



# ***Thrust 5: Applications and Testbeds***

*Thrust leader:  
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Princeton University*

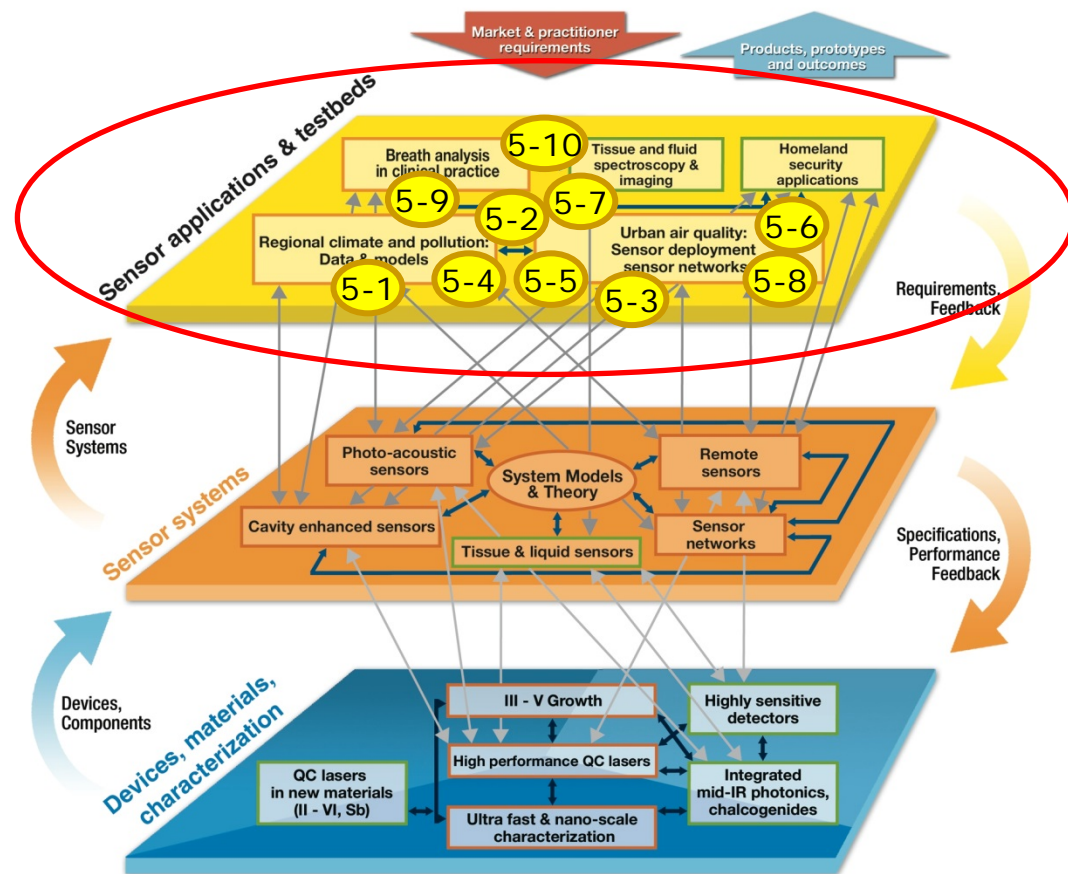
*NSF-ERC Cooperative Agreement EEC-0540832*





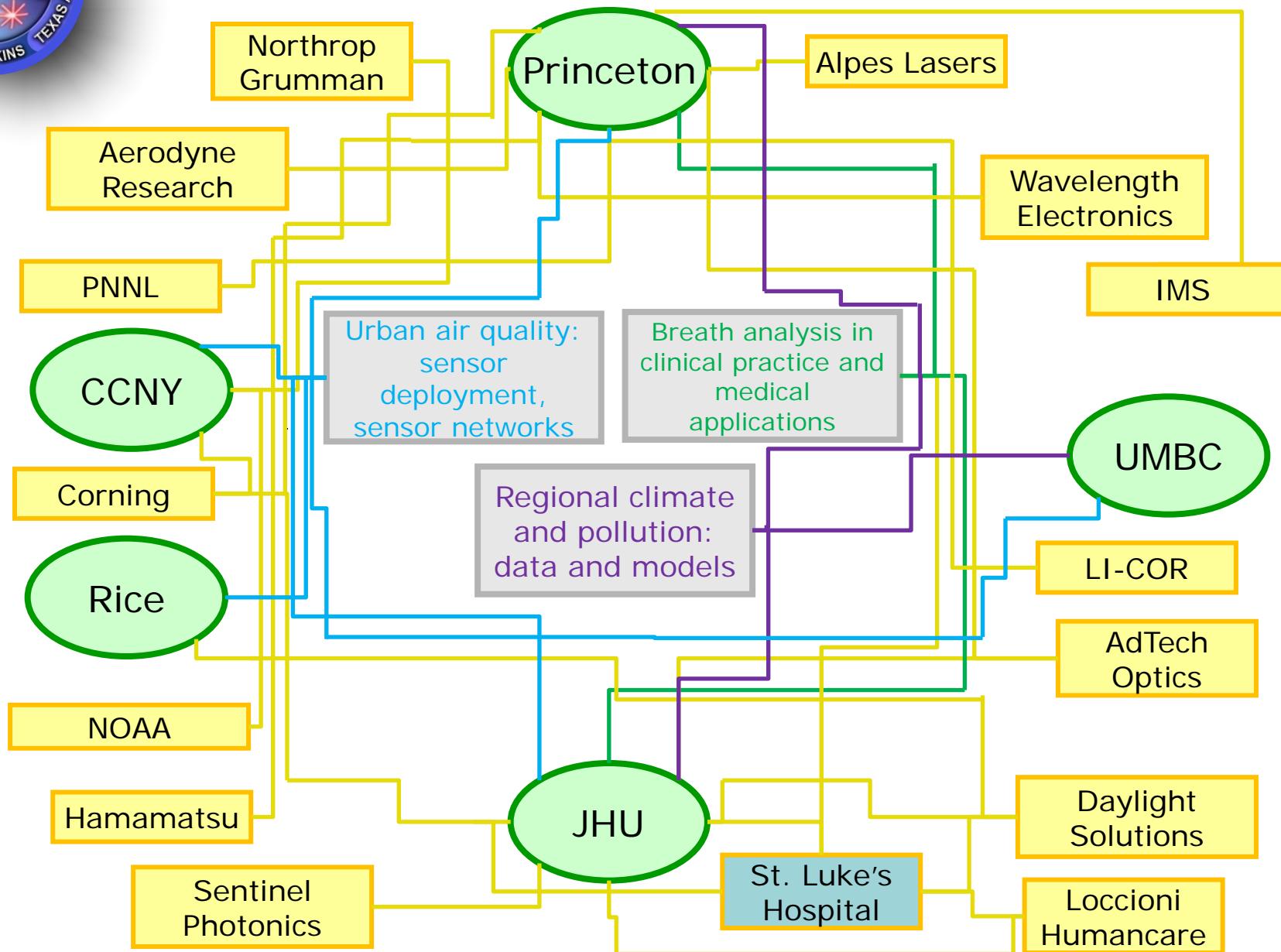
# Projects in Progress

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| 5.1   | A Multi-Sensor Field Deployment for Assessing Spatial and Temporal Variability of Carbon, Nitrogen and Water Fluxes |
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# Projects and Collaboration





## Thrust 5 Participants

- Faculty: 16
- Graduate Students: 16
- Undergraduates: 7
- Institutions: 5

### Key Companies:

Daylight Solutions, AdTech Optics, Aerodyne Research, LICOR, Hamamatsu, Alpes, Corning, Picarro, Wilmer Eye Clinic, Adtech Optics, Northrop Grumman, Wavelength Electronics, Intelligent Materials Systems

| Faculty          | Institution |
|------------------|-------------|
| Sam Ahmed        | CCNY        |
| Elie Bou-Zeid    | Princeton   |
| Claire Gmachl    | Princeton   |
| Rob Griffin      | Rice        |
| Barry Gross      | CCNY        |
| Jin U Kang       | JHU         |
| Fred Moshary     | CCNY        |
| Terrence Risby   | JHU         |
| James Smith      | Princeton   |
| Steve Solga      | St Luke's   |
| Lisa Spacek      | St Luke's   |
| Katalin Szlavecz | JHU         |
| Frank Tittel     | Rice        |
| Claire Welty     | UMBC        |
| Gerard Wysocki   | Princeton   |
| Mark Zondlo      | Princeton   |



# *Thrust Goals*

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- ***Applications:*** Air quality, regional climate, and carbon cycle assessments with a focus on urban environments and energy production; laser therapy and surgery; medical diagnostics using breath analysis.
- ***Goals:*** To develop monitoring technologies and analysis methods to address key societal problems concerning air quality, regional climate, the carbon cycle, and public health.



# Deliverables

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- **Baltimore Testbed:** Wireless sensor network, point sensors, turbulent flux measurements; applications.
- **Princeton Testbed:** Turbulent flux measurements, wireless sensor networks, point sensors, mobile sensor platforms, lidar, open path remote sensing, applications.
- **New York City Testbed:** Lidar, open path remote sensing, point sensor networks, applications.
- **Texas Testbed:** Houston (Moody Tower), point sensors and mobile sensors, applications.
- **St Lukes Hospital Testbed:** Clinical trials for fast response breath analysis; applications.
- **Field Deployments of MIRTHE Sensors:** SLIP, Beijing, Colorado, Texas.



# Key Results / State-of-the-Art

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- Vehicle  $\text{NH}_3$  emissions in urban areas underestimated by factor of two, based on measurements from mobile platforms.
- Super-emitting well pads in the Marcellus shale dominate overall methane emissions.
- A compact, drone-based methane sensor was successfully flight tested.
- Hydrogen Peroxide sensor system based on multi-pass absorption using CW DFB-QCL was built and tested.
- Upland forests may sequester less methane than previously thought.
- Partitioning of evaporation between plant transpiration and soil evaporation exhibits pronounced seasonal and diurnal cycles.
- QCL open-path fence-line system to monitor methane and nitrous oxide was built and tested.
- Two Channel aerosol and cloud micro-pulse IR lidar was built and tested.
- Urbanization alters regional climatology of rainfall in New York, Baltimore and Beijing testbeds.
- Use of short term interventions to evaluate changes in ammonia for medical diagnostics.
- Freehand laser surgery techniques using QCL lasers developed and demonstrated.



## ***Response to Comments***

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The Thrust 5 Health Testbeds are a great opportunity for students of all levels to gain an appreciation of the real world application of sensor systems for disease monitoring, though MIRTHE has not demonstrated a clear way to inculcate students into these testbeds.

**To bring the topic closer to MIRTHE students, we included a tutorial on medical applications in the 2014 MIRTHE Summer Workshop.**





# Urban Emissions of Greenhouse Gases and Air Pollutants

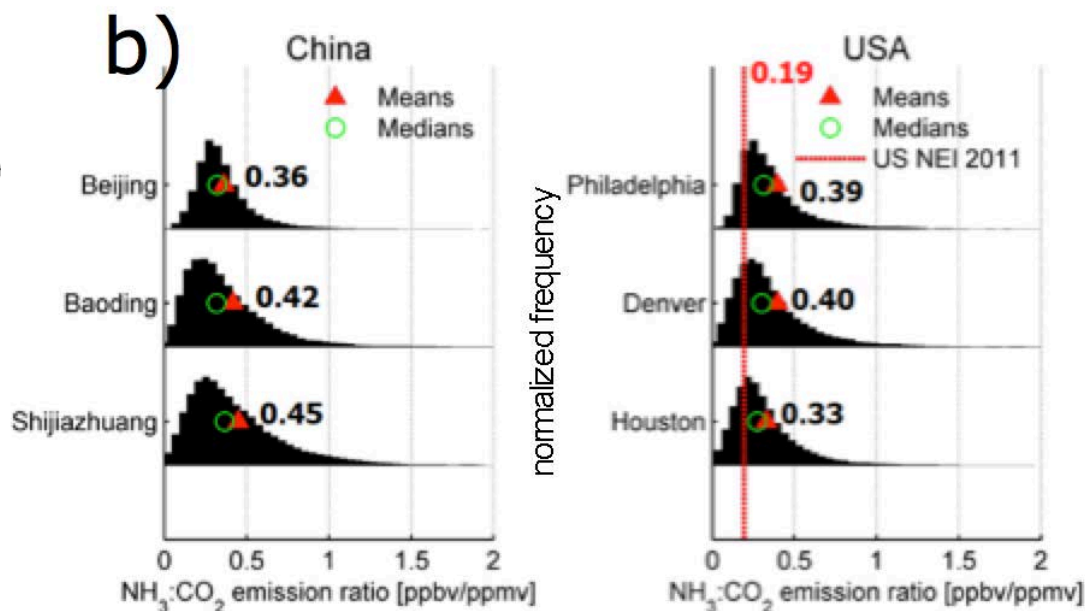
Multi-species measurements (> 8000 km) allows for fingerprinting of emissions in two field studies:

CAREBEIJING 2014, China  
NASA DISCOVER-AQ, CO

Fleet-wide,  $\text{NH}_3:\text{CO}_2$  emission ratios in US/China cities are comparable ( $0.39 \pm 0.07$ )

Vehicle  $\text{NH}_3$  emissions in urban areas underestimated by factor of two (US National Emissions Inventory = 0.19)

First validation of the NASA Tropospheric Emissions Spectrometer (TES) satellite  $\text{NH}_3$  measurements at the single-pixel scale:



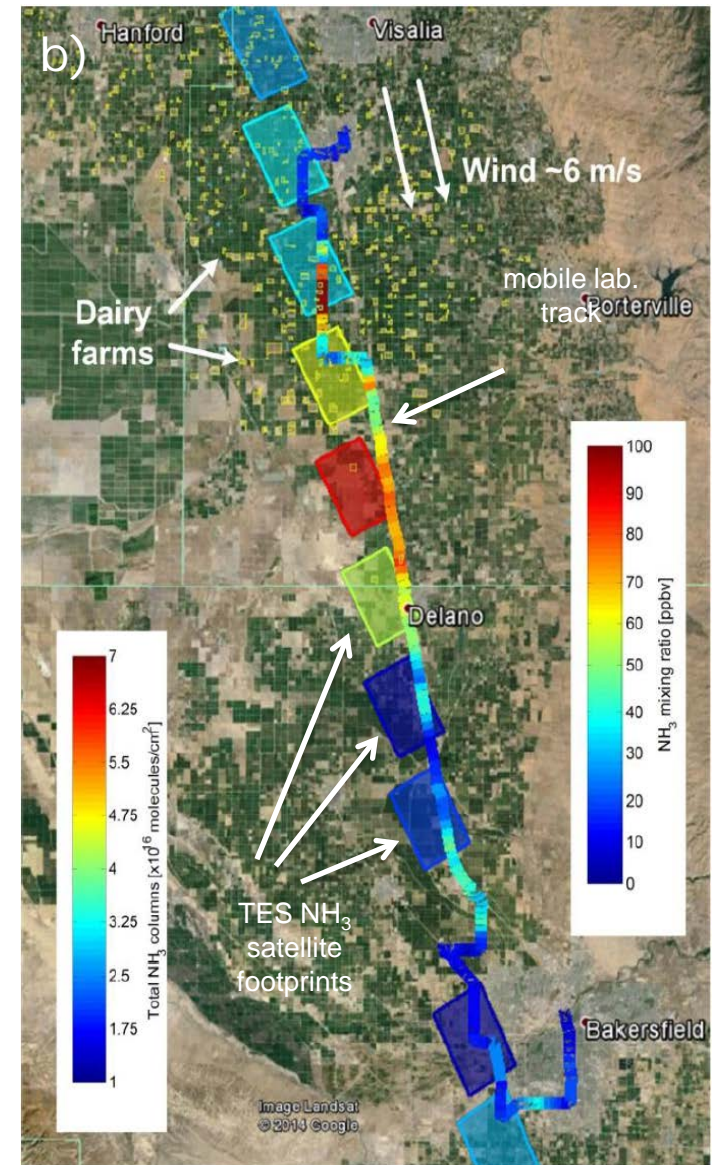


# Urban Emissions of Greenhouse Gases and Air Pollutants

First validation of the NASA Tropospheric Emissions Spectrometer (TES) satellite  $\text{NH}_3$  measurements at the single-pixel scale.

TES agrees within 6% of mobile/airborne  $\text{NH}_3$  data

increased confidence in global  $\text{NH}_3$  measurements





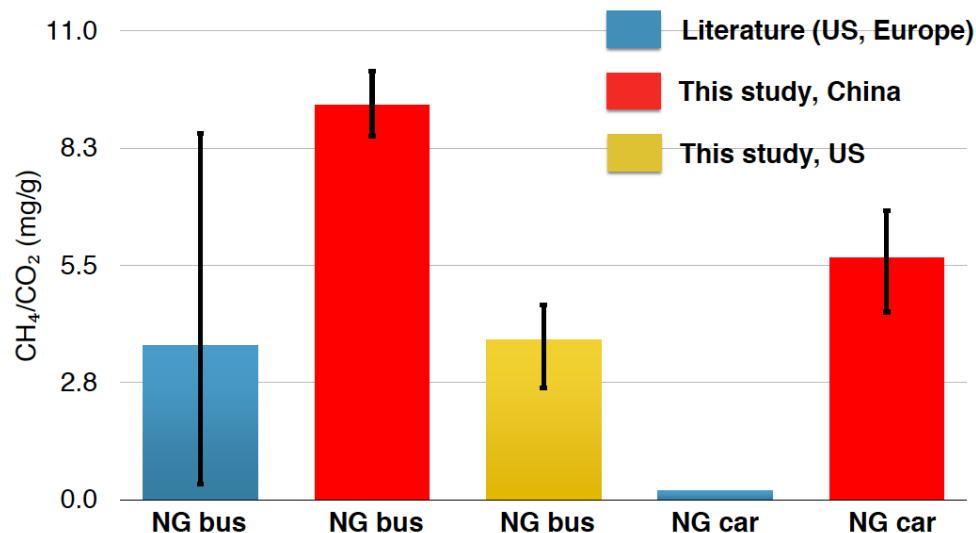
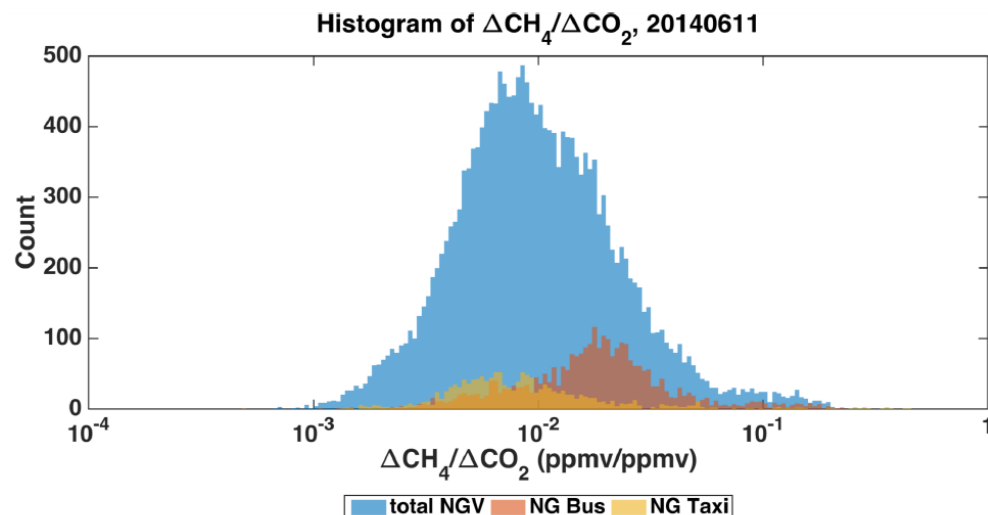
# Fugitive Methane from Petrochemical Activities

Super-emitting well pads in the Marcellus shale dominate overall emissions

- 80% of emissions from only 12% of well pads
- identification of super-emitters is key for mitigation

Natural gas vehicles (NGVs) in China have no climatic benefit due to leaks

- $\text{CH}_4$  from NGVs is 755 ( $\pm 240$ ) Gg  $\text{CH}_4$  / year
- every 1% of vehicle fleet converted to natural gas results in a 1.5% increase in  $\text{CH}_4$  emissions



(a) histogram of measured  $\Delta\text{CH}_4/\Delta\text{CO}_2$  emission ratios from natural gas vehicles in China; (b)  $\text{CH}_4/\text{CO}_2$  emission factors for natural gas cars and buses (red, yellow = present study); .

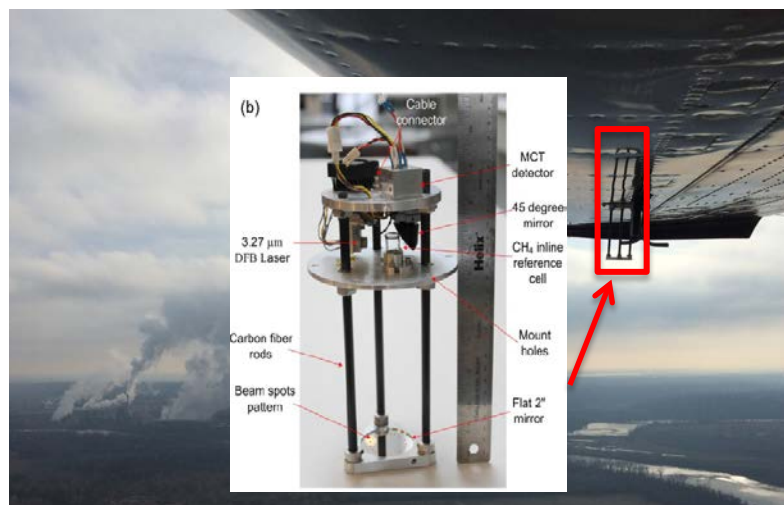
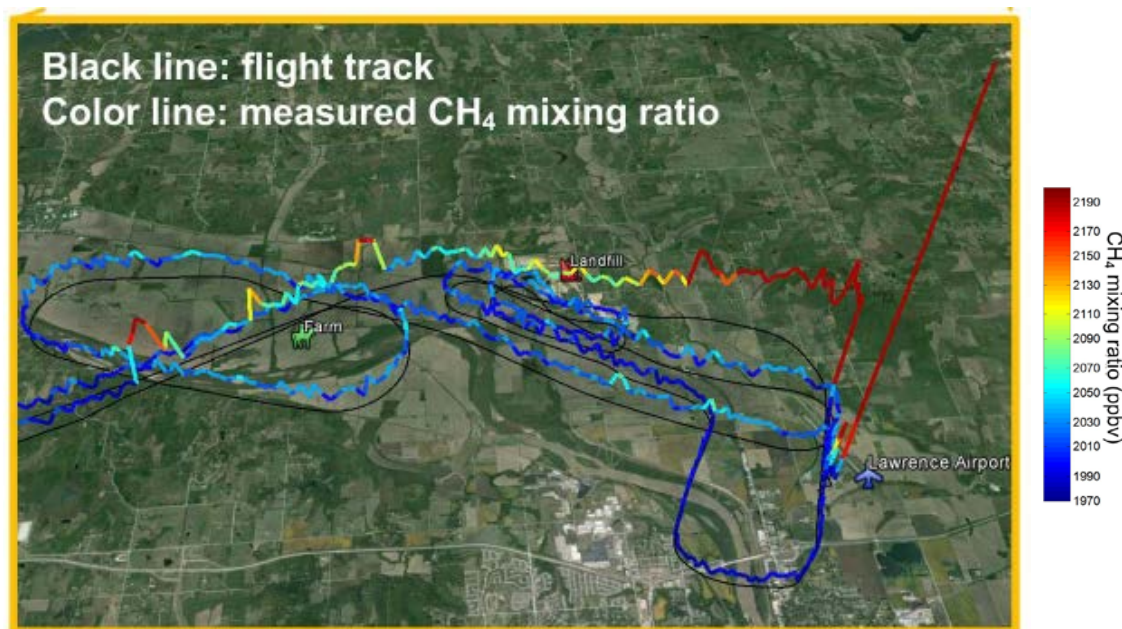




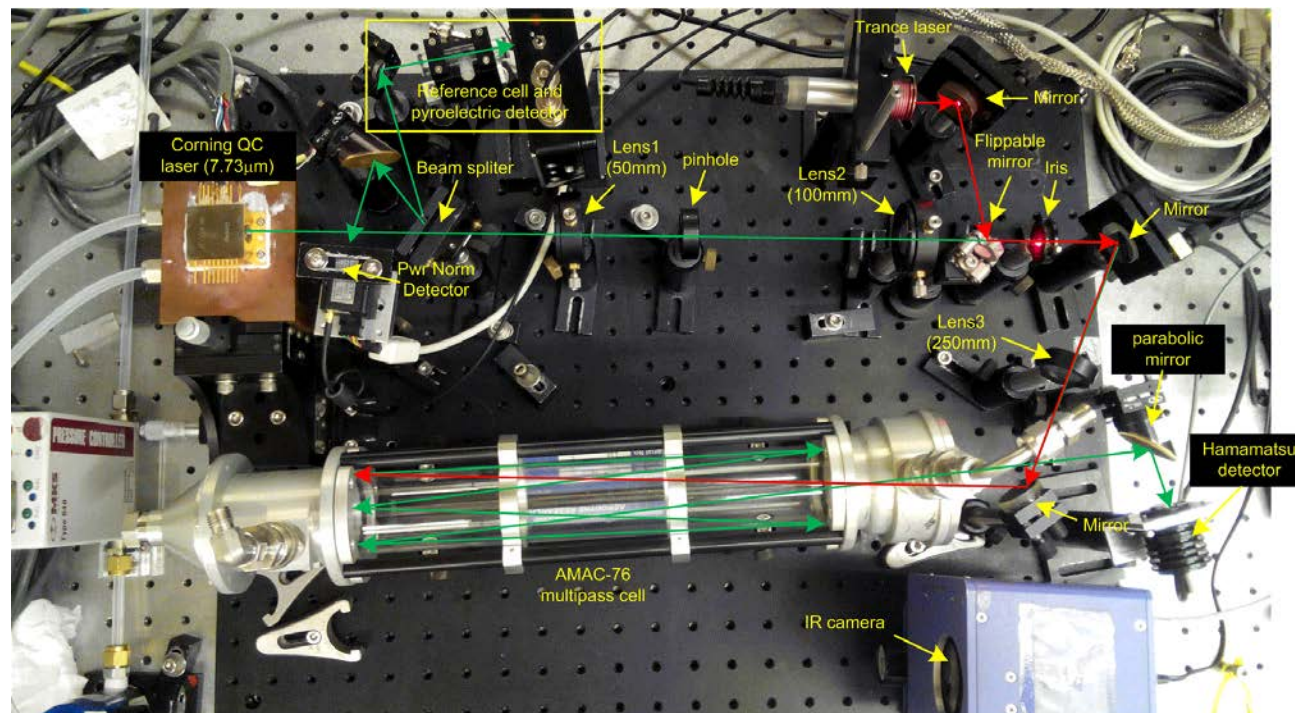
# Fugitive methane from petrochemical activities

A compact, drone-based  $\text{CH}_4$  sensor was successfully flight tested

- laser: 3.27 micron GaSb DFB
  - precision: 2 ppbv at 10 Hz
  - total mass: 1.81 kg (sensor + electronics)
  - flight stability < 30 ppbv over 2 h
  - agreement  $\pm(0.5\% + 5 \text{ ppbv})$
- drone-based flights along pipeline in May 2015



- Sensor system based on multi-pass absorption using CW DFB-QCL and targeting  $H_2O_2$  absorption line at  $1296.2\text{ cm}^{-1}$  was built .
- System deployed at Rice University campus and compared with commercial fluorescence-based instrument (AeroLaser AL2021).
- Further reduction of detection limit is needed for atmospheric monitoring of  $H_2O_2$  (sub-ppbv level).
- Significant interference from other atmospheric constituents (e.g.,  $H_2O$ ,  $N_2O$  and  $CH_4$ ) at the targeted spectral region was identified.

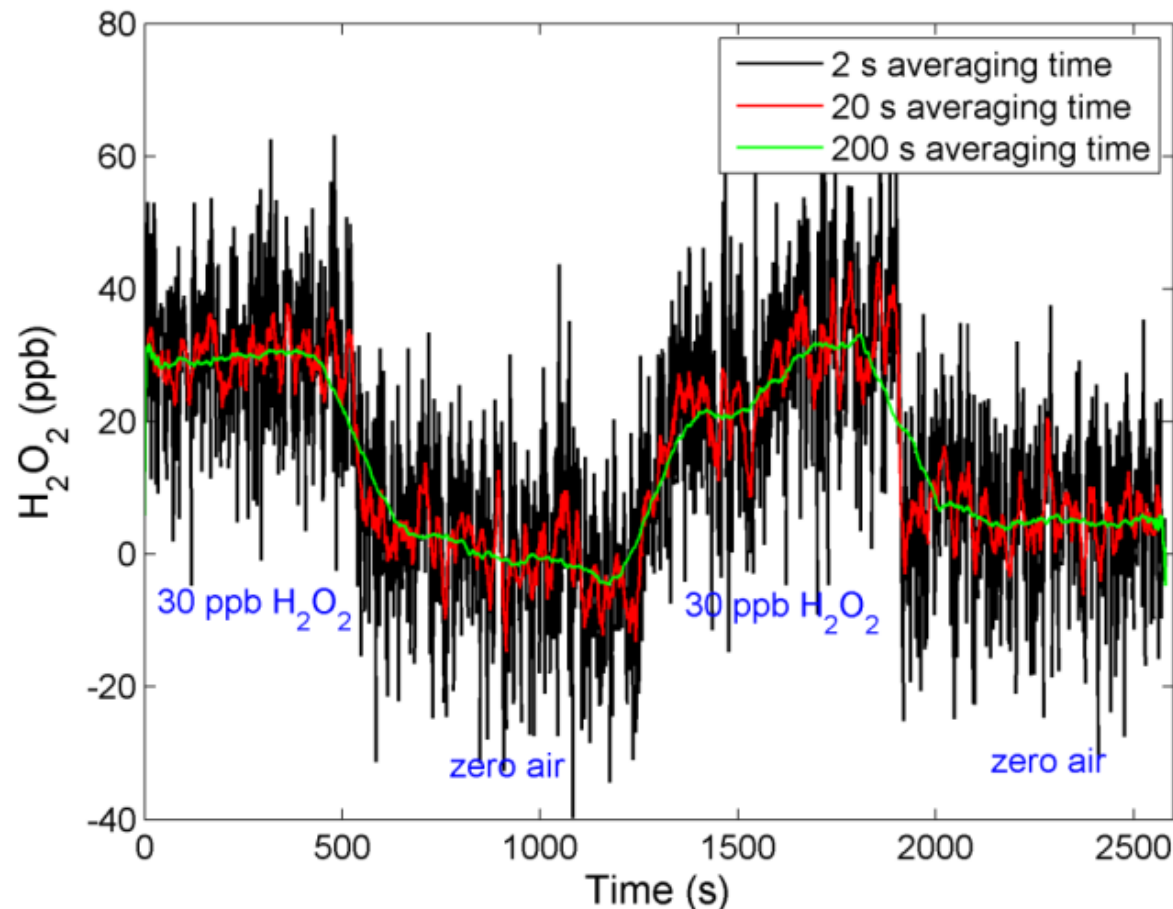


*Multi-pass absorption-based sensor system for atmospheric  $H_2O_2$  detection*



# Sensor for Atmospheric Hydrogen Peroxide ( $\text{H}_2\text{O}_2$ )

- Minimum  $\text{H}_2\text{O}_2$  detection limit (MDL): 13.4 and 1.5 ppb (200 and 2 sec integration time respectively)
- Improved MDL compared with previous QEPAS-based sensor (75 ppb at 1 sec integration time)
- Improved detection will be achieved by targeting a new spectral region with minor interference from other atmospheric species ( $1249.45 \text{ cm}^{-1}$ )



*Detection of gas-phase  $\text{H}_2\text{O}_2$  at the ppb level using the multi-pass absorption-based sensor system*





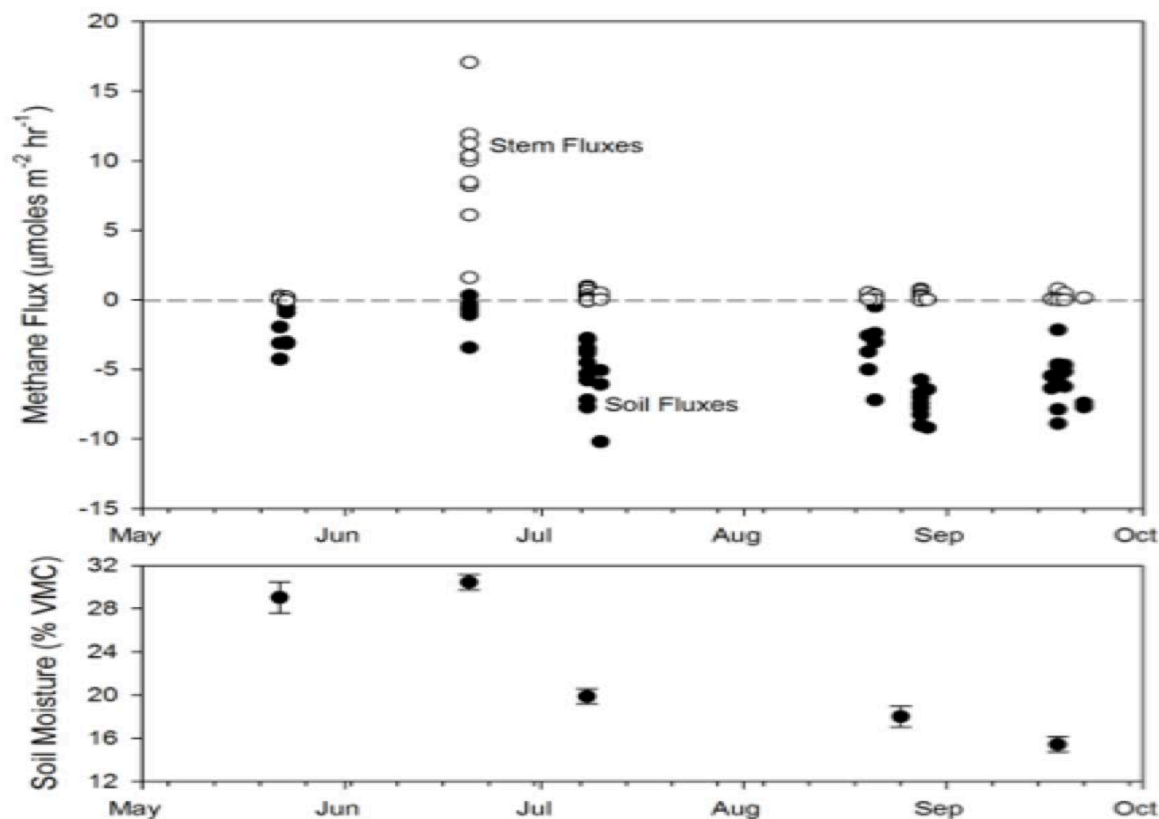
# Understanding the Carbon Cycle: the Contribution of Soil and Vegetation

Methane fluxes across tree stem and soil surfaces in during the 2014 growing season. Points above 0 indicates source, points below are sinks. Each point represents a significant flux ( $R^2 > 0.8$ ).



Upland forests may not be the uniform  $\text{CH}_4$  sinks as previously thought.

*In situ* data demonstrate that  $\text{CH}_4$  is emitted from the stems of dominant tree species, and that tree emissions occur throughout the growing season while soils adjacent to the trees are consuming  $\text{CH}_4$



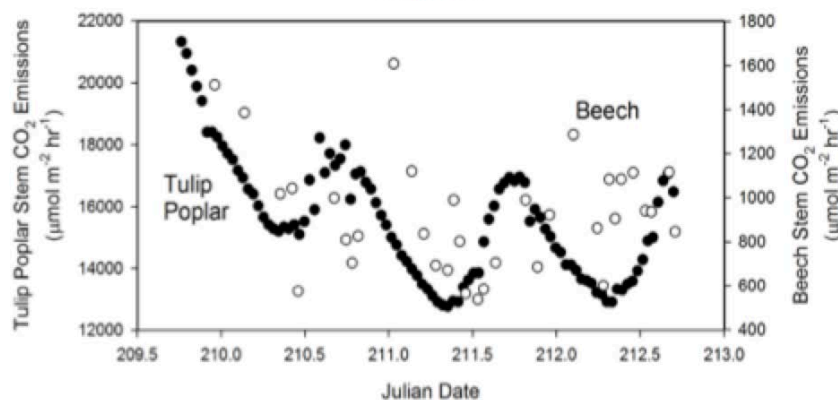
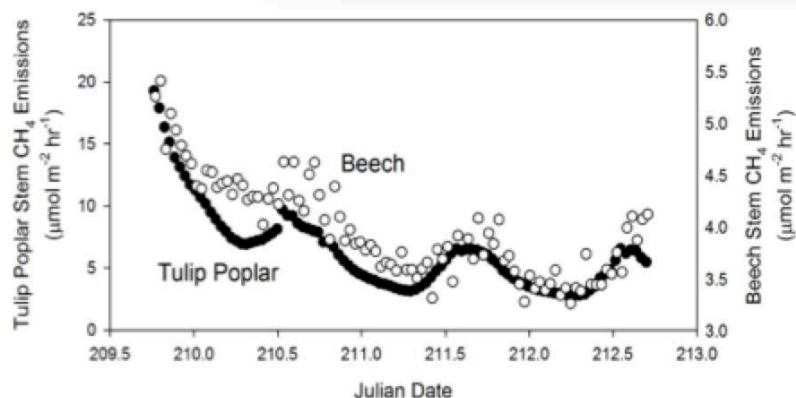


# Understanding the Carbon Cycle: the Contribution of Soil and Vegetation

High frequency measurements revealed diurnal cycling in the rate of  $\text{CH}_4$  emissions, pointing to soils as the  $\text{CH}_4$  source and transpiration as the most likely pathway for  $\text{CH}_4$  transport.

Findings may reduce global estimates for temperate forests as  $\text{CH}_4$  sinks.

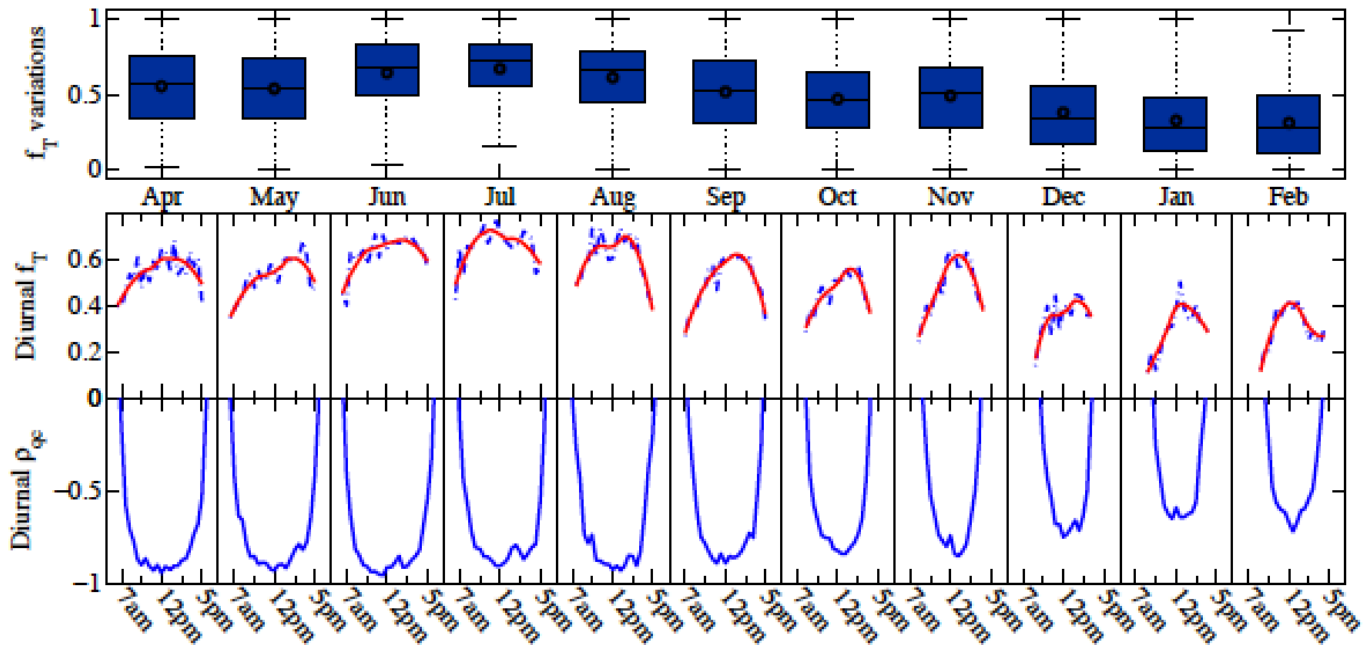
Stem emissions can be particularly significant in upland tropical forests, characterized by high rainfall and transpiration. Transpiration-driven  $\text{CH}_4$  transport may help explain observations of unexpectedly high pools of atmospheric  $\text{CH}_4$  over tropical forests and help resolving differences between models and measurements.







# Coupled Water, Carbon and Nitrogen Cycles in Urban Environments



Water Vapor – CO<sub>2</sub>  
correlation

Partitioning of evaporation  
between plant  
transpiration and soil  
evaporation exhibits  
pronounced seasonal and  
diurnal cycles.

Validation of QCL-based  
water vapor isotopes  
analyzer.

Princeton Testbed

Environmental  
Sensors



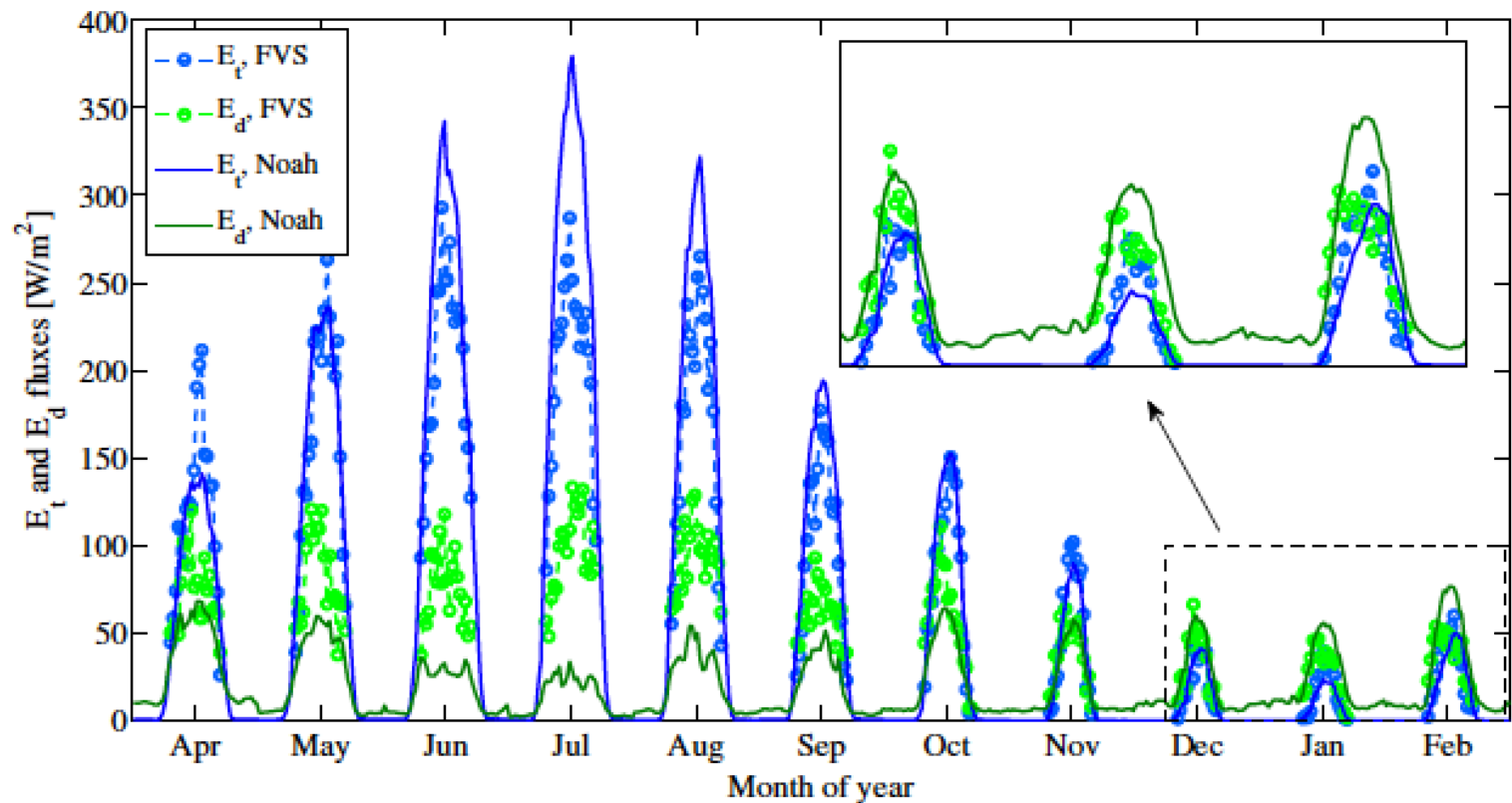
Broadmead  
Facility



# Coupled Water, Carbon and Nitrogen Cycles in Urban Environments

Climatology of transpiration and direct soil evaporation – seasonal and diurnal cycles

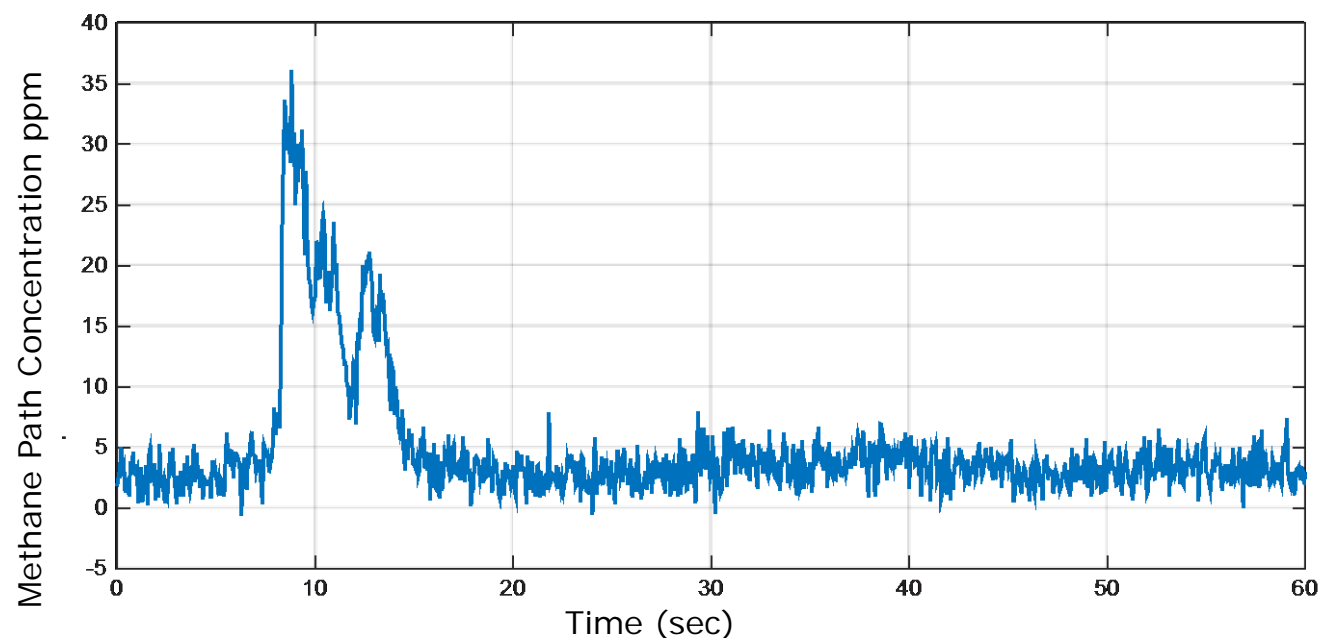
Validation of regional climate models used to assess urban impacts on climate





# Monitoring Trace Gas and Aerosol Properties in the Urban Environment

- \* QCL Open-path fence-line system to monitor methane and nitrous oxide with 1% accuracy over a 250 meter path.
- \* Two Channel aerosol and cloud micro-pulse IR lidar and field testing is ongoing.
- \* Demonstrated the high stability and reputability of a pulsed SG-DBR QCL system for spectroscopic applications



*Stand-off Detection of Methane Leak.*

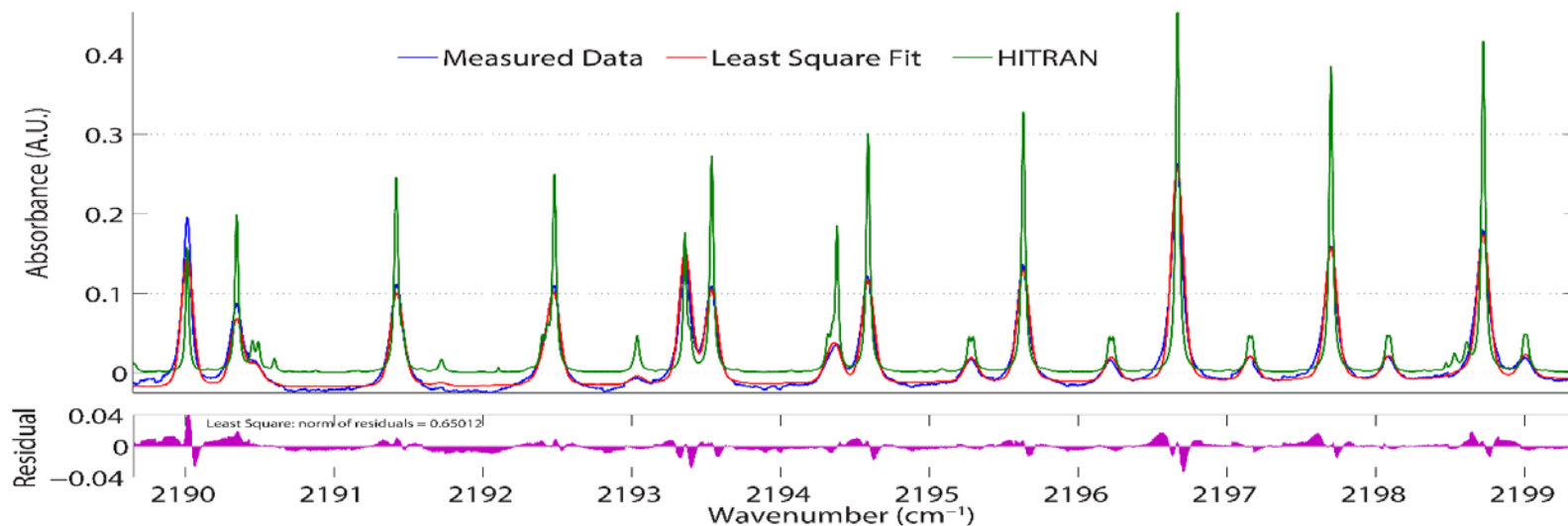
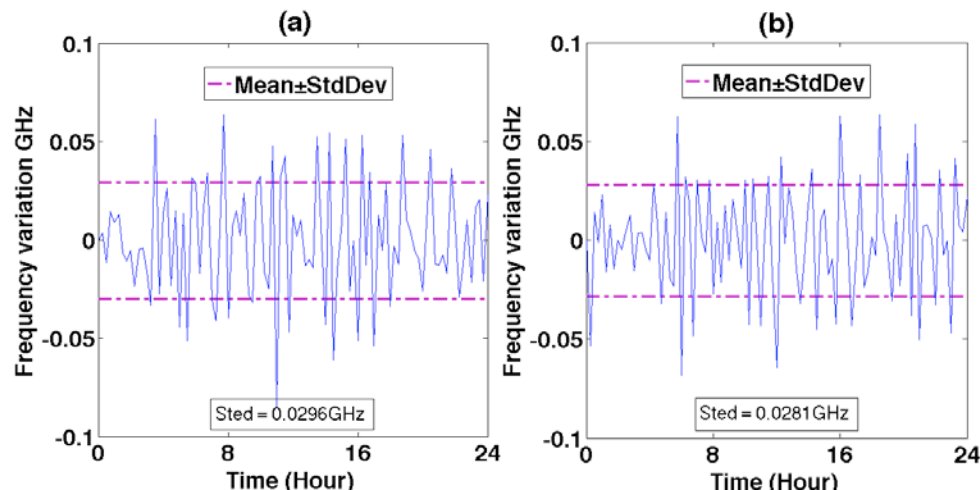


*Two Channel portable IR Micropulse Lidar at 1.5 and 4.5 microns for Clouds and Aerosols Observations*



# Monitoring Trace Gas and Aerosol Properties in the Urban Environment

*A stable and repeatable system:  
Relative pulsed SG-DBR frequency  
fluctuations measured using two  
different N<sub>2</sub>O absorption line peaks  
at 150 Torr. (a) 2198.7 cm<sup>-1</sup> and  
(b) at 2197.7cm<sup>-1</sup> respectively.*



*Broad electronic tunability at high resolution: Spectrum of simultaneous detection of H<sub>2</sub>O, CO, N<sub>2</sub>O .*

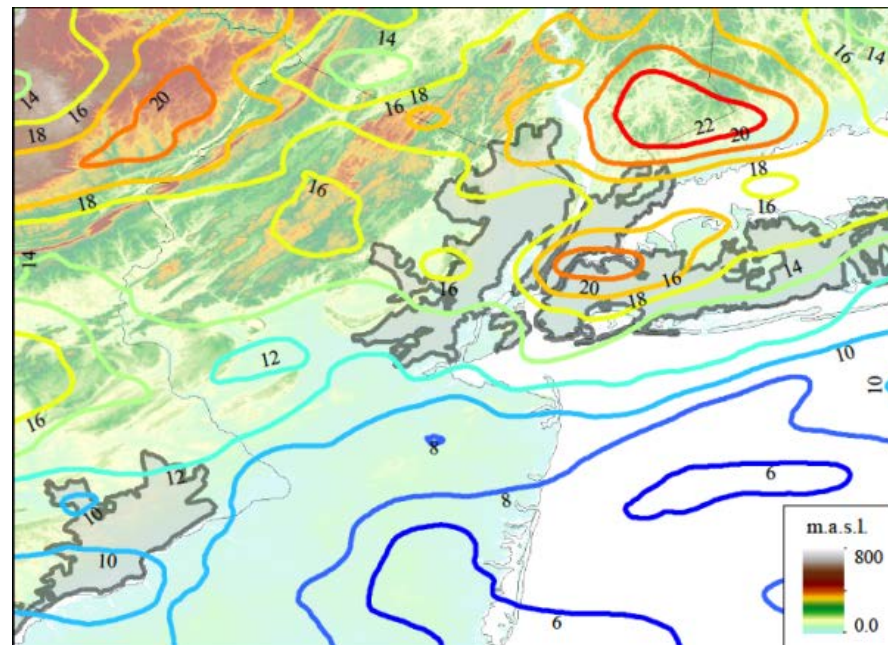
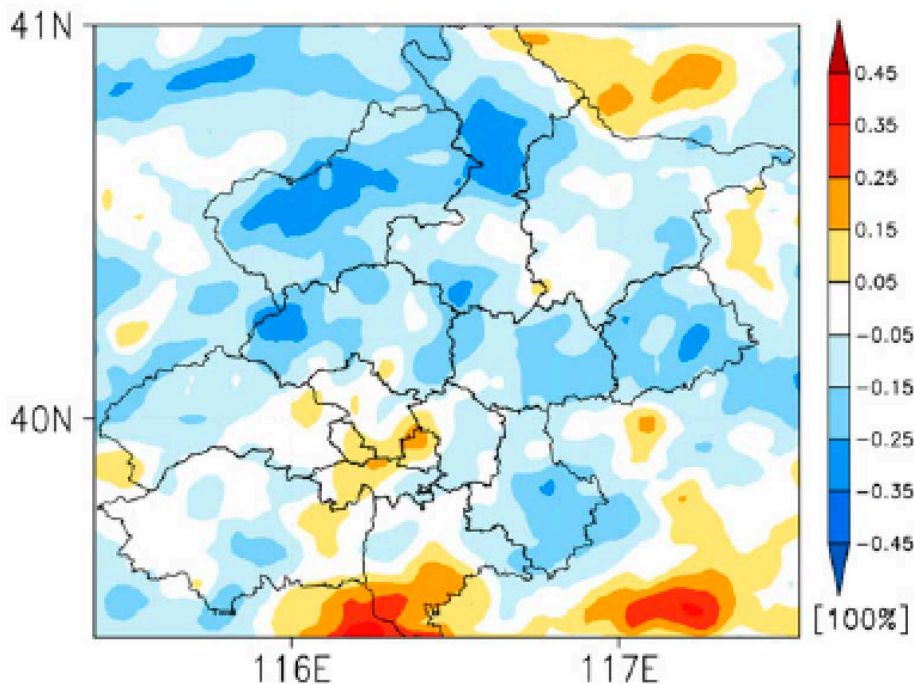




# Urban Climate Modeling

Urban Modeling of regional climate: New York, Beijing and Baltimore testbeds.

*Changes in the decadal-averaged (2000-2009) rainfall during August for the Beijing metropolitan region, associated with urban growth from 1993 – 2004.*



*Mean rainfall (mm) for the 50 most intense thunderstorm systems over the New York – New Jersey metropolitan region during the period from 2001 – 2009.*



# Quantum Cascade Lasers for Breath Analysis

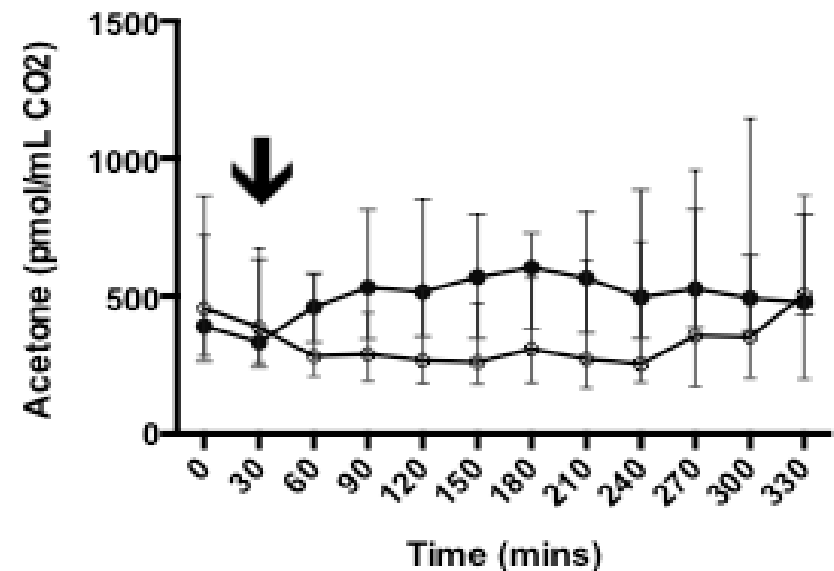
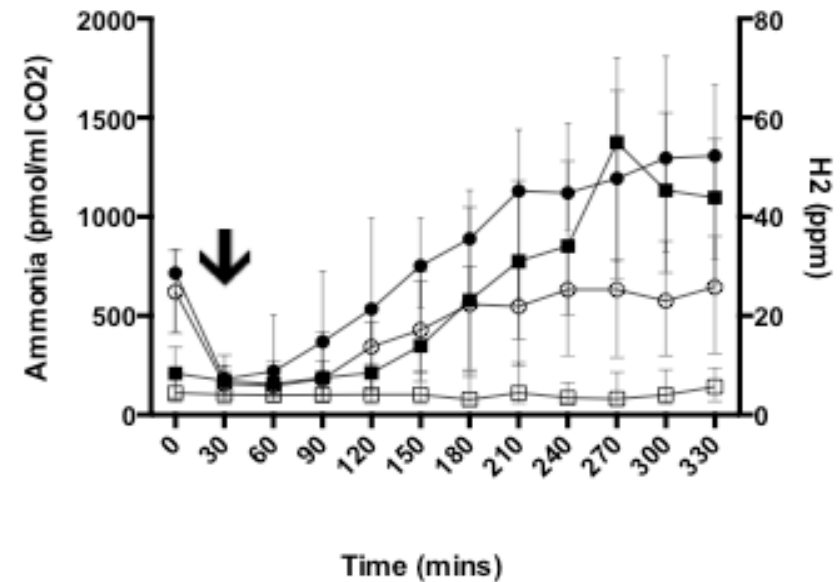
**Simultaneous multi-metabolite breath analysis provides a unique and powerful approach to evaluate gut metabolism and nutrition physiology in vivo.**

In 30 healthy subjects, we measured ammonia, acetone, and hydrogen serially for 6 hours in a control trial (glucose) and after a 60 gm high protein intervention.

Ammonia levels increase above baseline in response to a high protein intervention but not to control.

Acetone increase in intervention compared to decrease in control suggests that increased ammonia may be due to amino acid degradation.

Hydrogen peak marks time when the oral challenge enters the distal small bowel and colon





# Laser Therapy Using 6 $\mu\text{m}$ Quantum Cascade Lasers

**Capulorhexis is the most difficult part of cataract surgery and freehand laser incision could be a cost-effective alternative to femtosecond capulorhexis.**

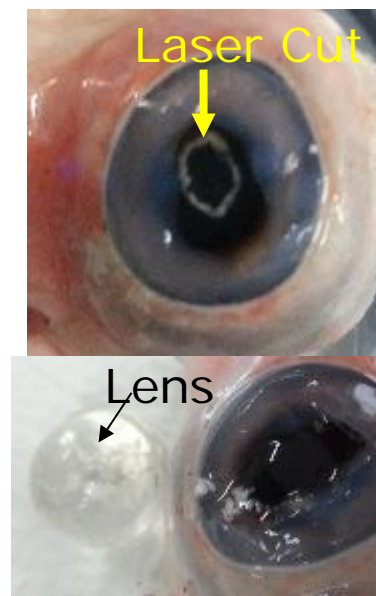
We performed studies to develop a freehand laser Capsulorhexis technique.

To achieve that goal, we first measured the absorption spectra of lens capsules.

In parallel we designed and fabricated ball lens based laser cutters and demonstrated free-hand laser capulorhexis of ex vivo cow eyes.



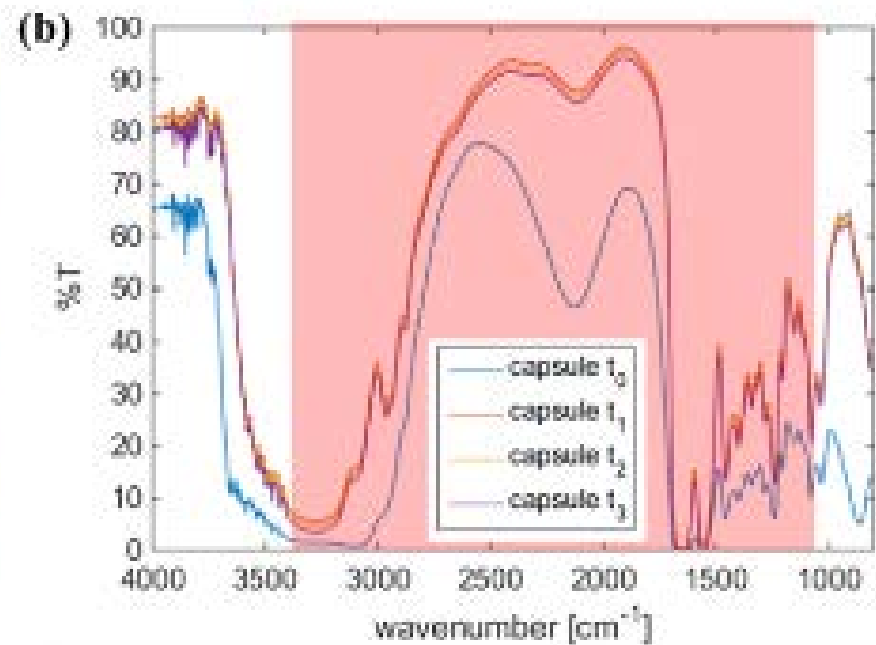
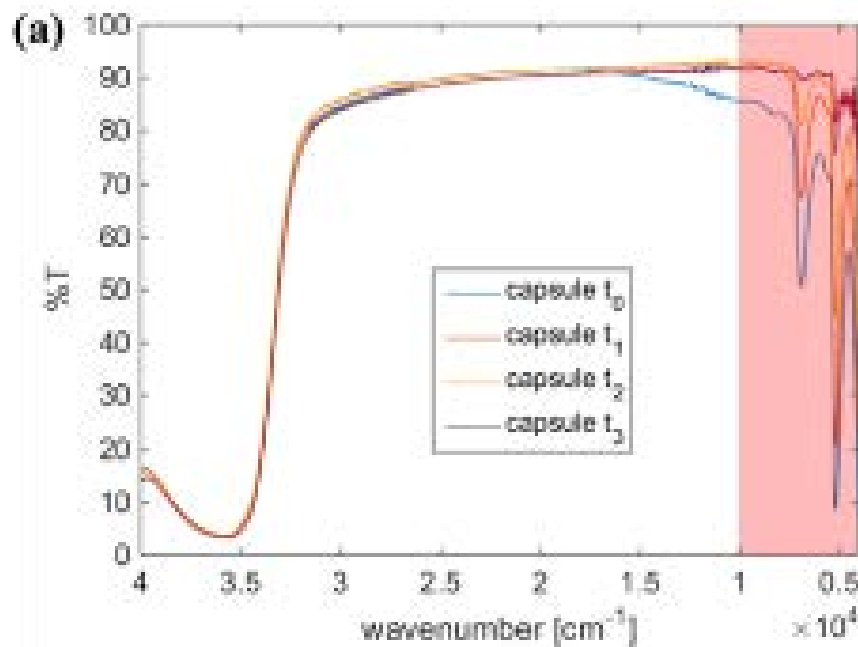
*Stainless laser cutting tip using ball lens for freehand laser capulorhexis*



*Laser cutting of lens capsule, Below: lens removed*



# Laser Therapy Using 6 $\mu\text{m}$ Quantum Cascade Lasers



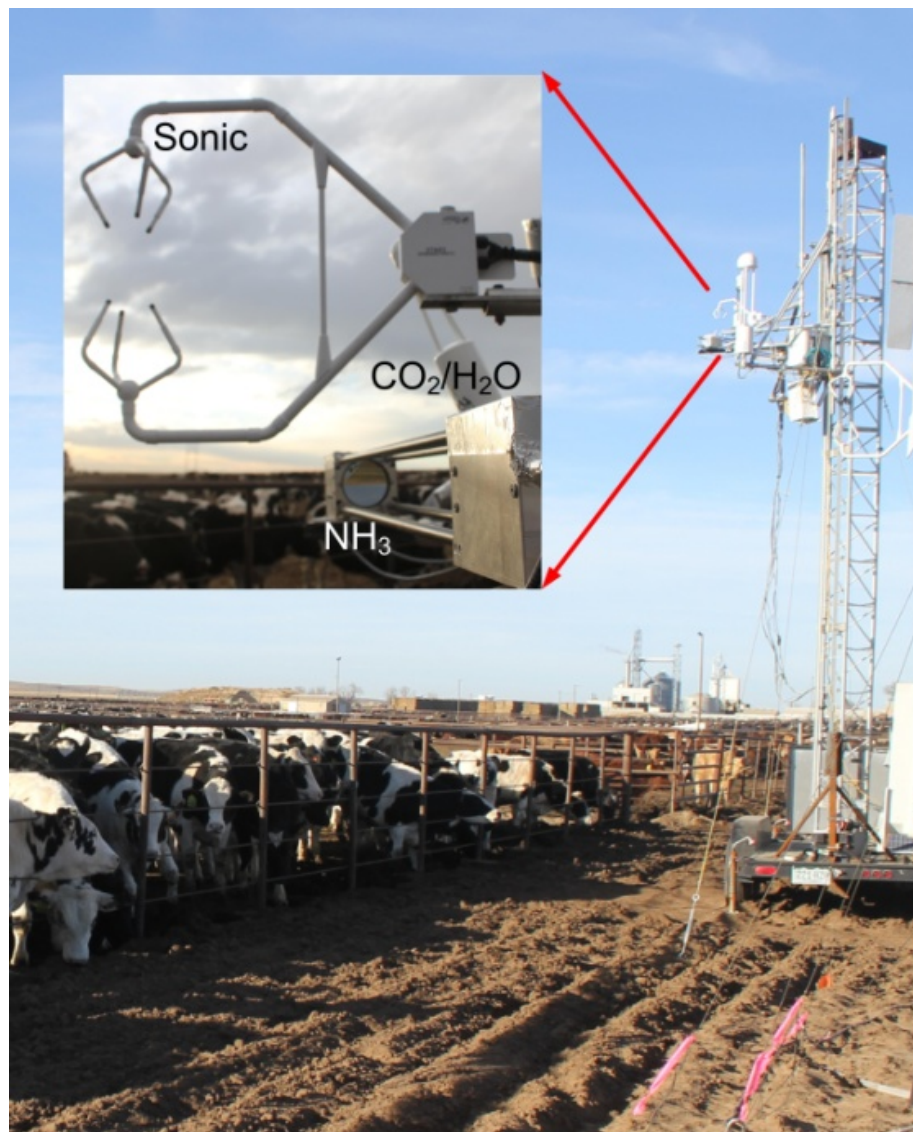
Transmittance measurement in (a) UV-visible-near IR region and (b) infrared region. Red regions indicates where water vaporization occurs during the temporal measurement over 2 hours between  $t_0$  to  $t_3$ .





## ***SLIP I: Multi-Sensor Deployment for Assessing Spatiotemporal Variability of Carbon, Nitrogen and Water Fluxes***

- Open-path  $\text{NH}_3$  EC flux measurements were demonstrated at a cattle feedlot
- A new open-path, quantum cascade laser-based sensor was used in the EC setup and showed advantage over commercial sensors
- A detection limit of  $1.3 \pm 0.5 \text{ ng m}^{-2} \text{ s}^{-1} \text{ NH}_3$  flux was achieved

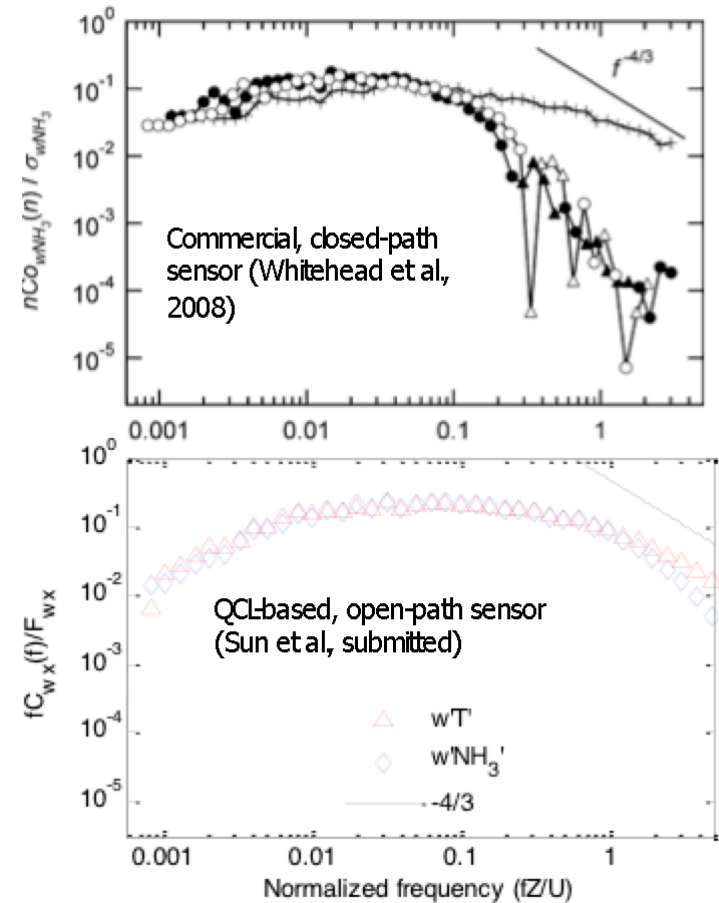
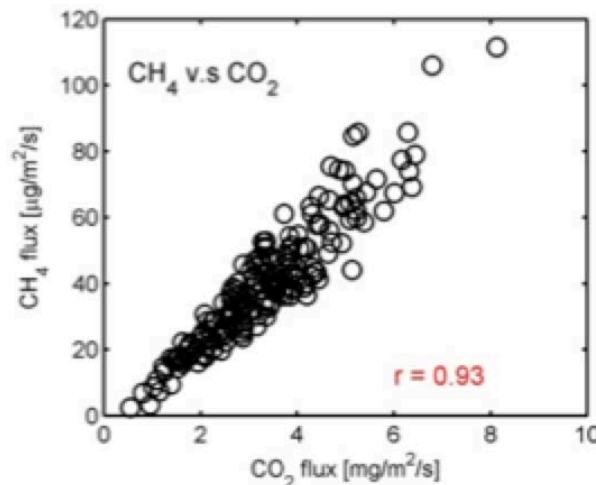
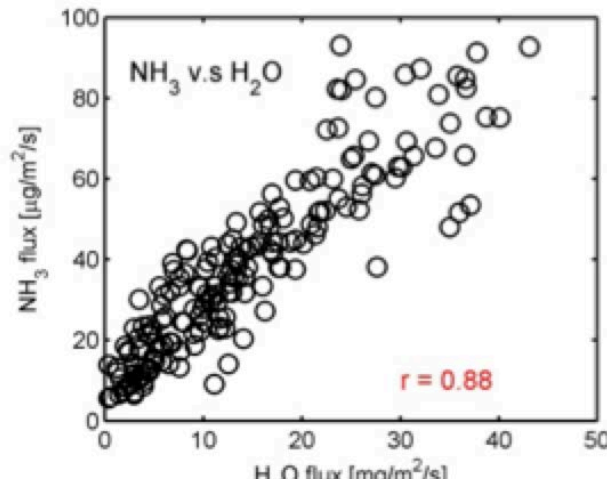


*Experimental setup of the eddy covariance measurements above a 25,000-animal cattle feedlot*



# SLIP I: Multi-Sensor Deployment for Assessing Spatiotemporal Variability of Carbon, Nitrogen and Water Fluxes

NH<sub>3</sub> fluxes showed a strong diurnal cycle and correlated well with latent heat; CH<sub>4</sub> fluxes correlated with CO<sub>2</sub> fluxes:



*Cospectra of NH<sub>3</sub> fluxes measured by closed-path sensors (top) and by open-path sensor (bottom)*



# Summary

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- Continued expansion in field deployment of environmental sensors have lead to important scientific advances in air quality and regional climate.
- Rapid growth in deployment of sensors on mobile platforms.
- Testbeds continue to provide key resources for development, testing and demonstration of QCL-based environmental and public health sensor systems.
- Field deployments have demonstrated ability of Thrust 5 projects to contribute cutting-edge advances to sensor technologies.