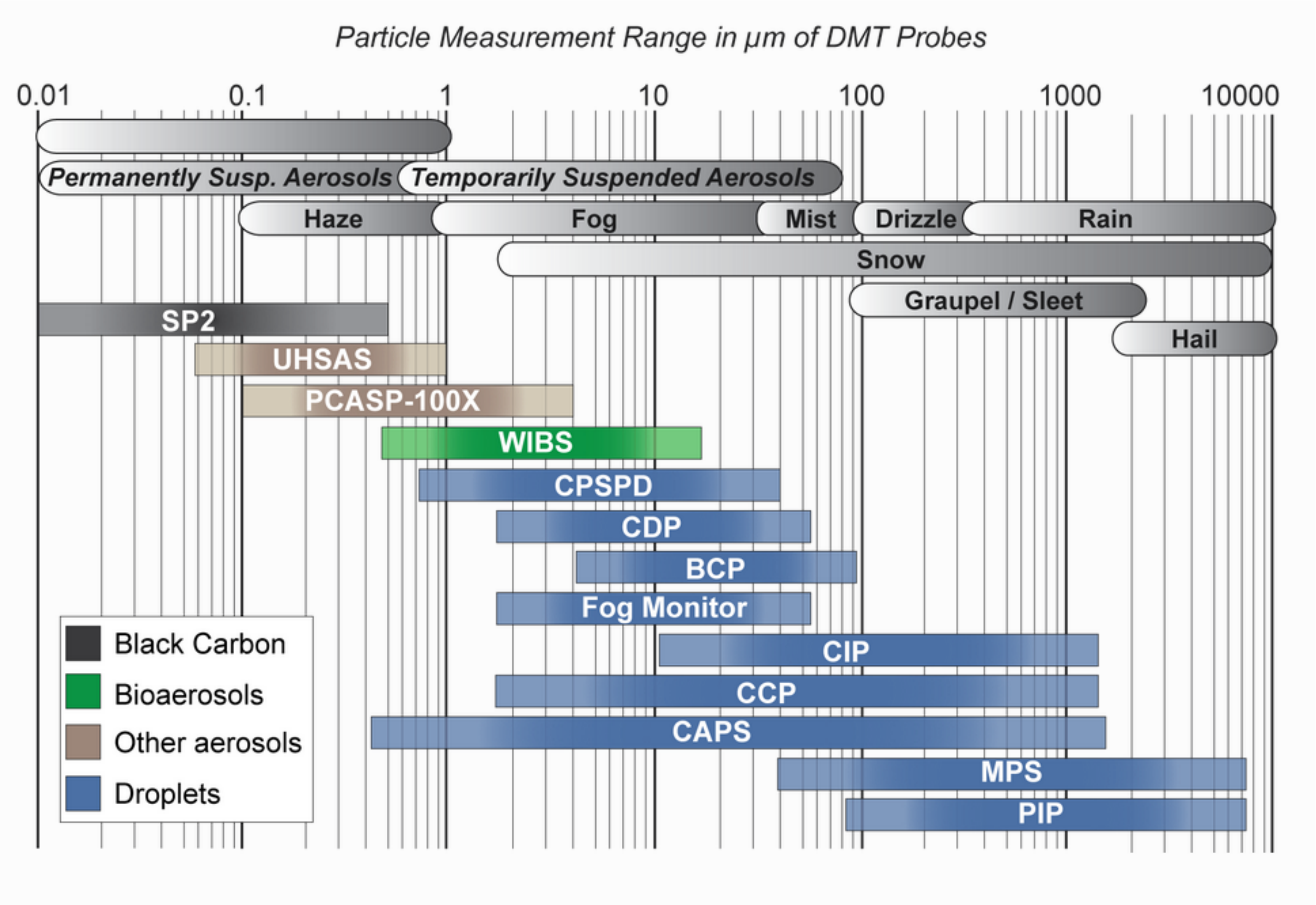
- methane,
- nitrous oxide, nitric oxide, nitrogen dioxide,
- carbon monoxide, carbon dioxide, formaldehyde,
- formic acid, ethylene, acetylene, carbonyl sulfide,
- acrolein, ammonia



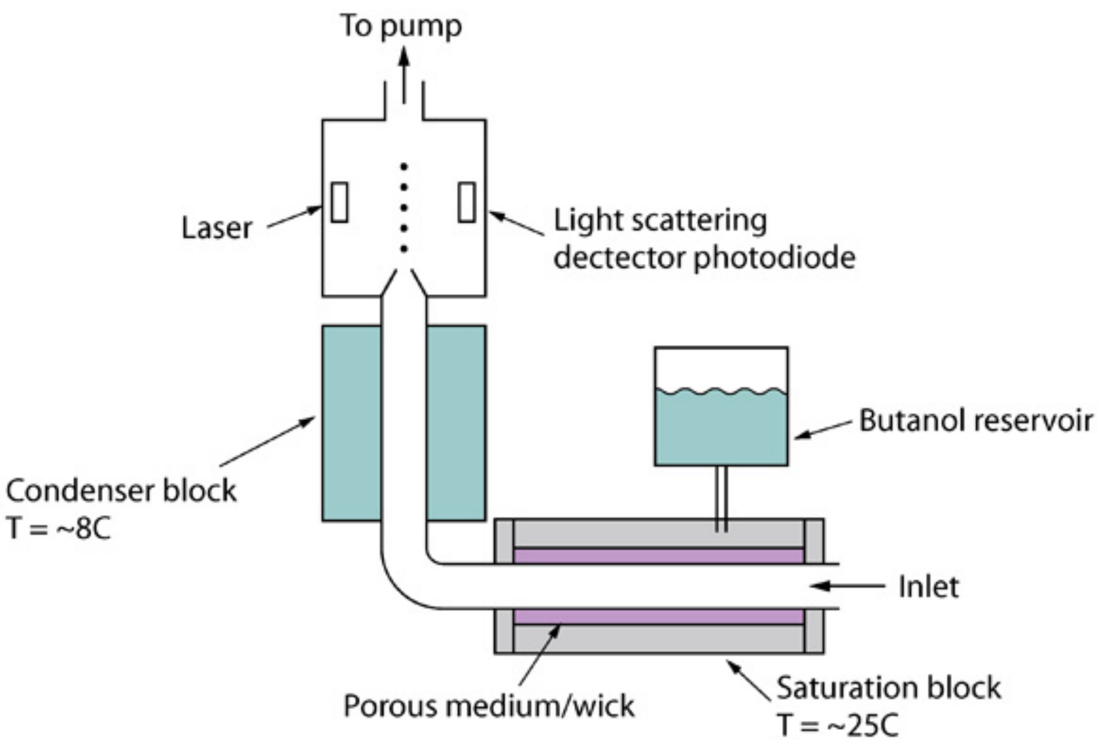
# *Aerosol Instrumentation*



# Particle measurement instruments

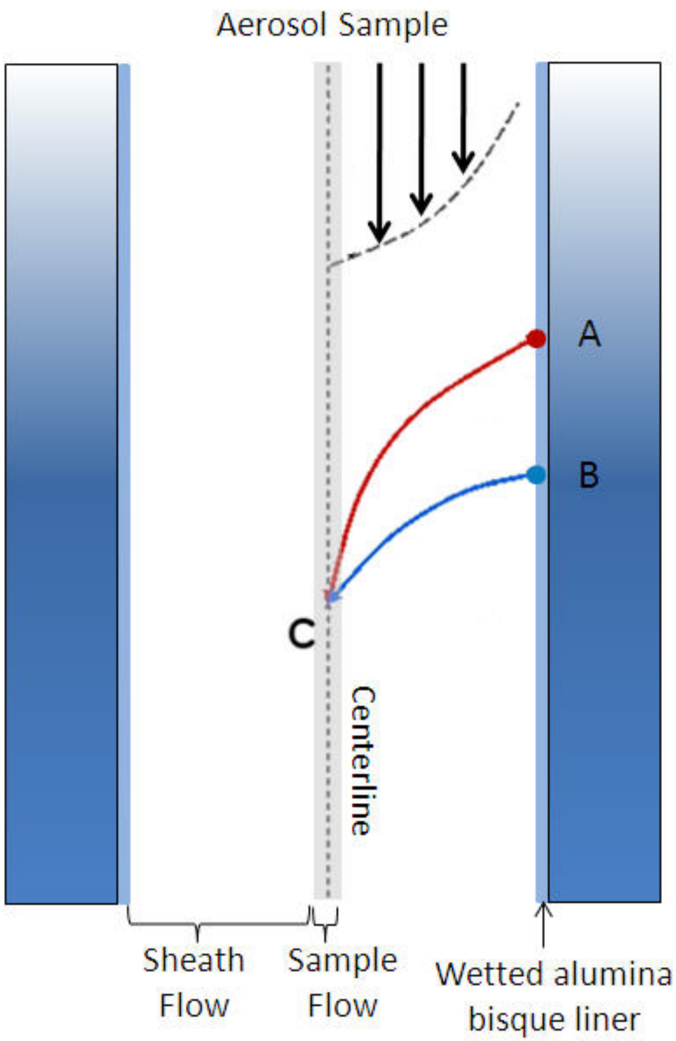


# *Condensation Nucleus Counter (CN)*




Particles > 5  (11) nm – depending on type of CN counter

# Cloud Condensation Nucleus Counter (CCN)





Thermal gradient diffusion chamber : measures particles that activate at controlled supersaturations

# *Ultra High Sensitivity Aerosol Spectrometer (particle sizes)*

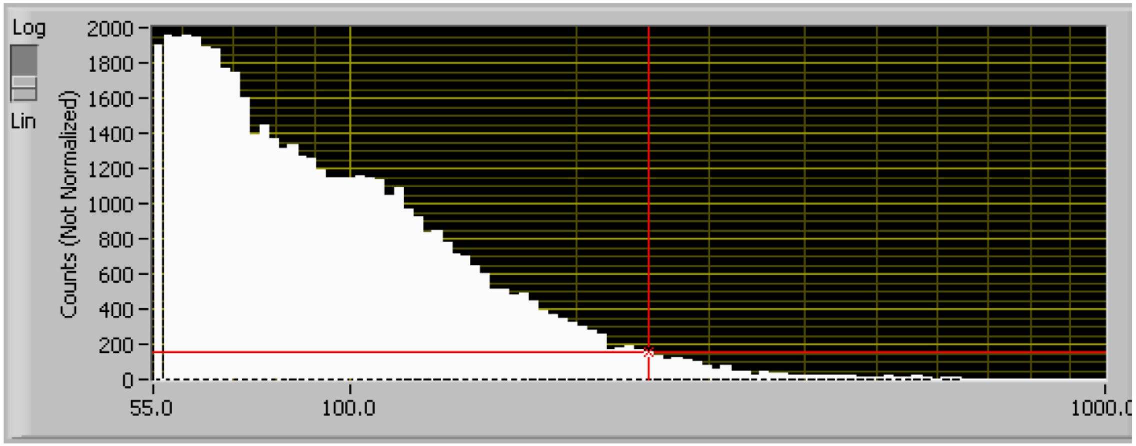



*Figure 14: Ambient-Air Distribution on a Properly Calibrated Instrument*

# *Ultra High Sensitivity Aerosol Spectrometer (particle sizes, 60 – 1000 nm)*

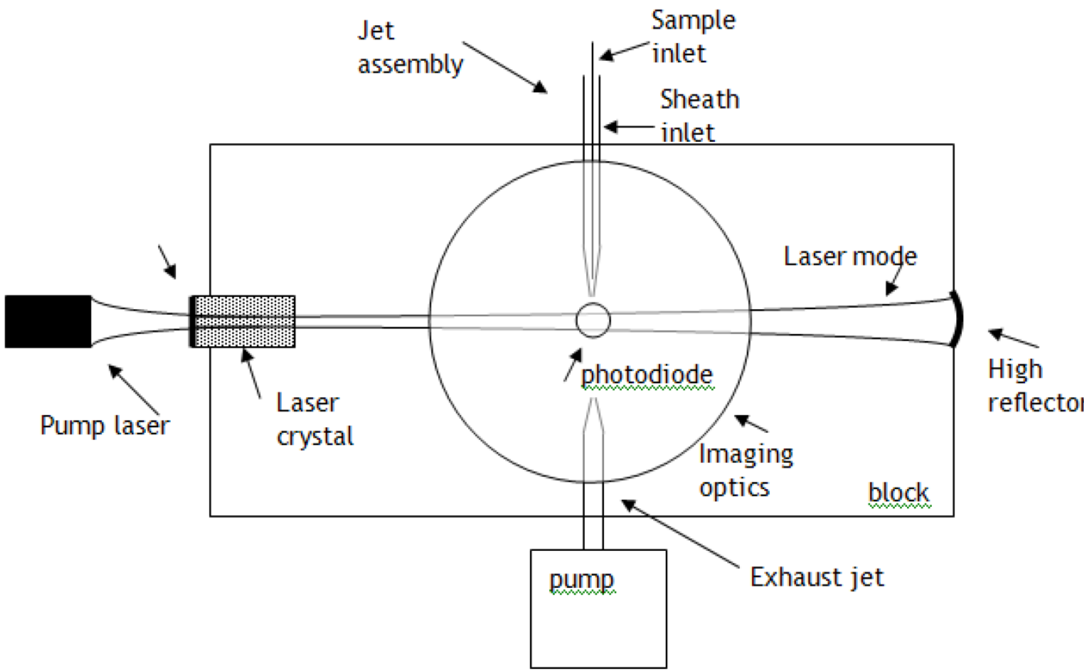



*Figure 3: Side View of Optical Block*

# *Single Particle Soot Photometer*

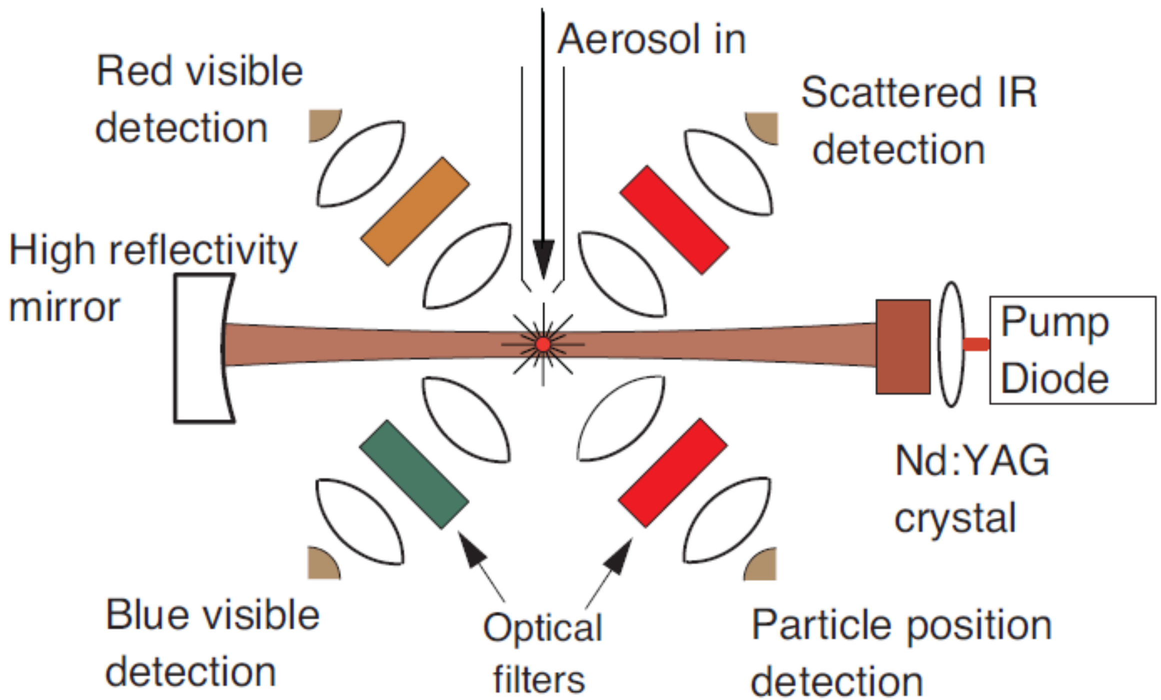
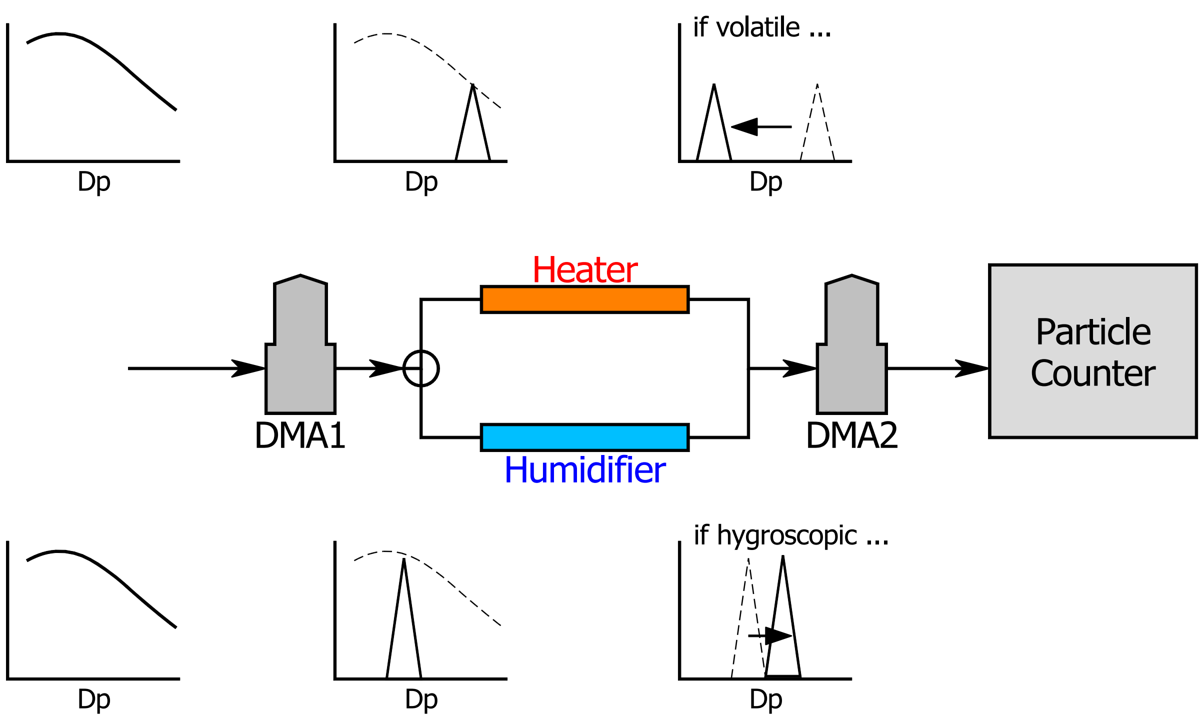


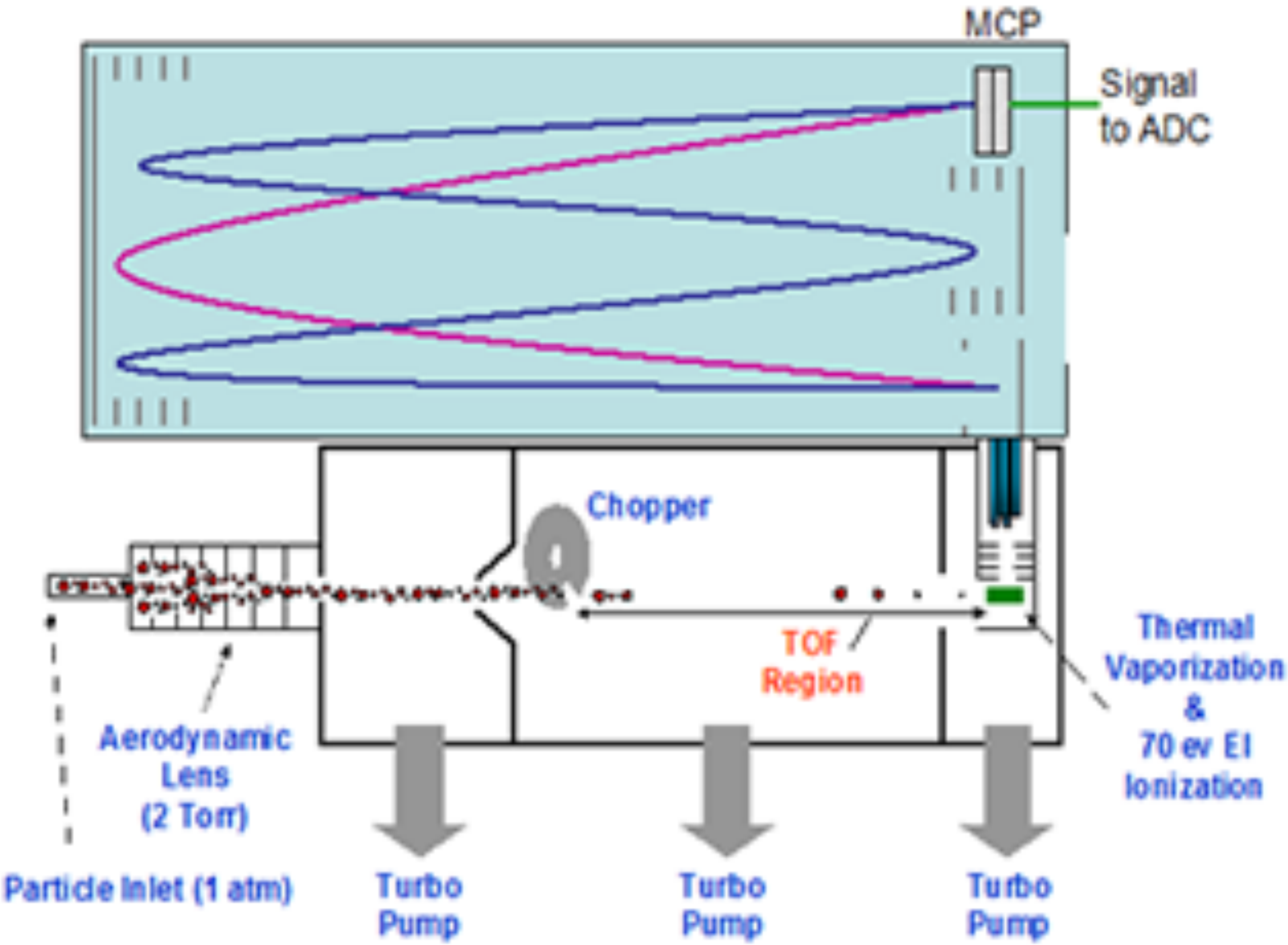

**Figure A3.** Schematic diagram of the SP2 photometer showing the basic optics and laser-induced incandescence and scattering detectors.

# Tandem Differential Mobility Analyzer (TDMA)

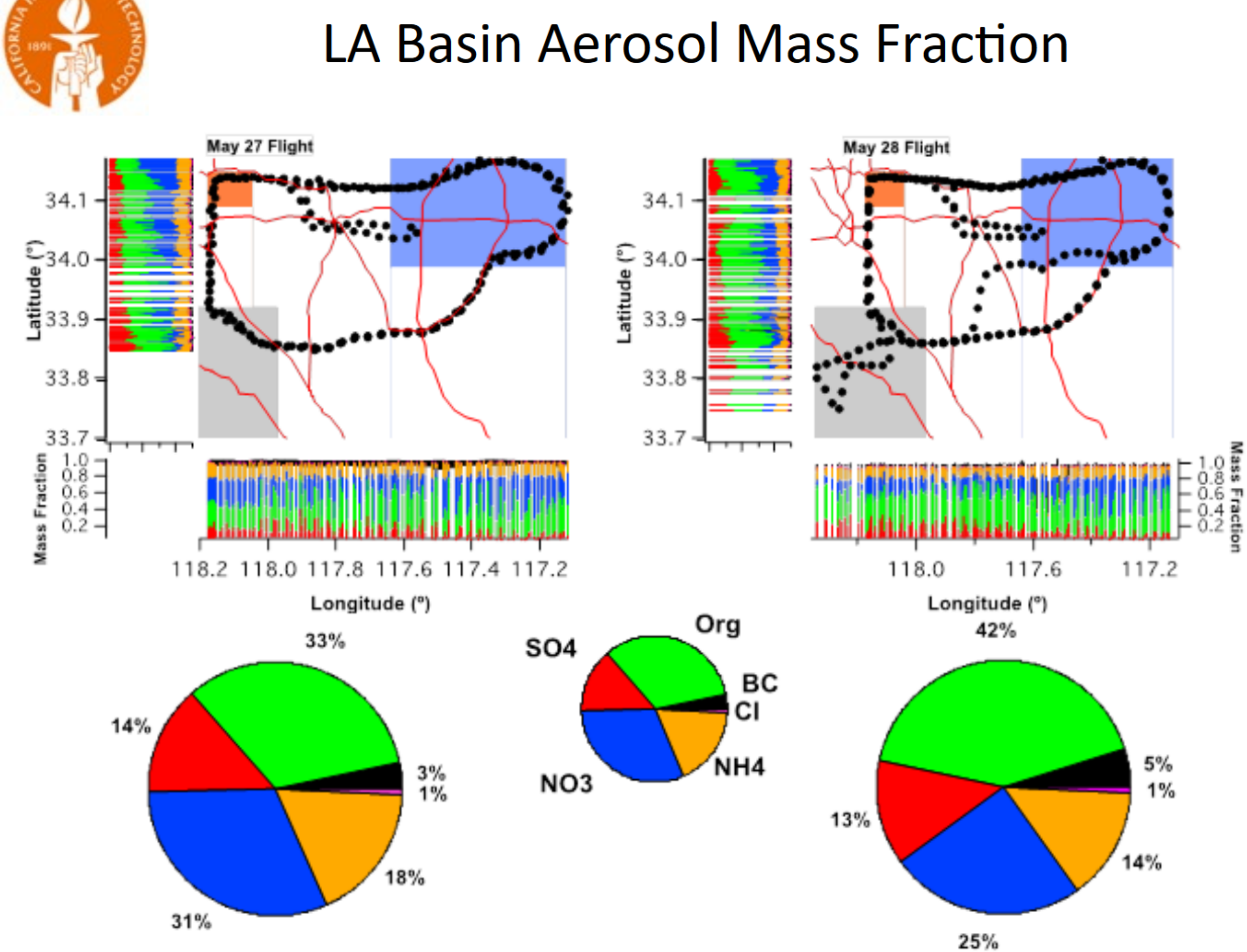



| | Volatility (~100 °C) | Hygroscopicity |
|---|---|---|
| **Sulfuric acid** | Volatile | Very hygroscopic |
| **Sulfates** (Totally or partially neutralized by ammonia) | Non-volatile | Very hygroscopic |
| **Organic carbons** | Volatile | Not or only slightly hygroscopic |

# *Aerosol HR – TOF - MS*

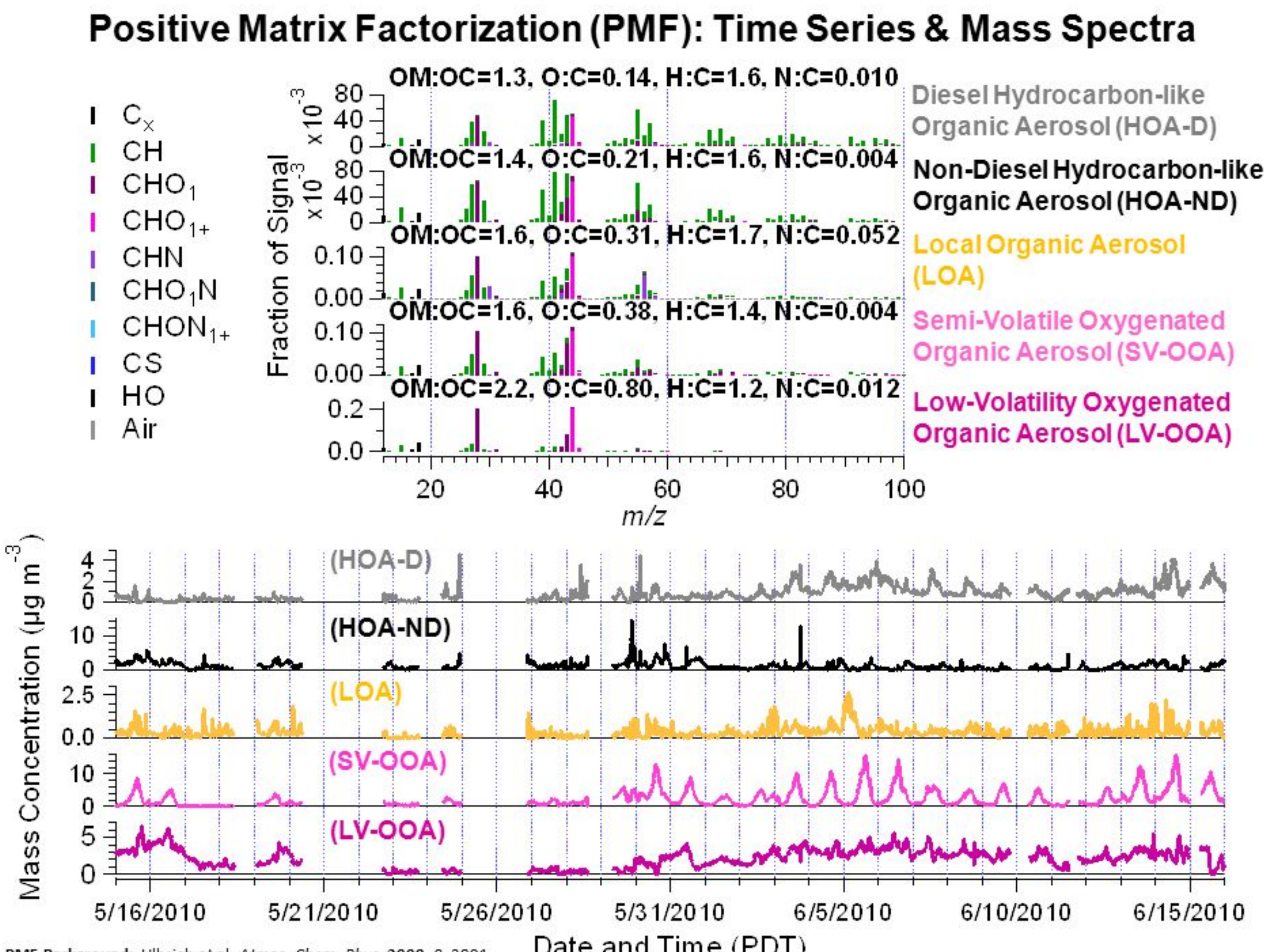


# *Aerosol composition over Los Angeles*




From J. Craven, CalTech, Calnex workshop

# Example of aerosol MS analysis




**PMF Background:** Ulbrich et al. *Atmos. Chem. Phys.* **2009**, *9*, 2891.

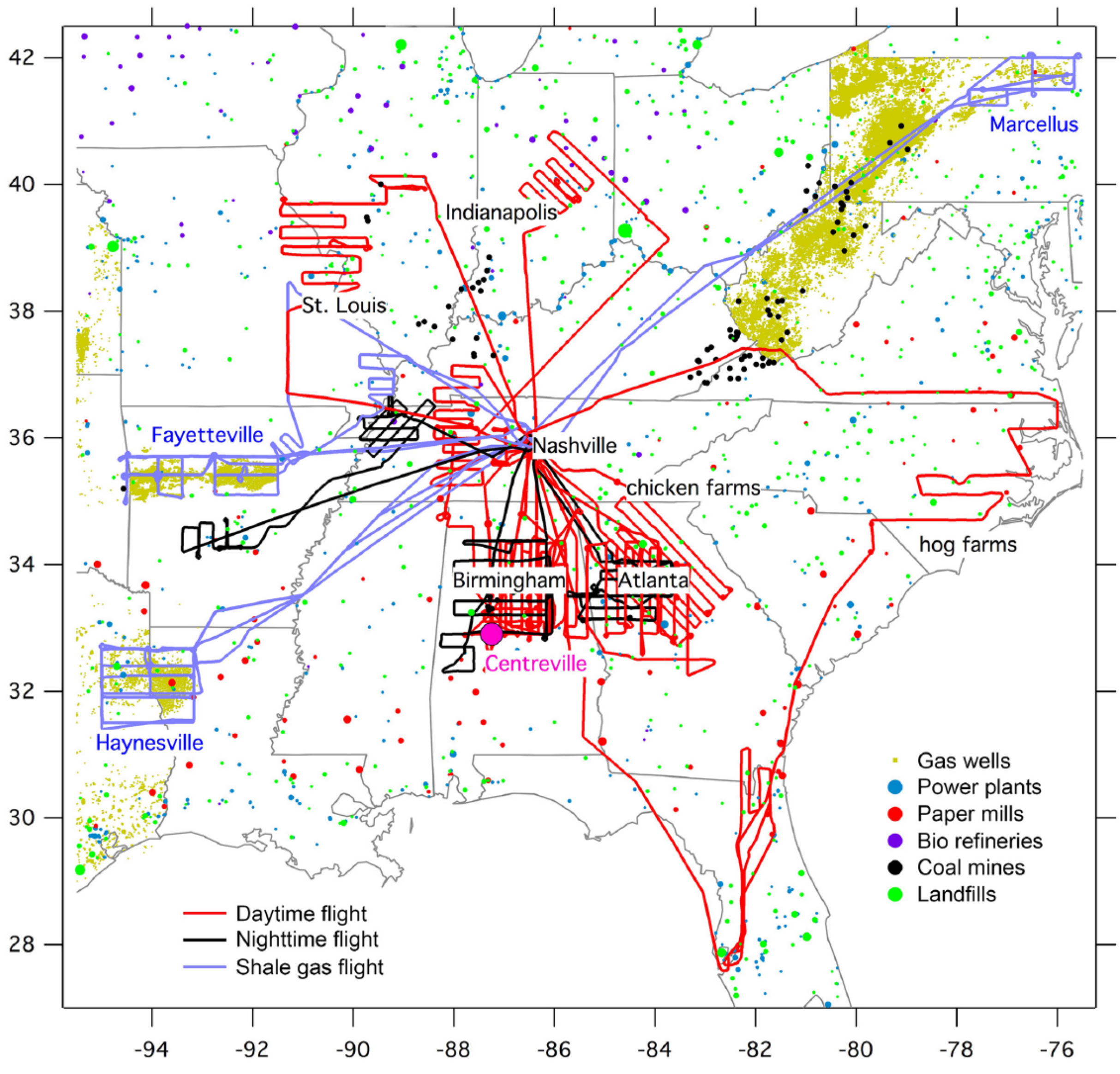
# *Airborne Research Campaign Examples*

# *SENEX Campaign (NOAA)*

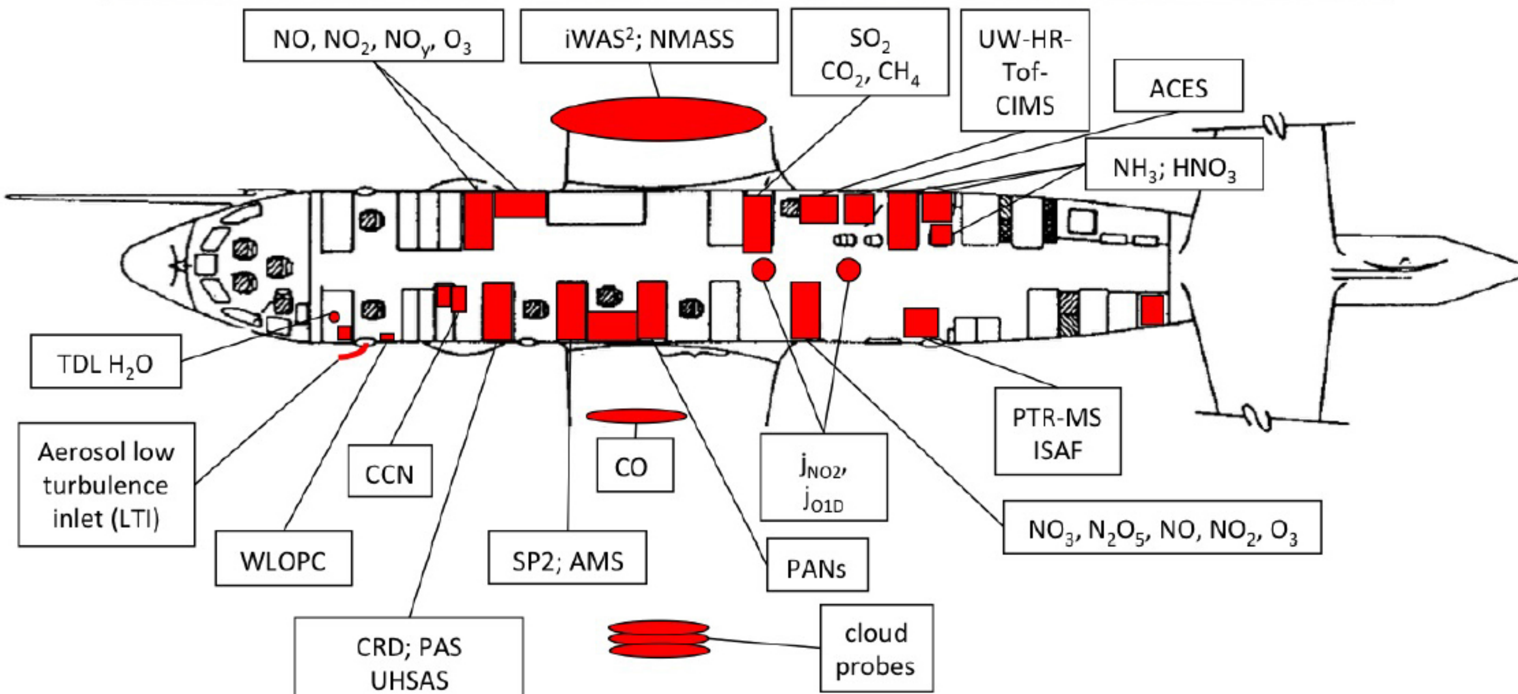
- Southeast Nexus - *Studying the Interactions between Natural and Anthropogenic Emissions at the Nexus of Climate Change and Air Quality*

  - *Understanding emissions of aerosols, ozone/aerosol precursors, greenhouse gases*
  - *Understanding formation mechanisms of secondary organic aerosol*
  - *Determine composition of aerosols*
  - *Determine climate relevant properties of aerosols*
  - *Quantify $CH_4$ and VOC emissions from shale gas operations*

# *SENEX aircraft flight tracks*



# C. Warneke et al.: Instrumentation and measurement strategy for the NOAA SENEX aircraft campaign


Atmos. Meas. Tech., 9, 3063–3093, 2016

| Aircraft parameters | Technique | Units | Uncertainty |
|---|---|---|---|
| Aircraft position | GPS latitude | ° | ±16 m |
| | GPS longitude | ° | ±16 m |
| | GPS altitude | m | ±16 m |
| | pressure altitude | m | ±10 m |
| | radar altitude above ground | m | ±15 m or 1–2 % |
| Aircraft meteorology | ambient temperature | °C | ±0.5 °C |
| | dew point temperature | °C | ±0.5 °C |
| | TDL dew point temperature | °C | 5 % |
| | $H_2O$ mixing ratio* | g $kg^{-1}$ | 5 % |
| | potential temperature | °K | ±0.5 K |
| | relative humidity* | % | ±5 % |
| | static pressure | mb | ±2.2 mb |
| | vertical wind speed | m $s^{-1}$ | ±0.5 m $s^{-1}$ |
| | wind direction | ° | 5° |
| | wind speed | m $s^{-1}$ | 1 m $s^{-1}$ |
| Aircraft miscellaneous | attack angle | ° | ±0.2° |
| | cabin pressure | mb | N/A |
| | ground speed | m $s^{-1}$ | ±3.4 m $s^{-1}$ |
| | heading | ° | ±0.5° |
| | pitch angle | ° | ±0.05° |
| | roll angle | ° | ±0.05° |
| | slip angle | ° | ±0.2° |
| | true air speed | m $s^{-1}$ | ±0.5 m $s^{-1}$ |

# Aerosol Instrumentation

| Measurement | Name/technique | Accuracy | Precision | Sample Interval |
|---|---|---|---|---|
| Low turbulence inlet | LTI: decelerating inlet to provide sample air to aerosol instruments in fuselage | N/A | N/A | N/A |
| Size distributions fine (0.004–1 µm) and coarse (1–8.3 µm) | parallel CPCs, and white and laser light scattering | | | 1s |
| Cloud condensation nuclei (CCN) spectra from 0.1–0.8 % supersaturation | CCN: Continuous-flow streamwise thermal-gradient CCN counter with scanning flow CCN analysis (SCFA) | Number: 10 % super-saturation: 0.04 % | 10 CCN $cm^{-3}$ | 60 s |
| Eight-cell optical extinction (dry 405, 532, 662 nm, 70 and 90 % RH 532 nm, thermodenuded 405 and 662 nm) | CRD: Cavity ring-down aerosol extinction spectrometer | < 2 % | 10 % 0.1 $Mm^{-1}$ | 1 s |
| Five-cell optical absorption (dry 405, 532, 662 nm, thermodenuded 405 and 662 nm) | PAS: Photoacoustic Absorption Spectrometer | 10 % | 1 $Mm^{-1}$ | 1 s |

# *Aerosol Instrumentation – cont'd*

| Measurement | Name/technique | Accuracy | Precision | Sample Interval |
|---|---|---|---|---|
| Refractory BC mass content of individual particles | SP2: Single-Particle Soot Photometer with laser-induced incandescence | 30 % | 0.5 fg (0.08 μm mass-equiv. diameter with 2 g $cc^{-1}$ density) | 1 s |
| Non-refractory, submicron sulfate, nitrate, ammonium, organic, and chloride mass concentrations | AMS: Aerosol Mass Spectrometer | 50 % | 0.05, 0.07, 0.24, 0.36, and 0.05 μg $sm^{-3}$ (study average) | 10 s |
| Cloud particle size distribution (0.6–50 μm)<br>(3–50 μm)<br>(50–6000 μm) | Cloud probes: Laser light forward and back scattering<br>laser light forward scattering<br>droplet imaging probe | | | 1 s |

# *Gas phase instrumentation*

| Measurement | Technique | Accuracy | Precision or Detec. Limit | Sample Interva |
|---|---|---|---|---|
| $CH_4$<br>$CO_2$ | wavelength-scanned cavity ring-down absorption spectroscopy | 0.07 ppm<br>1 ppb | 0.11 ppm<br>0.4 ppb | 1 s |
| CO | vacuum UV resonance fluorescence | 5 % | 0.5 ppb | 1 s |
| $SO_2$ | pulsed UV fluorescence | 20 % | 250 ppt | 1 s |
| NO<br>$NO_2$<br>$NO_y$<br>$O_3$ | Gas phase chemiluminescence | 3 %<br>4 %<br>12 %<br>2 % | 10 ppt<br>30 ppt<br>40 ppt<br>15 ppt | 1 s |
| Various VOCs | PTR-MS: proton transfer reaction mass spectrometer using $H_3O^+$ as reagent ion | 25 % | depending on signal and species | 1 s every 17 s |
| Hydrocarbons, oxygenated VOCs | iWAS: whole air sampler with immediate GC-MS analysis | 12–20 % | 4–7 ppt<br>ppt<br>ppt | 72/flight (3–8 s) |
| $HNO_3$<br>HCOOH<br>HONO | $HNO_3$-CIMS: chemical ionization mass spectrometer with $I^-$ as reagent ion | 20 % + 50 ppt<br>20 % + 120 ppt<br>40 % + 30 ppt | 25 ppt<br>40 ppt<br>25 ppt | 1 s |

# Gas phase instrumentation

| | | | | |
|---|---|---|---|---|
| $NH_3$ | $NH_3$-CIMS: chemical ionization mass spectrometer with protonated acetone dimers as reagent ion | 25 % + (0.02–0.5) ppb (depending on flight) | 0.02–0.07 ppb (depending on flight) | 1 s |
| PAN<br>PPN<br>APAN<br>$ClNO_2$ | PAN-CIMS: chemical ionization mass spectrometry with $I^-$ as reagent ion | 0.04–0.05 ppb<br>0.04–0.1 ppb<br>0.01–0.02 ppb<br>0.01–0.02 ppb | 0.01 ppb<br>0.003 ppb<br>0.006 ppb<br>0.02 ppb | 2 s |
| Various oxygenated VOCs<br>$ClNO_2$<br>$N_2O_5$<br>Alkyl nitrates | UW HR-ToF-CIMS: chemical ionization mass spectrometer with $I^-$ as reagent ion | 50 % | depending on signal and species | 1 s |
| glyoxal<br>$NO_2$ | ACES: cavity enhanced absorption spectroscopy | 5.8 %<br>5 % | 34 pptv<br>80 ppt | 10 s<br>5 s |
| NO<br>$NO_2$<br>$O_3$<br>$NO_3$<br>$N_2O_5$ | CRDS: cavity ring-down absorption spectrometer | 5 %<br>5 %<br>10 %<br>20 %<br>12 % | 1 ppbv<br>0.2 ppbv<br>0.2 ppbv<br>3 pptv<br>3 pptv | 1 s |
| HCHO | In Situ Airborne Formaldehyde (ISAF): laser induced fluorescence | 10 % | 36 ppt | 1 s |
| $j_{NO_2}$ and $j_{O1D}$ | $j$-heads: filter radiometers | 10 % | | 1 s |

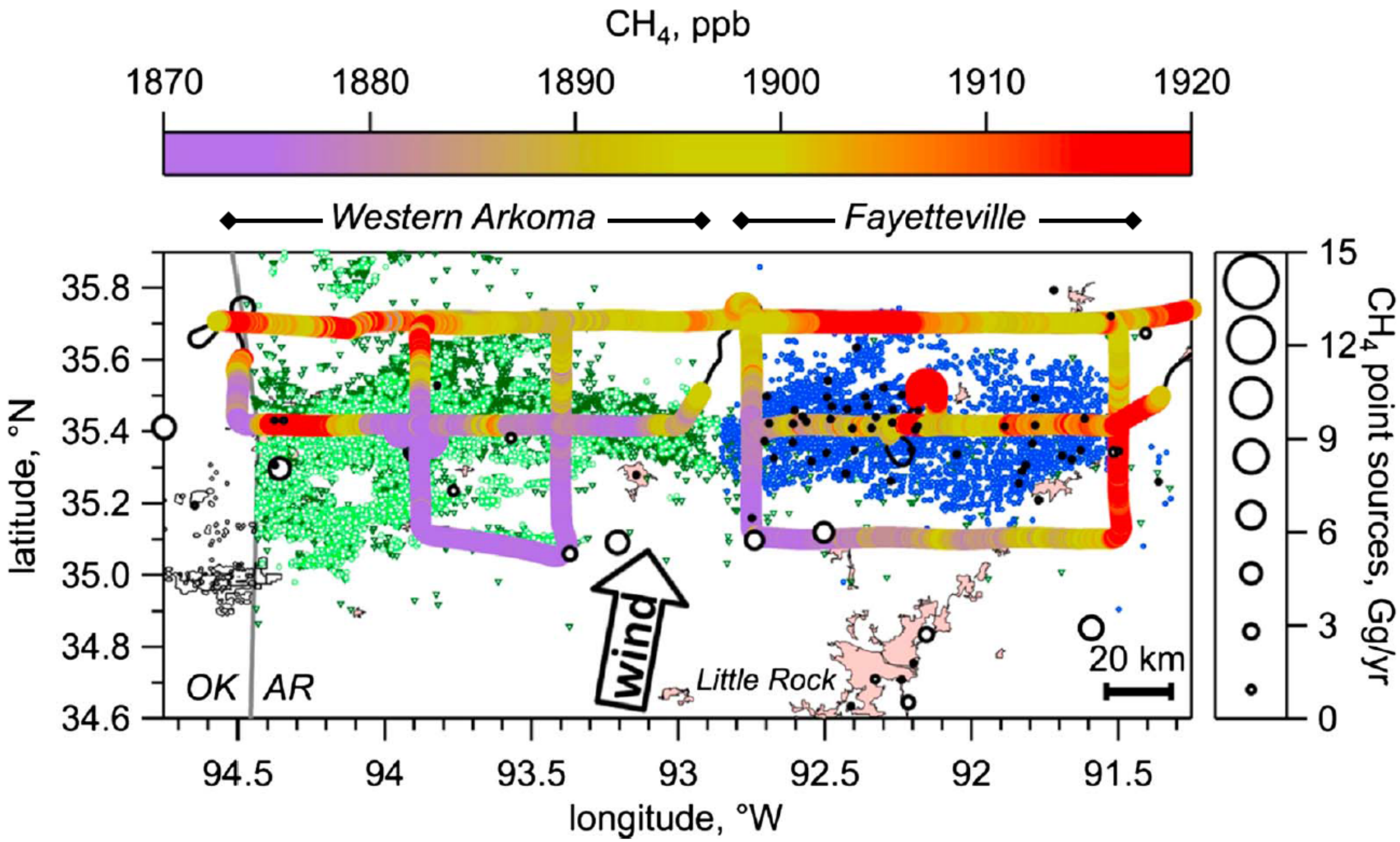
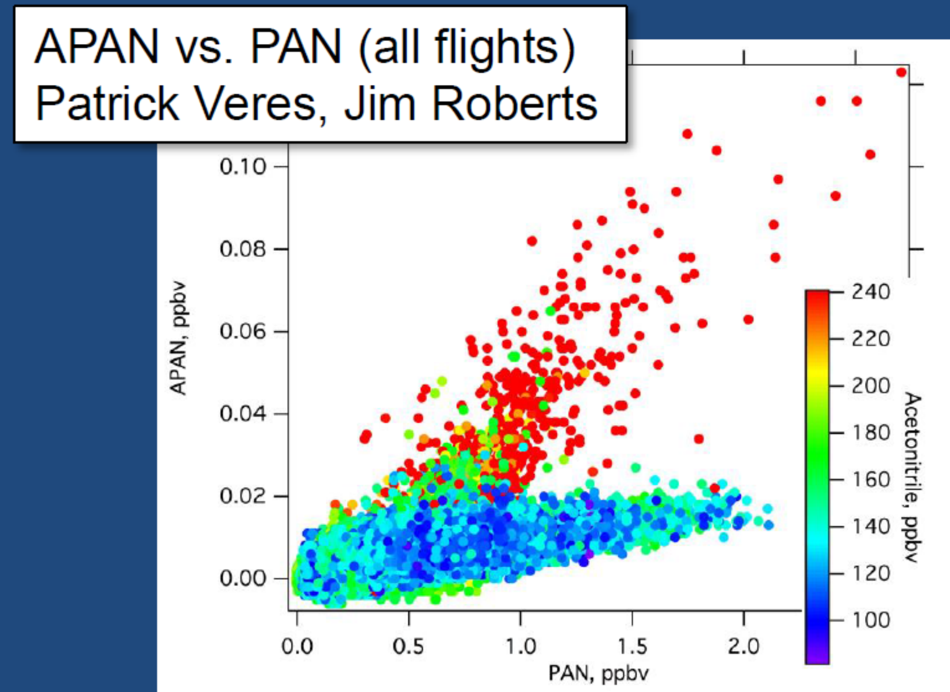


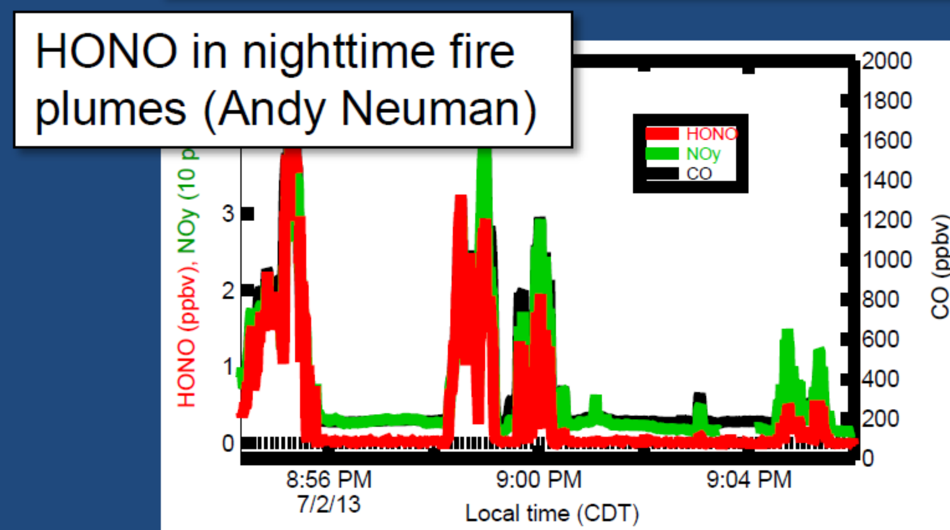

**Table 2.** Summary of $CH_4$ Emissions From Study Regions

| Region | Haynesville | Western Arkoma | Fayetteville | Marcellus |
|---|---|---|---|---|
| $CH_4$ flux ($10^7$ g/h) | 8.0 ± 2.7 | 3.3 ± 1.5 | 3.9 ± 1.8 | 1.5 ± 0.6 |
| $CH_4$ from livestock and non-oil-and-gas point sources ($10^7$ g/h) | 0.6 | 0.7 | 0.4 | 0.2 |
| Natural gas production in June 2013 ($10^7$ $m^3$/d) | 20 ± 3 | 0.9 | 7.6 | 18 ± 1 |
| $CH_4$ in natural gas | (90 ± 7)% | (95 ± 5)% | (94 ± 5)% | (96 ± 3)% |
| Natural gas loss rate | 1.0–2.1% | 6–20% | 1.0–2.8% | 0.18–0.41% |

Peischl et al., 2016, JGR

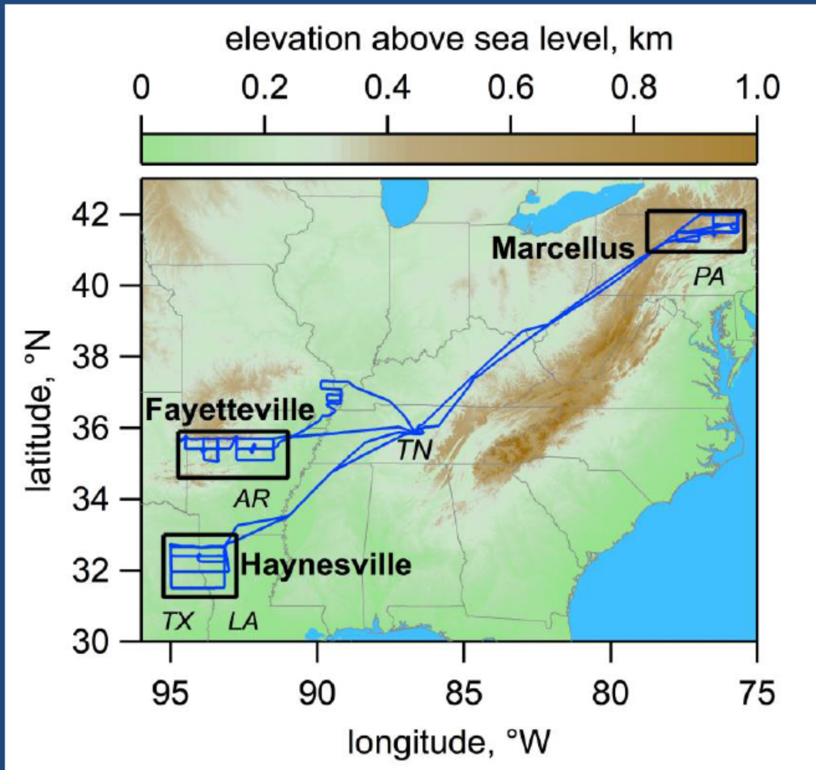
# What is the Importance of Biomass Burning Emissions?

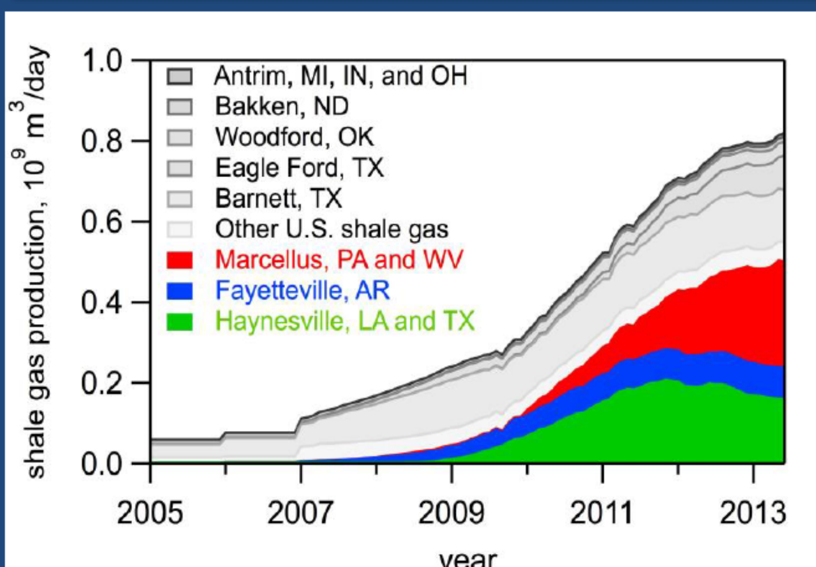



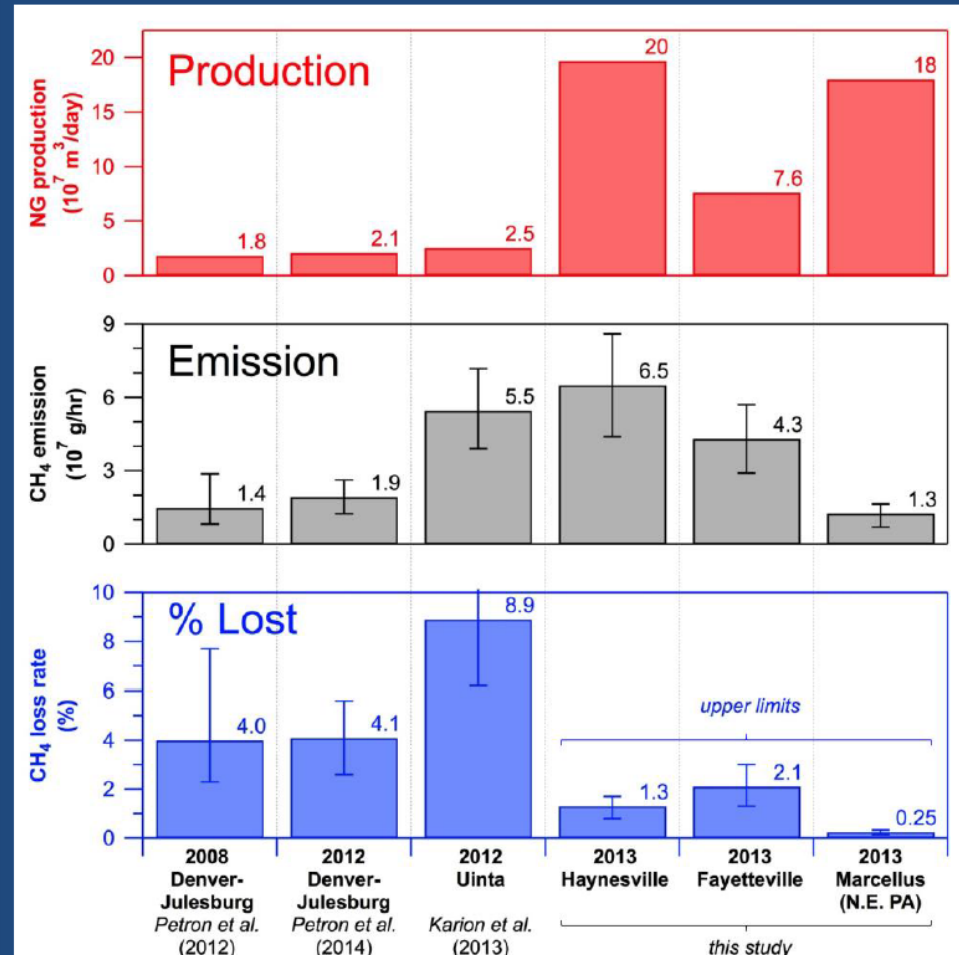




From J. DeGouw, et al. presentation

# Emissions from Production of Natural Gas




Studied basins have lower leak rates than basins in Utah and Colorado
Peischl et al. [JGR 2015]

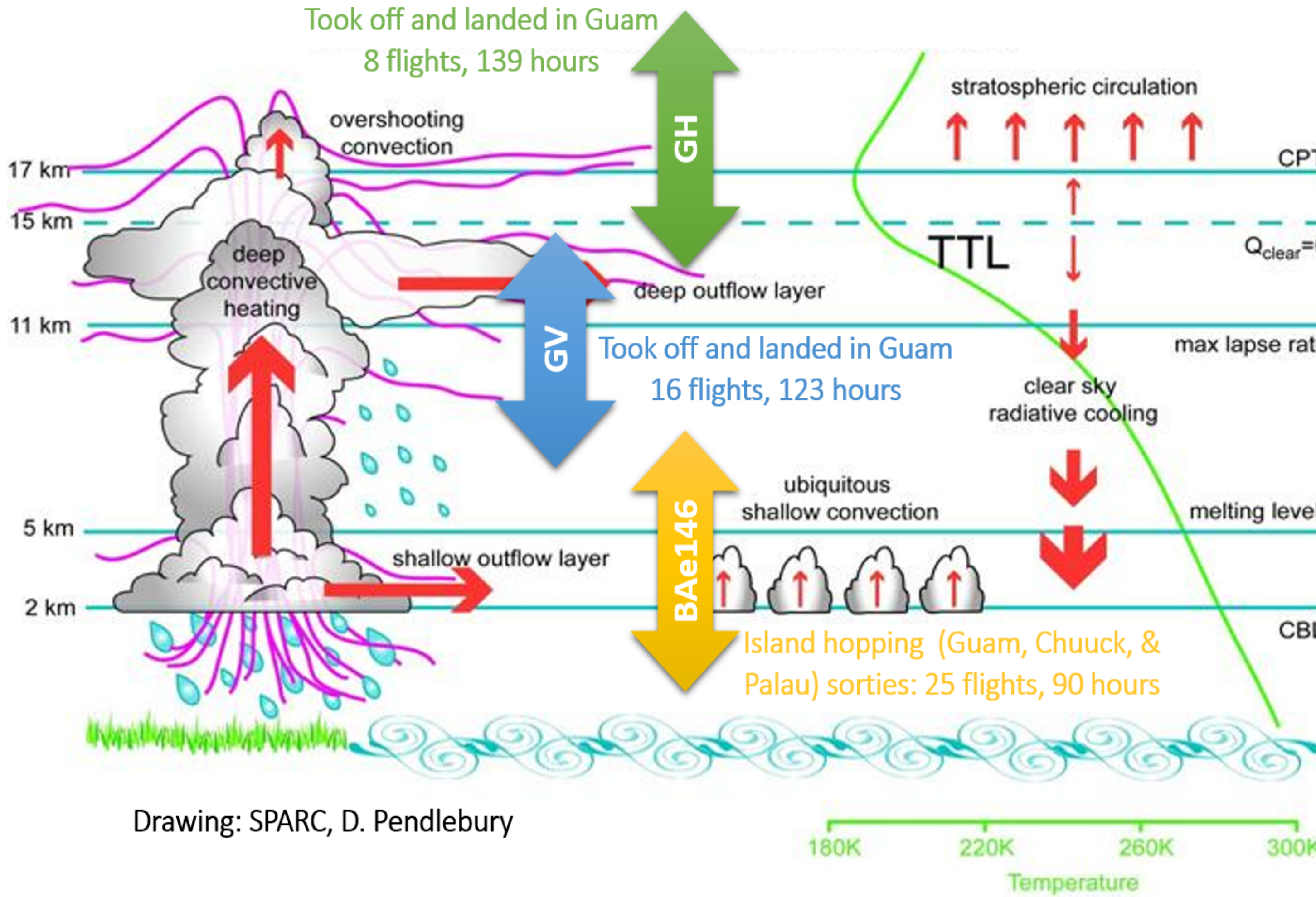
## *CONTRAST – Convective Transport of Reactive Species in the Tropics*

- Characterize chemical composition and $O_3$ photochemical budget at level of convective outflow in the Western Pacific during the deep convective season

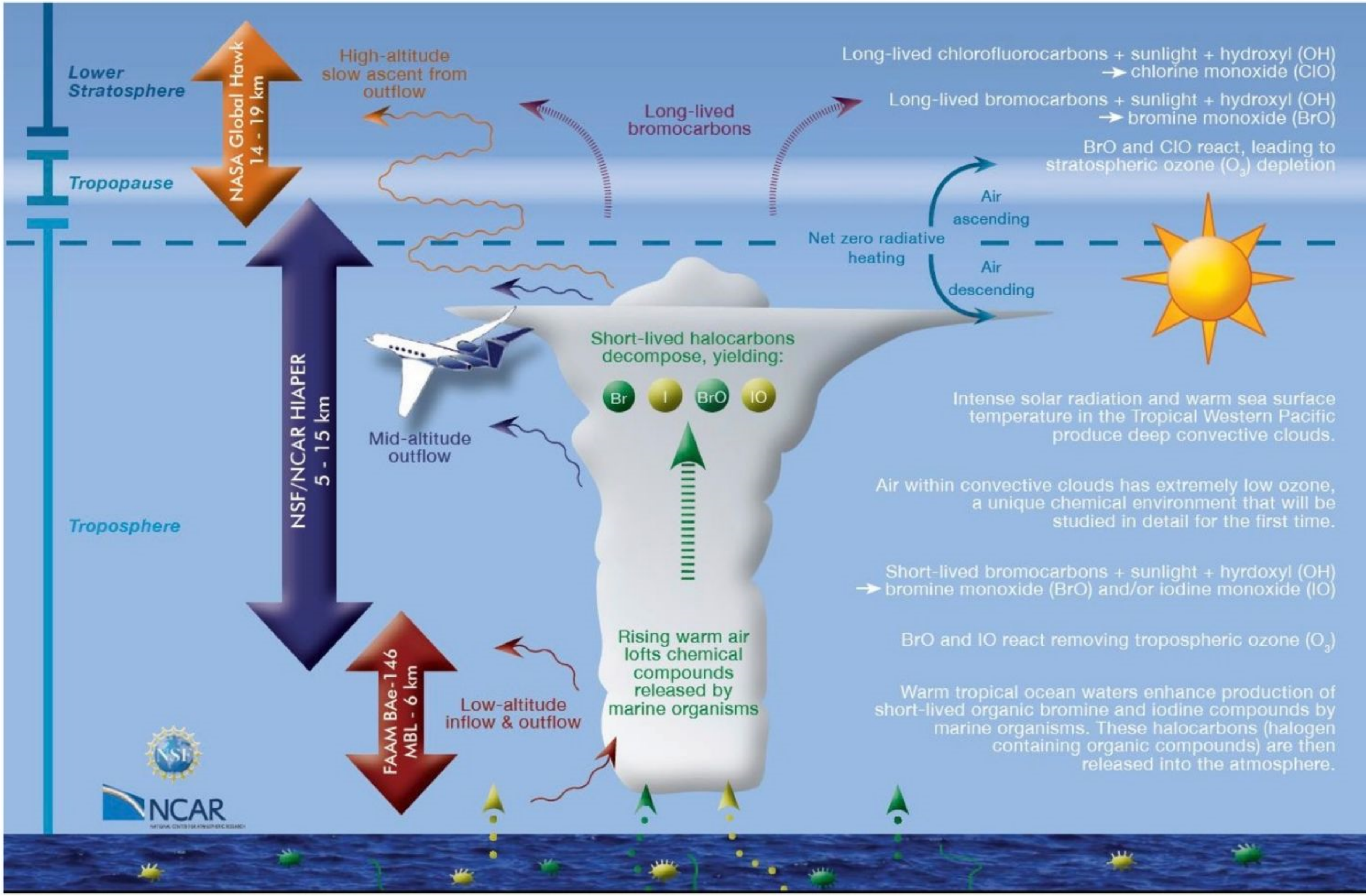
- Evaluate the budget of organic and inorganic halogens in the tropical TTL

- Investigate transport pathways from the ocean surface to the tropopause via coordinated flights of the GV (CONTRAST), BAe-146 (CAST), Global Hawk (ATTREX) & data from ozone sondes (SOWER & CAST) and water sondes (ATTREX & SOWER)

# Synergistic sampling of ATTREX (GH), CONTRAST (GV) and CAST (BAe-146) Aircraft

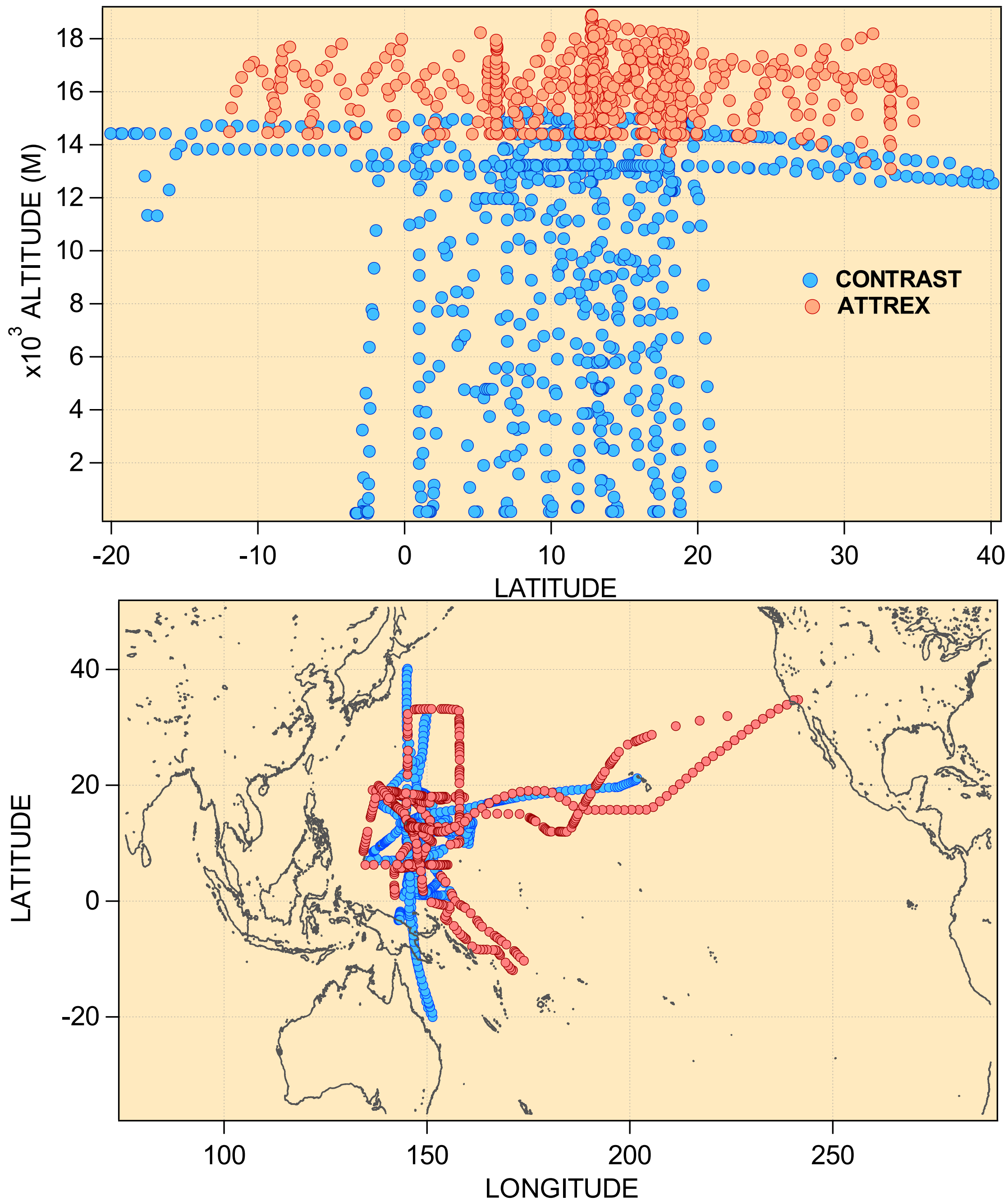



Drawing: SPARC, D. Pendlebury



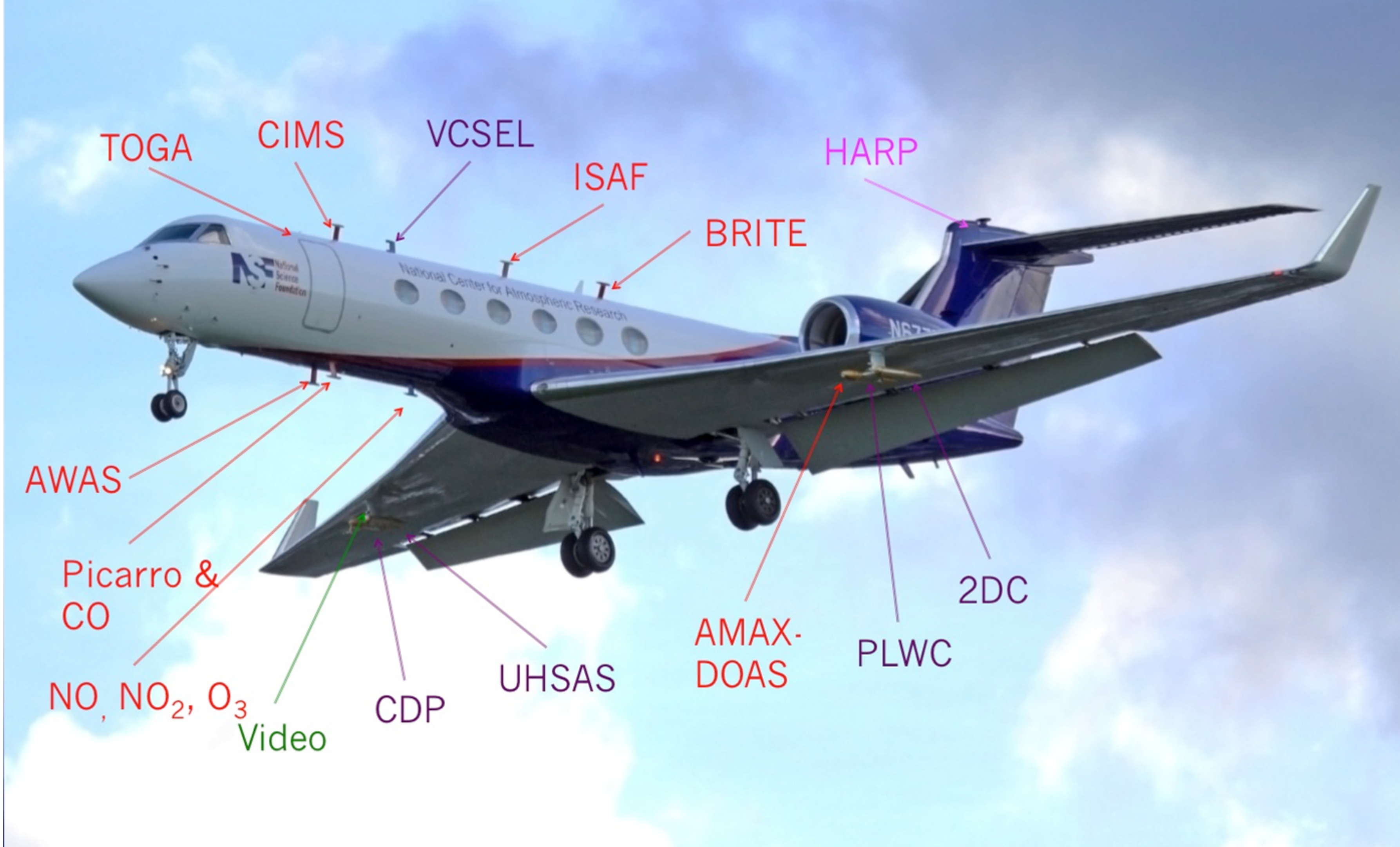
Lower Stratosphere
Tropopause
Troposphere
NASA Global Hawk 14 - 19 km
NSF/NCAR HIAPER 5 - 15 km
FAAM BAe-146 MBL - 6 km
High-altitude slow ascent from outflow
Long-lived bromocarbons
Long-lived chlorofluorocarbons + sunlight + hydroxyl (OH) → chlorine monoxide (ClO)
Long-lived bromocarbons + sunlight + hydroxyl (OH) → bromine monoxide (BrO)
BrO and ClO react, leading to stratospheric ozone ($O_3$) depletion
Air ascending
Net zero radiative heating
Air descending
Short-lived halocarbons decompose, yielding:
Br
I
BrO
IO
Mid-altitude outflow
Intense solar radiation and warm sea surface temperature in the Tropical Western Pacific produce deep convective clouds.
Air within convective clouds has extremely low ozone, a unique chemical environment that will be studied in detail for the first time.
Short-lived bromocarbons + sunlight + hyrdoxyl (OH) → bromine monoxide (BrO) and/or iodine monoxide (IO)
BrO and IO react removing tropospheric ozone ($O_3$)
Rising warm air lofts chemical compounds released by marine organisms
Low-altitude inflow & outflow
Warm tropical ocean waters enhance production of short-lived organic bromine and iodine compounds by marine organisms. These halocarbons (halogen containing organic compounds) are then released into the atmosphere.
NSF
NCAR

# AWAS/GWAS Sample Locations



# NSF/NCAR Research Aircraft Gulfstream V (GV)

## the GV Payload for the CONTRAST Campaign



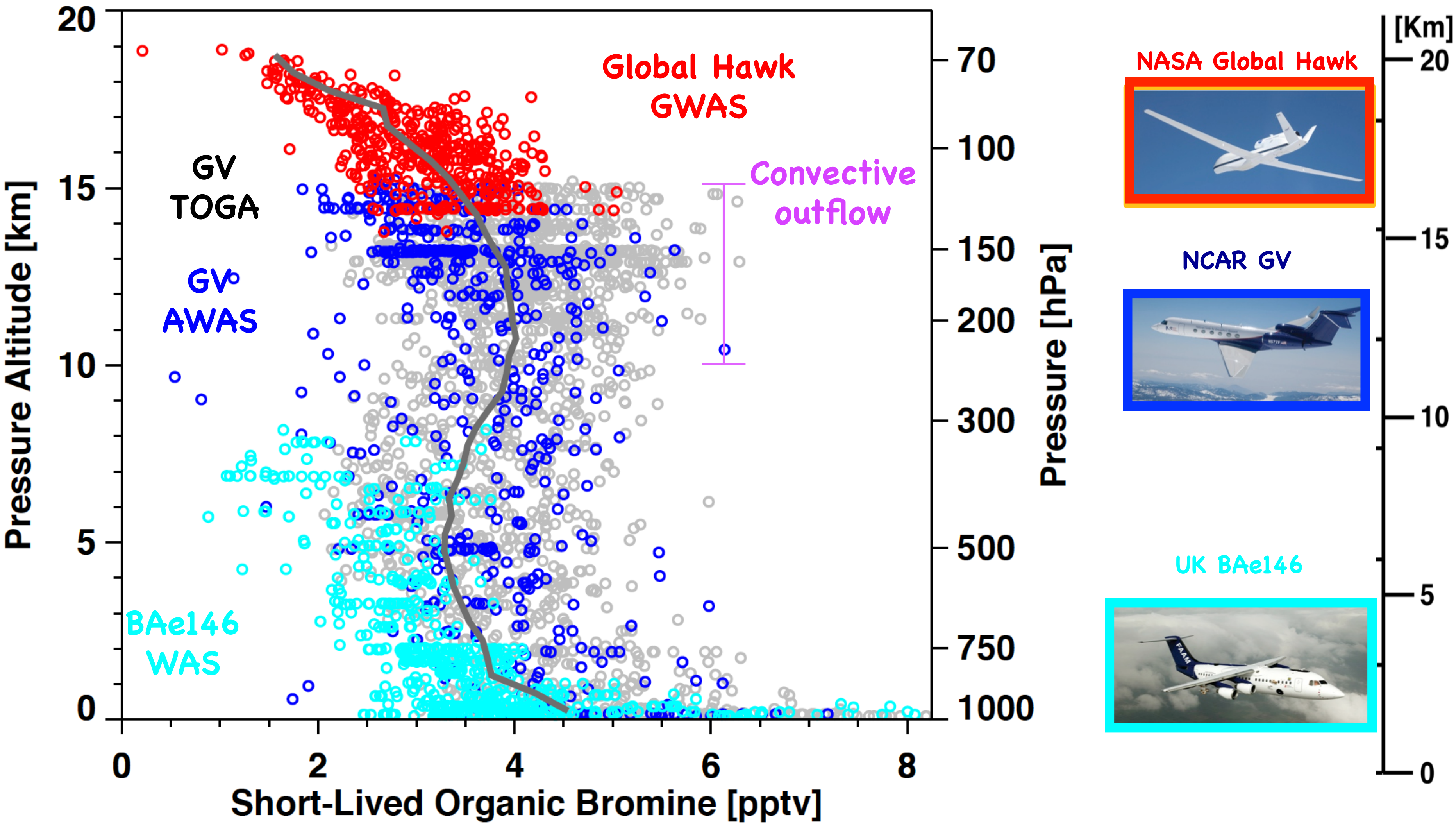
# CONTRAST – Payload (1)

| Chemistry | | Investigator | GH | BAe-146 |
|---|---|---|---|---|
| **$NO_x$** | NO, $NO_2$ | Weinheimer/NCAR ACD | NO | YES |
| **Fast Ozone** | $O_3$ | Weinheimer/NCAR ACD | YES | YES |
| **VUV Carbon Monoxide** | CO | Campos/NCAR ACD | YES | YES |
| **Picarro** | $CO_2$, $CH_4$ | Campos/NCAR ACD | YES | YES |
| **TOGA** | NMHCs, OVOCs | Apel, Hornbrook/NCAR ACD & Riemer / U Miami | NO | YES |
| **GT-CIMS** | BrO, BrCl, HOBr, ClO | Huey/GIT | NO | YES |
| **AMAX** | BrO, IO, $H_2CO$ (remote) | Volkamer/CU | YES | NO |
| **HAIS Advanced Whole Air Sampler (AWAS)** | Trace gases | Atlas/U.Miami | YES | YES |
| **In Situ Airborne Formaldehyde (ISAF)** | $H_2CO$ | Hanisco/ NASA GSFC | NO | NO |
| **Inorganic Br (BRITE)** | Br* (Σ BrO + Br) | Atlas/U.Miami & Flocke/ACD | NO | NO |
| | | | | |
| **Radiation** | | | | |
| **HARP** | Spectral Actinic Flux | Hall /NCAR ACD | YES | YES |

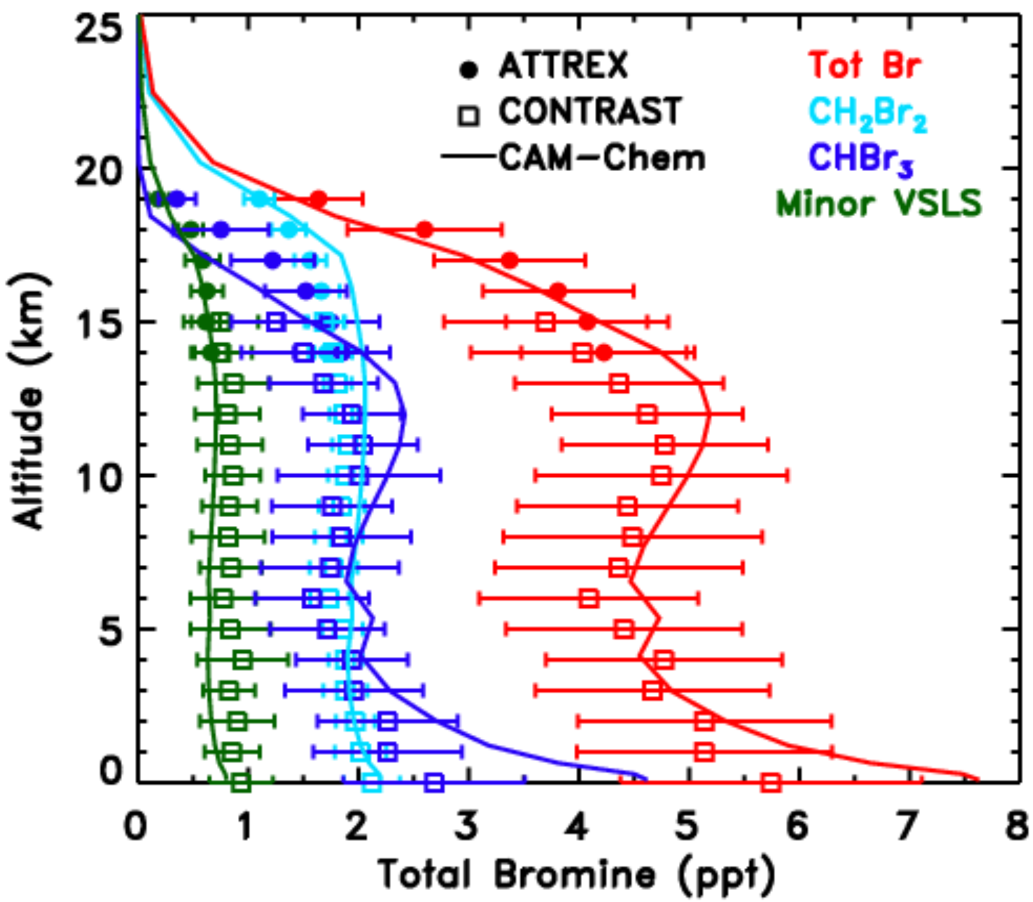
# CONTRAST – Payload (2)

| | | |
|---|---|---|
| State parameters | | |
| **State Parameters** | Lat/Lon, P, T, 3D wind | Jensen/NCAR RAF |
| **RAF Digital Video** | Four Direction views | Jensen/NCAR RAF |
| | | |
| **Microphysics** | | |
| **CDP Cloud Probe** | 2 - 50 um, water droplets, ice crystals | Jensen/NCAR RAF |
| **2D-C Precipitation Probe** | 25-1600 um, ice, water | Jensen/NCAR RAF |
| **UHSAS Aerosol Probe** | 0.075 - 1 um, aerosols | Jensen/NCAR RAF |
| **WCN CN Counter** | 0.01 - 3 um, aerosols | Jensen/NCAR RAF |
| **VCSEL Laser Hygrometer** | water vapor | Jensen/NCAR RAF |

# How does convection redistribute short-lived species in the tropics?

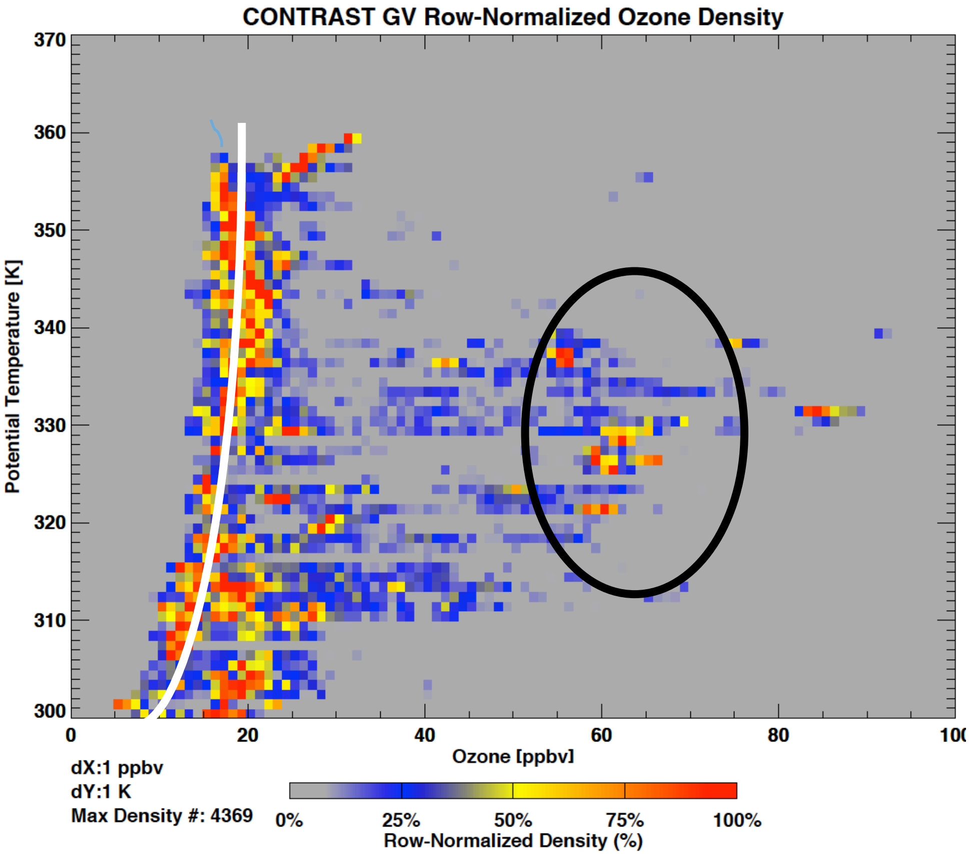


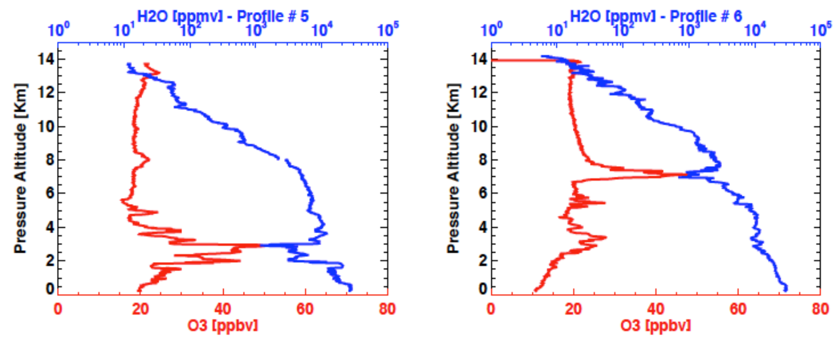
## How well are the vertical distributions of halogenated species represented in the CCMs ?



# What controls the ozone structure in the tropics?

## - Is the ozone enhancement produced by the dry intrusions or biomass burning?




- bi-modal structure: 20 and 60 ppbv
- Enhancement was often observed as filaments anti-correlated with water vapor
- Also observed positive correlation of ozone-HCN

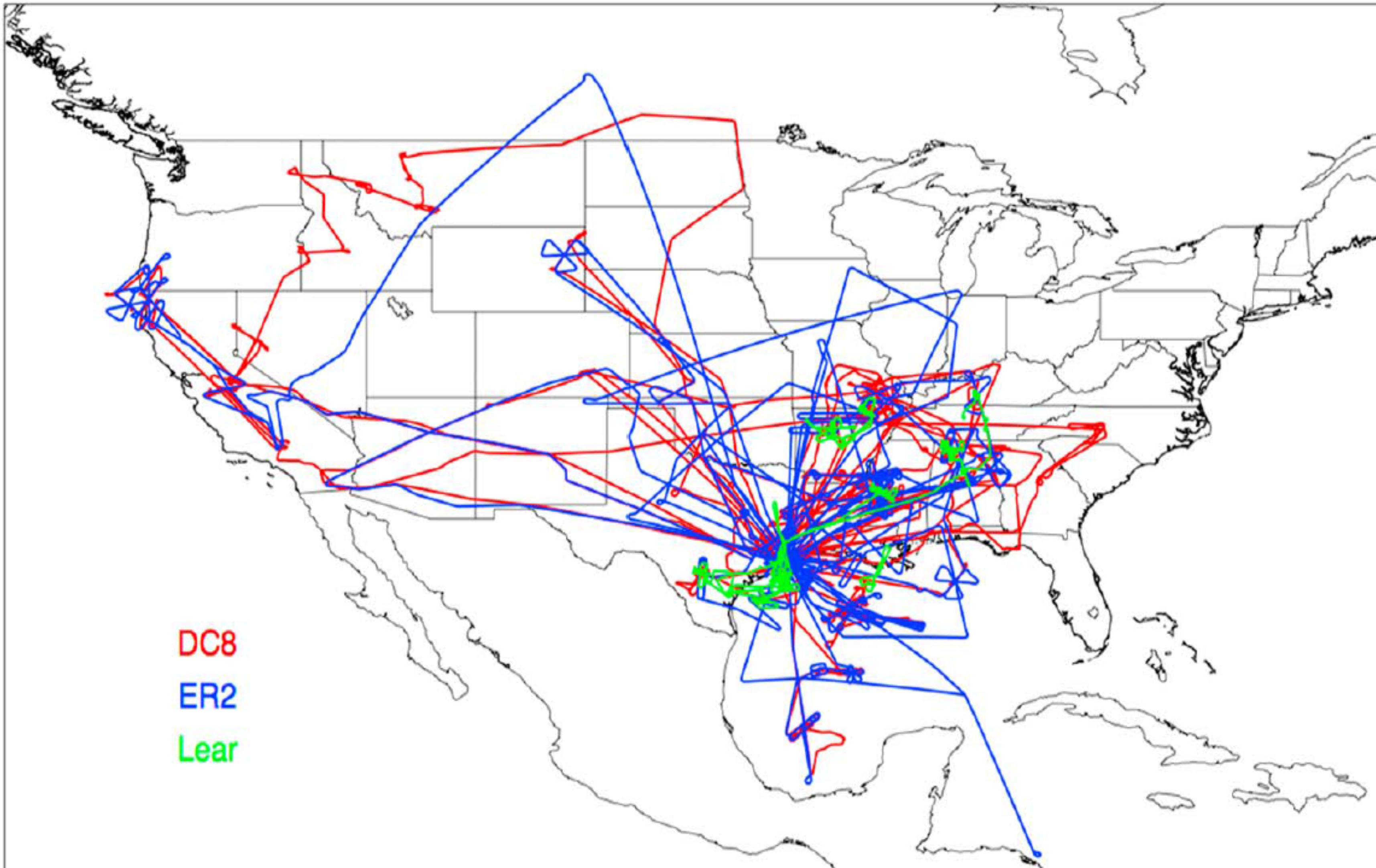
## *The Studies of Emissions and Atmospheric Composition, Clouds and Climate Coupling by Regional Surveys SEAC⁴RS*

**Table 1.** Major Goals of SEAC$^4$RS

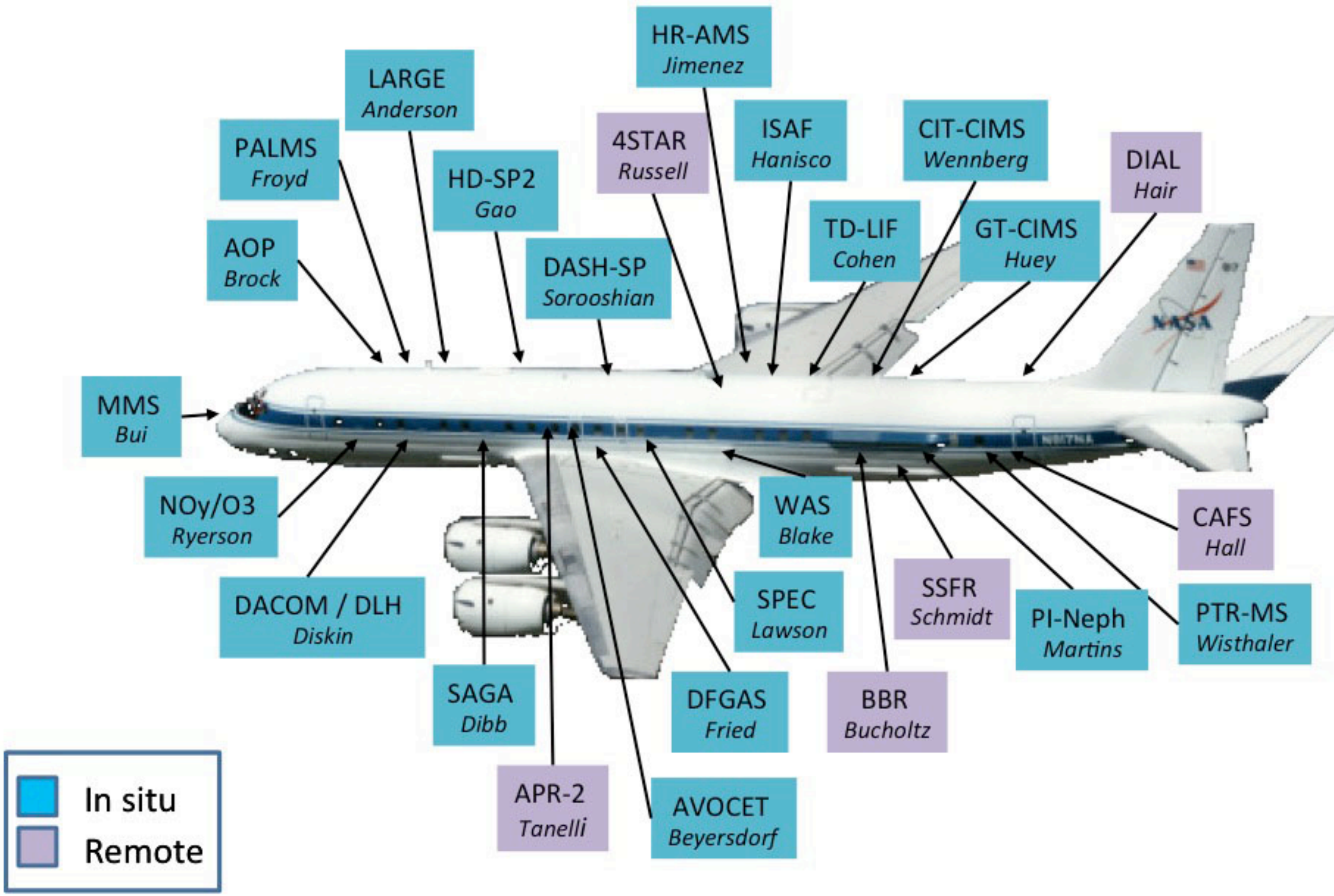
| | Goal |
|---|---|
| 1. | To determine how pollutant emissions are redistributed via deep convection throughout the troposphere. |
| 2. | To determine the evolution of gases and aerosols in deep convective outflow and the implications for chemistry in the upper troposphere and lower stratosphere. |
| 3. | To identify the influences and feedbacks of aerosol particles from anthropogenic pollution and biomass burning on meteorology and climate through changes in the atmospheric heat budget or through microphysical changes in clouds. |
| 4. | To understand how anthropogenic and biogenic emissions interact to control tropospheric ozone and aerosol concentrations. |
| 5. | To serve as a calibration/validation test bed for future satellite instruments and missions. |

From B. Toon et al., JGR, 2016

# *The Studies of Emissions and Atmospheric Composition, Clouds and Climate Coupling by Regional Surveys*
# *SEAC[4]RS*



# SEAC4RS DC-8 Payload

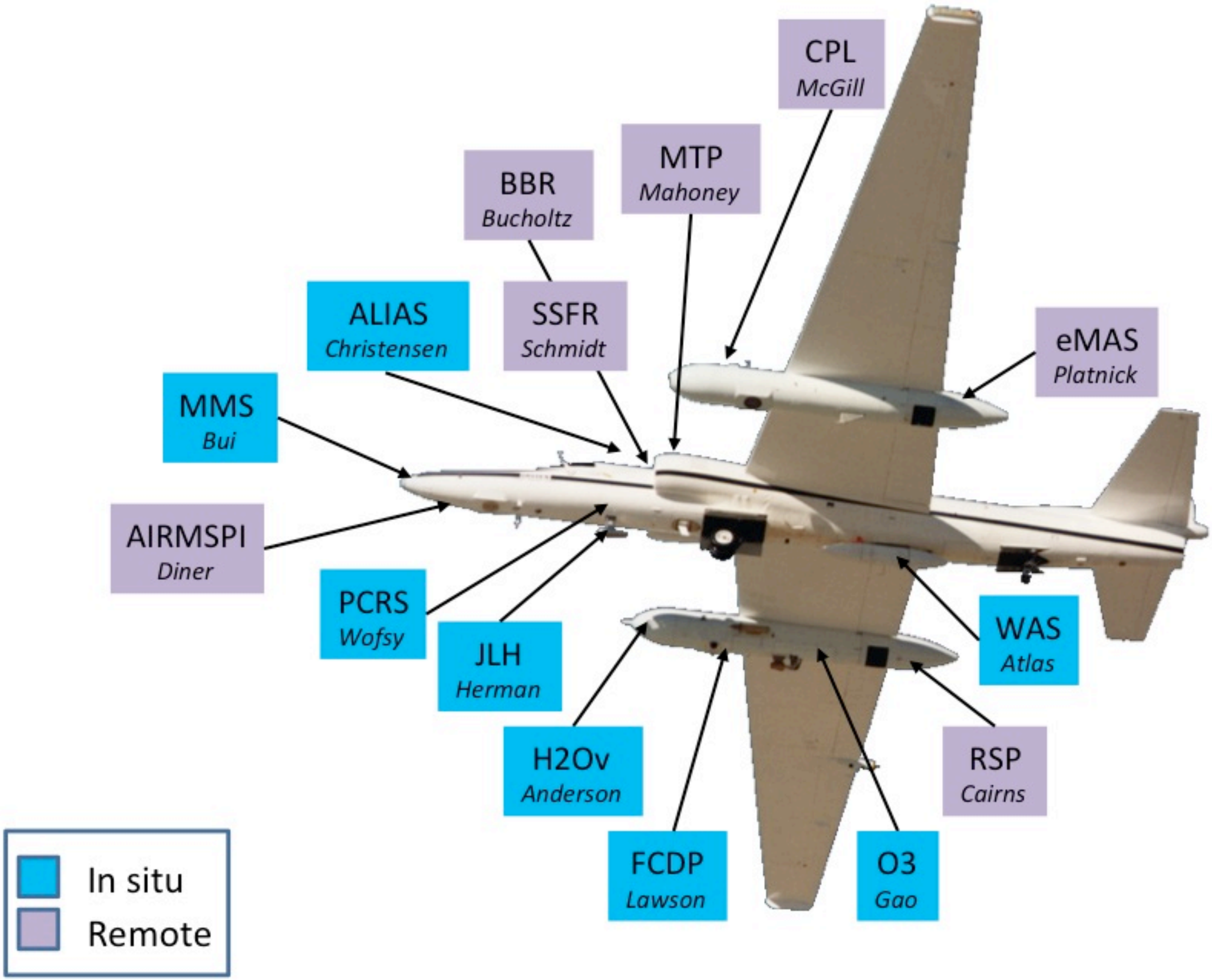


# *DC-8 Instruments*

**Table 4.** DC-8 Instruments

| Name | Technique | Primary Investigator | Products |
|---|---|---|---|
| 4-STAR | Sky scanning spectrometer | P. Russell, NASA Ames | Aerosol optical thickness, water vapor column |
| AOP | Aerosol optical properties | C. Brock, NOAA | Aerosol extinction, absorption, particle size |
| APR-2 | Dual frequency Doppler Radar | S. Tanelli, JPL | Reflectivity, precipitation, vertical velocity |
| AVOCET | IR spectroscopy of $CO_2$ | A. Beyersdorf, NASA LaRC | $CO_2$ |
| BBR | Broadband radiometers | A. Bucholtz, NRL | Solar and IR radiative fluxes and heating rates |
| CAFS | UV-Vis actinic flux | S. Hall, UCAR | Spectrally resolved actinic flux and photolysis frequencies |
| CAMS | Compact atmospheric multispecies spectrometer | A. Fried, UCAR | $CH_2O$ |
| CIT-CIMS | Chemical ionization mass spectrometer | P. Wennberg, CalTech | $HNO_3$, organic acids |
| DACOM | Tunable diode laser spectroscopy | G. Diskin, NASA LaRC | CO, $CH_4$, $N_2O$ |
| DASH SP | Differential aerosol sizing and hygroscopicity | A. Sorooshian, UAz | Hygroscopic growth factor |
| DIAL-HSRL | UV lidar | J. Hair, NASA LaRC | $O_3$, aerosol and cloud heights, aerosol extinction |
| DLH | Open path TDL | G. Diskin, NASA LaRC | $H_2O$ |
| GT-CIMS | Chemical ionization mass spectrometer | G. Huey, Georgia Tech | $SO_2$, HCl, $HO_2NO_2$, PAN |
| HD-SP2 | Laser-induced incandescence | R. Gao, NOAA | Black carbon mass, size, coating thickness, hygroscopicity |
| HR-AMS | Aerosol mass spectrometer | J. Jimenez, U. Colorado | Aerosol composition |
| ISAF | Laser-induced fluorescence | T. Hanisco, GSFC | $CH_2O$ |
| LARGE | Aerosol spectrometers | B. Anderson, NASA LaRC | Particle size distribution, optical properties, CCN |
| MMS | Meteorological measurements system | P. Bui, NASA ARC | Temperature, pressure, winds |
| $NO_y$, $O_3$ | Chemiluminescence | T. Ryerson, NOAA | $NO_x$, $NO_y$, $O_3$ |
| PALMS | Single particle composition mass spectrometer | K. Froyd, NOAA | Particle composition |
| PI Neph | Polarized imaging nephelometer | J. Vanderlei Martins, UMBC | Aerosol scattering phase matrix |
| PT-RMS | Proton transfer mass spectrometry | A. Wisthaler, U. Innsbruck | Volatile organic compounds |
| SAGA | Mist CHAMBER, ion chromatograph, filter | J. Dibb, U. New Hampshire | $HNO_3$, sulfate, soluble ions |
| SPEC | Cloud particle probes | P. Lawson, SPEC | Four-particle probes covering sizes from 1 µm to 10 cm |
| SSFR | Solar spectral flux radiometer | S. Schmidt, U. Colorado | Solar spectral fluxes and heating rates |
| TD-LIF | Thermal dissociation laser induced fluorescence | R. Cohen, U. C. Berkeley | $NO_2$, alkylnitrates, peroxynitrates, $CH_3O_2NO_2$ |
| WAS | Whole air sampler | D. Blake, U. C. Irvine | >70 trace gases |
| DC-8 CAM | Forward and nadir cameras | Rick Shetter, U. N. Dakota | Nadir and forward video |

# SEAC4RS ER-2 Payload

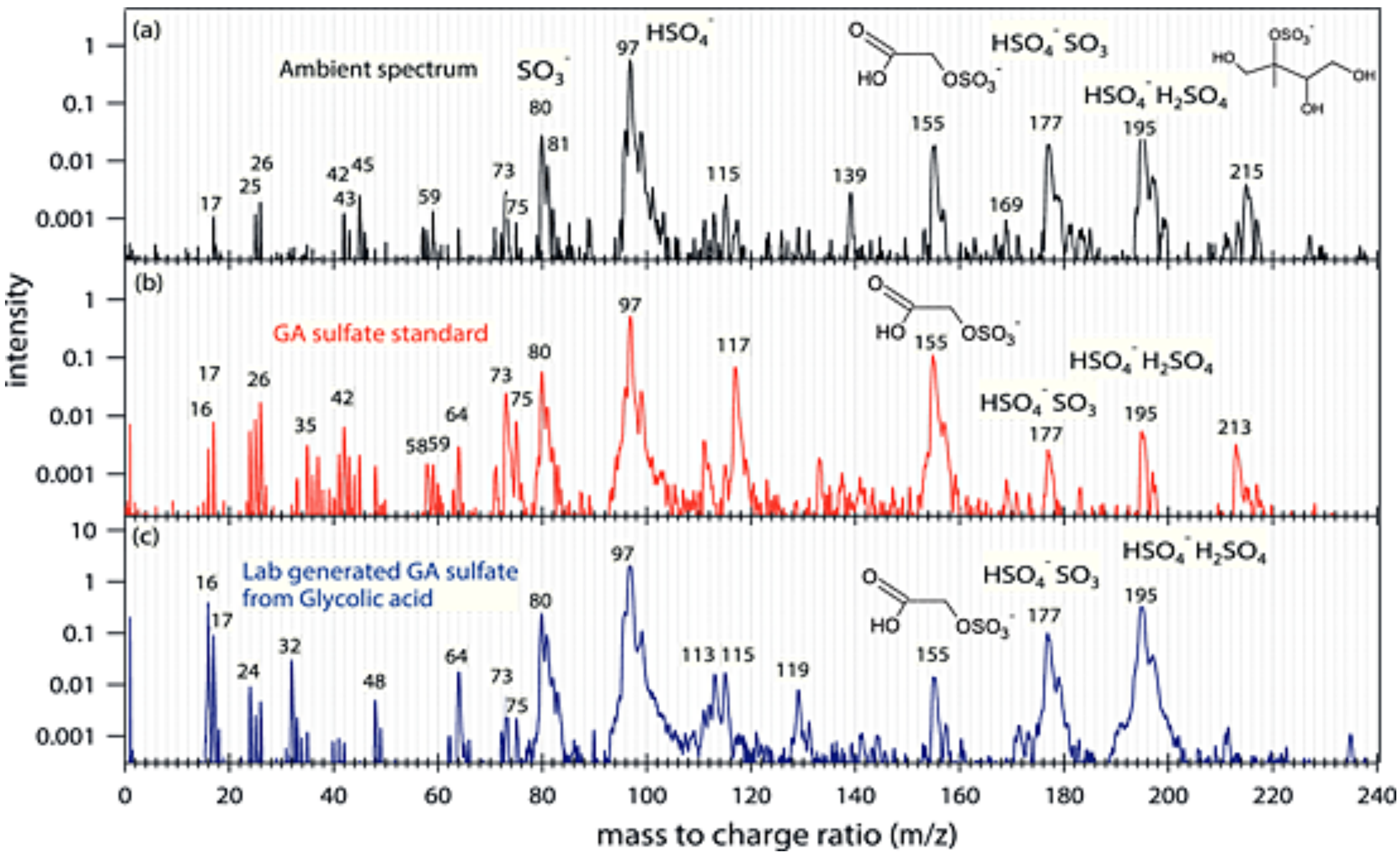


# *ER-2 Instruments*

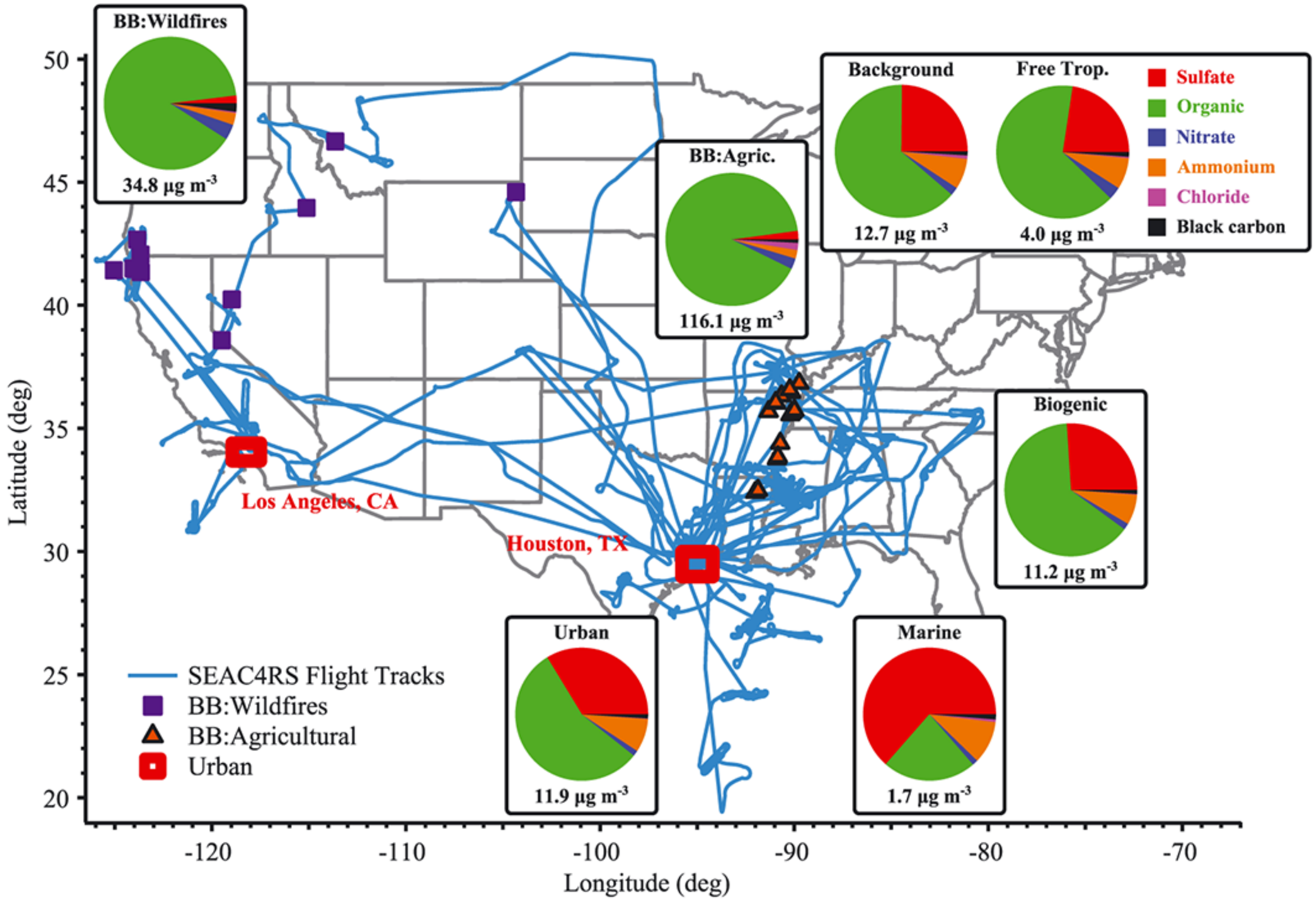
**Table 5.** ER-2 Instruments

| Name | Technique | Primary Investigator | Products |
|---|---|---|---|
| AirMSPI | Multiangle spectropolarimetric imaging | D. Diner, JPL | Multiangle polarization images |
| ALIAS | Laser infrared absorption spectrometry | L. Christensen, JPL | CO, $N_2O$ |
| BBR | Broadband radiometers | A. Bucholtz, NRL | Solar and IR radiative fluxes and heating rates |
| CPL | Lidar | M. McGill, NASA Goddard | Attenuated backscatter |
| eMAS | Multispectral scanning MODIS simulator | S. Platnick, NASA Goddard | Spectral images |
| FCDP | Optical particle sizing | P. Lawson, Spec Inc. | Particle size 1–50 μm |
| H2Ov | Lyman $\alpha$ + tunable diode laser | J. Anderson, Harvard | Water vapor |
| JLH | Tunable diode laser | R. Herman, JPL | Water vapor |
| MMS | Meteorological measurements system | P. Bui, NASA ARC | Temperature, pressure |
| MTP | Microwave radiometry | M.J. Mahoney, JPL | Temperature profiles |
| PCRS | Cavity ringdown spectrometer | S. Wofsy, Harvard | $CO_2$, $CH_4$, CO |
| RSP | Scanning polarimeter | B. Cairns, GISS | Multiangle polarization |
| SSFR | Solar spectral flux radiometer | S. Schmidt, U. Colorado | Solar spectral fluxes and heating rates |
| UAS-O3 | UV photometry | R.-S. Gao, NOAA | Ozone |
| WAS | Whole air sampling | E. Atlas, U. Miami | >50 trace gases |

*Liao et al., 2015, Airborne measurements of organosulfates over the continental U.S.*



*Shingler et al.,*
*Airborne characterization of subsaturated aerosol hygroscopicity and dry refractive index from the surface to 6.5 km during the SEAC4RS campaign*



*New Missions???*

# *Plan the next mission!*

- Identify research problem and questions
- Create mission acronym (important!)
- Use one (or more) aircraft
  - Ground-based measurements possible, too.
- Select payload to address science questions
- Suggest mission plan
  - Nominal flight patterns
- Present 5-minute summary
  - Explain rationale and plan

# *Potential problems*

- Role of emissions from the IGP on ozone and aerosol formation in the ASM
- Identification of sources and transport pathways of pollutants in the ASM
- Impact of primary and secondary aerosols on clouds and precipitation
- Impact of VSL halogen compounds from marine or anthropogenic origin on ozone in the UT/LS