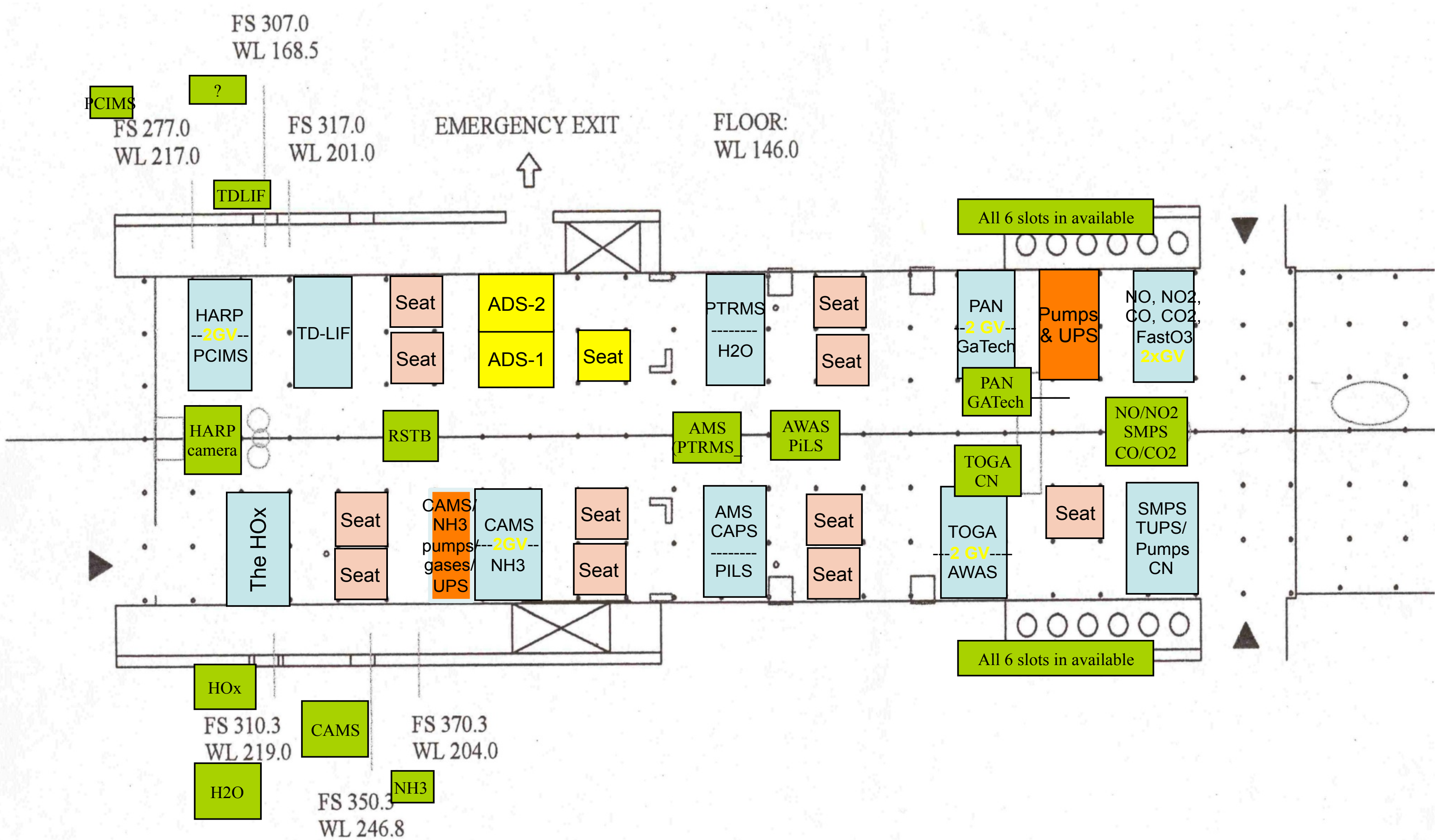
FRAPPÉ
C-130 instrumentation overview

C-130 Payload

Draft C-130 LAYOUT FOR FRAPPÉ
03/30/14



For those of you who thought it can't be done…

CARI chemistry

- **Picarro G1301-*c* Methane/Carbon Dioxide**
  - WS-CRDS
- **System Specifications**
  - **Concentration Range**
  - CO2: 0-1000ppmv, CH4: 0-10ppmv, (Precision/drift guaranteed for CO2 300-500ppbv; CH4 1-3ppbv)
- **Measurement Interval**
  - 5Hz (CO2 & CH4)

CARI chemistry

- **Instrument:** Aero-Laser 5002 G-V Carbon Monoxide Instrument (VUV flourescence)
- **Instrument Precision:** 2 ppbv for a 10-second averaging time
- **Resolution:** ~2 seconds
- **Overall Uncertainty:** ± (2 ppbv + 5 %)

In Situ Measurements of NO, NO_2, O_3 from the C130 in FRAPPE

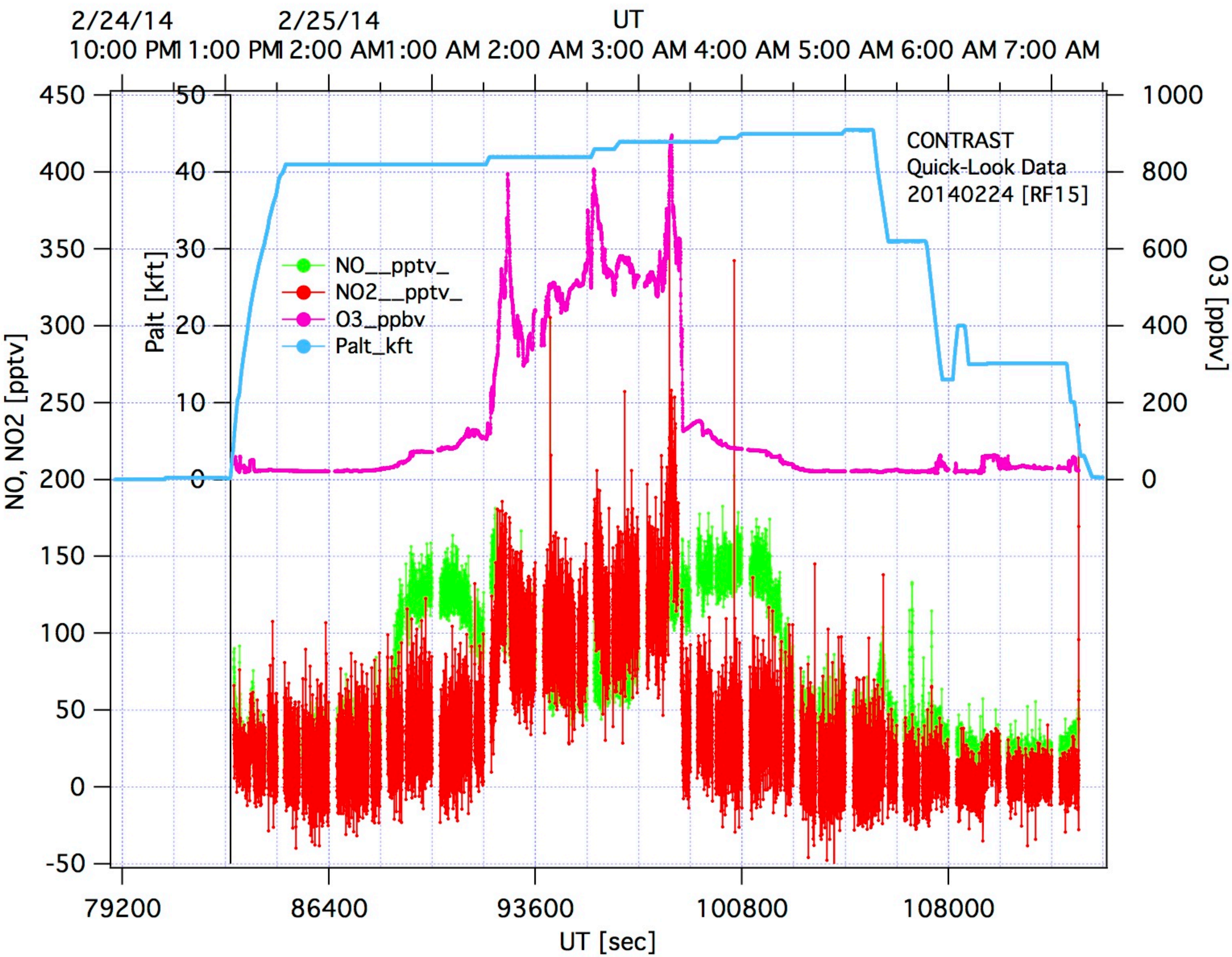
NO: chemiluminescence technique, using the addition of reagent O_3 to form excited NO_2, which is detected via photon counting.

NO_2: detected as NO (as above) after photolytic conversion.

O_3: chemiluminescence technique, using the addition of reagent NO to form excited NO_2, which is detected via photon counting.

Data are reported at 1 sec, with 1-2 sec time response for NO and NO_2, and < 1 sec for O_3.

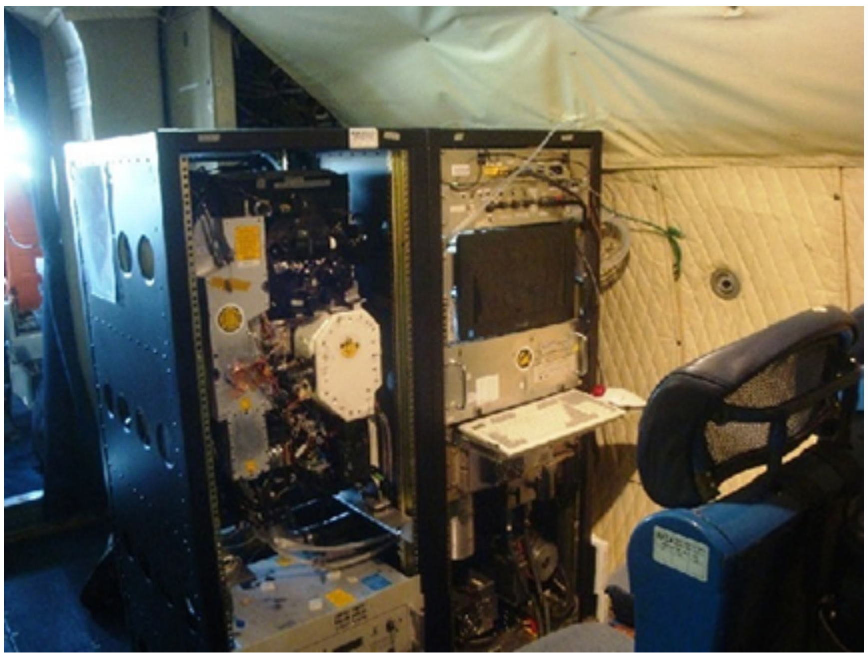
Typical 1-sec precisions (at C130 altitudes) are 10 pptv for NO, 20 pptv for NO_2, and better than 0.1 ppbv for O_3.



2/24/14
2/25/14
UT
10:00 PM 1:00 PM 2:00 AM 1:00 AM 2:00 AM 3:00 AM 4:00 AM 5:00 AM 6:00 AM 7:00 AM
CONTRAST
Quick-Look Data
20140224 [RF15]
NO__pptv_
NO2__pptv_
O3_ppbv
Palt_kft
NO, NO2 [pptv]
Palt [kft]
O3 [ppbv]
UT [sec]
79200
86400
93600
100800
108000

University of California, Berkeley / Ron Cohen

Thermal Dissociation - Laser Induced Fluorescence for NO_2 and related species (TD-LIF NO_2)



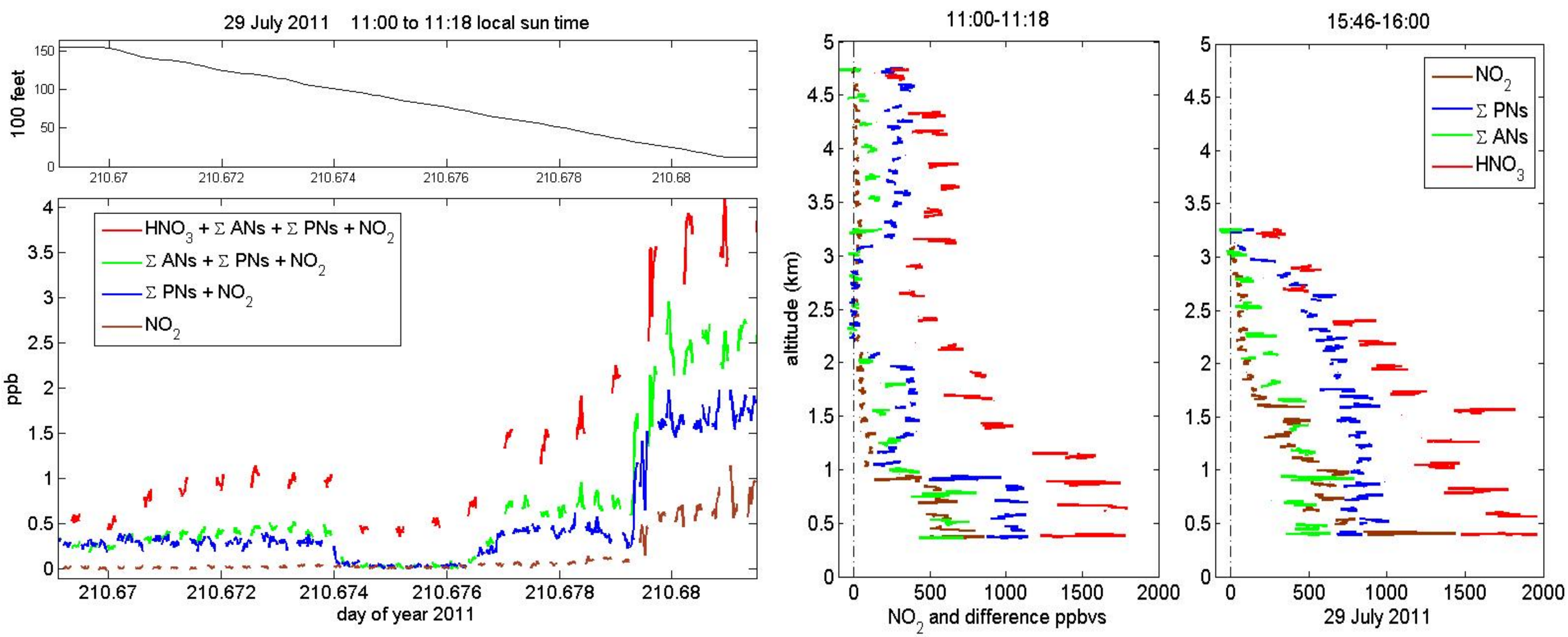
NO_2 is measured directly by LIF, with 5 pptv/10 sec (S/N=2).

Total peroxynitrates (ΣPNs), total alkylnitrates (ΣANs) and HNO_3 by differences between sample tubes heated to characteristic dissociation temperatures. Accuracy varies with concentrations, but is generally 15 to 30 pptv/10 sec.

NO_2 calibration accurate to $\pm$5%, and differences estimated at $\pm$15%

TD-LIF example data – Baltimore area profiles during DISCOVER-AQ 2011

Instrument multiplexes the 4 inlet channels into 2 measurement cells.

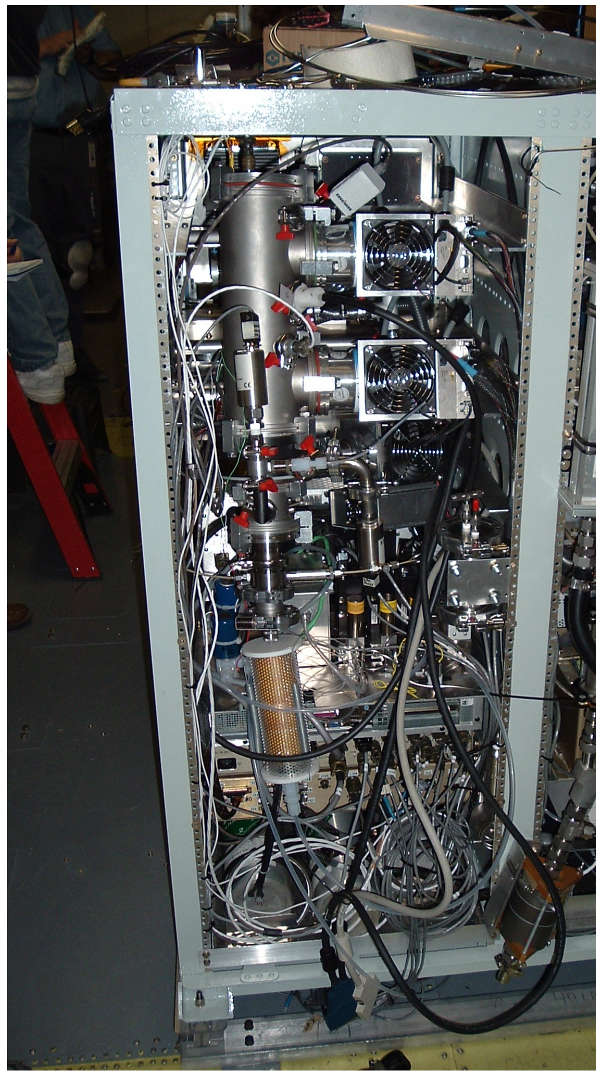


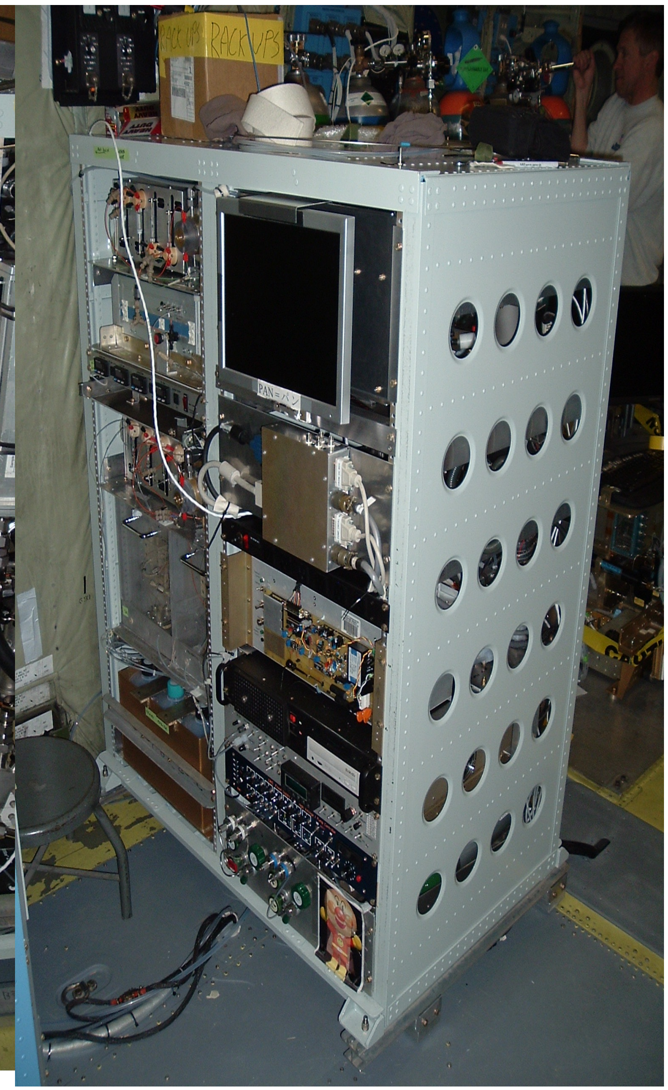
PAN / PPN NCAR CIMS

1 – second measurement of
- PAN
- PPN
- PANCal (C^{13}_2)
- Reagent ion (I-)

cyclic SIM

LOD ~ 10 ppt
Prec. ~ 10 ppt
Measurement error ~ 15%

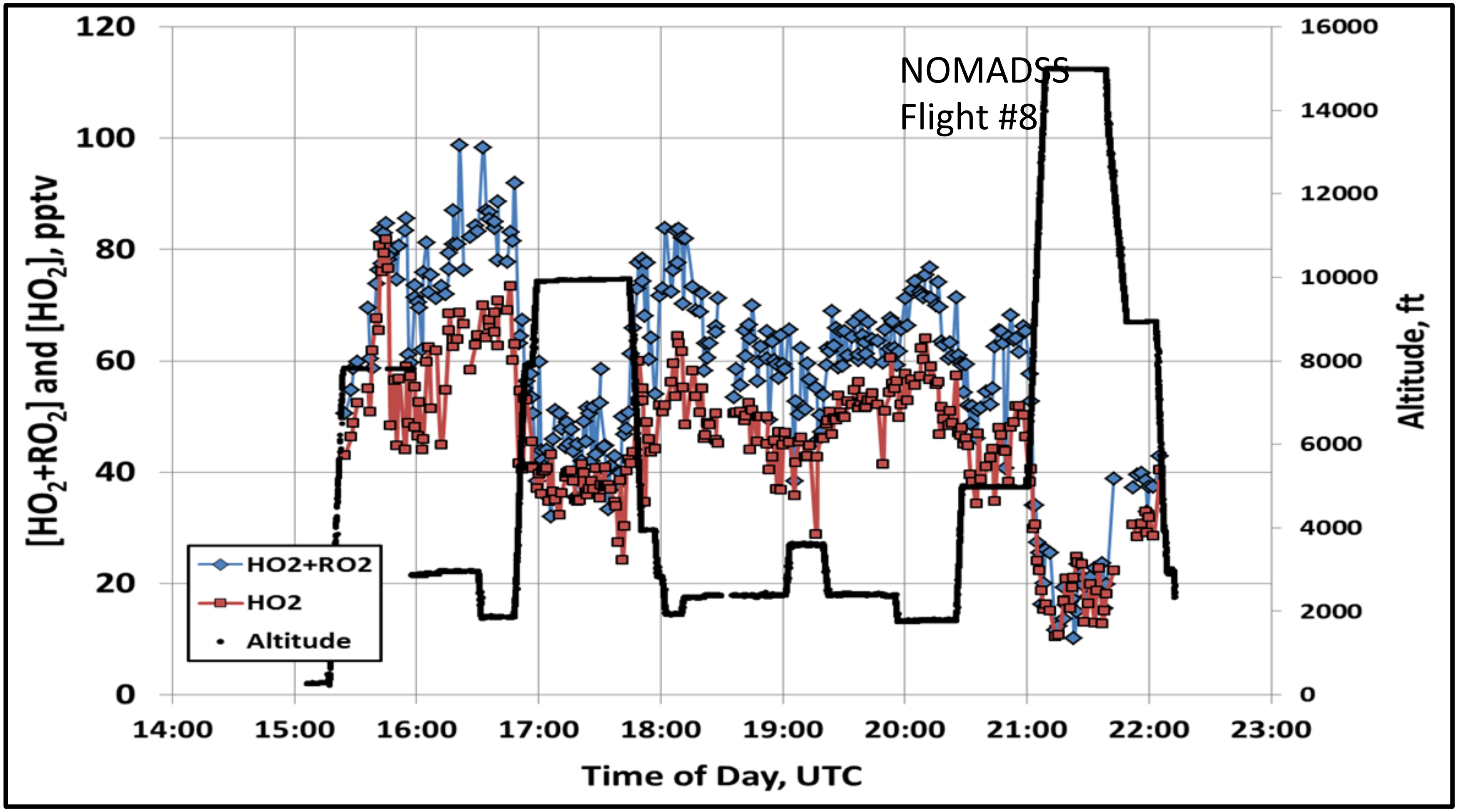




HOxCIMS: Four Channel CIMS

- For FRAPPE, 2 channels operating
  - OH/H_2SO_4/sCIs
    - Each quantity measured every 30 seconds; DL ~ 2 x 10^5 cm^{-3}
    - In flight calibration
    - Long heritage on C-130 – back to ACE-1, TOPSE, MIRAGE, PASE
  - HO_2/HO_2+RO_2
    - Each quantity measured once per minute; DL ~ 2 pptv
    - Deployed multiple times on C-130

Sample HOxCIMS Data

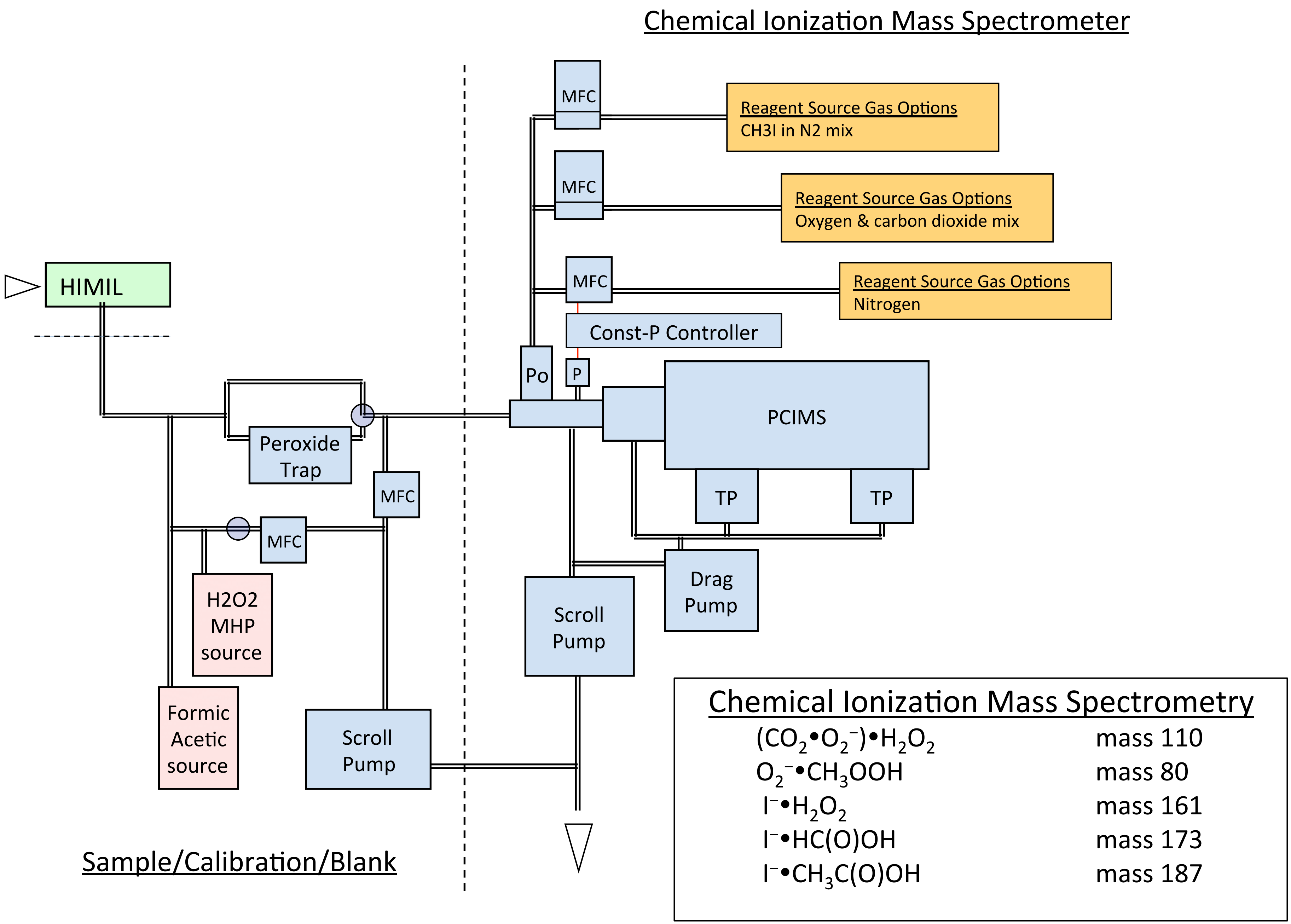


H_2O_2, CH_3OOH, HC(O)OH and $CH_3C(O)OH$

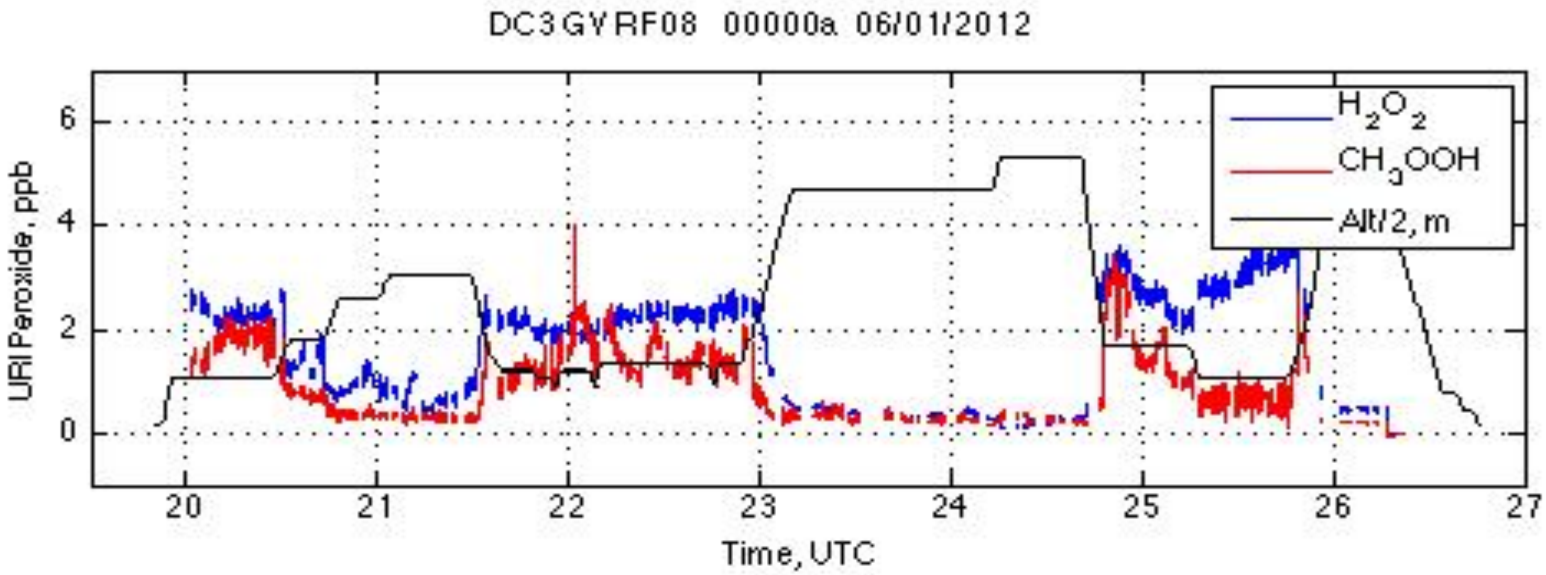
Brian Heikes and Daniel W. O'Sullivan

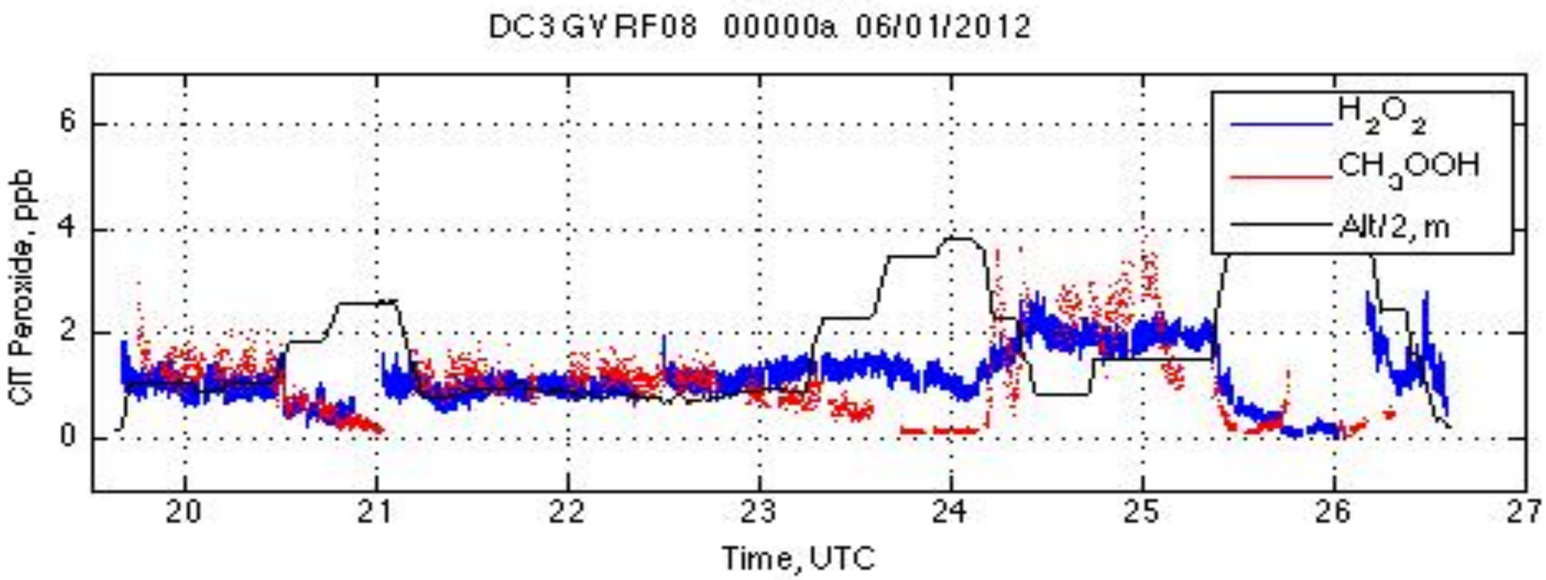
C-130 Airborne Platform, Relevance to the FRAPPE

- Photochemical HO_x cycles
- Oxygenated Volatile Organic Carbon Processing
- Emissions tracers
- Potential precursor/byproduct of Secondary Organic Aerosol
- Heterogenous/aqueous phase oxidants
- Heterogeneous/aqueous phase acidity

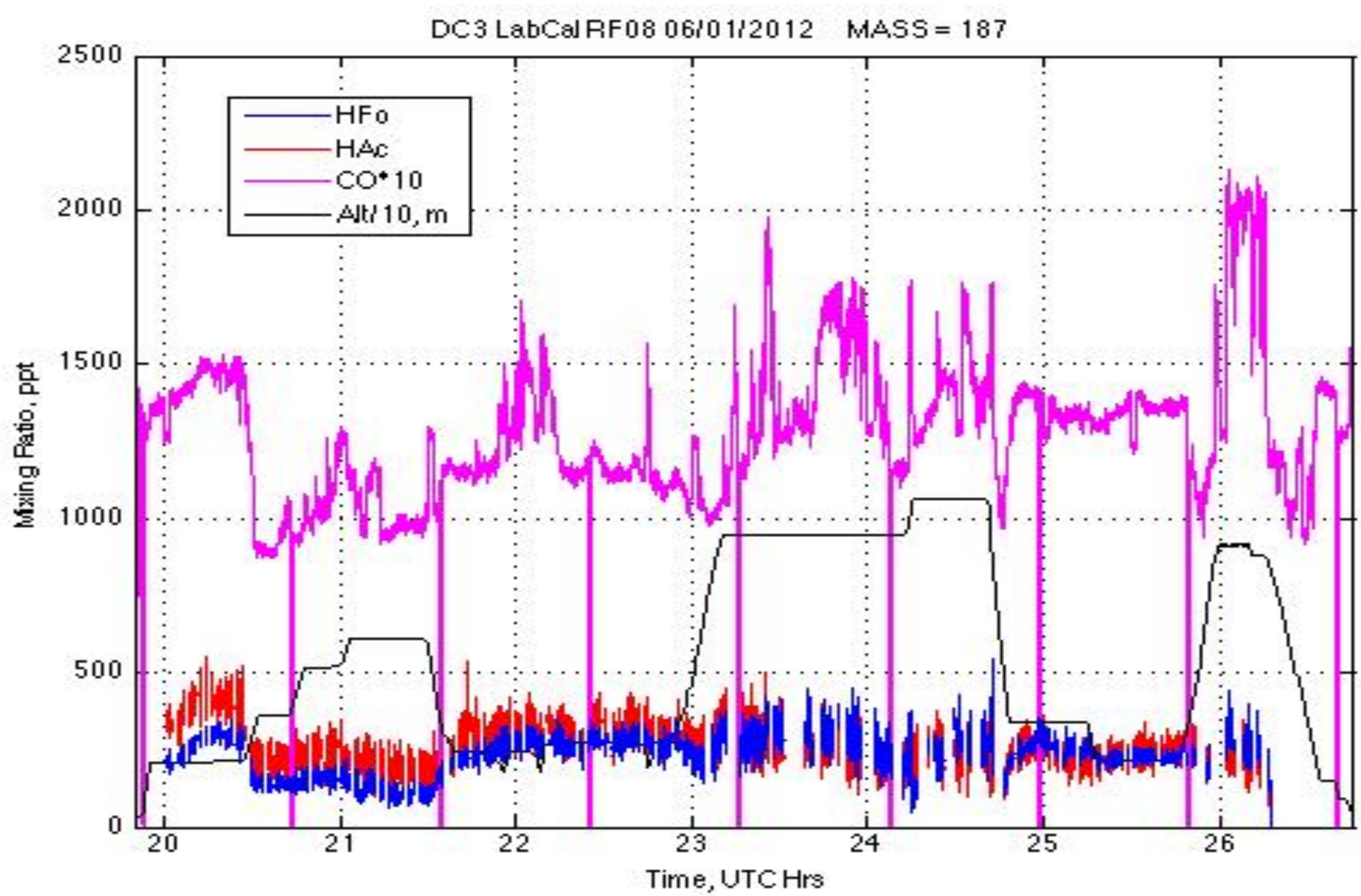

Chemical Ionization Mass Spectrometer
MFC
Reagent Source Gas Options
CH3I in N2 mix
MFC
Reagent Source Gas Options
Oxygen & carbon dioxide mix
MFC
Reagent Source Gas Options
Nitrogen
HIMIL
Const-P Controller
Po
P
PCIMS
Peroxide Trap
MFC
TP
TP
MFC
Drag Pump
H2O2 MHP source
Scroll Pump
Formic Acetic source
Scroll Pump
Sample/Calibration/Blank
Chemical Ionization Mass Spectrometry
$(CO_2\bullet O_2^-)\bullet H_2O_2$ mass 110
$O_2^-\bullet CH_3OOH$ mass 80
$I^-\bullet H_2O_2$ mass 161
$I^-\bullet HC(O)OH$ mass 173
$I^-\bullet CH_3C(O)OH$ mass 187

DC3 H_2O_2 and CH_3OOH





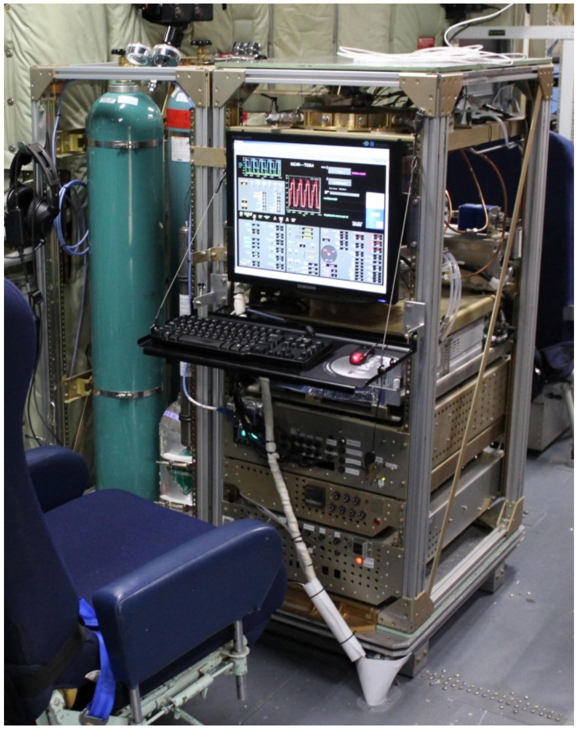
Preliminary HFo and HAc, DC3 near Denver



The Trace Organic Gas Analyzer (TOGA)

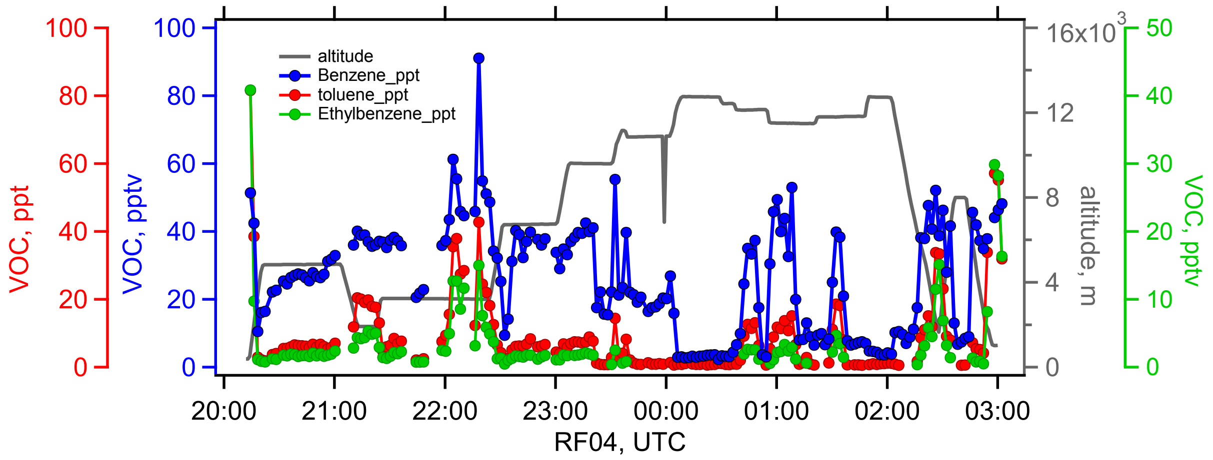
Eric Apel (PI), Alan Hills, Rebecca Hornbrook (ACD/NESL/NCAR)

- VOCs needed to understand chemistry leading to trop O_3 and aerosols. Halogenated species can impact both trop and lower strat
- Designed specifically for the G-V but also used on C-130
- Recently deployed on CONTRAST, NOMADSS, DC3, TORERO
- Designed to have very low LOD ppt to sub – pptv detection limits, over 70 VOCs measured simultaneously
- 30 second time resolution, 2 minute duty cycle



TOGA installed on C-130 for NOMADSS

Example of TOGA Data



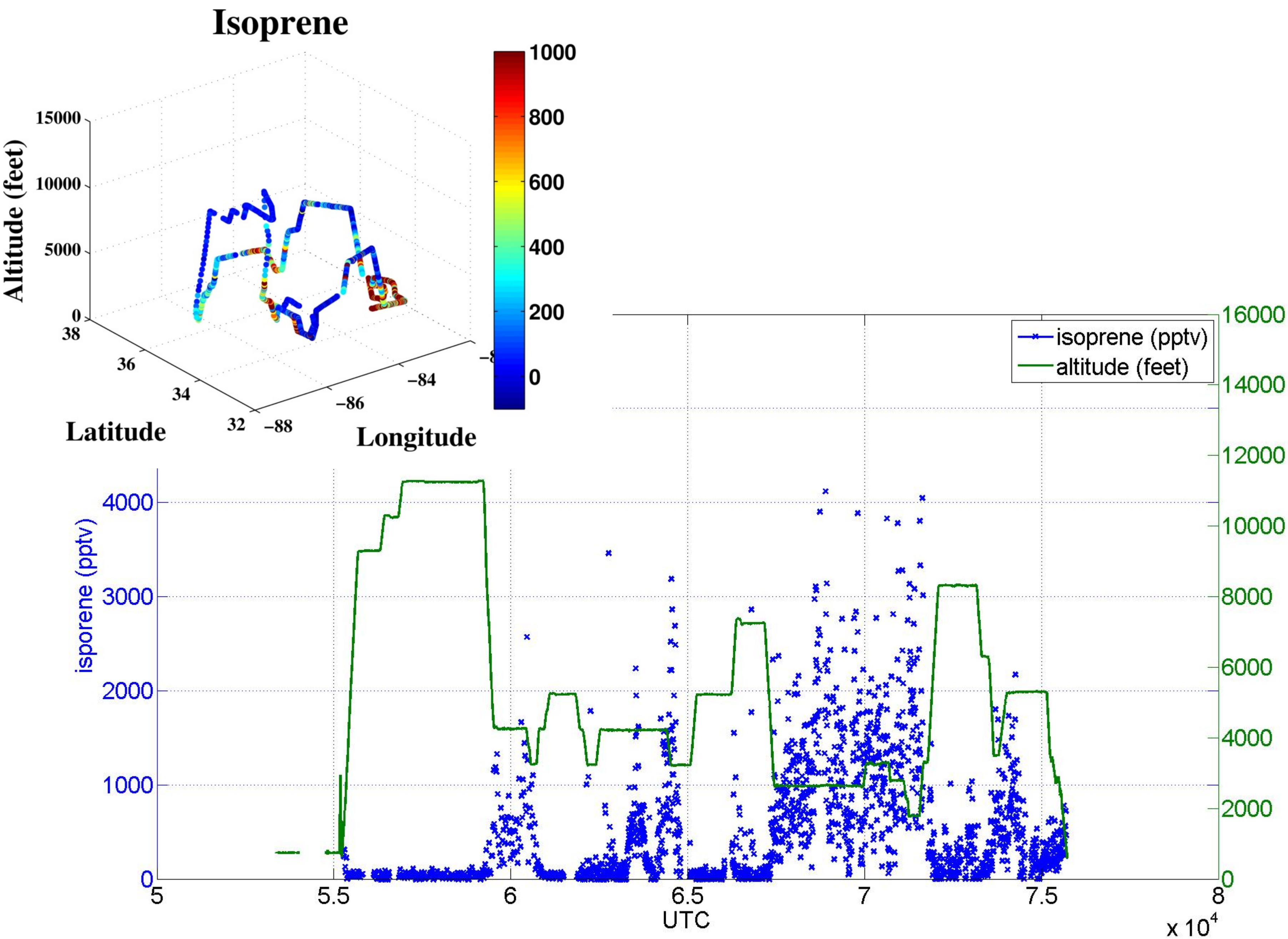
TOGA compounds

Hydrocarbons	Propane	Isoprene	
	1-Butene	*t*-2-Pentene	
	i-Butene	*c*-2-Pentene	
	Butane	*i*-Pentane	
	i-Butane	*o*-Xylene	
	Benzene	*m/p*-Xylene	
	Toluene	1,3,5-Trimethylbenzene	
	Ethyl Benzene	1,2,4-Trimethylbenzene	
	t-2-Butene	α-Pinene	
	c-2-Butene	β-Pinene	
	Pentane	Camphene	
	1,3-Butadiene	Myrcene	
	Limonene		
Oxygenates	Acetaldehyde	Methanol	
	Propanal	Ethanol	
	Butanal	Acetone	
	Pentanal	Butanone	
	Methacrolein	2-Pentanone	
	Methyl Vinyl Ketone	3-Pentanone	
	Methyl Butenol	Methyl t-Butyl Ether	
Halocarbons	Chloroform ($CHCl_3$)	Tetrachloromethane (CCl_4)	dibromomethane
	Methylene chloride (CH_2Cl_2)	CFC-113	diodomethane
	Methyl chloride (CH_3Cl)	HCFC-141b	bromocjhloromethane
	Methyl bromide (CH_3Br)	HCFC-134a	bromoiodomethane
	Tetrachloroethane (CH_2Cl_4)	1,2-Dichloroethane ($C_2H_4Cl_2$)	chloroiodomethane
	Tetrachloroethylene (C_2Cl_4)	Methyl Iodide (CH_3I)	
	Bromoform	iodoform	
Nitrogen and sulfur compounds	Acetonitrile	HCN	
	Dimethyl Sulfide (DMS)		

PTR-MS

Mass (amu)	Compound	
28	HCN	
30	HONO	
31	Formaldehyde	
33	Methanol	←
42	Acetonitrile	←
43	Multiple species	
45	Acetaldehyde	←
47	Formic acid	←
54	Acrylonitrile	
57	Butenes, MTBE, butanol	
59	Acetone	←
61	Acetic acid	←
63	DMS	
69	Isoprene Furan	←
71	MVK + MACR	←
73	MEK	←
75	Hydroxy acetone	
77	PAN	
79	Benzene	←
81	Monoterpenes Hexenal	←
83	Hexenol, hexanal, hexenyl acetate Methyl furan, isoprene hydroxy carbonyls	
85	Ethyl vinyl ketone	
87	MBO C_5-carbonyls, methacrylic acid	←
91	PPN	
93	Toluene	←
95	2-vinyl furan Phenol	
99	Hexenal	
101	Isoprene hydroperoxides	
103	MPAN	
105	Styrene, PiBN	
107	C_8-aromatics	←
115	Heptanal	
121	C_9-aromatics	←
129	Octanal Naphthalene	
135	C_{10}-aromatics	
137	Monoterpenes	
139	Nopinone	
143	Nonanal	
149	C_{11}-aromatics Methylchavicol	
151	Pinonaldehyde	
163	C_{12}-aromatics	

- Table shows all VOC's measured by PTR-MS in the atmosphere (deGouw and Warneke, Mass Spectrometry Reviews, 2007, 26, 223– 257)
- Blue arrows indicate the VOC's that we intend to measure by PTR-MS during FRAPPE
- Typical sensitivity: 200-400 cps/ppbv (depending uppon compound)
- Typical LOD: 20-300 pptv (depending upon compound)


Isoprene
Altitude (feet)
15000
10000
5000
0
38
36
34
32
Latitude
−88
−86
−84
Longitude
1000
800
600
400
200
0
isoprene (pptv)
altitude (feet)
isporene (pptv)
4000
3000
2000
1000
0
16000
14000
12000
10000
8000
6000
4000
2000
0
5
5.5
6
6.5
7
7.5
8
UTC
x 10^4

Ground and aircraft measurements of VOCs and stable isotopes of CH_4 in the Colorado Front Range

Donald R. Blake and the UCI team
Department of Chemistry
University of California Irvine (UCI)
Irvine, CA drblake@uci.edu

Amy Townsend-Small and the UC team
Departments of Geology and Geography
University of Cincinnati (UC)
Cincinnati, OH townseay@ucmail.uc.edu

UC measurements:

- Stable CH_4 isotopes
  - $\delta^{13}C$ and δD of CH_4

UCI measurements:

- CH_4, CO, CO_2
- 70 speciated C_1-C_{10} NMVOCs
  - C_2-C_8 alkanes (ethane, …)
  - C_2-C_5 alkenes (isoprene, …)
  - C_6-C_9 aromatics (benzene, …)
  - C_1-C_2 halocarbons (C_2Cl_4, …)
  - C_1-C_5 alkyl nitrates ($MeONO_2$, …)
  - Oxygenates (methanol, …)
  - Sulfur compounds (OCS, DMS)

Measurement strategy:

- Flask-based whole air samples (WAS)
  - Aircraft: 60 samples/flight
  - Ground-based: 168 samples

UCIrvine
University of California, Irvine

UNIVERSITY OF Cincinnati

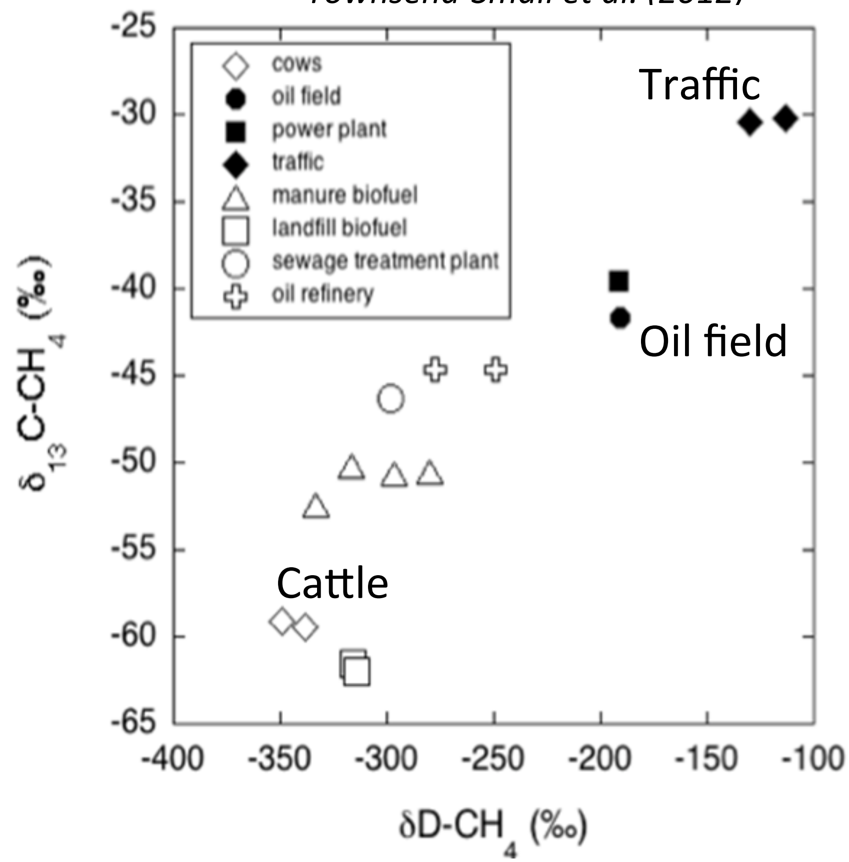
Ground and aircraft measurements of VOCs and stable isotopes of CH_4 in the Colorado Front Range

Main objective:

- Use VOC and CH_4 isotope measurements to characterize and help distinguish specific emission sources in the Colorado Front Range

Source	VOC tracer
Oil and gas	
- Natural gas	CH_4, ethane
- Gasoline	*i*-Pentane
- Oil	*n*-Butane, *n*-hexane
- Traffic	CO, ethyne
Agriculture	
- Cattle	CH_4
- Feedlots	Ethanol, methanol
Urban/Industry	C_2Cl_4
Biogenic	Isoprene
Biomass burning	CO, methanol

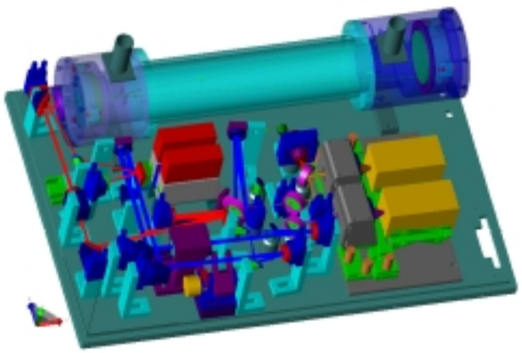
$\delta^{13}C$ and δD of CH_4 from biological and fossil fuel sources
Townsend-Small et al. (2012)



UCIrvine University of California, Irvine

University of Cincinnati

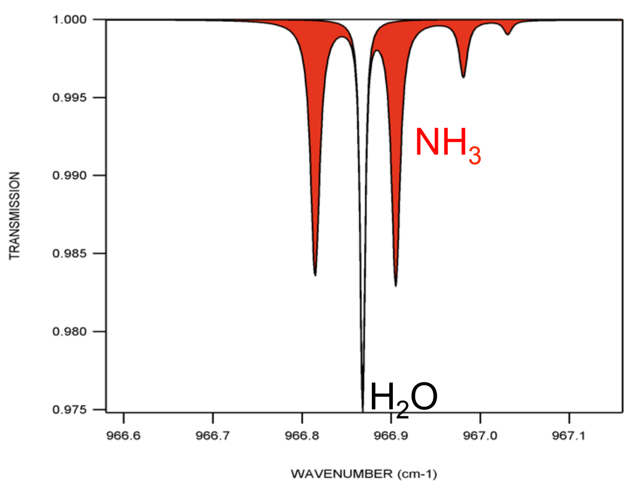
ARI NH_3/HNO_3 Dual QCL

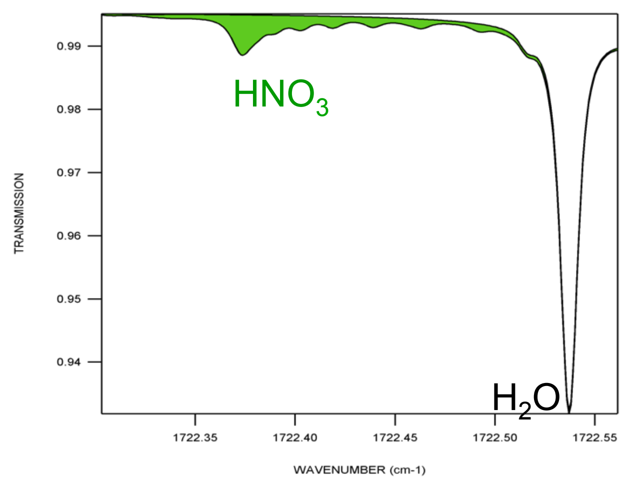


Dual Quantum Cascade Laser

- Absorption measurement of NH_3 and HNO_3

NH_3 and HNO_3 Absorption Features



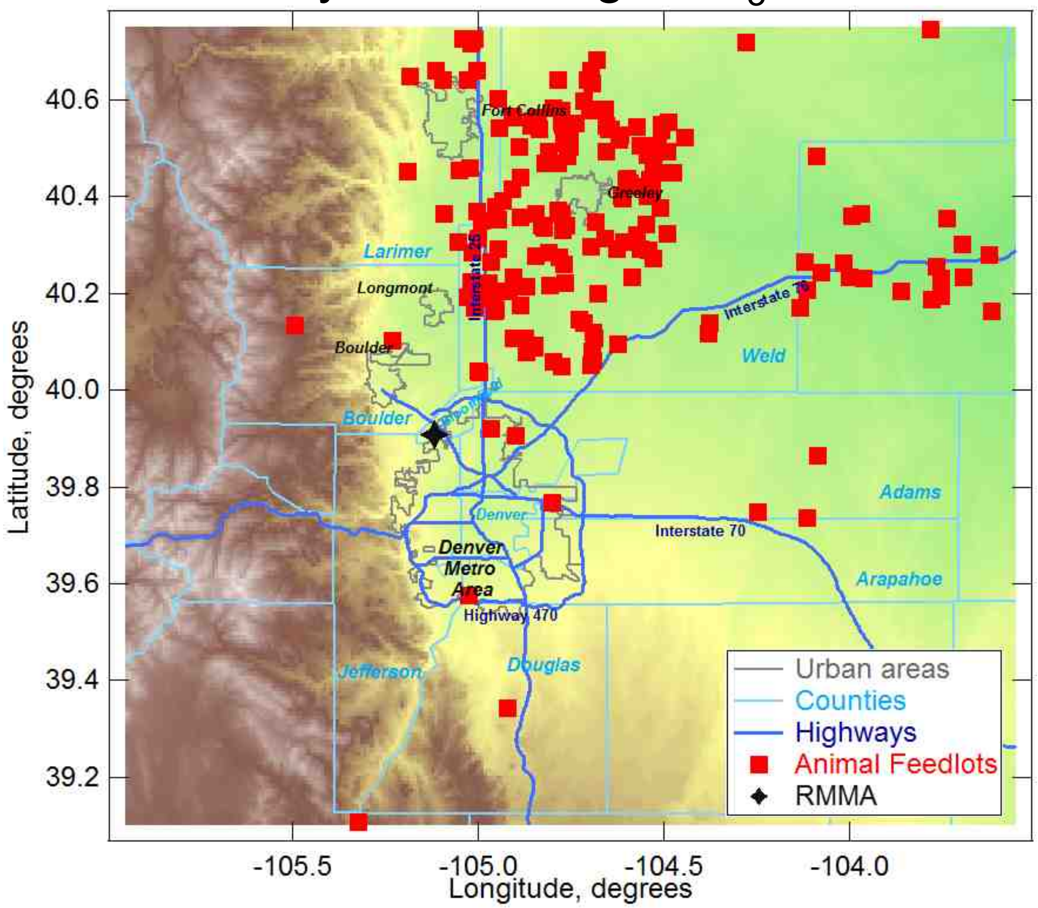


Time response: <5 s for NH_3
<5 s for HNO_3

Instrument Noise Floor: 30 ppt @ 1s for NH_3
50 ppt @ 1s for HNO_3

NH_3-centric Science

Primary Front Range NH_3 Sources



- Feedlots
- Other agricultural activities
- Automobile traffic

Science Goals

- *Identify NH_3 sources*
- *Quantify NH_3 emissions*
- *Characterize NH_3 transport as a source of excess N to RMNP*
- *Examine the impact of the NH_3 emission sources on particle formation and composition*

NCAR

HARP Actinic Flux Spectroradiometers

Samuel Hall, Kirk Ullmann

Measurement: Upwelling, downwelling actinic flux

Product: Photolysis frequencies based on cross-section and quantum yield calculations →→→

Calibrations

- NIST traceable absolute spectral sensitivity (primary, field)
- Wavelength assignment
- Angular, azimuthal and effective plane

Research areas

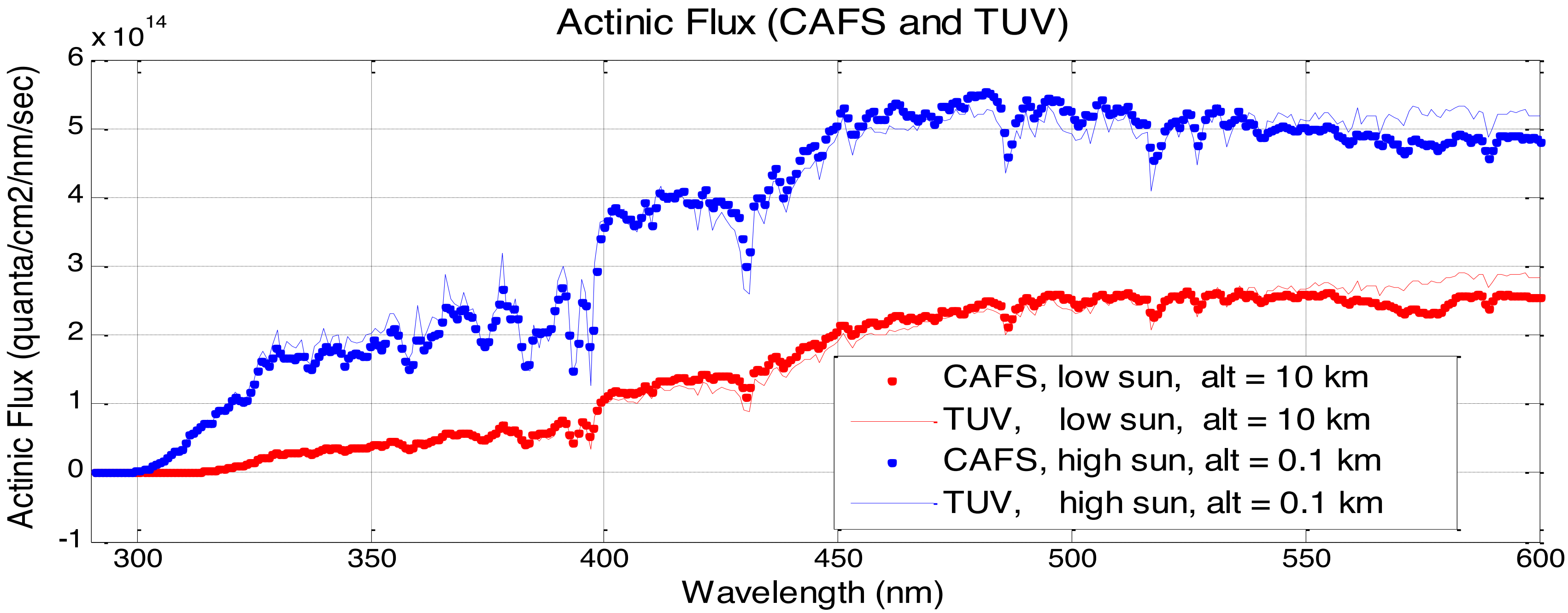
- Chemical evolution in pollution plumes
- Tropospheric oxidant chemistry
- Aerosol (anthropogenic and biomass burning) and cloud radiative impacts on photochemistry

Wavelengths	280-680 nm (unfiltered)
Resolution	~1.8 nm FWHM at 297 nm
Precision	1-2% wavelength dependent
Spectral Accuracy	5% (UV-B), 3% (UV-A/VIS) limited by NIST standards
Detection Limits	~0.04 mW/m2/nm at 300 nm
Data Rate	6 seconds

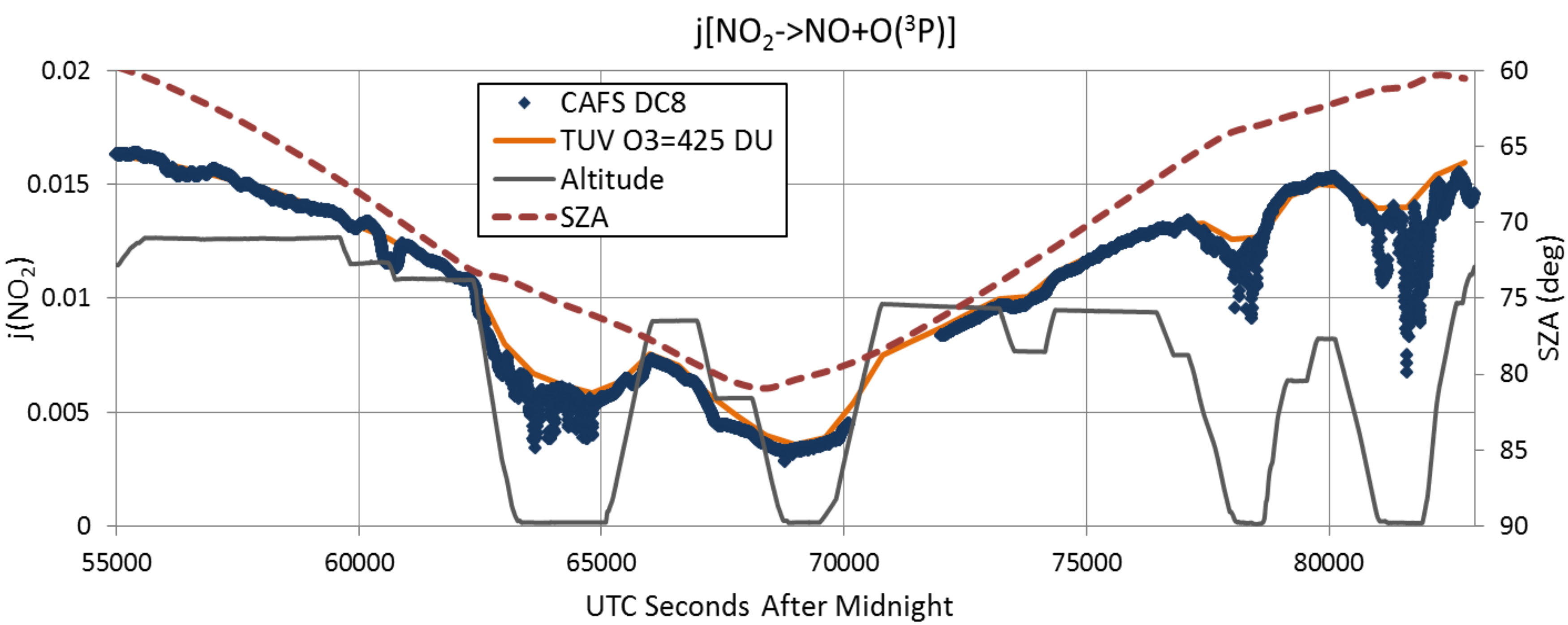
j [O3->O2+O(1D)]
j [NO2->NO+O(3P)]
j [H2O2->2OH]
j [HNO2->OH+NO]
j [HNO3->OH+NO2]
j [CH2O->H+HCO]
j [CH2O->H2+CO]
j [CH3CHO->CH3+HCO]
j [CH3CHO->CH4+CO]
j [C2H5CHO->C2H5+HCO]
j [CHOCHO->products]
j [CHOCHO->HCO+HCO]
j [CH3COCHO->products]
j [CH3COCH3->CH3CO +CH3]
j [CH3OOH->CH3O+OH]
j [CH3ONO2->CH3O+NO2]
j [PAN->products]
j [CH3COCH2CH3-> Products]
j [CH3CH2CH2CHO-> C3H7+HCO]
j [CH3CH2CH2CHO-> C2H4+CH2CHOH]
j [HO2NO2-->HO2+NO2]
j [HO2NO2-->OH+NO3]
j [CH3CH2ONO2-> Products]
j [Br2->Br+Br]
j [BrO->Br+O]
j [Br2O->products]
j [BrNO3->Br+NO3]
j [BrNO3->BrO+NO2]
j [BrCl->Br+Cl]
j [HOBr->HO+Br]
j [BrONO2->Br+NO3]
j [BrONO2->BrO+NO2]
j [Cl2+hv->Cl+Cl]
j [ClO->Cl+O]
j [ClONO2->Cl+NO3]
j [ClONO2->ClO+NO2]
j [CHBr3->Products]

Additional compounds may be included

MEASUREMENT



PRODUCT

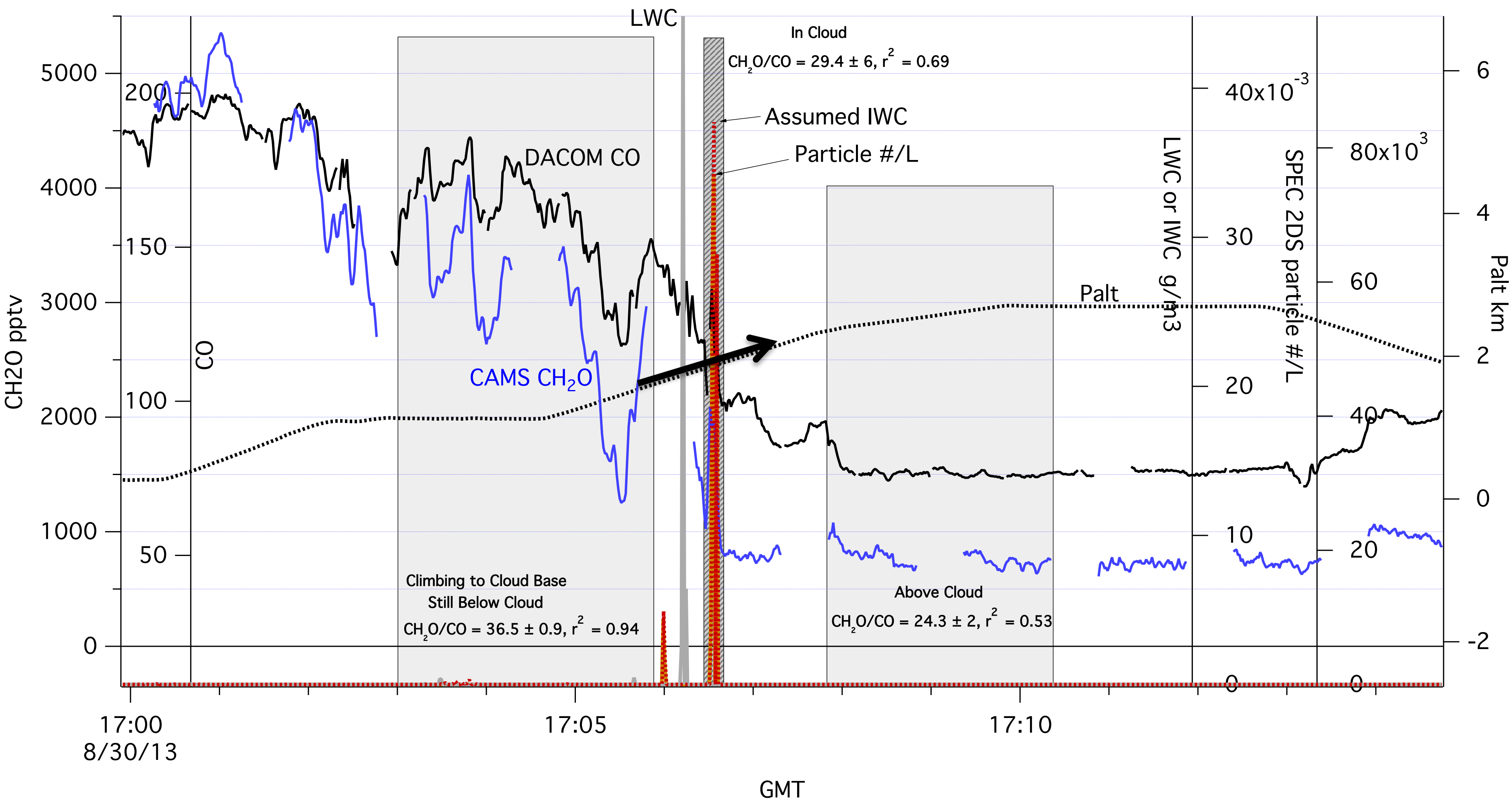


Compact Atmospheric Multi-Species Spectrometer (CAMS)

1-Second Time Response
1-Second CH_2O LOD (Actual)
15 – 30 pptv

1-Second Ethane LOD (Anticipated)
2- 5 pptv

CH_2O-CO Regression Slopes (pptv/ppbv) Below, In & Above Low Altitude Clouds During SEAC[4]RS 2013 Campaign



Highly correlated enhanced CH_2O-CO (Diskin group) with large enhancements in cloud particle number concentration when flying through low altitude clouds.

Airborne Aerosol Composition and Extinction Measurements During FRAPPE

PI: Roya Bahreini

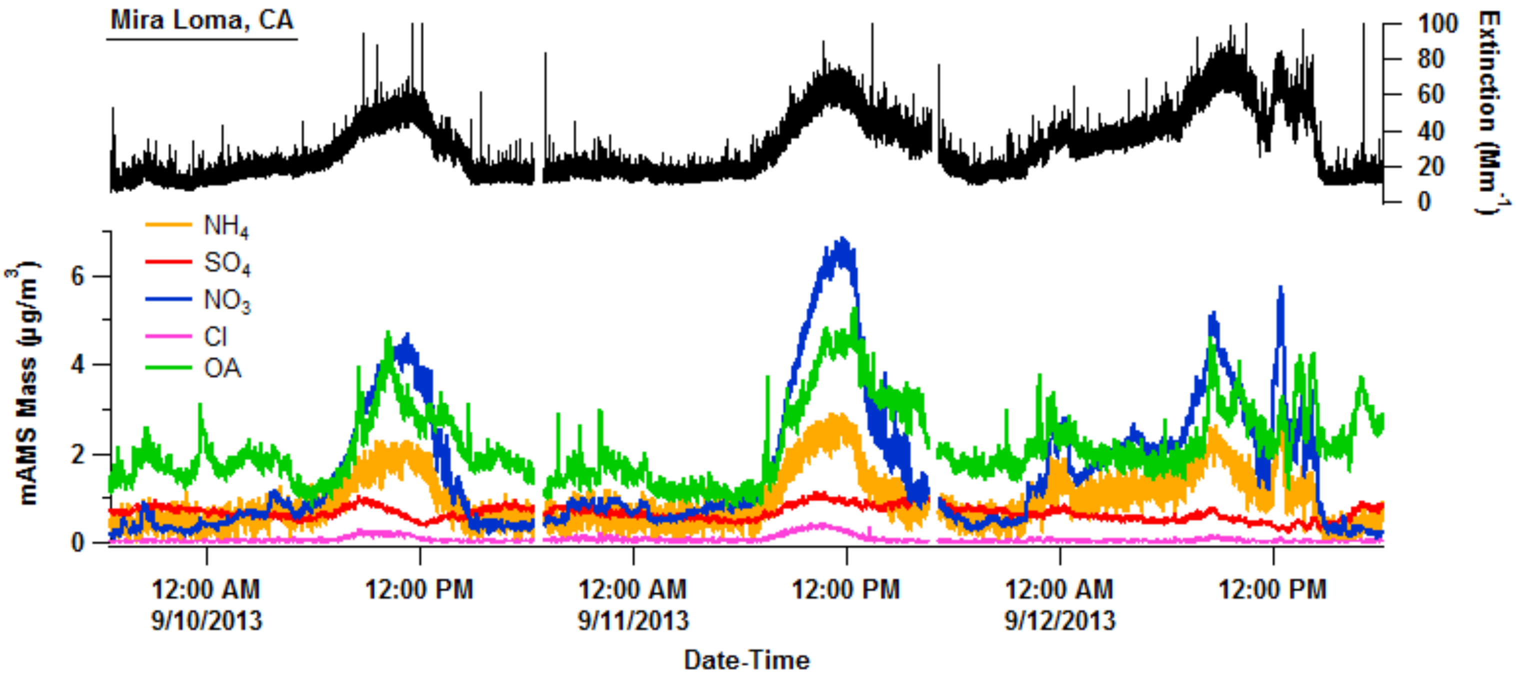
UC- Riverside

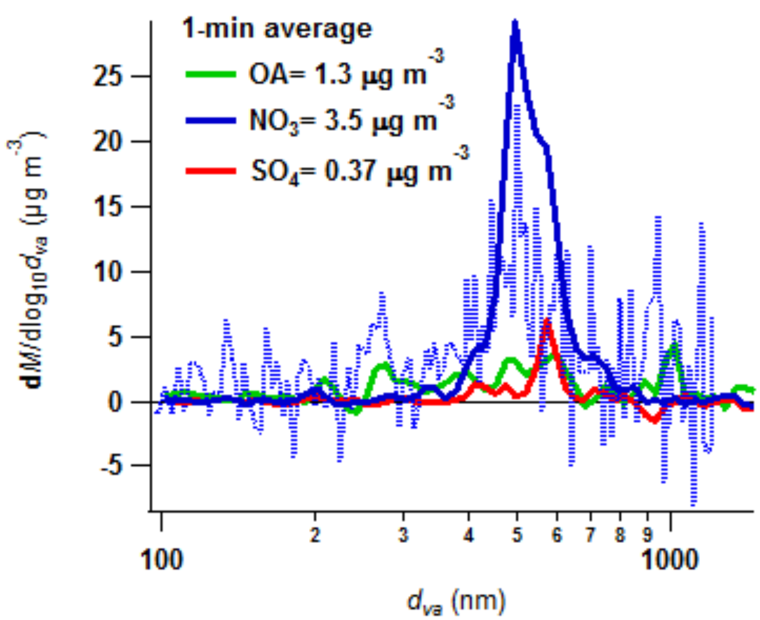
Measurements

- Size-dependent composition of sub-micron, non-refractory aerosol by mass spectrometry (mAMS)
- Aerosol extinction measurements at λ=632 nm (CAPS-PM_{ex})

Measured Parameter	Sampling Interval	Detection Limit	Uncertainty
Sulfate	15 s	0.09 mg m^{-3}	36%
Nitrate	15 s	0.13 mg m^{-3}	34%
Chloride	15 s	0.10 mg m^{-3}	36%
Ammonium	15 s	0.54 mg m^{-3}	34%
Organics	15 s	0.35 mg m^{-3}	38%
Aerosol Extinction (632 nm)	1 s	3 Mm^{-1}	3%

Data Output/Results





- Time series of NH_4, SO_4, NO_3, Cl, organic aerosol (OA)
- Time series of extinction at λ=632 nm
- Species-specific mass distributions ***with much improved sensitivity*** *(for comparison, the dashed line on the left indicates an average mass distribution of NO_3, for a similar averaging time and NO_3 loading, obtained with previous designs of the AMS)*
- Other parameters deduced from mAMS:
  - Estimates of aerosol organic nitrate
  - Time series of $C_xH_y^+$, $C_xH_yO^+$, $C_xH_yO_{z>1}^+$ ions
  - Time series of O:C and H:C

C-130: PILS + offline analysis NCAR (Smith) & CSU (Farmer)

Measurement		
Particle Into Liquid Sampler (Brechtel)	5 minute sampling	
	Ion Chromatography	(NO_3^-, NO_2^-, SO_4^{2-}, Cl^-, NH_4^+, oxalate, acetate, formate?, others?)
	TOC / TON	WSOC/WSON (subset of samples)