

Air Quality at the Urban-Agricultural Interfaces

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CrIS: K. Cady-Pereira

IASI: P.-F. Coheur, C. Clerbaux

NASA DISCOVER-AQ and CAREBEIJING science teams



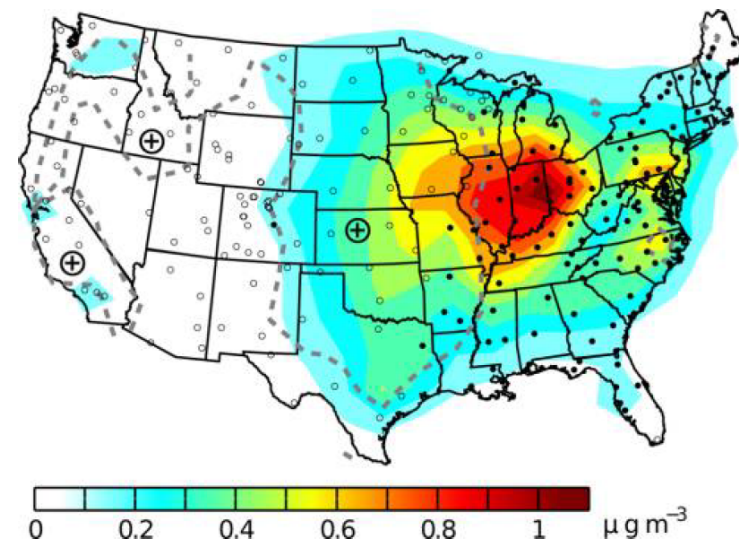
NASA H-AQAST Science Meeting
Seattle, Washington
February 28, 2017



Ammonia is critical precursor for PM2.5

Paulot, ES&T, 2014

- NH_4^+ a major component of aerosols
dominant atmospheric base (SO_4^{2-} , NO_3^-)
- NH_3 emissions unregulated in US
- Agricultural emissions large, episodic, though
all urban areas exhibit high $[\text{NH}_3]$
- Widespread PM2.5/haze in Europe
due to ag fertilization (Fortems-Cheiney, 2016)
- High mortality due to agricultural NH_3
emissions (Paulot et al., 2014; Lee et al., 2015)



Goals

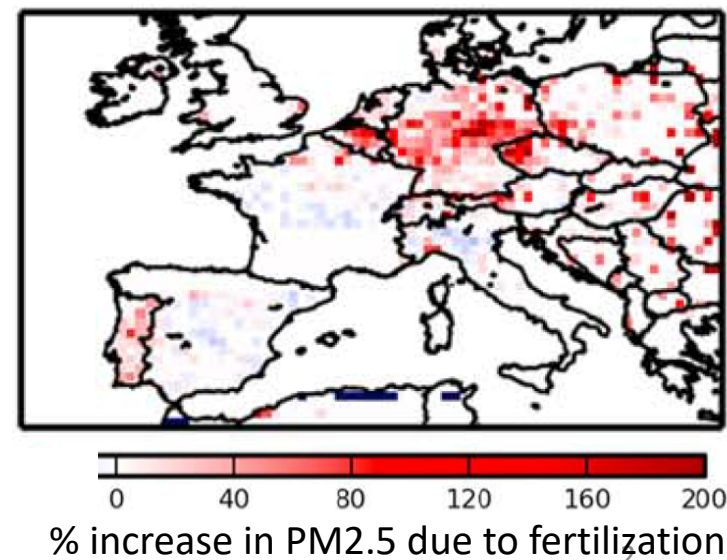
How accurate are satellite observations of NH_3 ?

To what extent does NH_x -rich air transport to cities?

How does massive fertilization impact regional air quality?

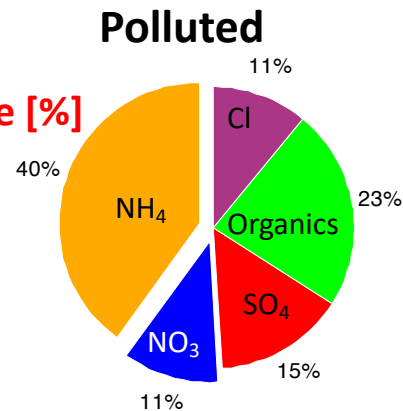
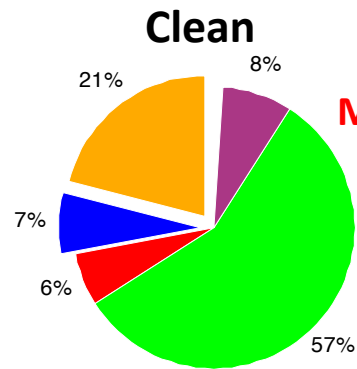
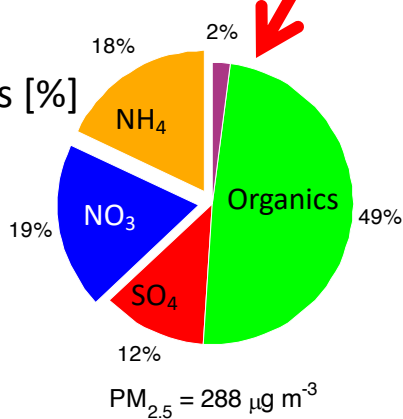
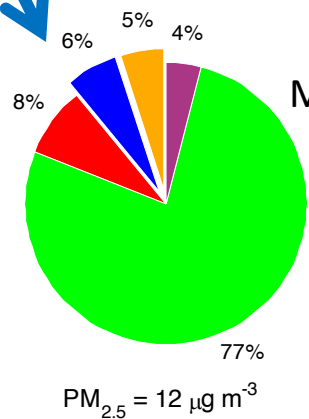
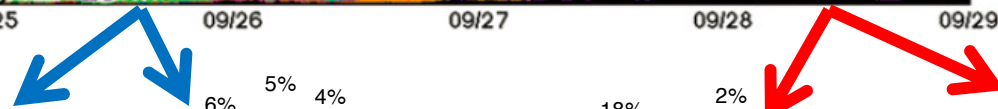
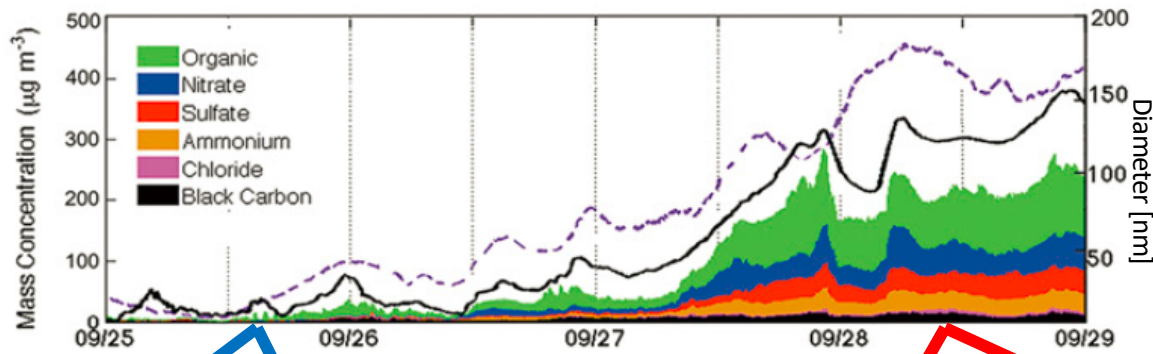
What are spatiotemporal patterns of emissions?

Fortems-Cheiney, GRL, 2016



Ammonia key PM2.5 precursor in cities

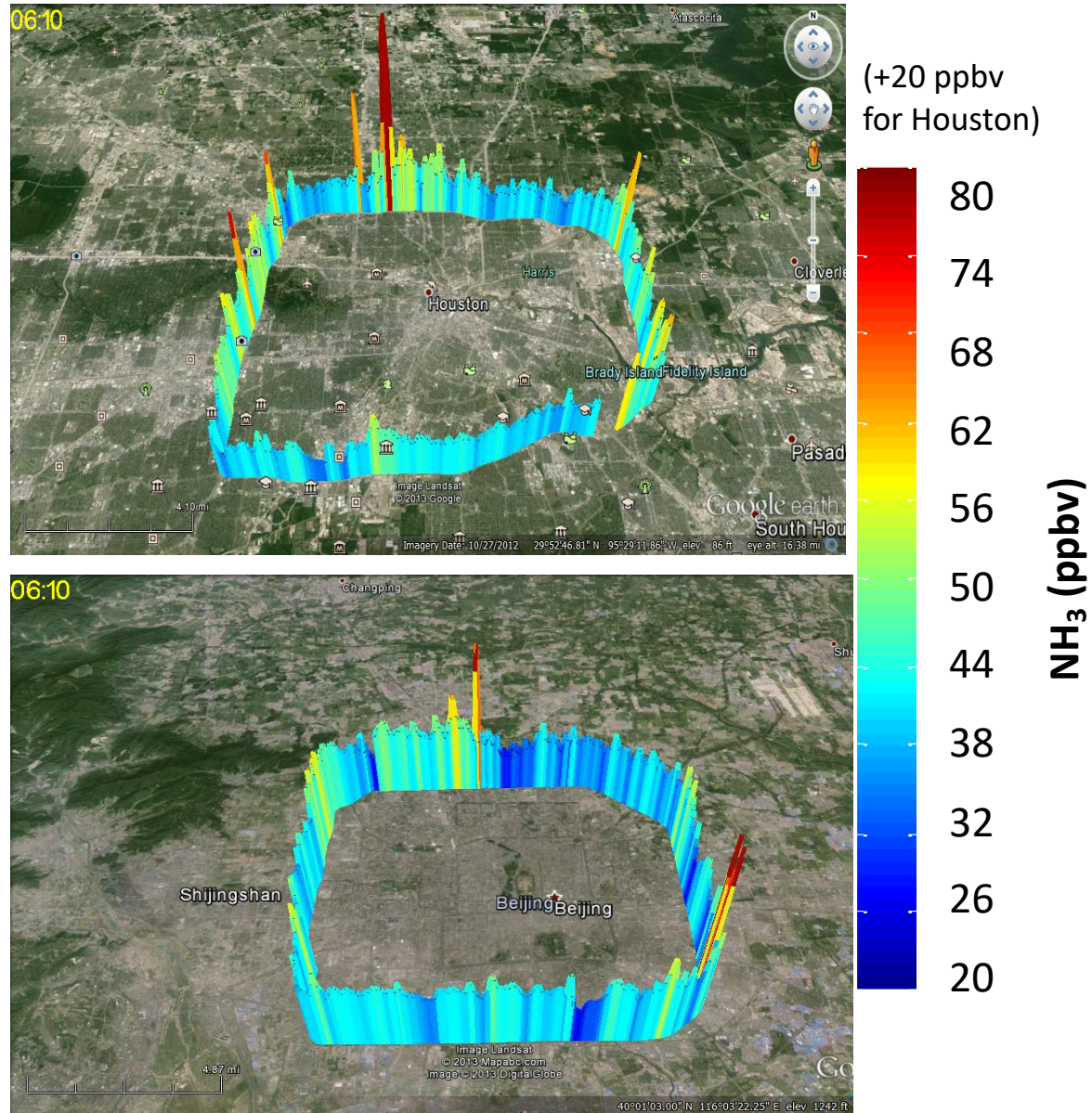
Beijing:



Source: Guo et al. (2014).

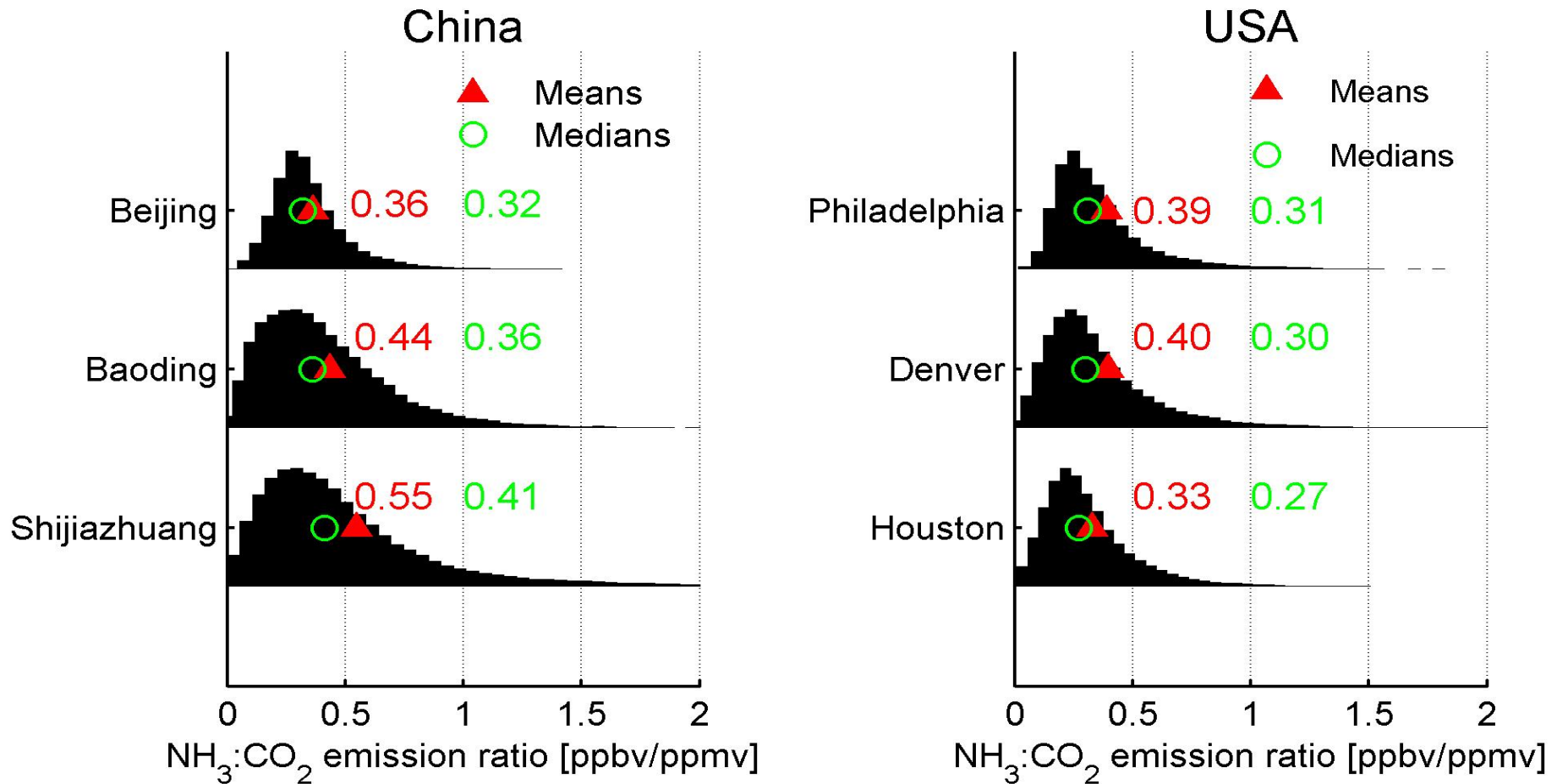
A closer look at vehicle emissions

Vehicle NH_3 emissions
co-located with NO_x , pulse
emissions with rush hours



Measured vehicle NH_3 emissions in 8 US and 3 large Chinese cities

Vehicle emissions in US and Chinese cities



- National Emissions Inventory (NEI) for NH_3/CO_2 for US cities ~ 0.16
- NH_3 vehicle emissions are underreported by a factor of two in US cities, an important source of unhealthy fine particulate matter (similar to Beijing)

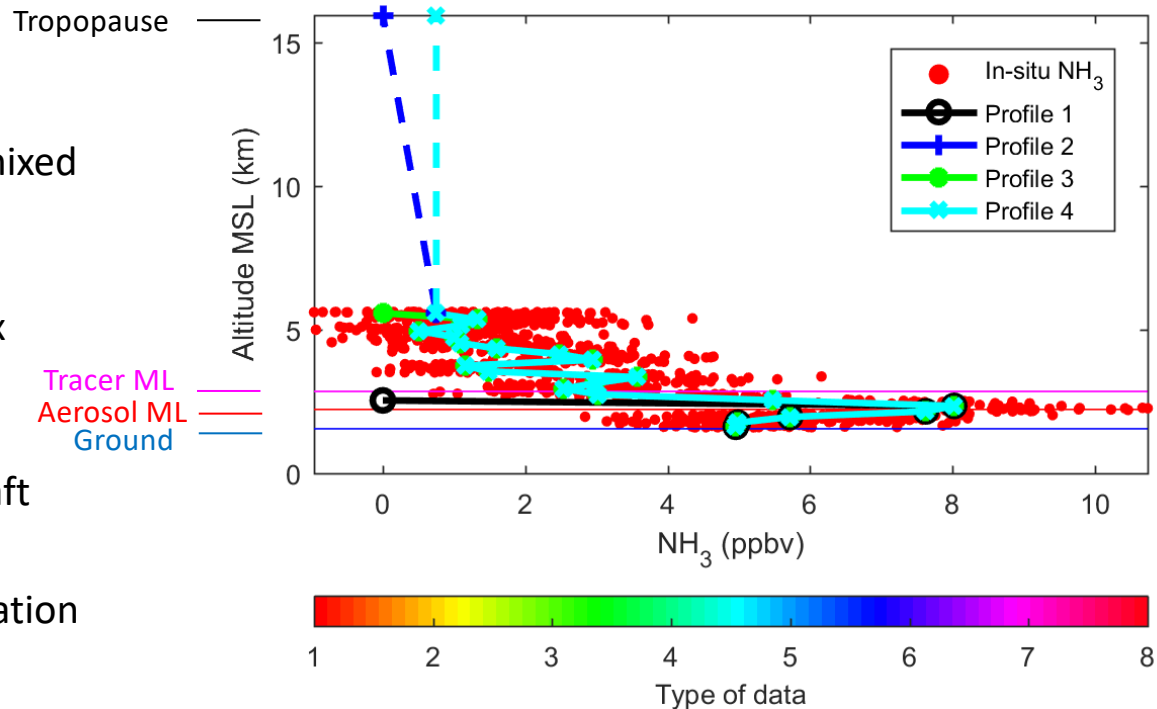
(Sun et al., ES&T, 2017)

IASI / in-situ NH_3 Vertical Profile

Validating IASI and CrIS with NASA DISCOVER-AQ and other in-situ datasets

Four cases to integrate in-situ NH_3 :

1. Assume negligible NH_3 above mixed layer (ML)
2. Linearly extrapolate NH_3 concentration to zero from max aircraft altitude to tropopause
3. Assume negligible NH_3 concentration above max aircraft altitude
4. Assume constant NH_3 concentration above max aircraft altitude



Case 1: Used average of tracer ML and aerosol ML heights

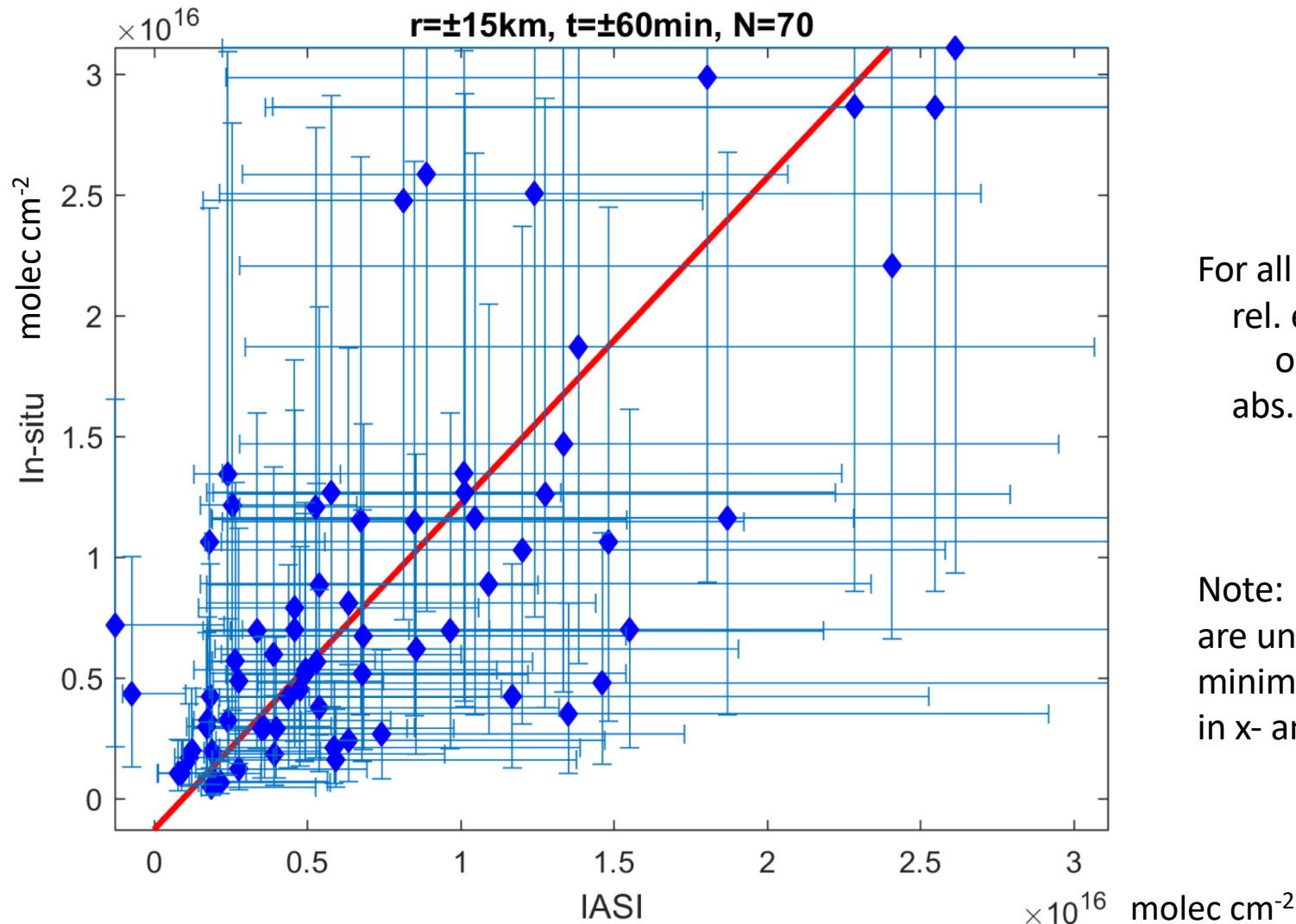
Case (1) avoids biases from aircraft when NH_3 outgasses in clean troposphere

**IASI ± 15 km, ± 1 hour: integrate NH_3 to
ML height only (DAQ-CO)**

$$m = 1.35 \pm 0.15$$

$$b = -1.3 (\pm 1.3) \times 10^{15} \text{ molec cm}^{-2}$$

$$r^2 = 0.54$$



For all data:
rel. error < 200%
or
abs. error < 5×10^{15}

Note: all linear fits
are unweighted,
minimized residuals
in x- and y-directions

Choice of spatiotemporal windows critical – more sensitive to space

Need to revisit urban NH₃ for PM_{2.5}

- vehicle NH₃ emissions double current NEI estimates
- agricultural emissions at minimum during cold season while vehicle emissions are largely constant through the year
 - 53% of US population has vehicle > agricultural emissions in winter
 - vehicle emissions peak with rush hours and co-located with NO_x
- deposition/loss of NH₃ during transport from agricultural to urban areas needs to be better understood
- satellite NH₃ can be used to quantify agricultural pollution and its impacts (IASI and CrIS more useful, accurate than Ammonia Monitoring Network)



Article

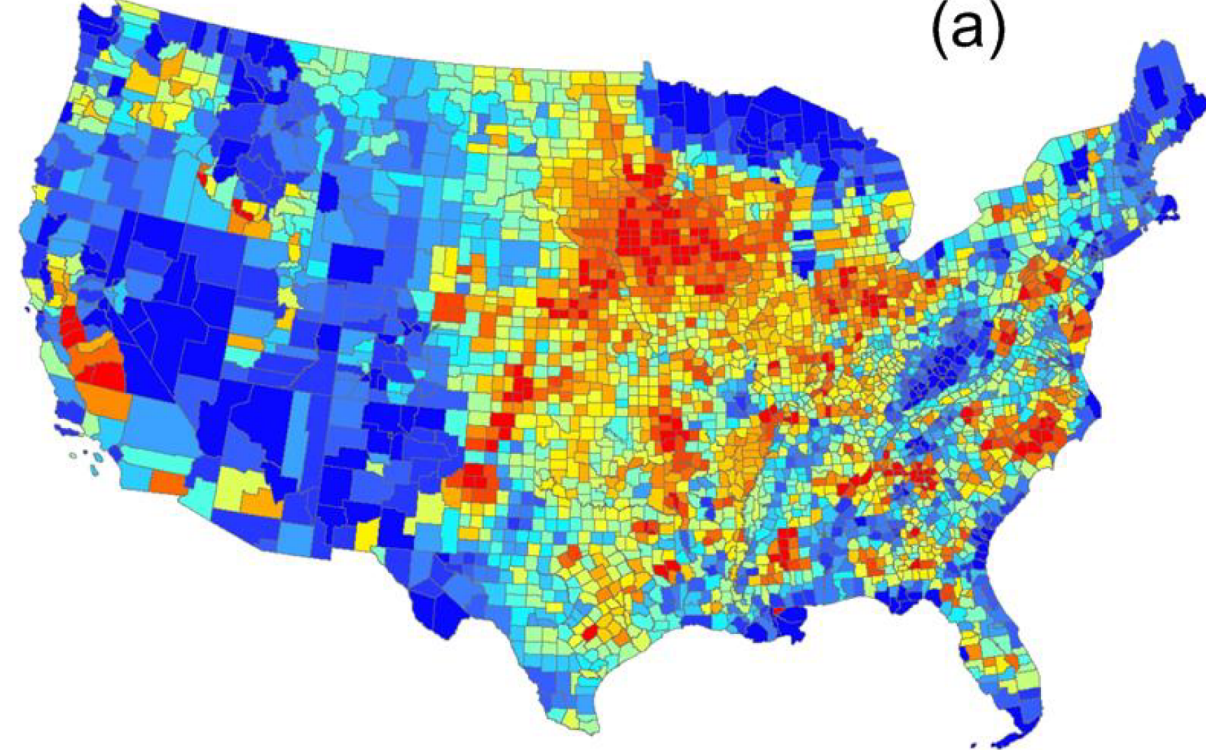
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Sun et al., *ES&T*, 51, 2472-2481, 2017

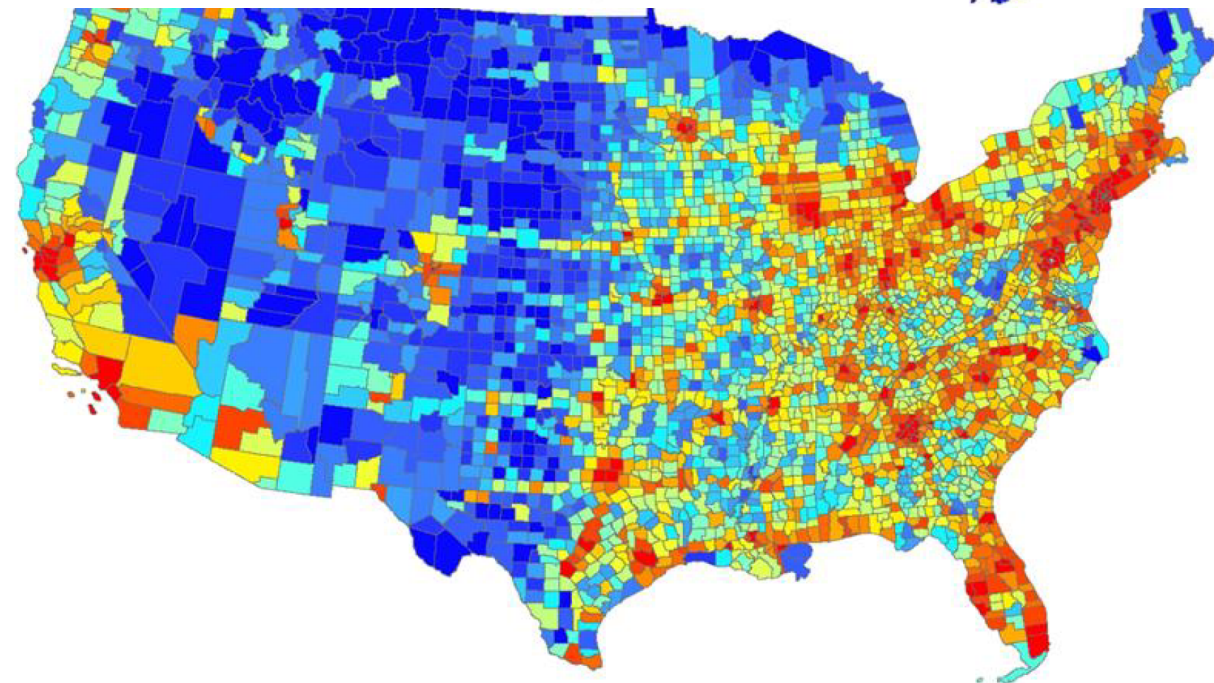
Vehicle Emissions as an Important Urban Ammonia Source in the United States and China

Kang Sun,^{†,‡,○} Lei Tao,^{†,‡,¶} David J. Miller,^{†,‡,∞} Da Pan,^{†,‡} Levi M. Golston,^{†,‡} Mark A. Zondlo,^{*,†,‡,Ⓢ}
Robert J. Griffin,[§] H. W. Wallace,[§] Yu Jun Leong,[§] M. Melissa Yang,^{||} Yan Zhang,[⊥]
Denise L. Mauzerall,^{†,‡,Ⓢ} and Tong Zhu[▽]

(a)



Agricultural



Vehicle

Sun et al., *ES&T*, 51, 2472-2481, 2017

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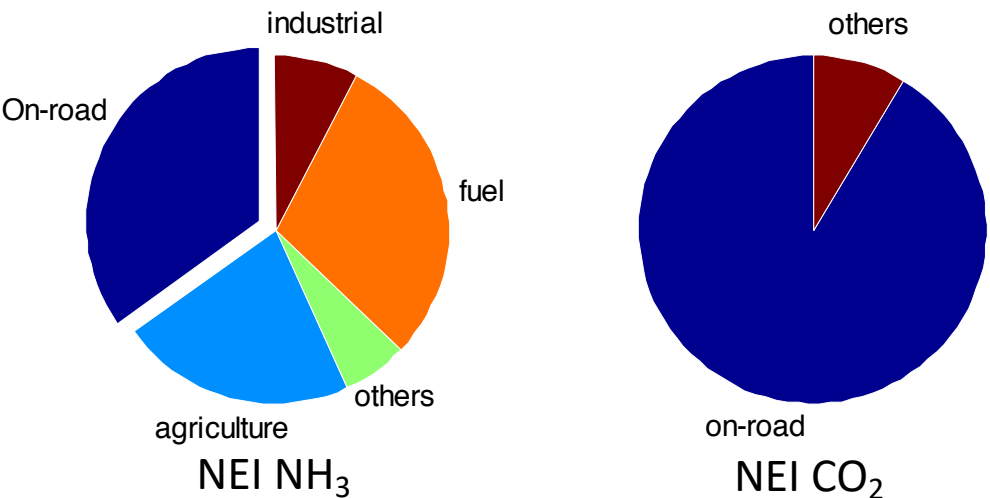
[⊥]Nanjing P&Y Environmental Technology Co., Ltd., Nanjing, Jiangsu 210014, China

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[▽]State Key Laboratory for Environmental Simulation and Pollution Control, College of Environmental Sciences and Engineering, Peking University, Beijing 100871, China

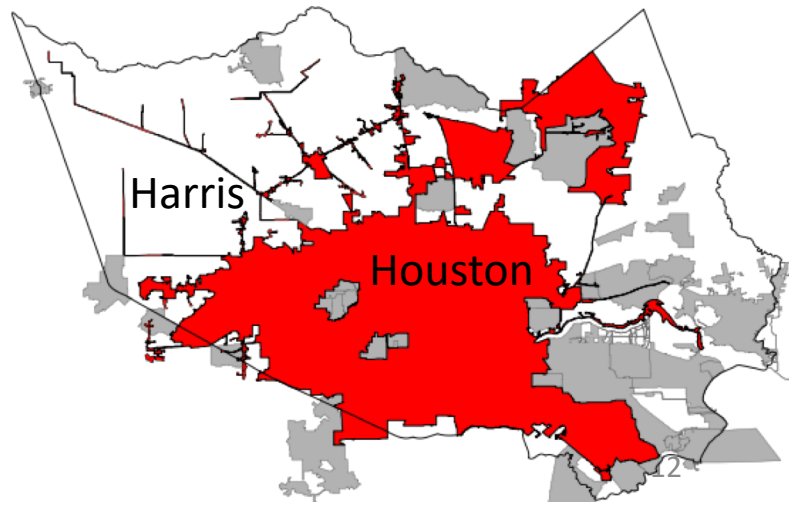
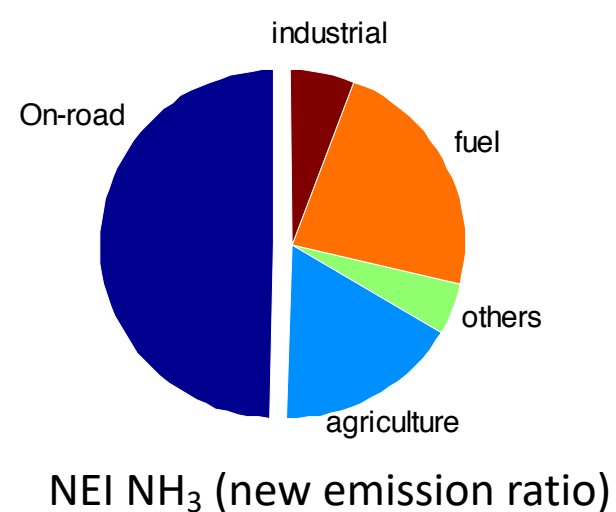
Vehicles as an important NH₃ source

- National Emission Inventory of Harris County, 2011

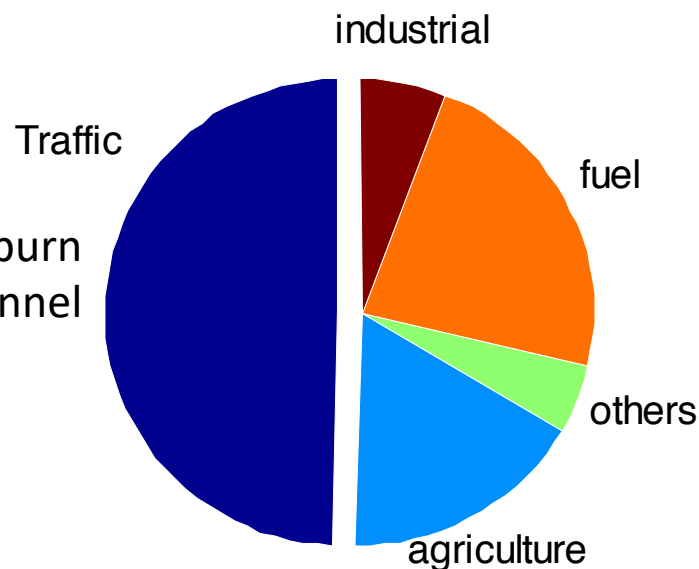
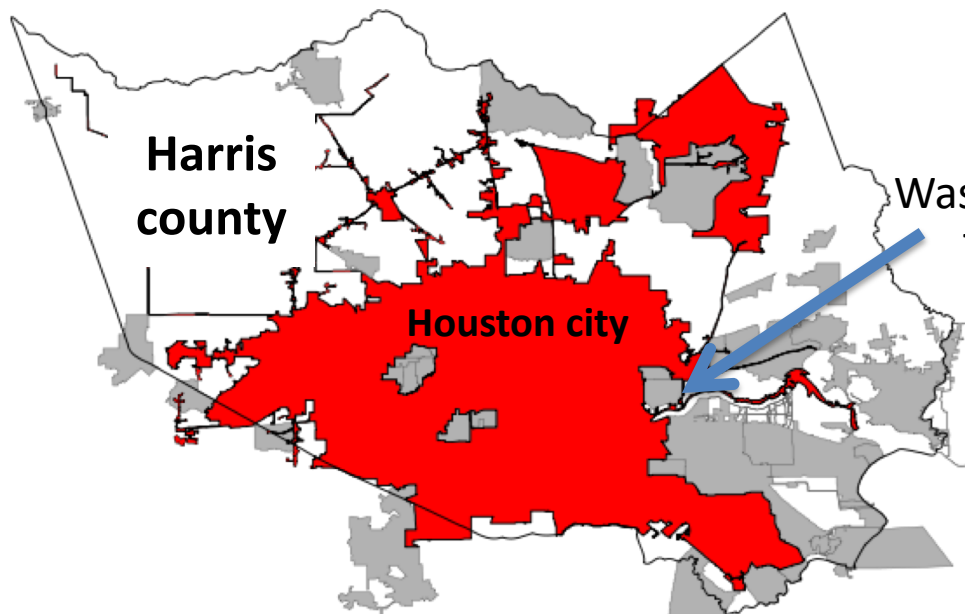


Inventory on-road emission ratio = 0.17 ppbv/ppmv

- Update with observed emissions (0.33 ppbv/ppmv)



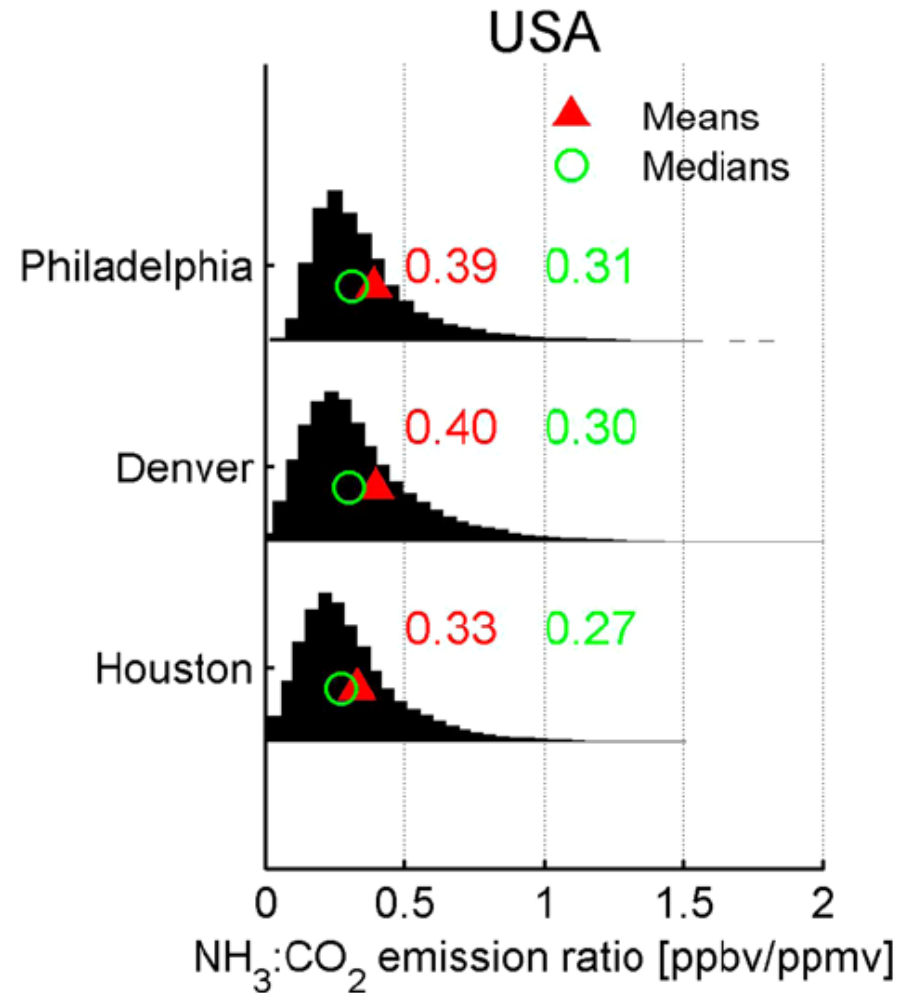
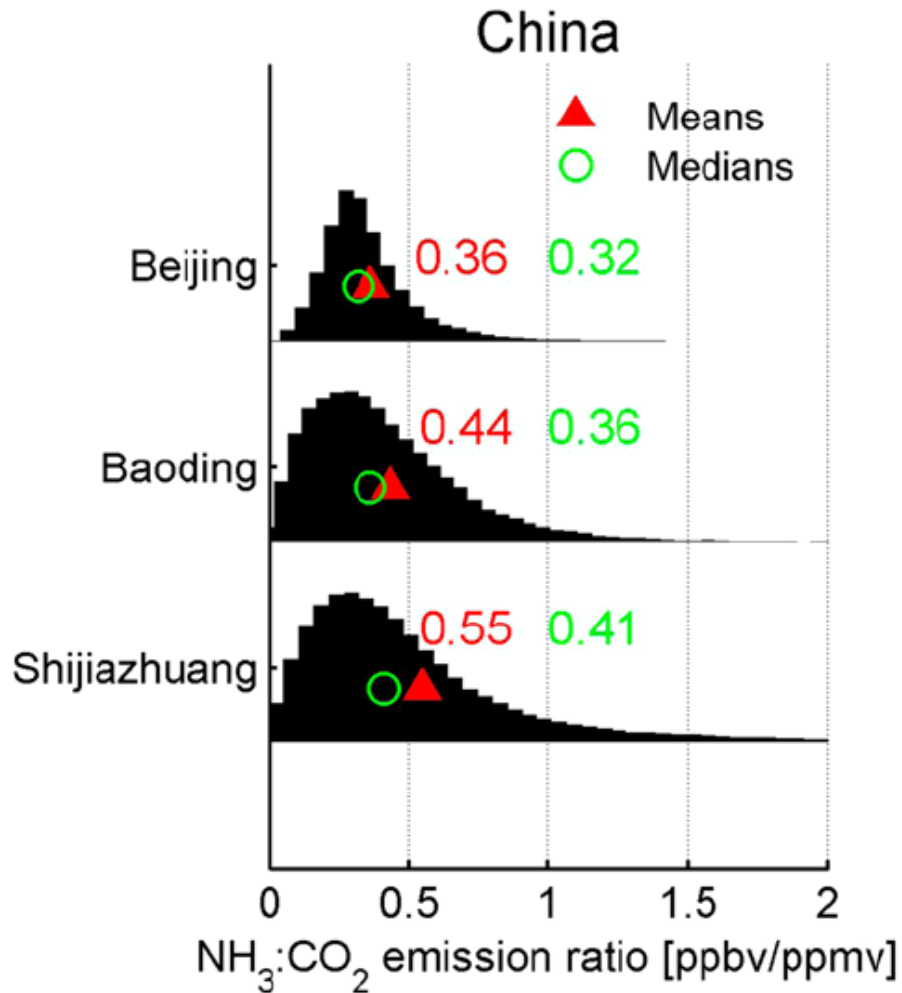
Case study: Houston



Harris county NH_3 inventory: NEI 2011

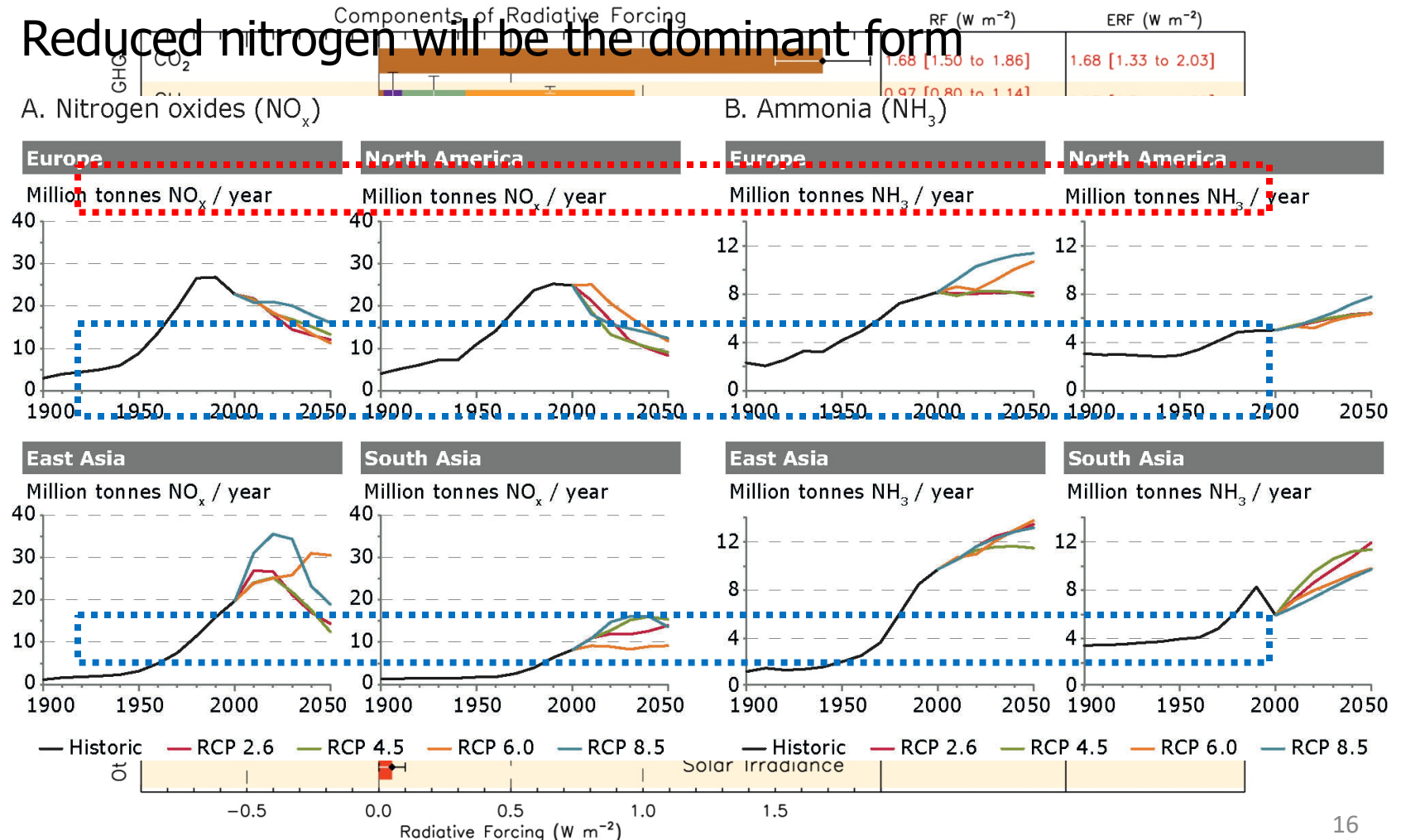
- Agricultural/industrial sources outside the city
- On-road emissions are dominant NH_3 sources in Houston city
- Average on-road ER: 0.33 ppbv/ppmv

Comparison of US and China emissions



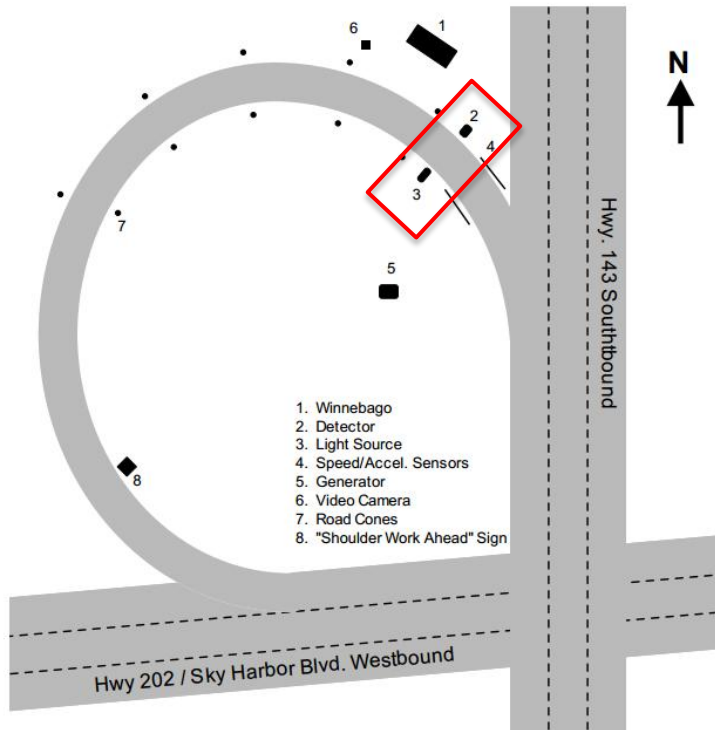
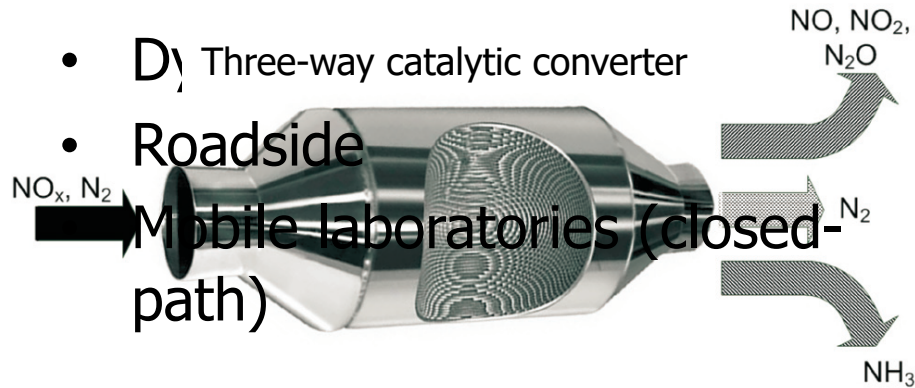
Motivation: RN and future climate

- Direct/indirect ammonium/nitrate aerosol climate impacts
- N_2O is a powerful greenhouse gas
- Reduced nitrogen will be the dominant form

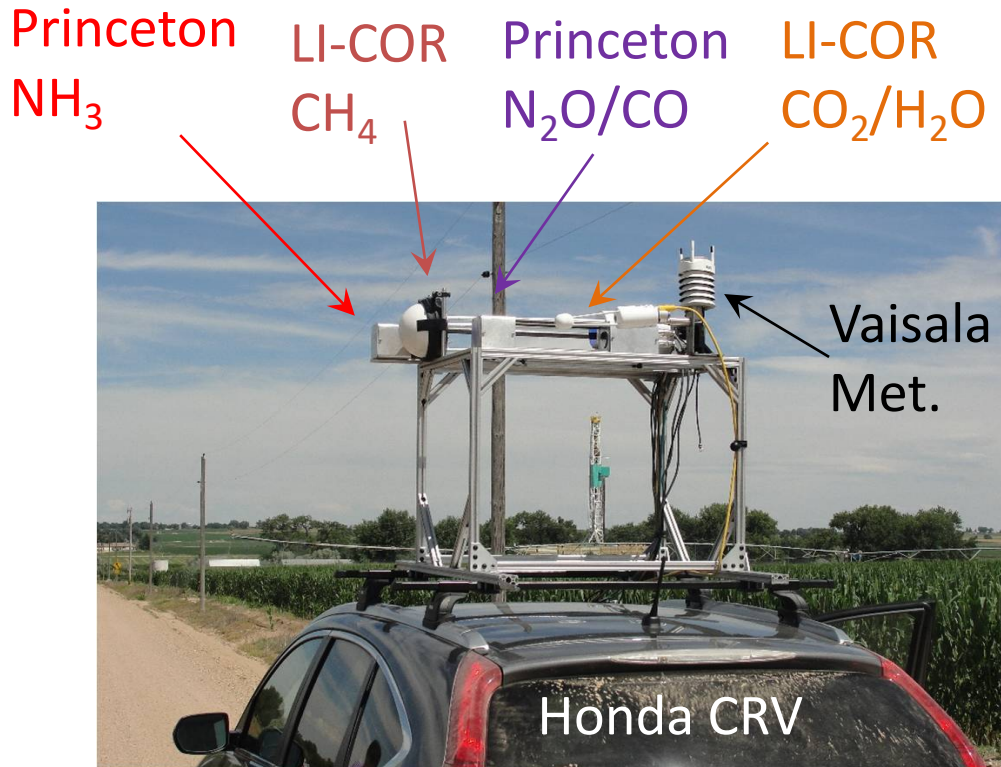


Sources: EEA (2014); IPCC (2013).

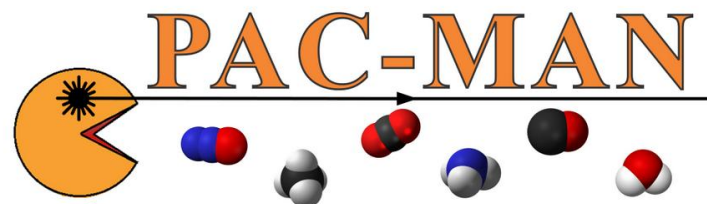
Previous measurements



Open-path mobile sensing platform



PrinAtmChemistry
Mobile Acquisition Node



PRINCETON
School of Engineering and Applied Science
<http://zondlo.princeton.edu/mobile>



Open-path design critical for:

- Fast, high-resolution
- Compact, low power sensor
- Avoiding sampling biases
- Enhancing response time

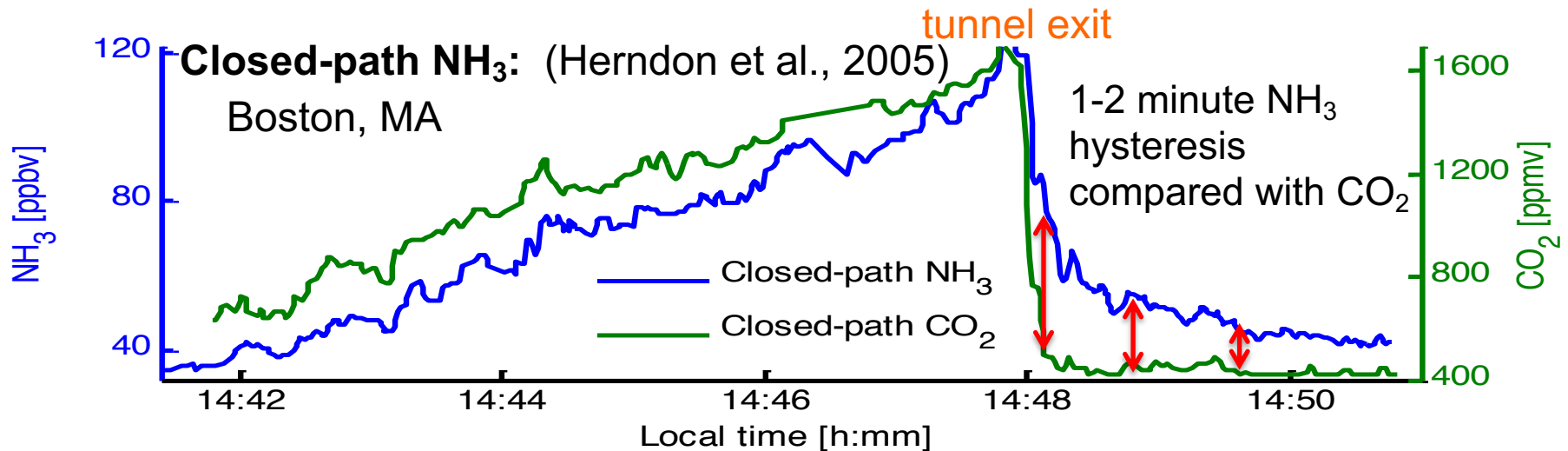
Sensor	Light sources	Sensitivity	Power	Weight
QCL NH ₃	9.06 μm QCL	150 pptv NH ₃	45 W	6.8 kg
QCL CO/N ₂ O	4.54 μm QCL	3 ppbv CO 0.2 ppbv N ₂ O	45 W	5.4 kg
LI-7500A	IR Lamp	0.11 ppmv CO ₂	12 W	0.75 kg
LI-7700	1.65 μm VCSEL	5 ppbv CH ₄	8 W	5.2 kg

NO sensor (5.26 μm) to be incorporated!

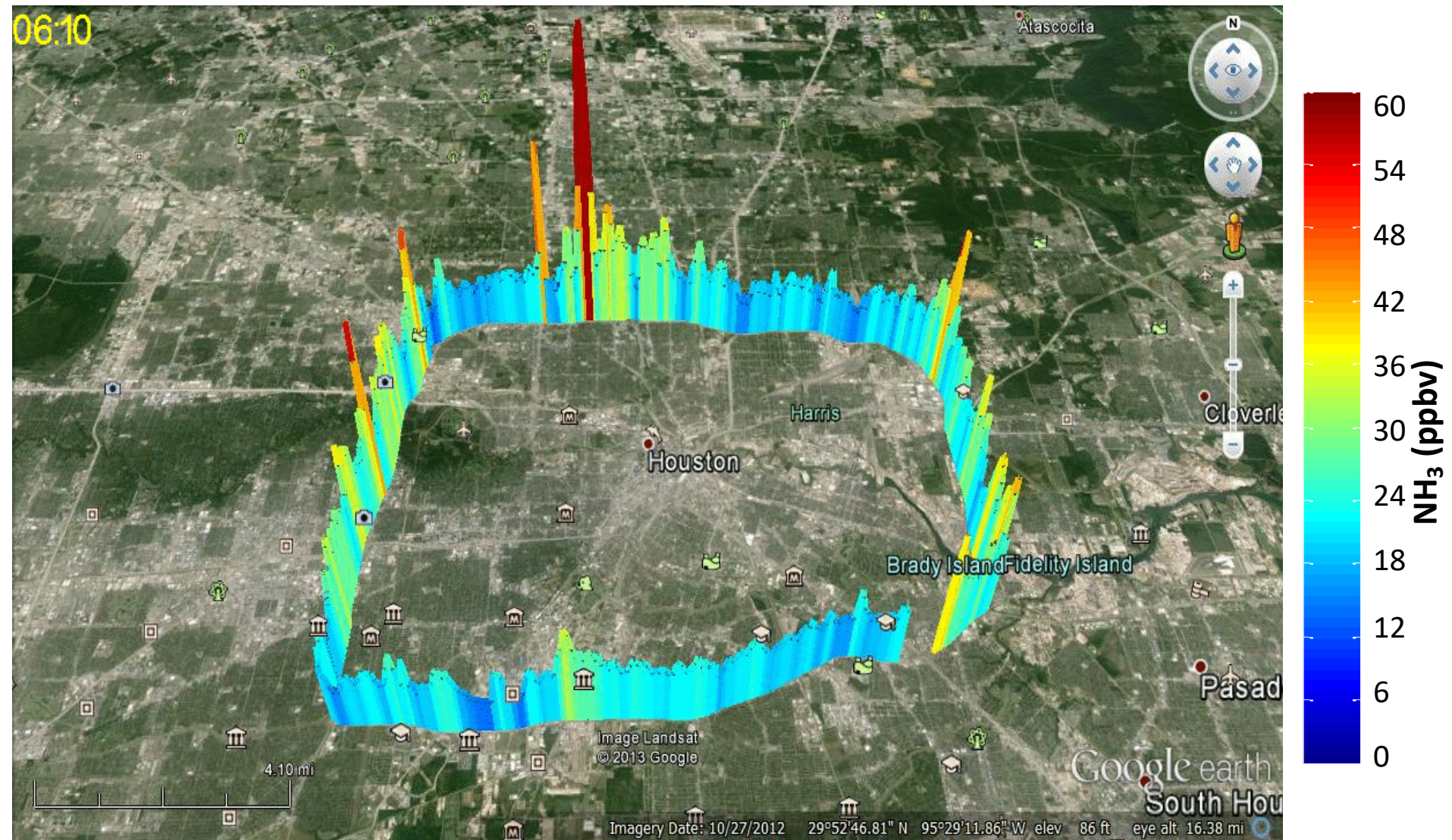
Instrument references:

McDermitt et al. (2011); Sun et al. (2014);
Miller et al. (2014); Tao et al. (2015).

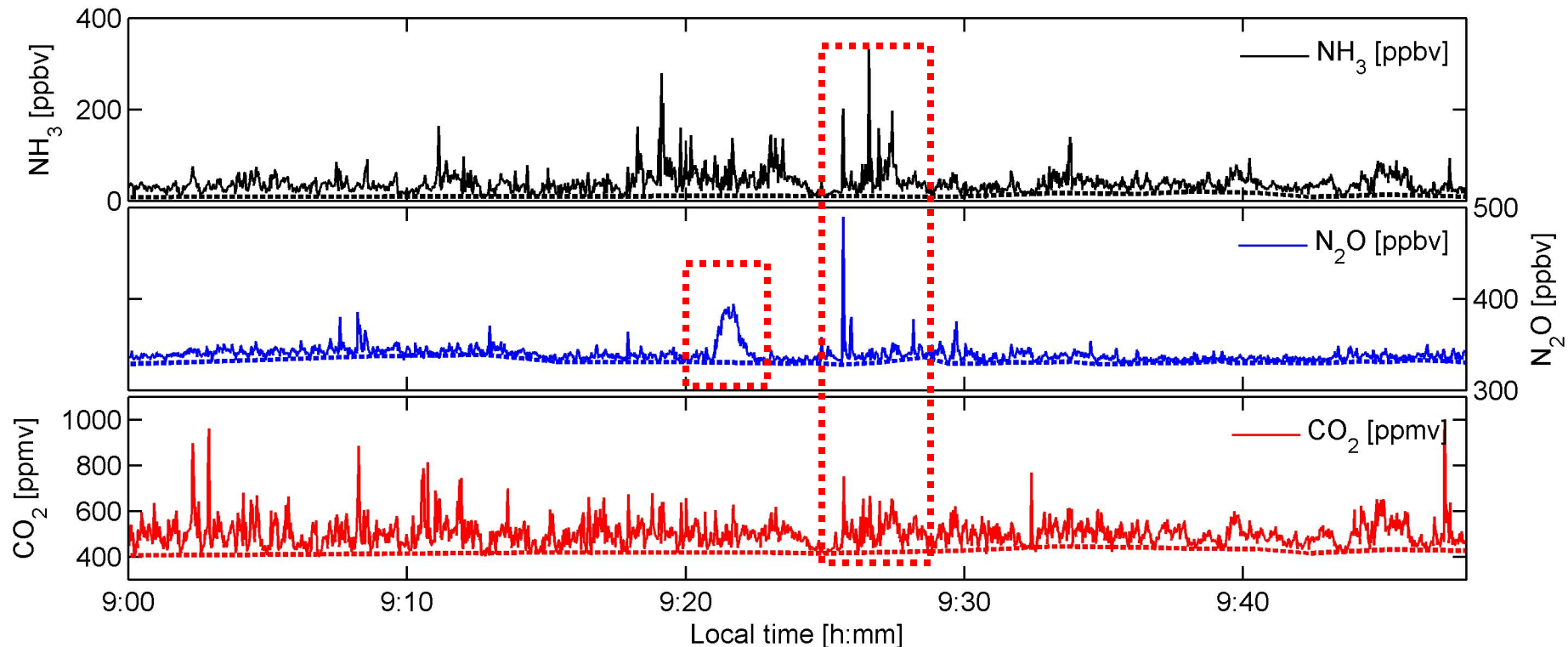
Open- vs. closed-path on-road measurement



Watching a city "breathe": Houston



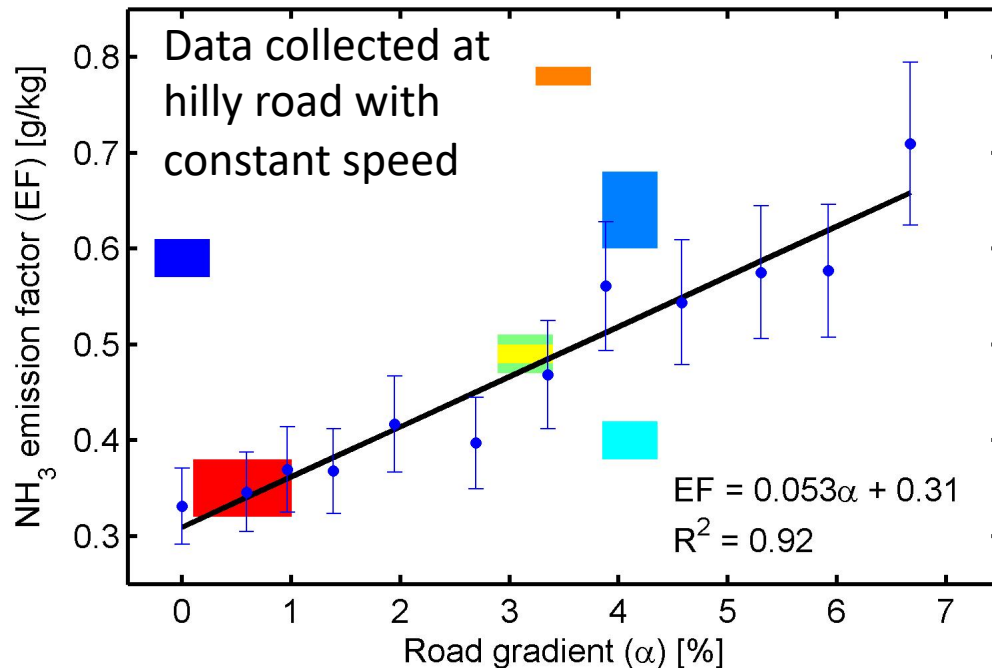
Quantifying vehicle emissions using ER/EF



- Concentrations = peaks (ΔRN , or ΔCO_2) + backgrounds
- Backgrounds: 1st percentile in 10 min window (uncertainty: 10%)
- RN: CO_2 emission ratios (ER) are defined as $\Delta\text{RN}/\Delta\text{CO}_2$
- Emission factors (EF) are calculated using emission ratios:

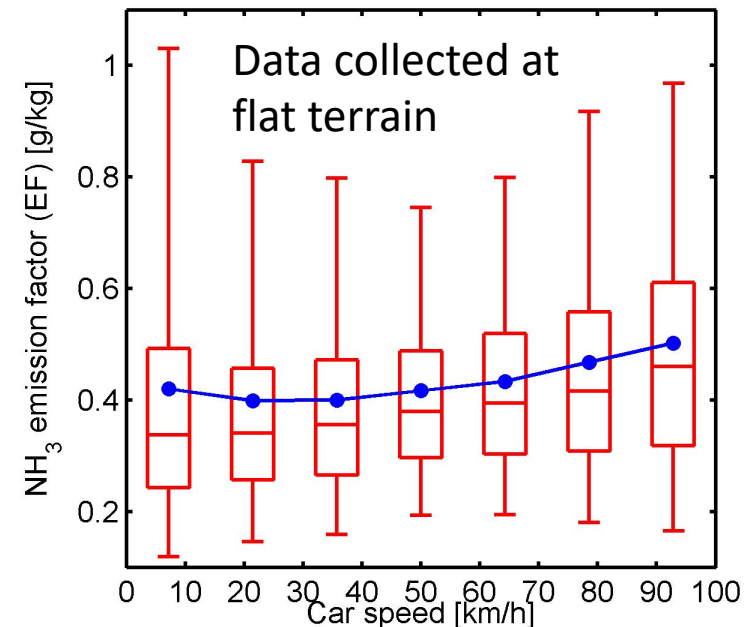
$$\text{EF} = \left(\frac{\Delta[\text{RN}]}{\Delta[\text{CO}_2] + \Delta[\text{CO}]} \right) \left(\frac{\text{MW}_{\text{RN}}}{\text{MW}_{\text{C}}} \right) w_{\text{C}} \quad \text{Unit: g/kg fuel}$$

Determining factors of on-road emissions



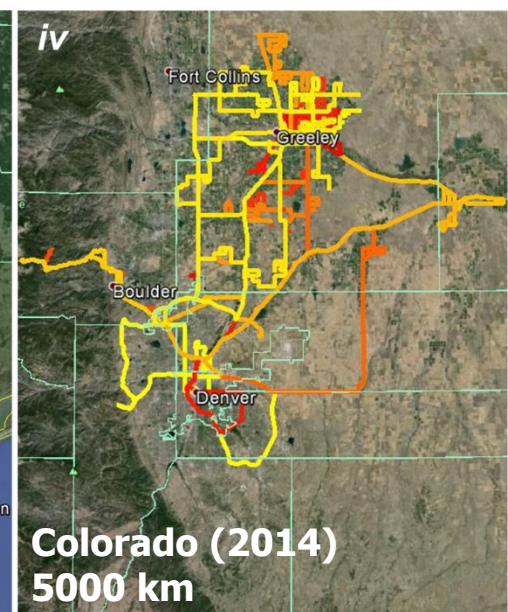
- LA (1999), "slightly uphill"
- Caldecott Tunnel (1999)
- Caldecott Tunnel (2006)
- San Jose (2008)
- Fresno (2008)
- West LA (2008)
- Van Nuys (2010)
- This study (2013)

- NH₃ emission factors depend on road gradient (top)
- and driving conditions (right)
- Stop-and-go and highway driving cause high emissions

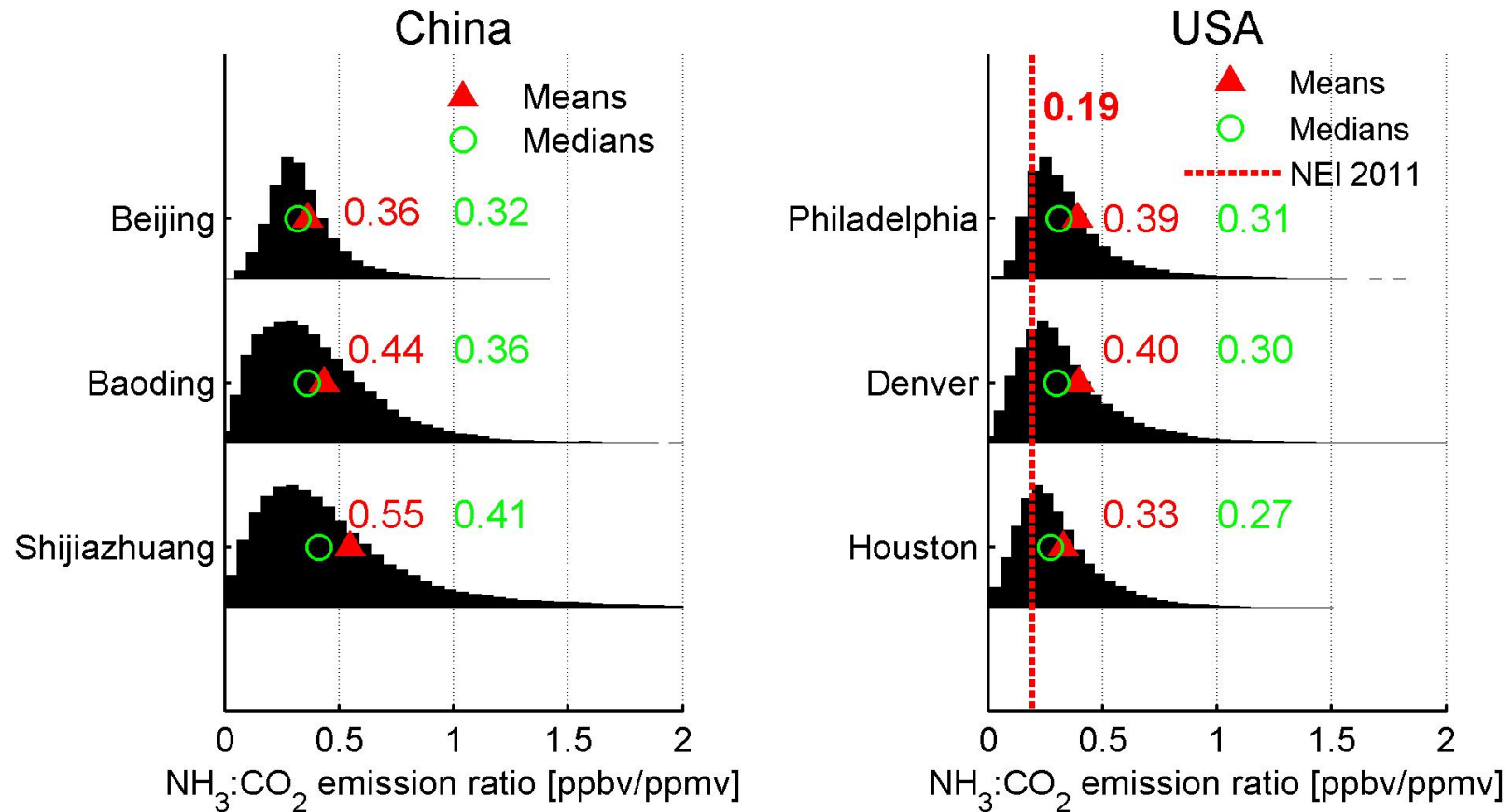


On-road measurements

- Mobile measurements during NASA DISCOVER-AQ in California (i), Texas (iii), and Colorado (iv)
- CAREBeijing/NCP in North China Plain (ii)
- Coverage $\sim 18,000$ km, 400 hours
- Multiple metropolitan regions in the US and China



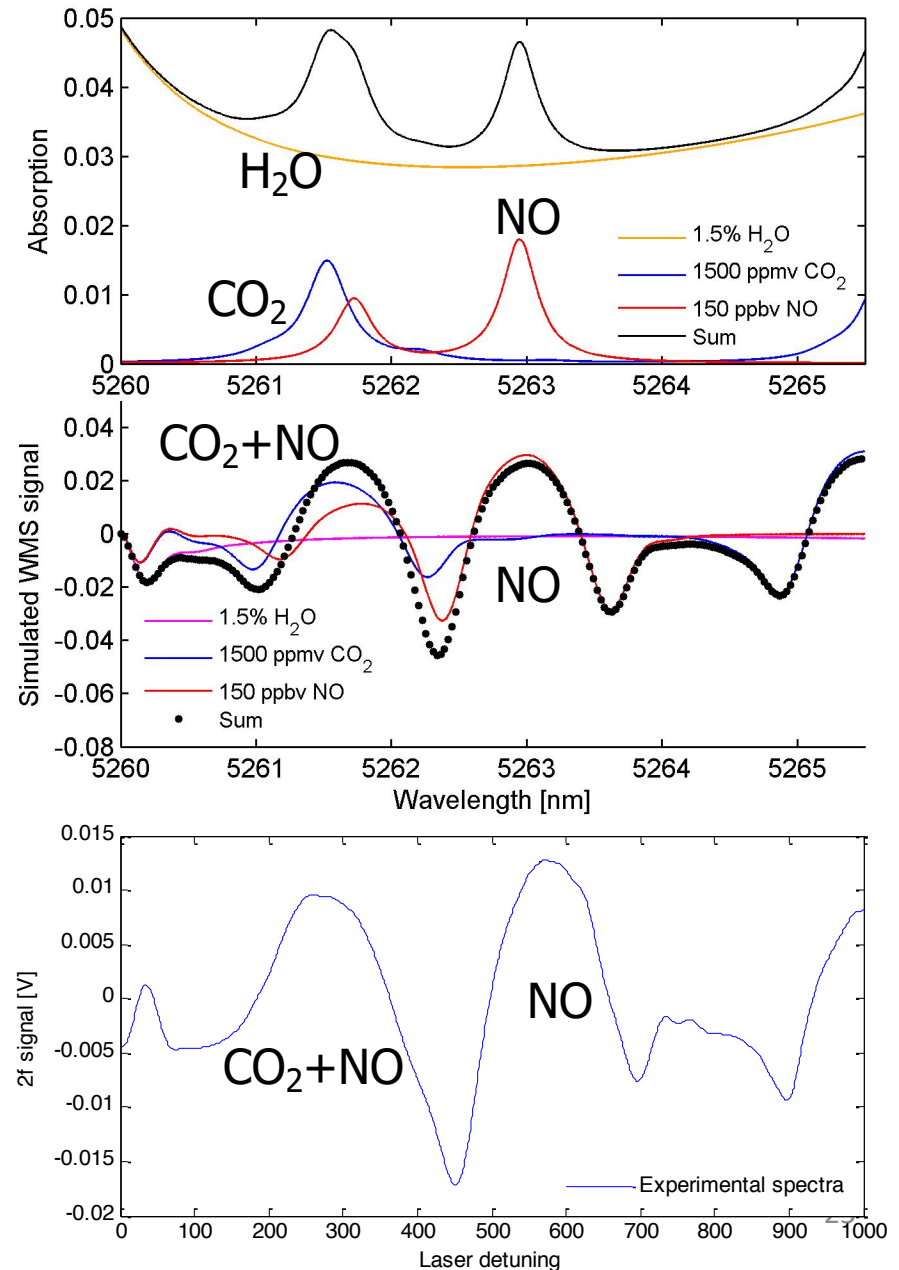
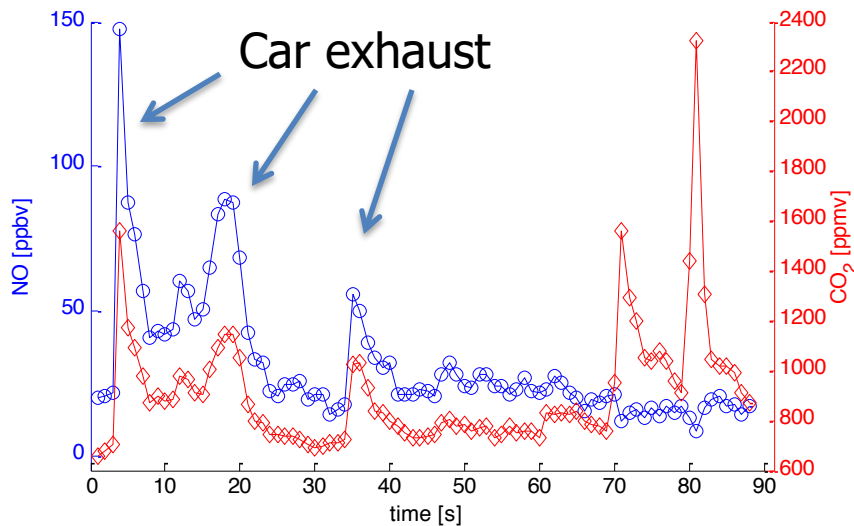
NH₃ emissions in Chinese & US cities



- “Developing” cities show higher NH₃ emissions
- NH₃:CO₂ ERs are comparable between Beijing & US cities
- NEI on-road NH₃ emission greatly underestimated (50%)

Developing open-path NO sensor

- QC laser at 5.26 μm
- Wavelength modulation spectroscopy: eliminating water vapor baseline
- Rapid detection of vehicle emissions

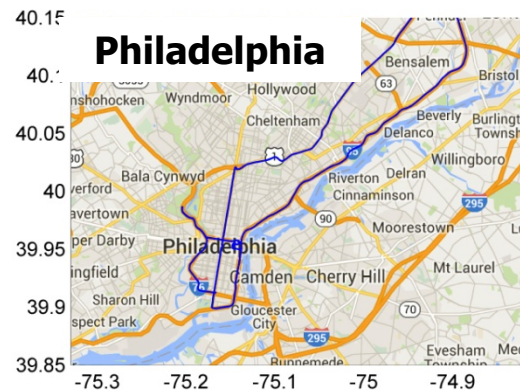
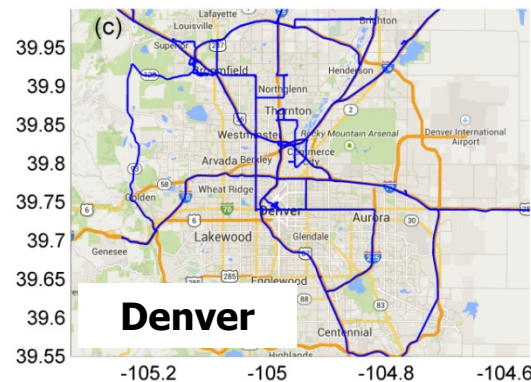
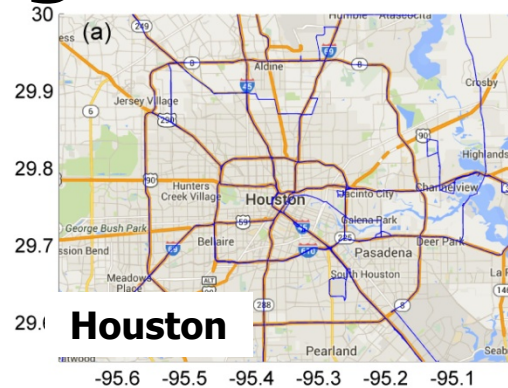


Conclusions

- Quantum cascade laser-based, open-path mobile laboratory
 - Established sensors for NH_3 (Miller et al., AMT, 2014), N_2O (Tao et al., OE, 2012); NO to be incorporated
 - Battery-powered, compact for flight carry-on
 - Extensive field deployments and intercomparisons
 - ➔ Wide coverage, fleet-integrated emissions: new discoveries
- Urban NH_3 emissions from vehicles
 - Road gradient strongly influence vehicle NH_3 emissions ($\times 2$ from 0 to 7%)
 - Beijing emission ratios similar to US cities, lower than “developing” cities
 - Traffic NH_3 underestimated by $\sim 50\%$ in the US, largest sources in cities
 - ➔ major source of urban PM formation
 - ➔ Nr deposition downwind of cities
- Future work
 - Agile DSP based electronics to control multiple sensor channels
 - Real-time data publishing and sharing; from nodes to network

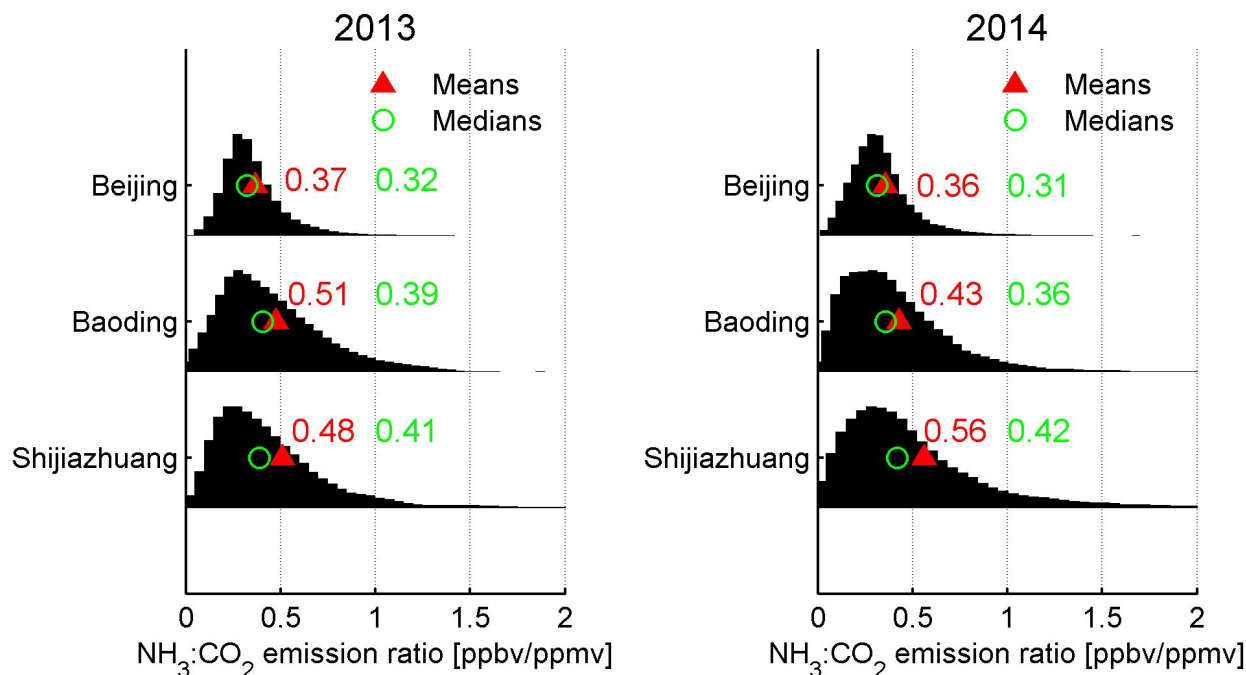
Spatial coverage in urban areas

- Houston
- Denver
- Philadelphia
- Beijing
- Baoding
- Shijiazhuang



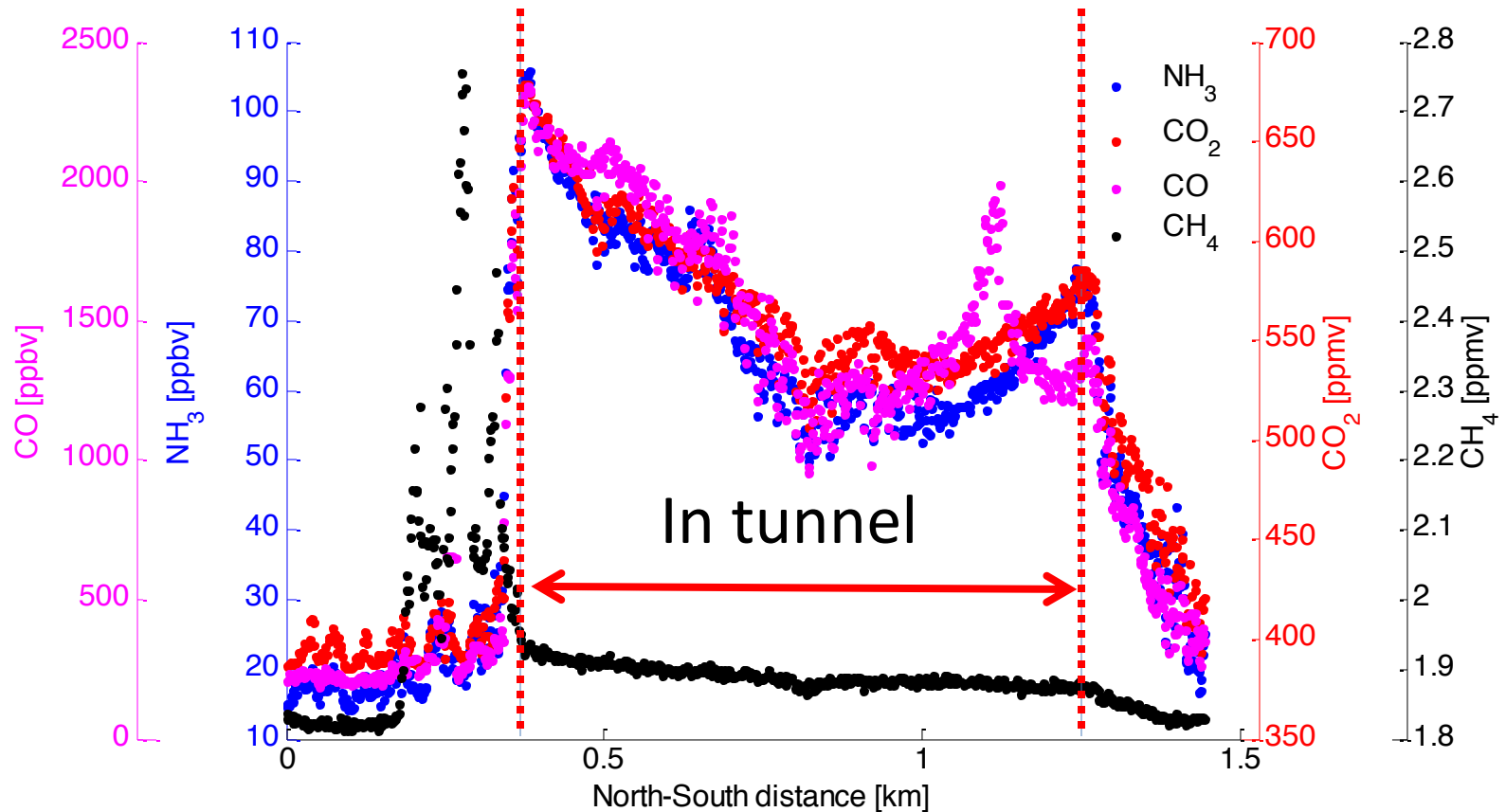
Interannual consistency

- Beijing, Baoding, and Shijiazhuang were sampled in both 2013 (blue) and 2014 (red)
- No significant interannual variation
- Beijing has lower emissions because of newer & more regulated fleet (Euro V standard v.s. Euro III in other two cities)



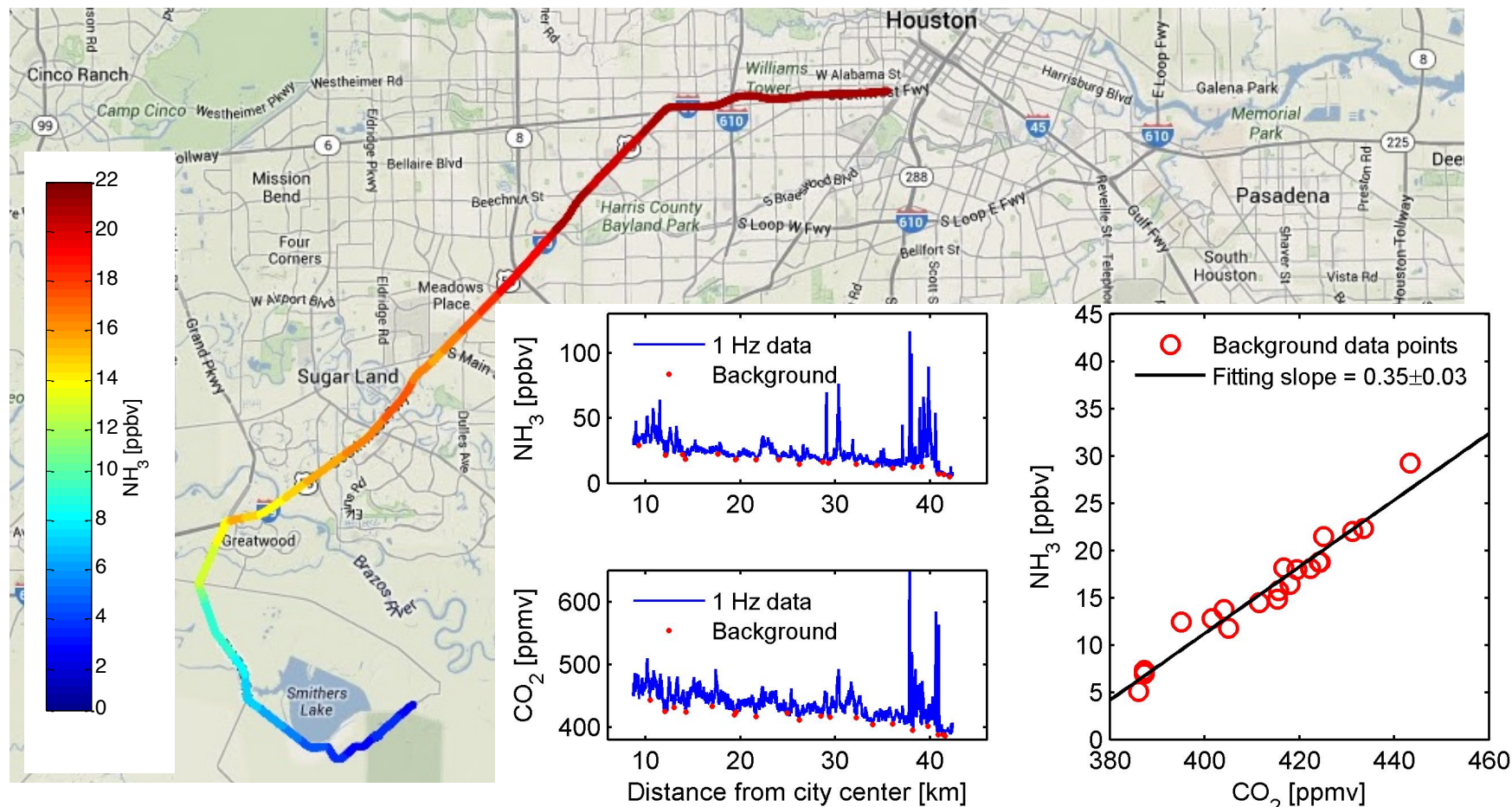
Tunnel measurements

- Seven transits were performed through Washburn tunnel



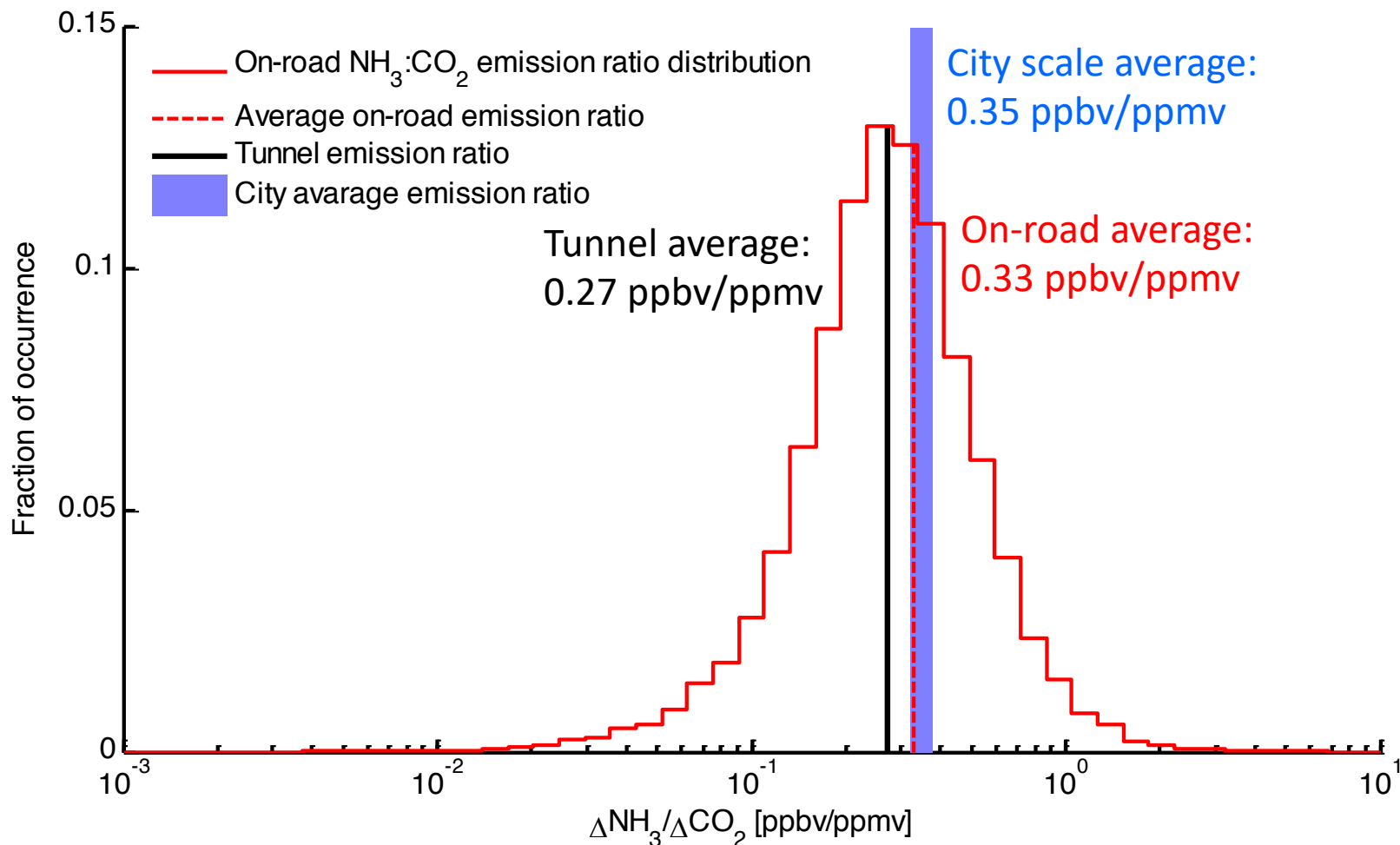
- Tunnel NH₃:CO₂ emission ratios are 0.27 ± 0.05 ppbv/ppmv
- Comparable to average on-road ER: 0.33 ppbv/ppmv

City scale gradients



- Mobile measurement from downtown Houston to the outskirts
- Particulate ammonium contribution was less than 1 ppbv (AMS measurements by William Wallace, Rice University).

Local vs. city scale measurements



- City scale emission ratio is consistent with on-road/tunnel data
- Possible integration of other NH_3 and CO_2 sources, likely minor, according to NEI at Harris County