Reactive Nitrogen, Ozone, and Radicals

Glenn M. Wolfe (Moderator)
NASA Goddard Space Flight Center

AGES Meeting
28 September 2022

Speaker	Measurement	Mission
Glenn (for Lee Mauldin)	RO_x, H_2SO_4	GOTHAAM
Glenn (for Ale Franchin)	NO_x, O_3	GOTHAAM
Andrew Rollins	NO_x, NO_y, O_3	AEROMMA
Ilana Pollack	NH_3	AEROMMA
Aaron Stainsby	OH Reactivity	AEROMMA
Saewung Kim	OH Reactivity	NYC-METS
Ezra Wood	$HO_2 + RO_2$	NYC-METS
Trevor VandenBoer	Acids, Total N_r	THE CIX
Paul Walter	Sondes	STAQS
Steve Brown	NO_y, O_3	CUPiDS
Steve Brown	"Night NO_x"	AEROMMA

OH, HO_2, HO_2+RO_2, H_2SO_4 Measurements

Lee Mauldin, Chris Cantrell, Emmanuel Assaf
University of Colorado, Boulder

OH

OH is measured by first converting it to $^{34}H_2SO_4$ via reaction with $^{34}SO_2$ and then measuring $H_2{}^{34}SO_4$. ^{34}S is used to discriminate between H_2SO_4 produced from OH and ambient H_2SO_4 – which is also measured.

HO_2 and HO_2+RO_2

HO_2 and **HO_2+RO_2** are also measured by converting them to H_2SO_4 via reaction with SO_2 and NO then measuring H_2SO_4.

HO_2 is measured in a low O_2, relatively high NO environment, in which most RO_2 are not converted to H_2SO_4.

HO_2 + RO_2 is measured in a high O_2, relatively low NO environment, in which both are converted to H_2SO_4 with high efficiency.

H_2SO_4

H_2SO_4 is measured using nitrate Chemical Ionization Mass Spectroscopy (CIMS)

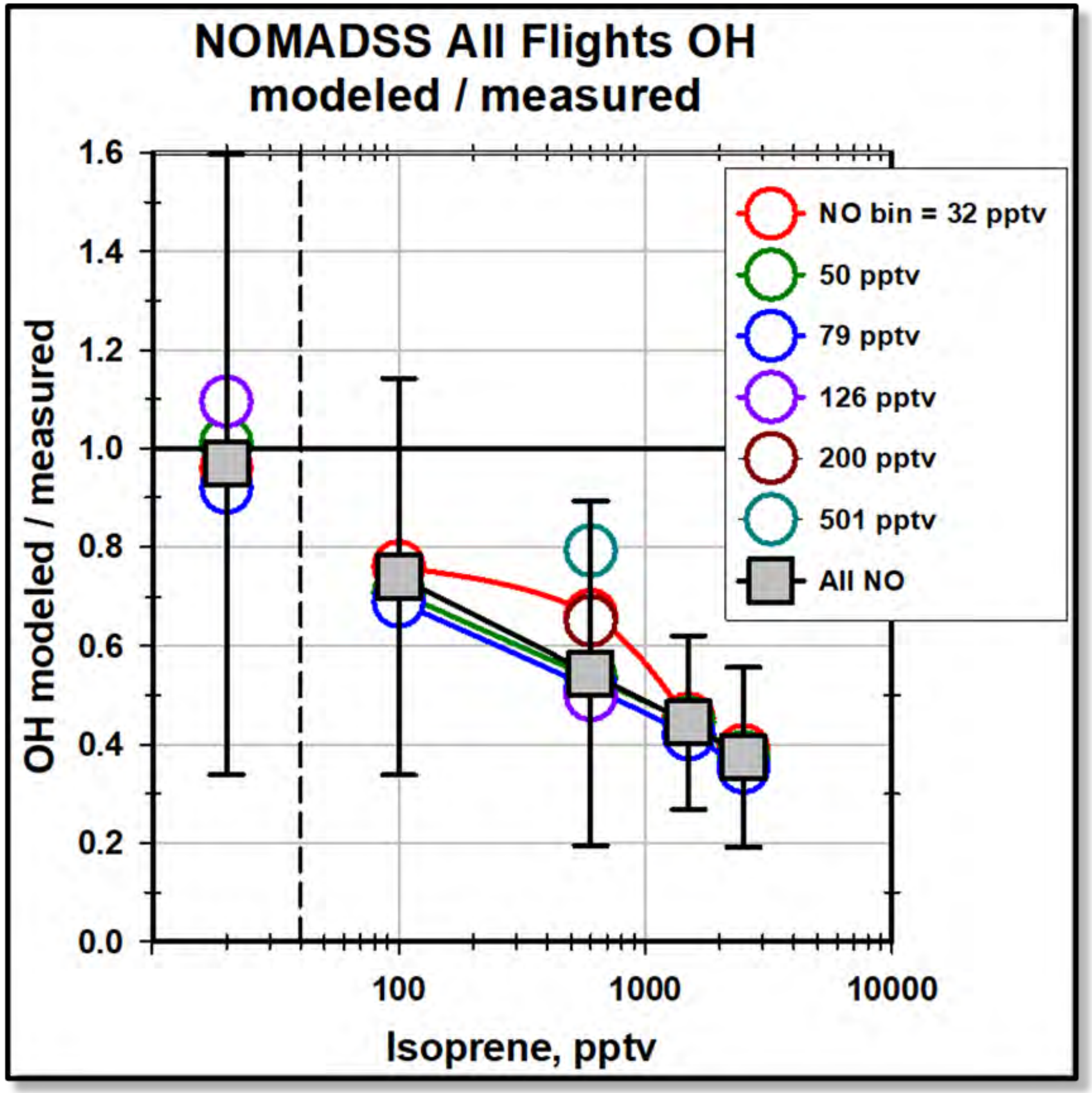
Detection Limits

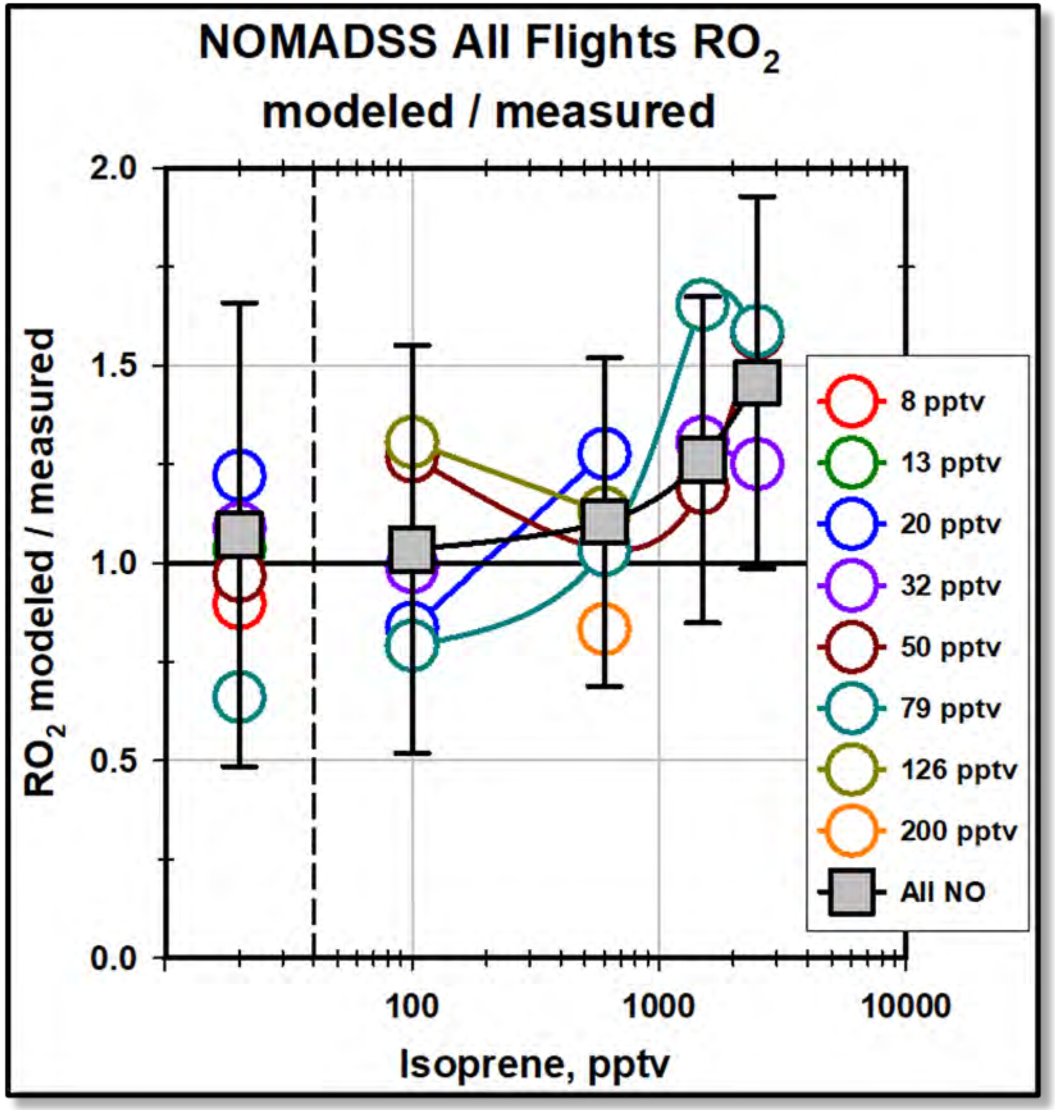
OH, H_2SO_4 - $3x10^5$ molecule cm^{-3} for 30 sec measurement

HO_2, HO_2+RO_2 - $5x10^5$ molecule cm^{-3} for 60 sec measurement

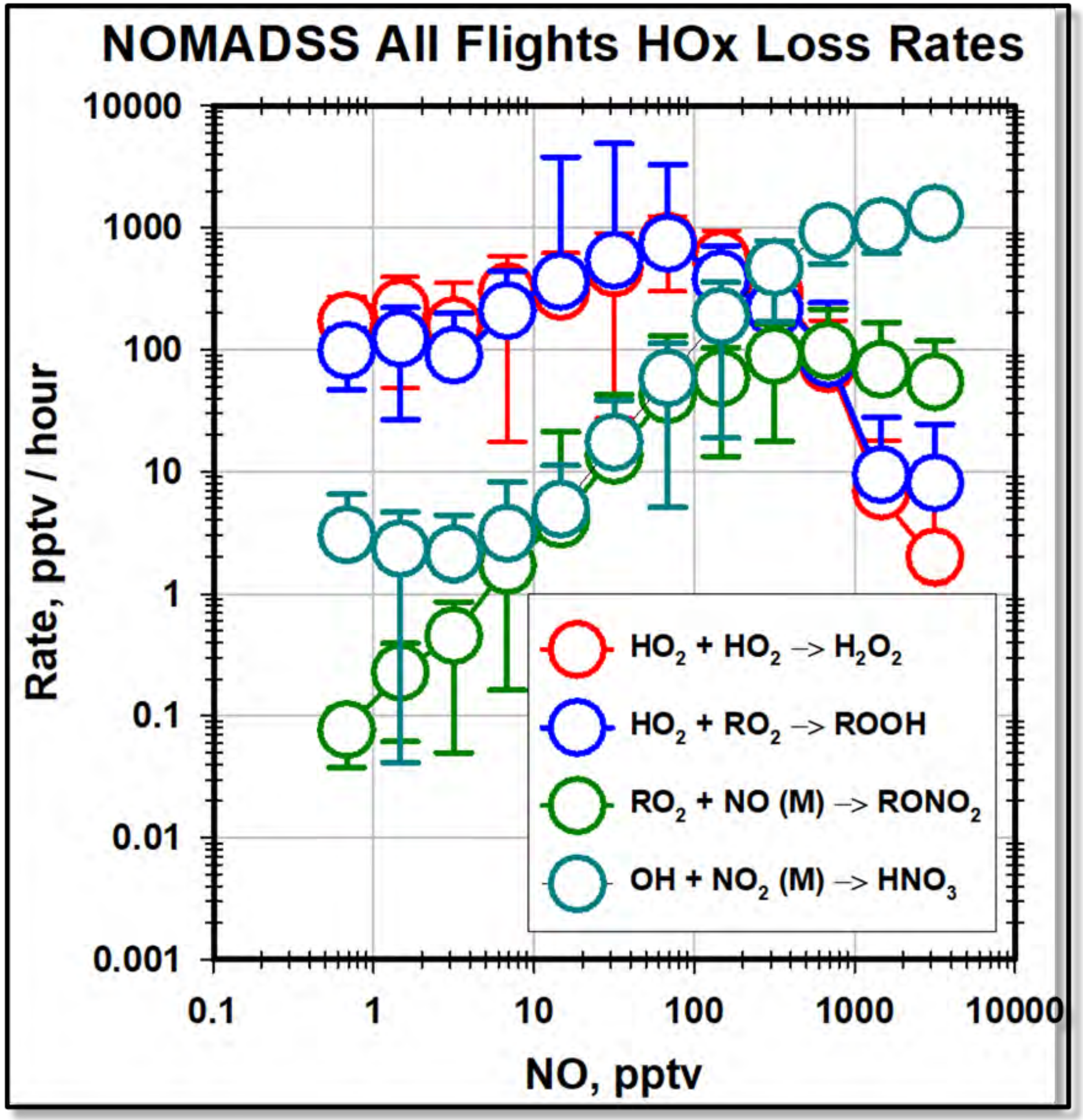
Hornbrook et al., AMT (2011), 10.5194/amt-4-735-2011

Box model underpredicts OH and overpredicts RO_2 at high isoprene





Direct Calculation of Radical Termination Rates



In Situ Measurements of NO, NO_2, and O_3

- For NO, reagent O_3 is added to the flow of ambient air.
- Photons are counted using dry-ice cooled PMT.
- For NO_2, first convert to NO in cooled photolytic cell.
- For NO_y, first convert to NO on heated gold catalyst.
- For O_3, reagent NO is added to flow of ambient air.

NCAR 2-Channel instrument
(NO & NO_2, integrated with O_3)

HAIS O3
(integrated with NO/NO2)

3 sample flows, each employing the chemiluminescent reaction:
$NO + O_3 \rightarrow NO_2^* + O_2$

Nominal detection limits:

NO:	10 pptv
NO_2:	20 pptv
O_3:	50 pptv

Data reported at 1s time resolution

Shared double rack with ACOM Carbon instrumentation, total installation taking up one station in C-130

People you might see around the NOx / O_3 /carbon rack:

Ale Franchin (PI)

Courtney Owen

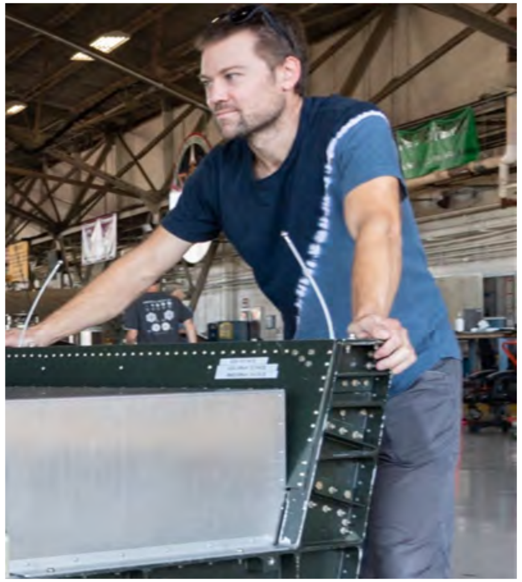
Kirk Ullmann

Kirk Lesko

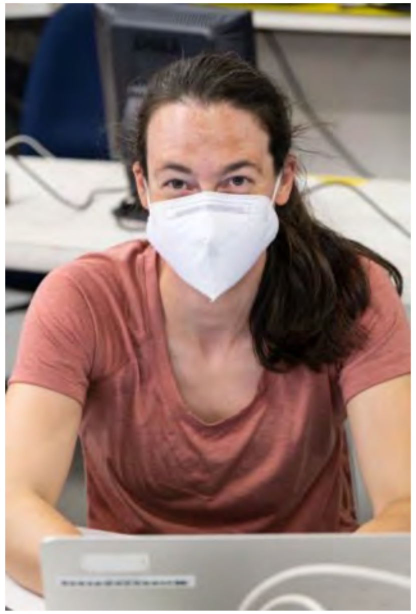
Teresa Campos

NOx/NOy and O_3 measurements on the DC-8 for AEROMMA

Kristen Zuraski



Drew Rollins



Eleanor Waxman

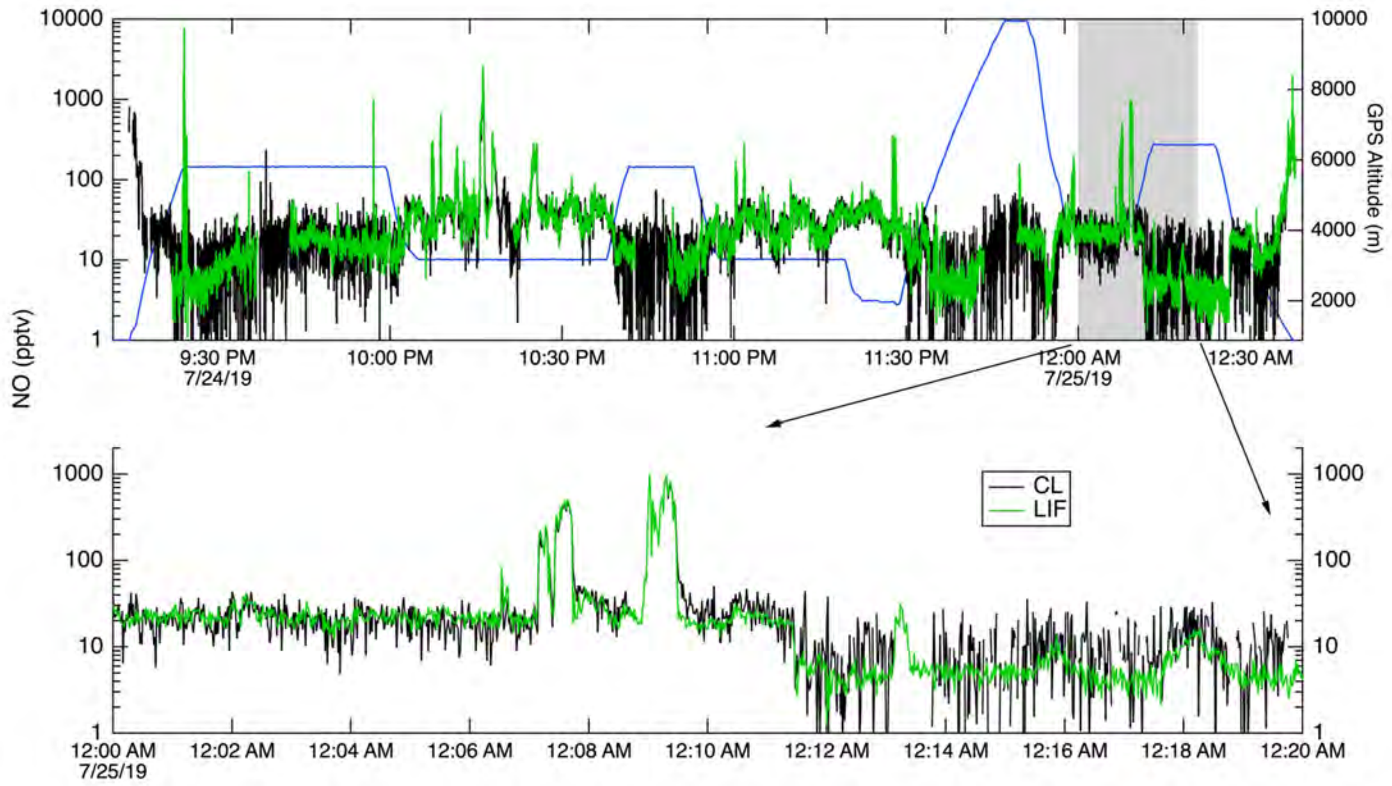
Jeff Peischl

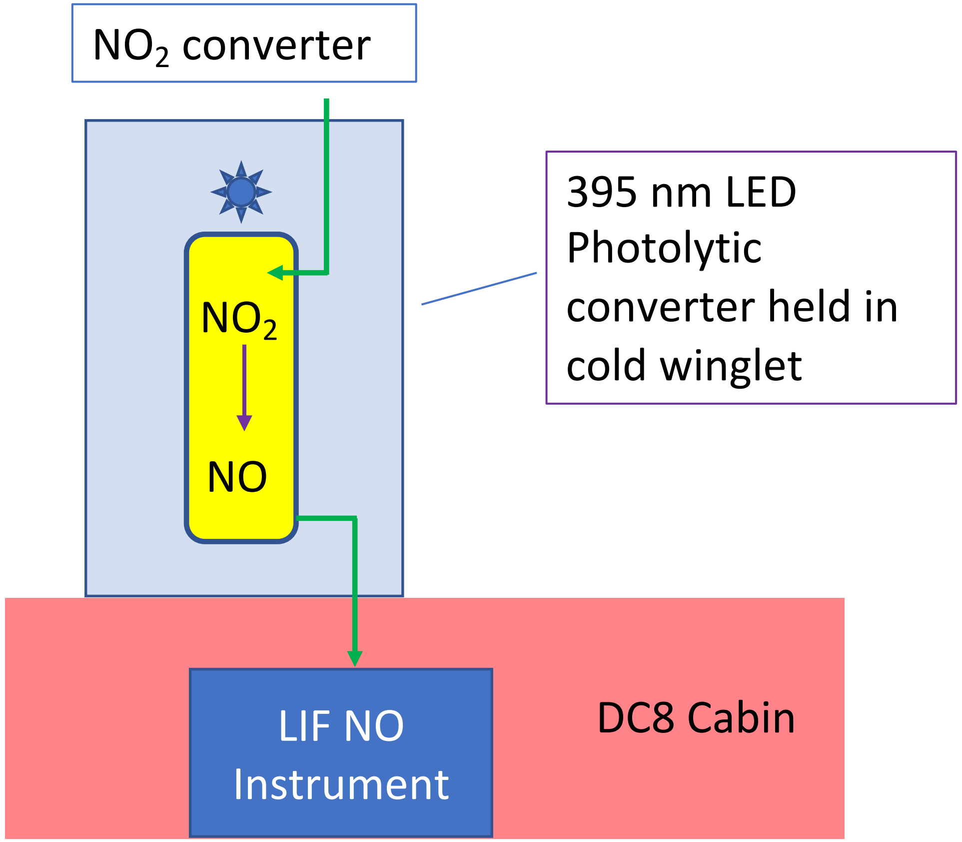
NO-LIF Technique / O_3 Chemiluminescence Technique

$NO/NO_2/NO_y$ Technique
- Laser excitation @ 215 nm
- Fluorescence collection ~250-260 nm
- 1 s detection limit: < 1 ppt
- 3 channel instrument for continuous measurements of NO, NO2, NOy

NO - LIF Heritage
- FIREX-AQ 2019 (DC-8)
- SABRE 2022 (WB-57)
- ACCLIP 2022 (WB-57)

O_3 CL Instrument:
- O_3 + NO -> light
- High precision
- No interferences





NOy / O_3 Science Foci

Marine

- Fluxes of NO and O_3
- NO_y closure in the MBL
- NO_x gradients in coastal regions and impact of peroxy radical fate on oxidation product distributions

Continental

- NO_x sources in urban areas
- Impact of NO_x on O_3 production
- Fate of peroxy radicals and impact of NO_x
- UT NO_2 / NO ratios and lightning NO_x

Gas-phase Ammonia Measurements for AEROMMA on the DC-8

Ilana Pollack
PI, Instrument Team Lead

Emily Lill
PhD Candidate, Team Member

Emily Fischer
co-PI, Team Member

Jeff Pierce
co-PI, Team Member

Colorado State University

Department of Atmospheric Science

Contact:
ilana.pollack@colostate.edu

Photo by Bonne Hottman

Gas-phase NH_3 on the DC-8 using a QC-TILDAS

Instrument features:
- Commercial Aerodyne QC-TILDAS mini-CS
- Filterless, aerodynamic separation of particles
- Vibration applied to laser obj. for reduced noise
- Isolation mounted for reduced motion sensitivity
- Active continuous passivation and heating of sampling surfaces for improved time response

Instrument performance*:

Meas. Freq.: 10 Hz sampled, 1 Hz reported

Time Res. (t_{90}): <1 s with, ~2 s w/out passivant

Precision: <60 ppt @ 1 Hz

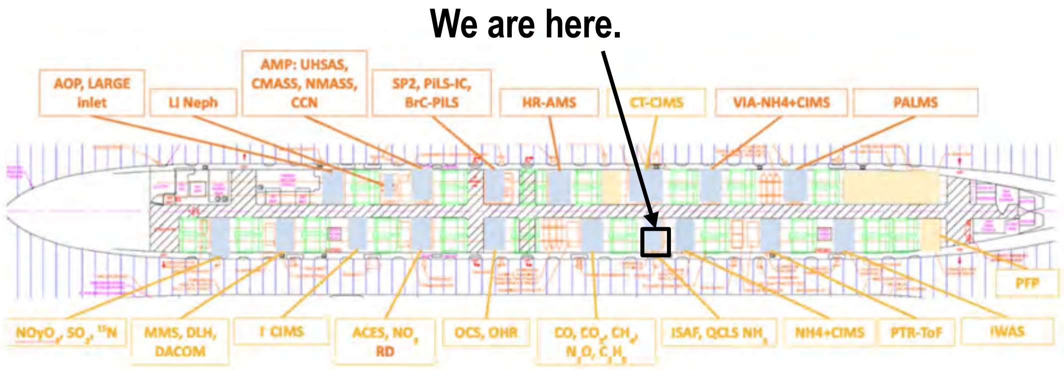
Detection Limit: <200 ppt @ 1 Hz

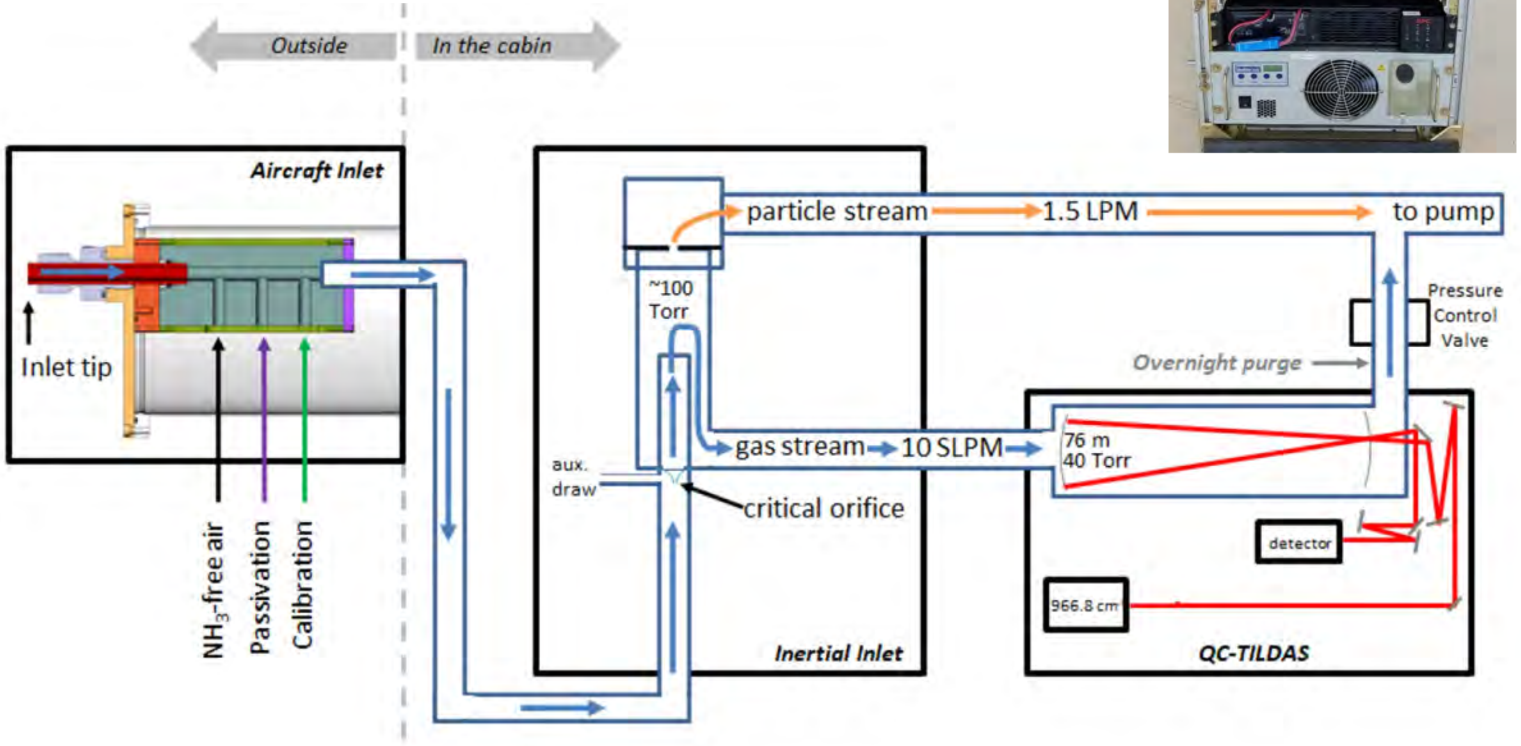
Accuracy: 12%

*As determined in flight on the NSF/NCAR C-130.

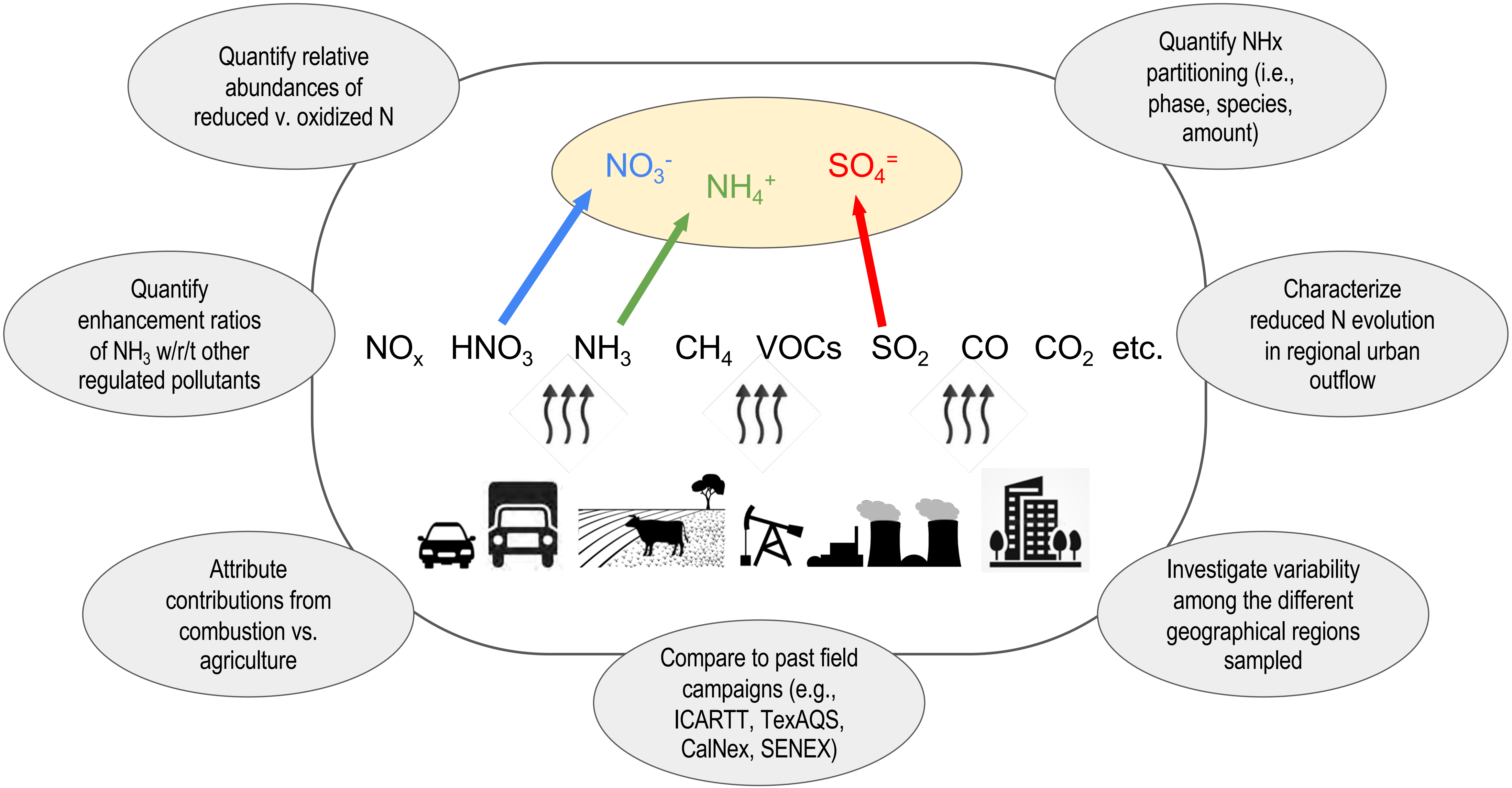
Key reference:

Pollack et al. (2019), AMT., 12, 3717–3742, DOI: 10.5194/amt-12-3717-2019.





Ammonia for AEROMMA Science Goals



OH REACTIVITY INSTRUMENT

Forschungszentrum Jülich
Institute of Energy and Climate Research

Hendrik Fuchs
Instrument PI

Anna Novelli
Scientist

Aaron Stainsby
PhD Student

SEPTEMBER 27, 2022

Mitglied der Helmholtz-Gemeinschaft

NOAA 2023 AEROMMA Atmospheric Emissions and Reactions Observed from Megacities to Marine Areas

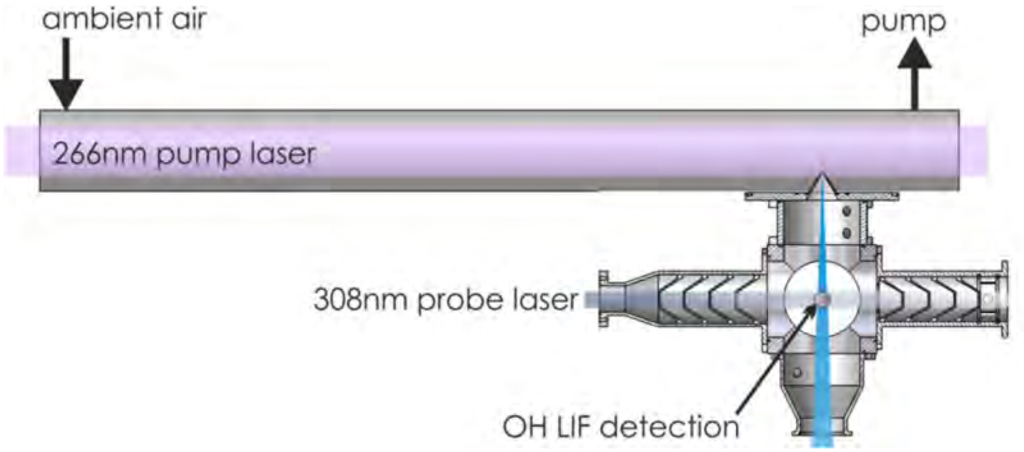
JÜLICH Forschungszentrum

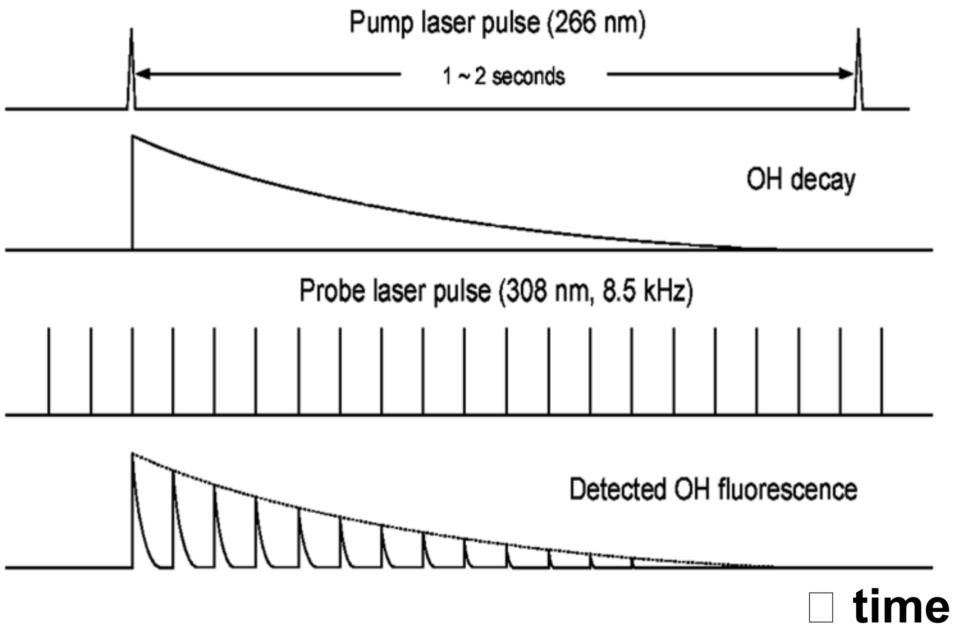
Contact: H.Fuchs@fz-juelich.de

LIF OH-REACTIVITY

$O_3 + h\nu\ (266nm) \rightarrow O_2 + O(^1D)$

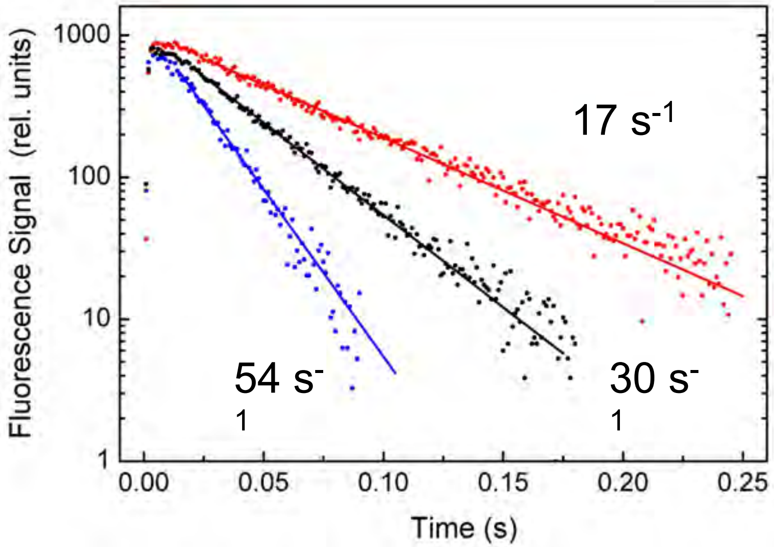
$O(^1D) + H_2O \rightarrow 2\ OH$





$$[OH](t) = [OH]_0 e^{-(k_{OH} t)}$$

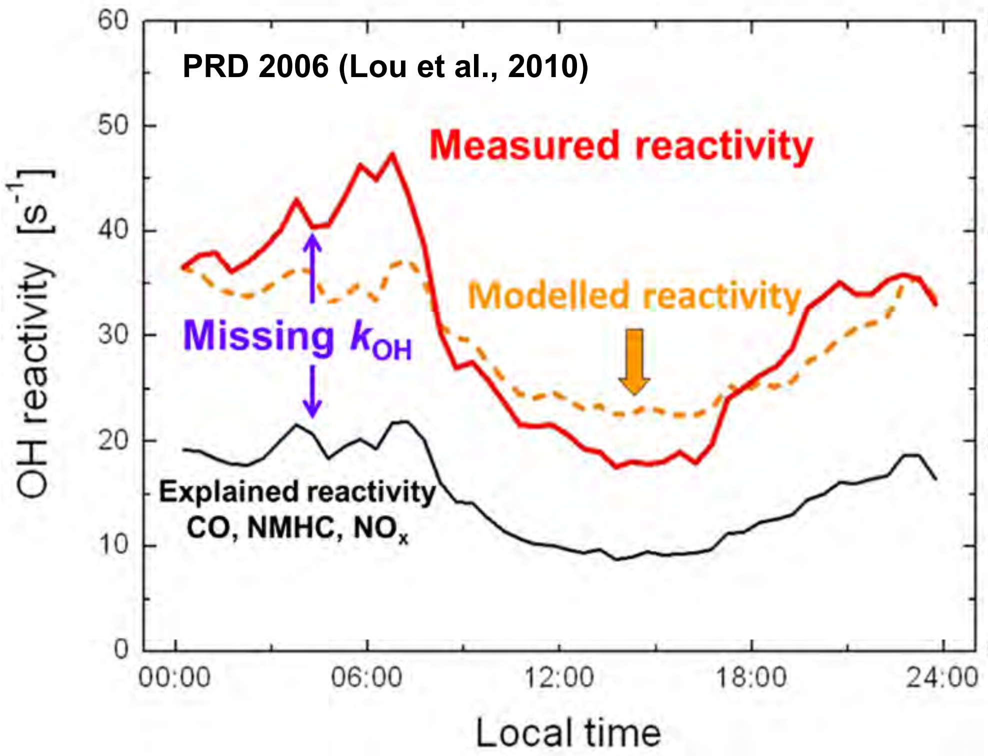
	k_{OH} instrument
Precision	0.2 s^{-1}
Accuracy	(5 – 10) % ± 0.7 s^{-1} for NO < 20 ppb
Limit of detection	2σ = 0.6 s^{-1}

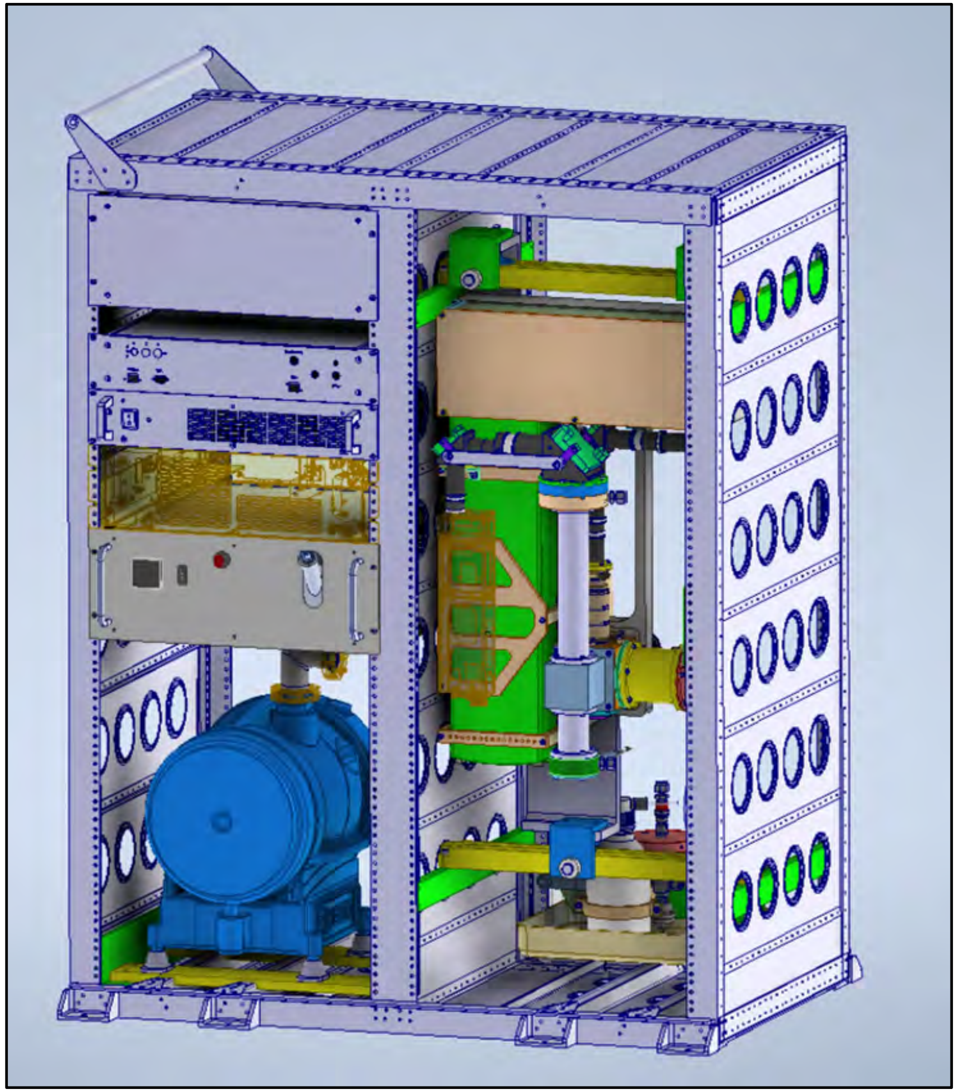


SCIENCE GOALS AND FOCI

Test completeness of $kOH_{calculated}$ by comparison with $kOH_{measured}$

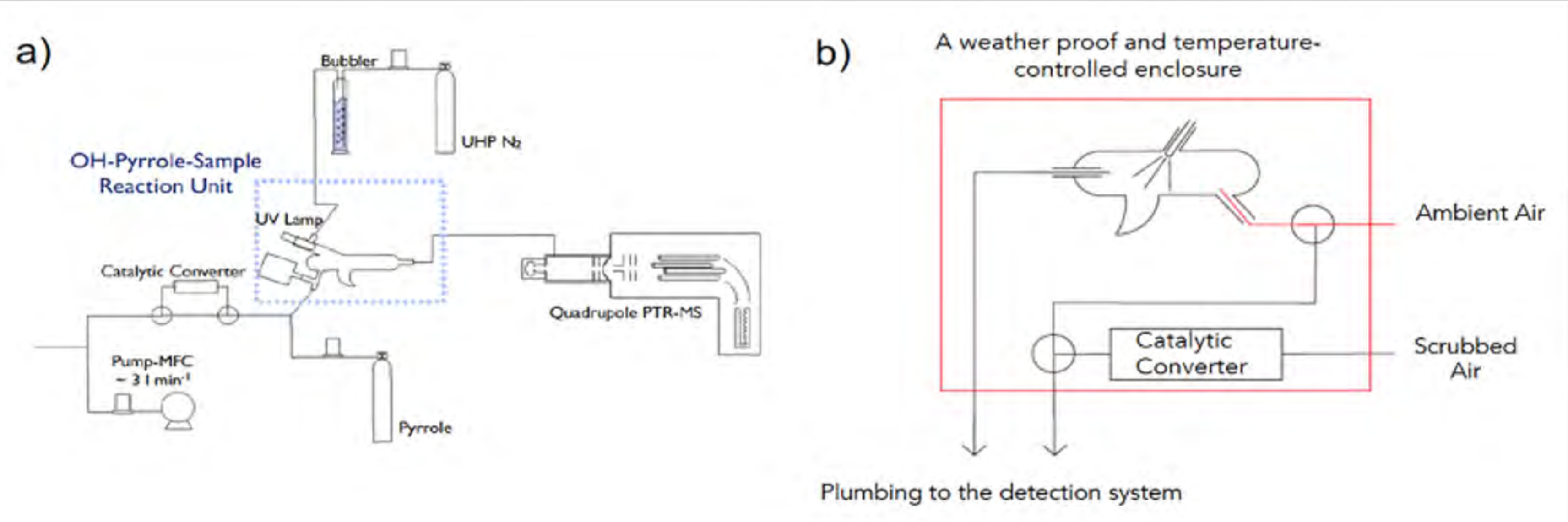
$$k_{OH} = \underbrace{\sum k_{OH+Xi}\,[X_i]}_{\text{known species } X_i} + k_{OH}^{missing}$$





Determination of Instantaneous Ozone Production Regime with total OH reactivity measurements in the New York Metropolitan Area during the AEROMMA campaign

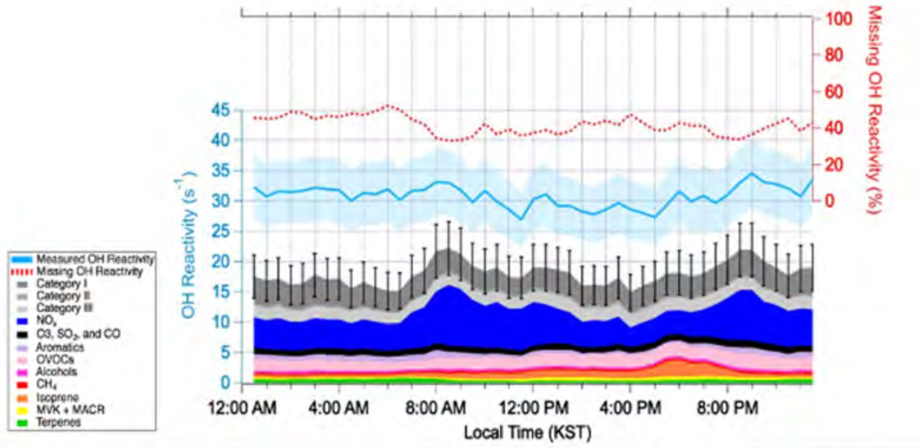
UC Irvine - Saewung Kim, Alex Guenther, Sanjeevi Nagalingam, Gracie Wong, Julie Devlin, and Katherine Paradere



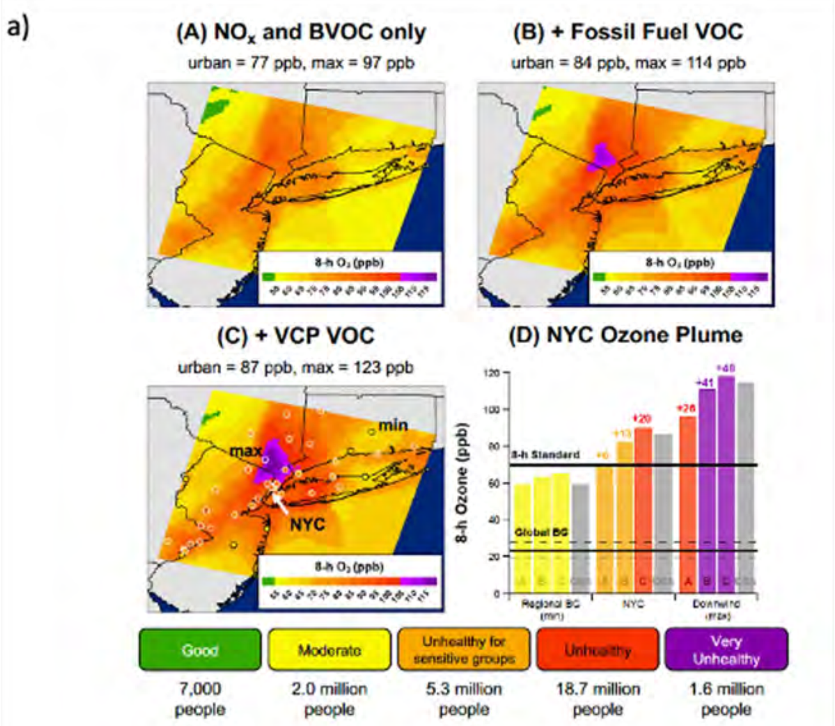
- Ground OH reactivity Observations using the Comparative Reactivity Method (Sinha et al., 2009) with an updated inlet system
- Possible ground observations for the CA deployment

Specific science questions

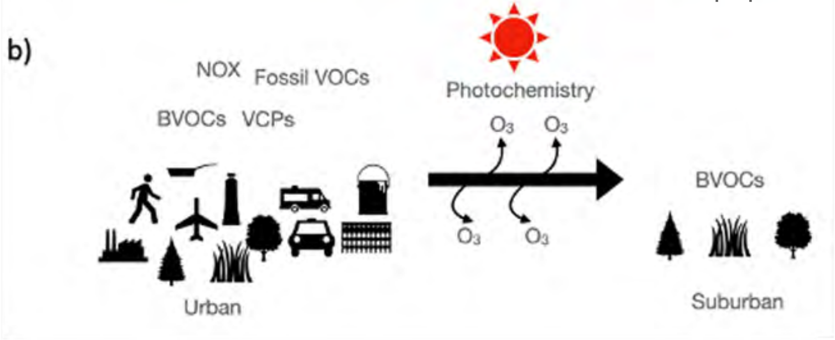
Sanchez et al., (2020)



- Identifying any unmeasured/unidentified compounds
- Source appointments for the unaccounted/unknown
- Wholistic identifications for the ozone production regimes



From AEROMMA white paper



Additional Observations

TOF CIMS Measurements (SF_6^-) to quantify radical precursors: HONO, HO_2NO_2, and HCl

BVOC

distribution

Drexel ECHAMP (HO_2 & RO_2) at CUNY ASRC (NYC-METS)

Ezra Wood
Instrument PI

Tauhidur Rahman
Grad Student

Khaled Joy
Grad Student

Contact:
Ezra.Wood@drexel.edu

Drexel Ethane CHemical AMPlifier $HO_2 + RO_2$ at CUNY Advanced Science Research Center (NYC-METS)

Targeted Species

"Total" Peroxy Radicals.

Only detects peroxy radicals that react with NO to form NO_2 and propagate HOx cycle

Instrument Performance

Time resolution: 2 minutes

Detection limit: 2-4 ppt

Precision: 1-2 ppt

Accuracy: 20 - 30%

Measure NO_2 ←

$HO_2 + NO \rightarrow OH + \mathbf{NO_2}$

$OH + C_2H_6 + O_2 \rightarrow C_2H_5O_2 + H_2O$

$C_2H_5O_2 + NO + O_2 \rightarrow CH_3CHO + \mathbf{NO_2} + HO_2$

← Air

NO, C_2H_6

References:

Anderson et al. (2019) *ACP* 19.5: 2845-2860

Wood et al. (2017) *ES&T Letters* 4.1: 15-19

Anderson et al. (2021), *ES&T* 55.8: 4532-4541

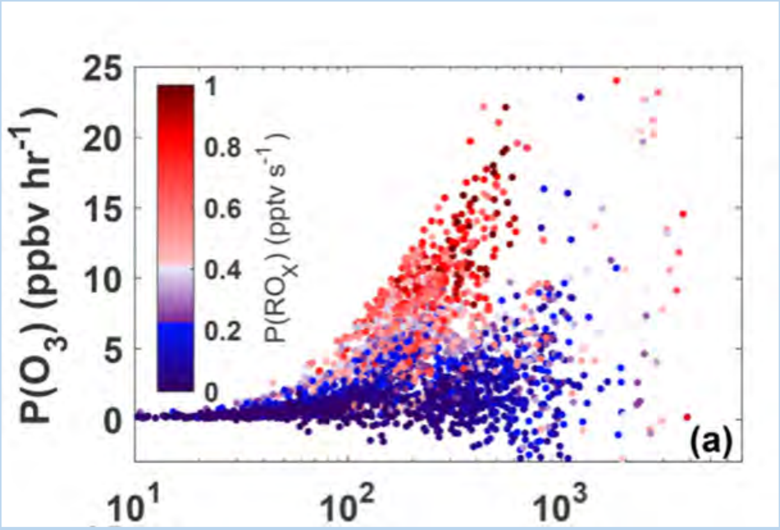
Science Goals & Questions

Characterize Instantaneous Ozone Production Rate $P(O_3)$ and dependence on NOx & VOCs (especially VCPs)

Determine Instantaneous Ozone Production Rates:

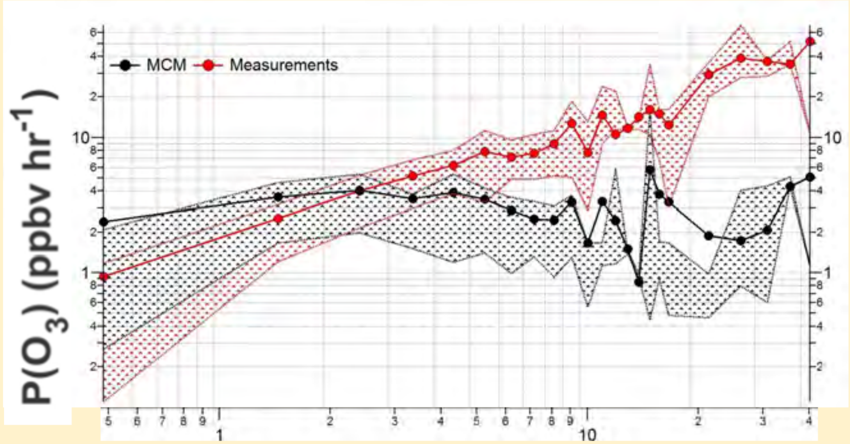
$P(O_3) = k([HO_2]+[RO_2])[NO]$

Example from San Antonio, 2017:



[NO] (pptv)

Do we understand high-NOx ozone chemistry? Investigate with 0-D models (collaborative)



[NO] (ppbv)

Large model-measurement discrepancies observed in London (Whalley et al. ACP 2018), Beijing, Wangdu, Colorado.

Bonus activities:

- Provide NO and NO_2 measurements (chemiluminescence/CAPS)
- Quantify on-road NOx emission factors (C-balance method)
- Provide photolytic HONO calibration source for I^- CIMS (Lindsay and Wood, AMT 2022)

York University - Reactive Nitrogen Measurements

SEYED DANIAL NODEH FARAHANI

ToF-CIMS Instrument (acetate)

PhD Student
Department of Chemistry
York University

MOXY SHAH

Nitrogen Oxides Instrumentation

MSc Student
Department of Chemistry
York University

TREVOR VANDENBOER

Team Leader

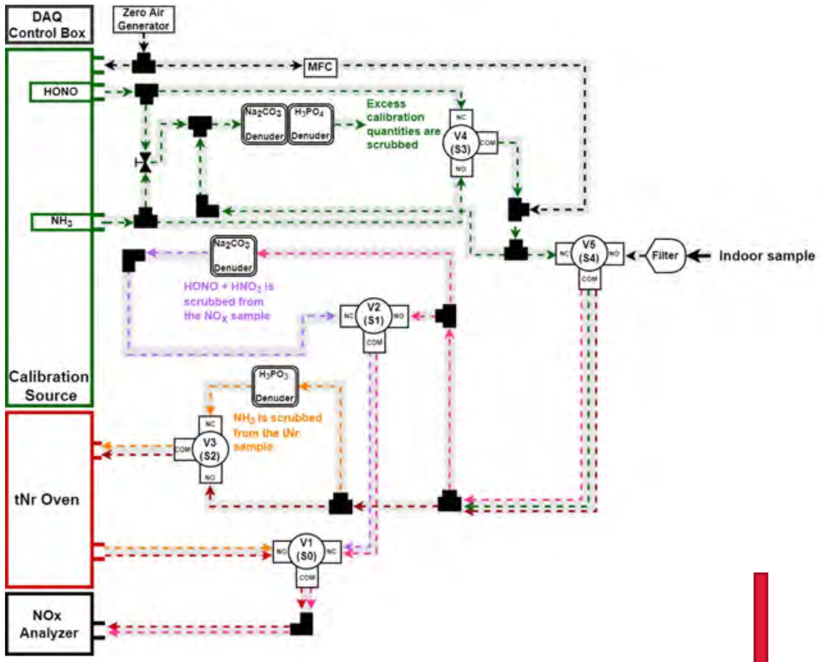
Assistant Professor
Department of Chemistry
York University

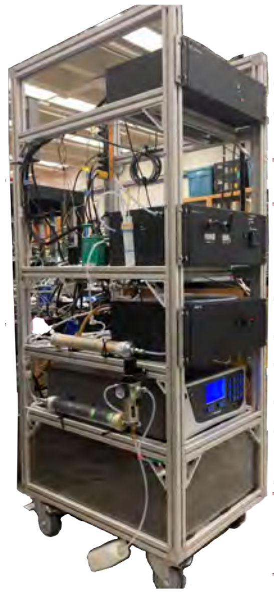
PROSPECTIVE GROUP MEMBER

ToF-CIMS and Total Reactive Nitrogen Instrumentation

Graduate Student and/or Postdoc
Department of Chemistry
York University

York University –H-ToF-CIMS (Acetate) and Total-N_r





DAQ Control System (LabJack & LabView)

Laptop Area

HONO/NH_3 Calibration Source (Lao et al. 2020)

Total Reactive Nitrogen Oven (Stockwell et al. 2018)

NO_x Analyzer (American Ecotech, Serinus 40)

Pumps (2)

T-Slotted Framing Rails & Casters (McMaster Carr)

Targeted Species

Total N_r

Gases: HONO+HNO_3, NR_3, NO, NO_2

Particulate: All condensed N_r

Time resolution: 5 – 20 minutes

Detection limits: 0.4 ppb for 1 min

Precision: signal/analyte dependent

Accuracy: ~±20 %

H-ToF-CIMS

Inorganic Acids: HCl, HONO, HNO_3

Organic Acids

Persistent Acids (PFCAs): TFA

Haloacetic acids: monochloroacetic acid

Performance: Currently under determination

YORK U

York University –H-ToF-CIMS (Acetate) and Total-N_r

Science Goals

Total N_r

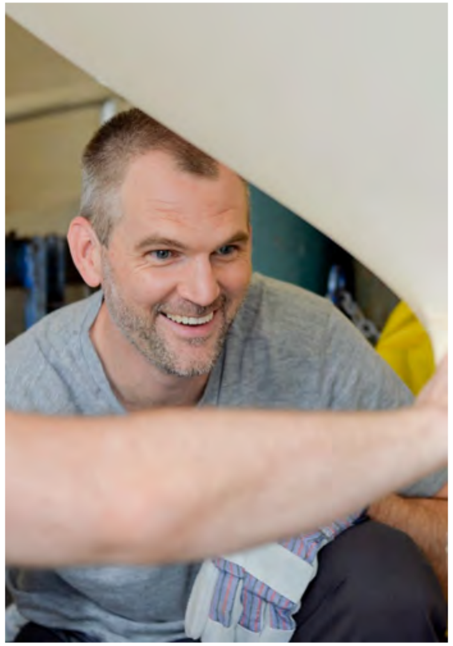
- NO_x contributions to O_3 and radical reservoir formation
- Urban gas and particle phase N_r budgets
- Inorganic vs organic N in PM
- Validate through CIMS and AIM-IC measurements

H-ToF-CIMS

- Impacts of HONO on radical budget
- Acid impacts on secondary inorganic PM formation
- Formation and fate of persistent halogenated acids in urban air

YORK U

Ozondesondes during STAQS

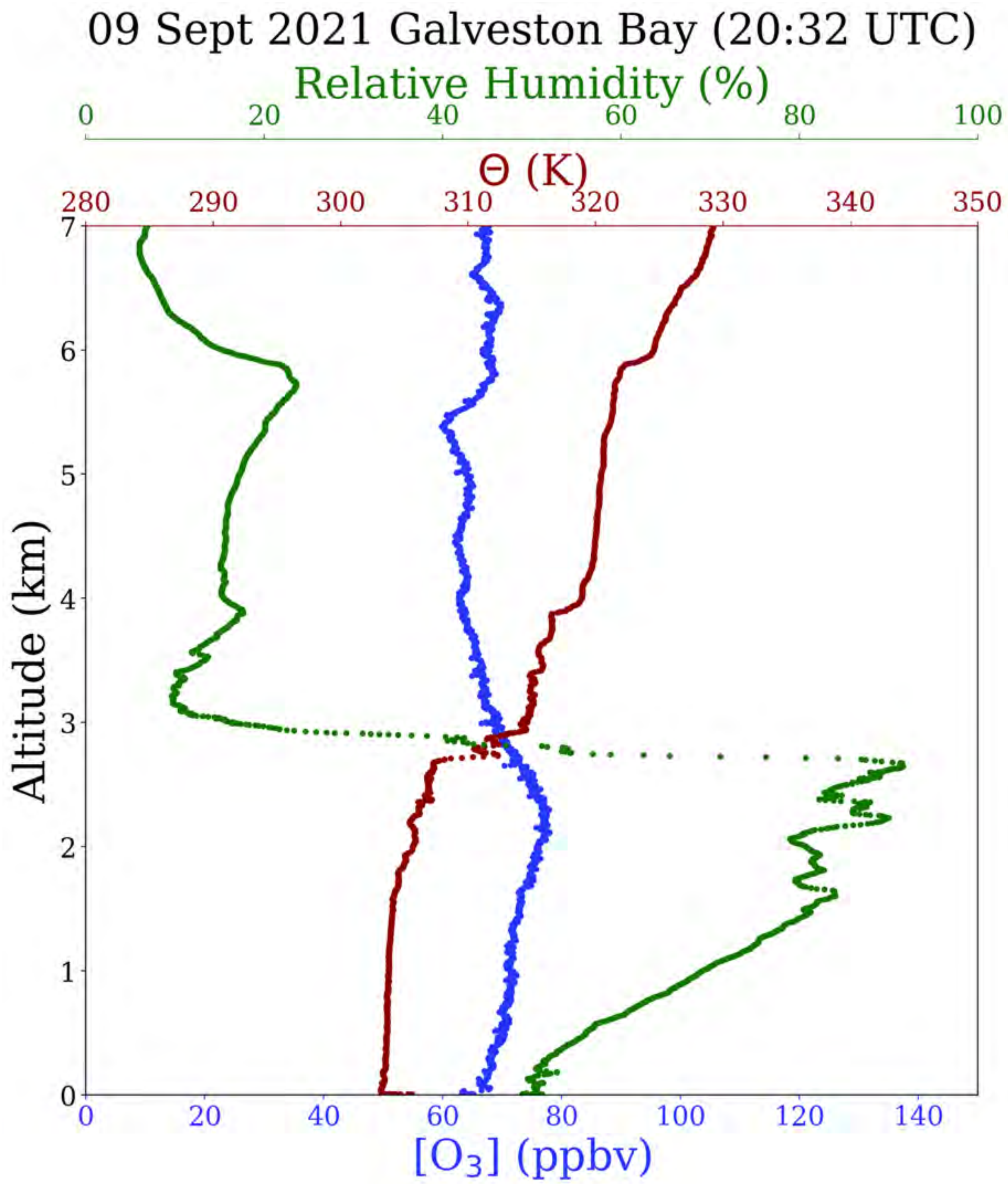


Paul Walter
St. Edward's University

John Sullivan
NASA Goddard

ST. EDWARD'S UNIVERSITY

NASA



Ozonesondes during STAQS

Balloon-based Instruments:
En-Sci 2Z Ozonesonde
iMet-4RSB Radiosonde

Data Collected:
Vertical Profiles of O_3 and meteorological data

Altitude range:
Surface to 24-30 km depending on balloon size
Rise rate of ~5 m/s

Instrument Performance:
Ozone
Accuracy: 5-10%
Response time: 25 s
(vertical resolution ~125 m)

Time Resolution: 1 Hz

Ozonesondes during STAQS

50-60 ozonesondes near Long Island Sound

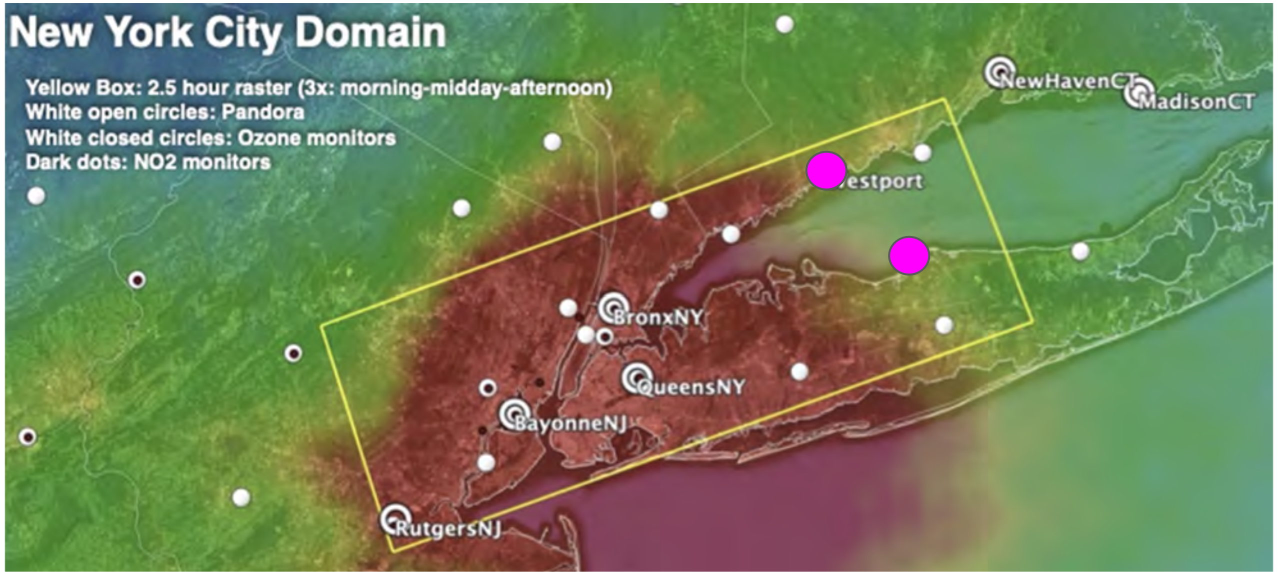
- ~20 collocated at each TOLNet ground-based ozone lidar site
  - NASA GSFC ozone lidar (Flax Pond, NY)
  - NASA LaRC ozone lidar (Westport, CT)
- 10-20 from other locations

Validation of

- ground-based & airborne ozone lidars
- TEMPO
- Pandoras

Characterize ozone episodes

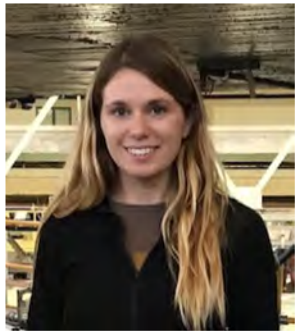
- Boundary layer and residual layer ozone
- Identification of possible ozone transport
- Boundary Layer heights
- Vertical profiles of U and V winds



Ground-based ozone lidar locations shown in pink. Image courtesy of Laura Judd.

NOAA Nitrogen Oxide Cavity Ring Down Spectrometer (NO_xCaRD)

4 Channel, one color CRDS instrument for NO, NO_2, NO_y, O_3



Kristen Zuraski

?

1. Direct detection of **NO_2** @ 405

1. Convert NO to NO_2 in excess O_3 to measure NO_x

$$NO + O_3 \text{ (20 ppm)} \rightarrow \mathbf{NO_2} + O_2$$

2. Convert O_3 to NO_2 in excess NO to measure O_x

$$O_3 + NO \text{ (20 ppm)} \rightarrow \mathbf{NO_2} + O_2$$

3. Thermally dissociate NO_y to NO_2

$$NO_y + \Delta \text{ (650 °C)} \rightarrow \mathbf{NO_2}$$

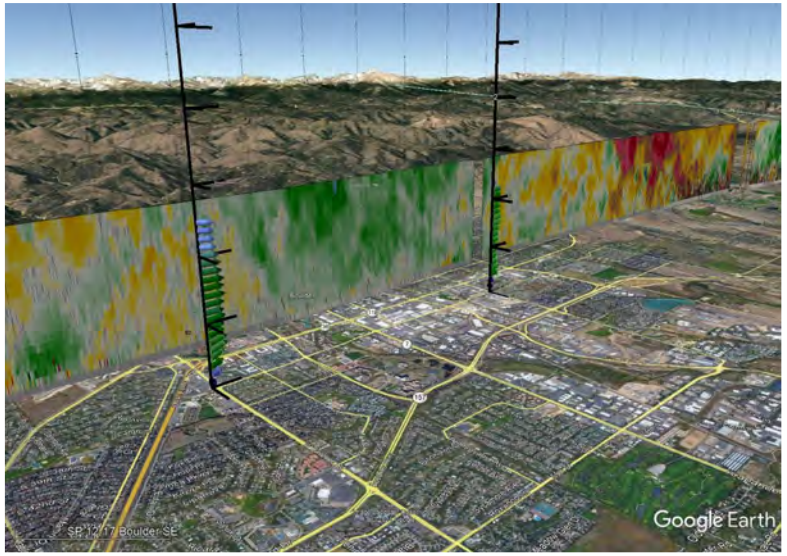
NO_2: ≥ 20 pptv, 5% accuracy / 1 Hz
NO, O_3: ≥ 50 pptv, 7% accuracy/ 1 Hz
NO_y ≥ 20 pptv, 12% accuracy / 1 Hz

Science Objectives: Coastal Urban Plume Dynamics Study (CUPiDS)

- Vertical profiles and cross boundary layer gradients of NO_2
- Air mass aging and photochemistry (NO_x/NO_y)
- Urban ozone production efficiency

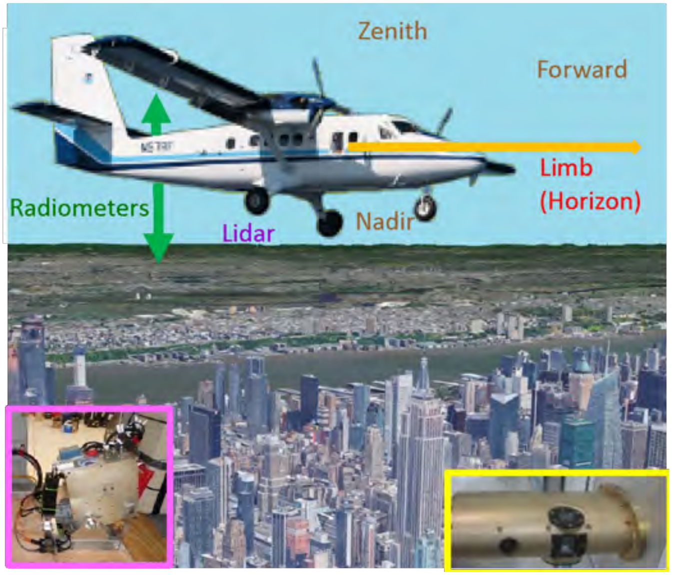
Scanning Doppler Lidar (CSL)

- Wind, Turbulence and Aerosol profiles
- Boundary Layer Depth



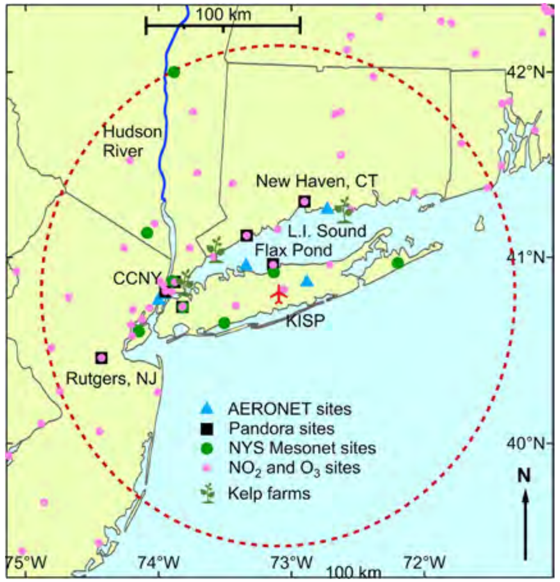
MAX-DOAS (CU – AC4 supported)

- NO_2, Formaldehyde, Glyoxal, IO profiles
- Surface albedo



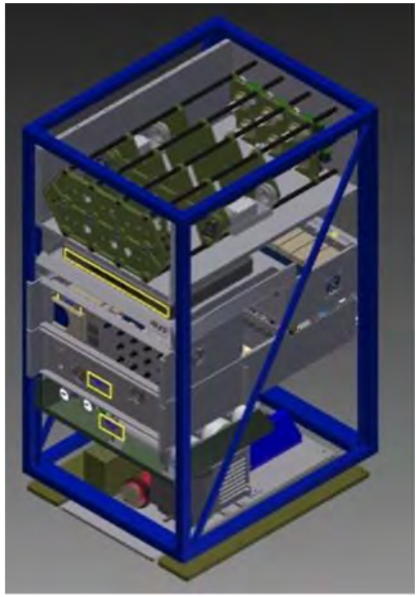
In-Situ Airborne (CSL,GML)

- GHG, NO_2, NO, NOy, O_3
- Temp, Press, RH



NOAA Nighttime Nitrogen Oxides Cavity Ring Down Spectrometer (NNOx)

P-3 Instrument: Developed 2004



Single Bay: 2022

Wyndom Chace

Carrie Womack

4 Channel, 2 Color CRDS Instrument for NO_3, N_2O_5, NO_2, O_3

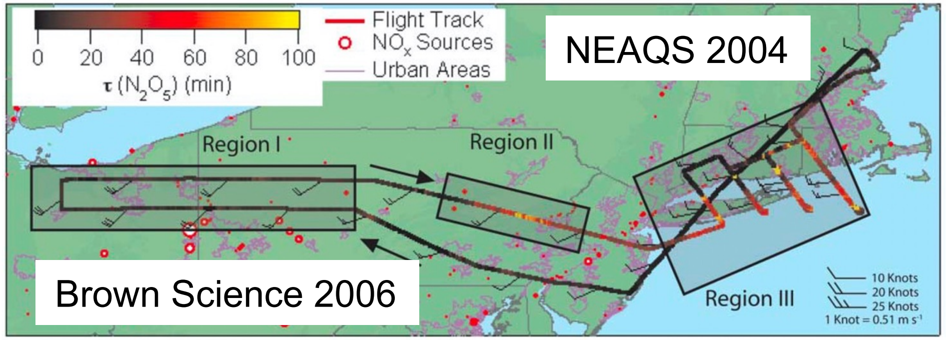
- 2 Channels @ 662 nm for detection of NO_3 (direct) and N_2O_5 (thermal dissociation to NO_3)
  $N_2O_5 + \Delta\ (140°C) \rightarrow NO_2 +$ **NO_3**
  NO_3 by 662 nm optical extinction, sensitivity ≥ 0.2 pptv / 1 Hz

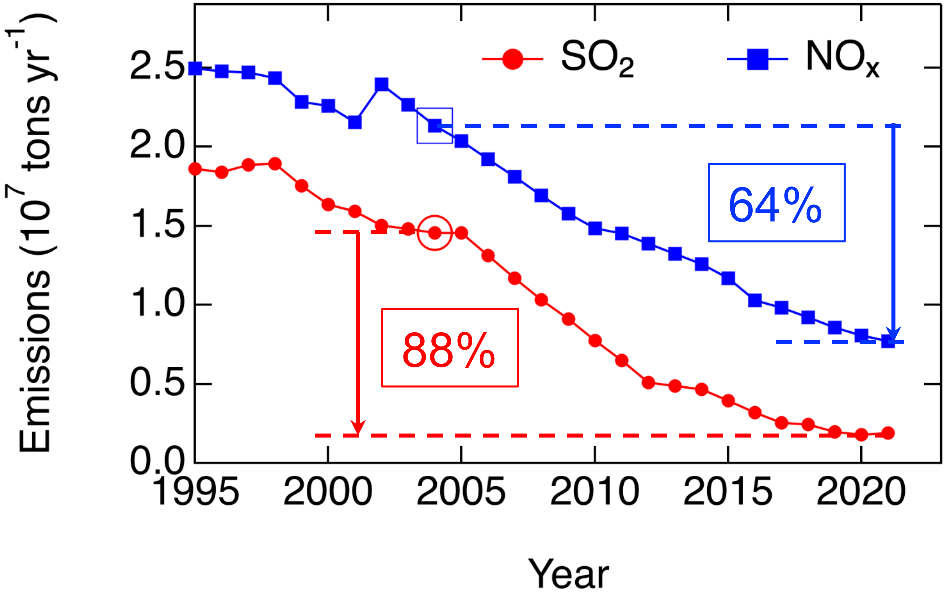
- 2 Channels @ 405 nm for detection of NO_2 (direct) and O_3 (via conversion to NO_2)
  O_3 + NO (excess, ~20 ppm) → **NO_2** + O_2 (*or* sum of $NO_2 + O_3 = O_x$)
  NO_2 by 405 nm optical extinction, sensitivity ≥ 20 pptv / 1 Hz

Science Objectives

Limited time for flying after dark, and no dedicated night flights !

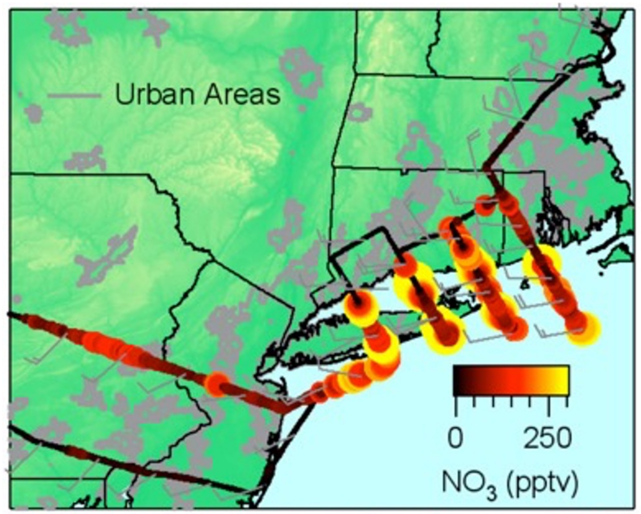
1. N_2O_5 heterogeneous uptake

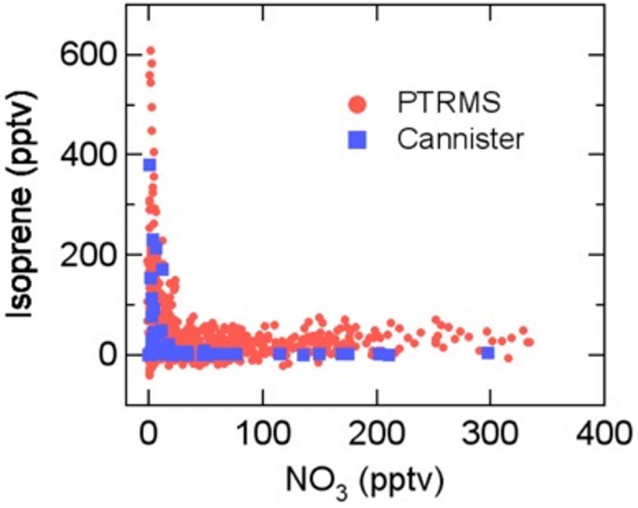




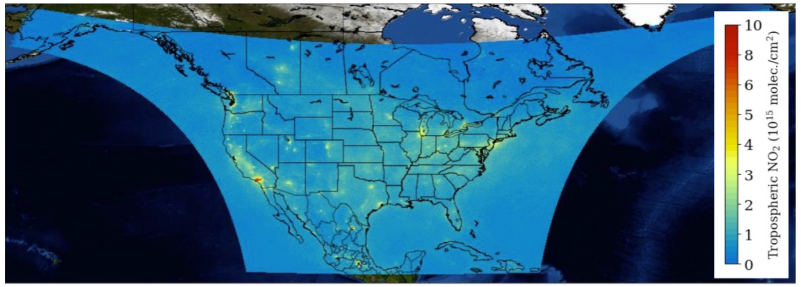
Change in sulfate N_2O_5 uptake ?

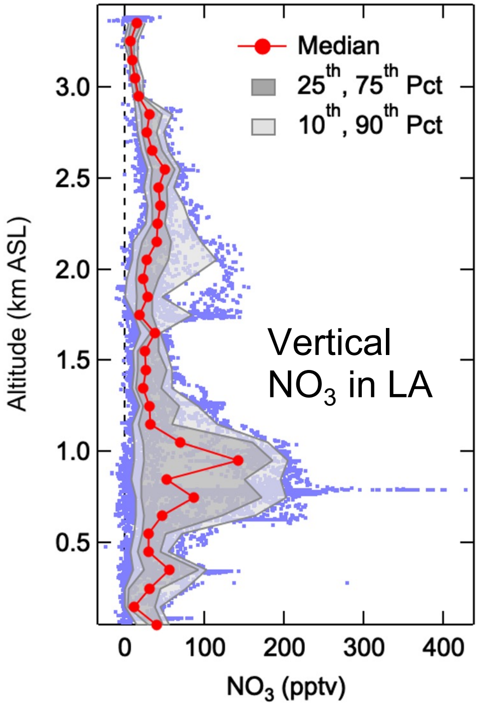
2. Isoprene Oxidation





3. Satellite NO_3 ?





Red channels on TEMPO and GCAS (G-V)

Twilight measurement of nighttime species

Reactive Nitrogen, Ozone, and Radicals

Glenn M. Wolfe (Moderator)
NASA Goddard Space Flight Center

AGES Meeting
28 September 2022

Speaker	Measurement	Mission
Glenn (for Lee Mauldin)	RO_x, H_2SO_4	GOTHAAM
Glenn (for Ale Franchin)	NO_x, O_3	GOTHAAM
Andrew Rollins	NO_x, NO_y, O_3	AEROMMA
Ilana Pollack	NH_3	AEROMMA
Aaron Stainsby	OH Reactivity	AEROMMA
Saewung Kim	OH Reactivity	NYC-METS
Ezra Wood	$HO_2 + RO_2$	NYC-METS
Trevor VandenBoer	Acids, Total N_r	THE CIX
Paul Walter	Sondes	STAQS
Steve Brown	NO_y, O_3	CUPiDS
Steve Brown	"Night NO_x"	AEROMMA