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Environmental ammonia monitoring for urban and rural areas of Texas using optical EC-QCL based sensor platform

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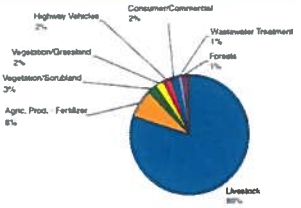
- Motivation: Environmental monitoring of ammonia (NH_3) based on an optical sensor platform
- NH_3 sensor platform architecture
- NH_3 absorption line selection
- Detection results and long term measurements
- Summary and Future Directions

Special acknowledgement to Prof. Barry Lefer (University of Houston) for his hospitality

Ammonia (NH_3) facts

- NH_3 plays an important role in atmospheric chemistry.
- The total estimated global emission of NH_3 to the atmosphere is ~ 45 TgN/year
- Industrial and motor vehicles activities can be important in urban areas.
- In the atmosphere, NH_3 reacts with different acid pollutants forming ammonium particulates and aerosols.
- Ammonia is a potential source of atmospheric NO and N_2O.



Ammonia emissions by major source category in Texas [1]

$$NH_3 + OH^{\cdot} \rightarrow NH_2^{\cdot} + H_2O$$
$$NH_2^{\cdot} + O_2 \rightarrow NH, NHO, NO$$
$$NH_2^{\cdot} + NO_2 \rightarrow N_2 \text{ or } N_2O \ (+ H_2O)$$

[1] R. T. Pavlovic, U. Nopmongcol, Y. Kimura and D. T. Allen, Atmospheric Environment 40, 538-551 (2006)

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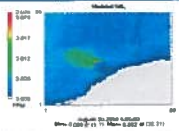
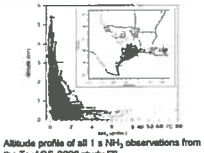
Estimated ammonia levels for Houston

- Atmospheric NH_3 concentrations for urban and industrial areas vary between 0.1 and 10 ppbv [1].
- The modeled ammonia concentration for Houston was estimated to range between 1 and 15 ppb [2].
- The typical NH_3 mixing ratios from area sources range from 0.2 to 3 ppbv, but for unexpected industrial accidents or events can increase even to 80 ppbv [3].



Modeled ammonia concentrations at times of maximum nitrate concentrations. [2]



Altitude profile of all 1 s NH_3 observations from the TexAQS 2006 study [3].

[1] J.H. Seinfeld, S.N. Pandis Atmospheric Chemistry and Physics, John Wiley and Sons, Inc., Hoboken, NJ (2006)
[2] R. T. Pavlovic, U. Nopmongcol, Y. Kimura and D. T. Allen, Atmospheric Environment 40, 538-551 (2006)
[3] Nowak J. B., et al. J. Geophys. Res., 115, D22304, (2010)

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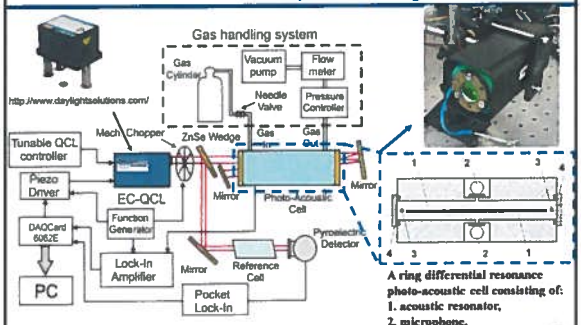
Mid-IR EC-QCL based AM-PAS sensor architecture for atmospheric NH_3 detection



A ring differential resonance photo-acoustic cell consisting of:
1. acoustic resonator,
2. microphone,
3. gas input and output,
4. window

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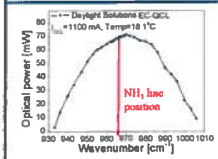
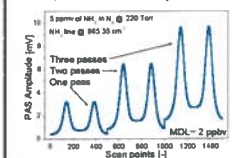
PAS based NH_3 measurements with a 10.34 µm Daylight Solutions CW EC-QCL source

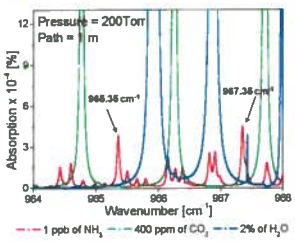


Tuning range and optical power profile for a Daylight Solutions, Inc mid-IR CW EC-QCL system



AM-PAS signal for 5 ppmv NH_3 in N_2 after one, two, and three QCL output beam passes through the photoacoustic cell

Available EC-QCL power P_{EC-QCL} up to **72 mW (CW)**
Wavelength tunability **73 cm^{-1}** (933 cm^{-1} – 1006 cm^{-1})



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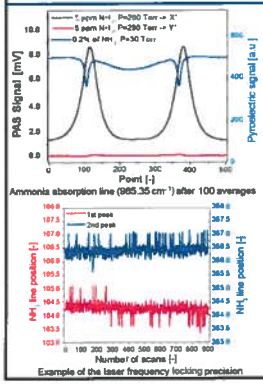
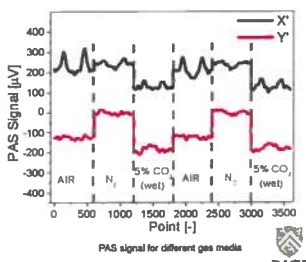
Data Acquisition Procedure



Example of the laser frequency locking precision

Scan period: T = 10 s
Lock-In TC: τ = 200 ms
Res. freq: f=1800 Hz (40°C)



PAS signal for different gas media

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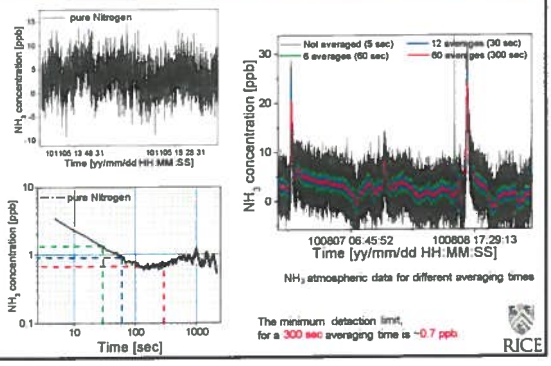
Stability of NH_3 sensor platform after Moody Tower installation



NH_3 atmospheric data for different averaging times

The minimum detection limit, for a 300 sec averaging time is ~0.7 ppb

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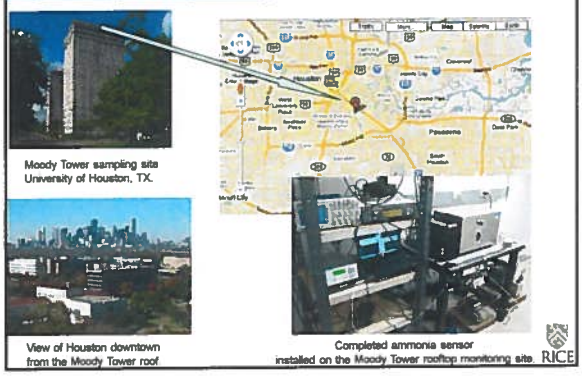
NH_3 sensor deployment (University of Houston campus)



Moody Tower sampling site University of Houston, TX.

View of Houston downtown from the Moody Tower roof

Completed ammonia sensor installed on the Moody Tower rooftop monitoring site.

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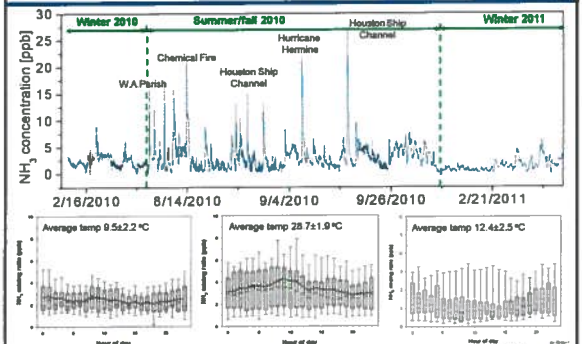
Data of Atmospheric NH_3 Concentration Levels for Houston



Diurnal trends representing atmospheric NH_3 concentration levels during the Feb 12, 2010–March 1, 2010; Aug 5, 2010–Oct 15, 2010; and Feb 9, 2011–March 7, 2011 sampling periods.

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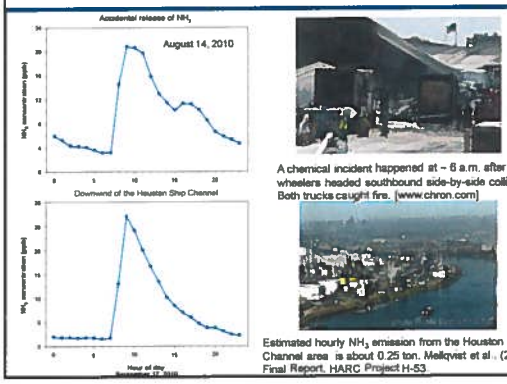
NH_3 detection due to fire resulting from a truck collision



A chemical incident happened at ~ 6 a.m. after two 18-wheelers headed southbound side-by-side collided. Both trucks caught fire. [www.chron.com]

Estimated hourly NH_3 emission from the Houston Ship Channel area is about 0.25 ton. Mellqvist et al. (2007) Final Report, HARC Project H-53

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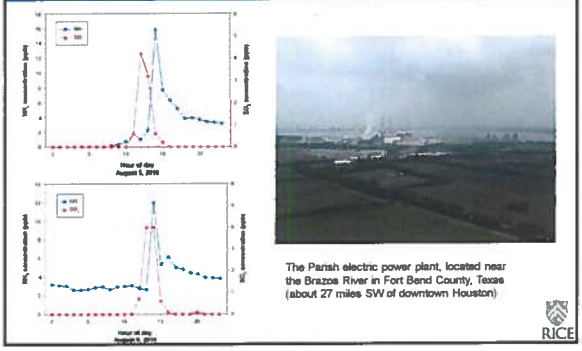
Sporadic increased NH_3 concentration levels related to emissions by the Parish electric power plant, TX



The Parish electric power plant, located near the Brazos River in Fort Bend County, Texas (about 27 miles SW of downtown Houston)

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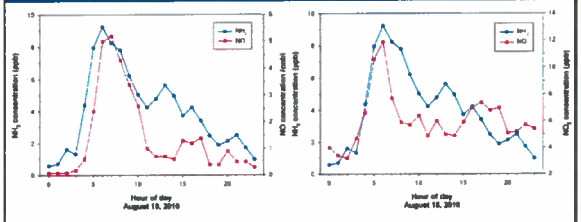
Increased NH_3 concentrations related to traffic emissions during Houston, TX rush hour



NH_3 concentrations significantly increased on Aug 18, 2010 during rush hour and the wind direction was from the northwest to the Moody tower. During the same time period the TCEQ Site No.408 located in northwest Houston measured NO and NO_2 enhancements that coincided with increased NH_3 concentration levels measured at the UH Moody Tower monitoring test site.

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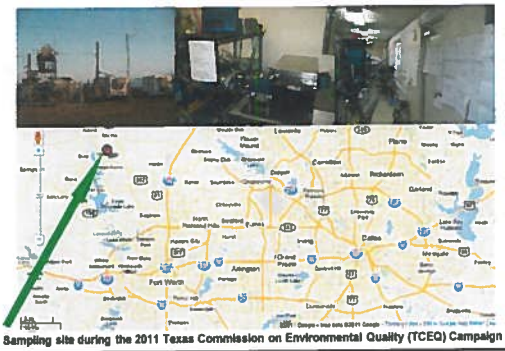
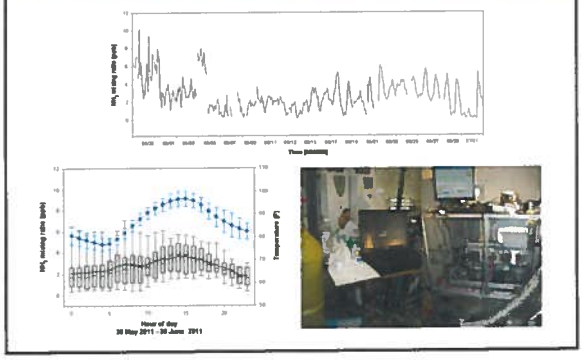
NH_3 sensor deployment in Fort Worth (CAMS 75)



- Sampling site during the 2011 Texas Commission on Environmental Quality (TCEQ) Campaign

Preliminary results for a May-June 2011 TCEQ campaign - Fort Worth, TX



Summary

- A 10.4 μm EC-QCL based ammonia sensor, employing conventional photo-acoustic spectroscopy, was demonstrated.
- The minimum detection limit, obtained for the NH_3 absorption line at 965.35 cm^{-1}, was ~0.7 ppb for a 300 sec averaging time.
- The NH_3 sensor is capable of unattended operation and continuous data acquisition for extended periods of time.
- Remote access via internet, enabling real-time monitoring of the sensor performance was established.
- Several unexpected episodes of high NH_3 mixing ratios were observed.
- The Houston Ship Channel is a significant contributor. However, NH_3 source attribution is influenced by factors such as boundary layer dynamics, meteorology, and the lack of sufficient emission inventory data.
- The AM-PAS based NH_3 sensor was also field tested at the CAMS75 monitoring site in the Fort Worth/Dallas area, between May 31, 2011 and June 30, 2011, as part of the Summer 2011 Texas Commission on Environmental Quality (TCEQ) Campaign.

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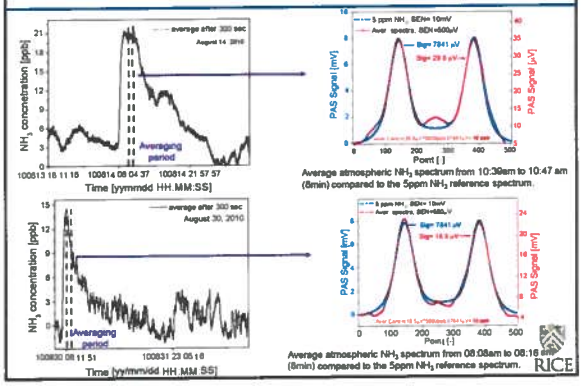
NH_3 Measurements in Air



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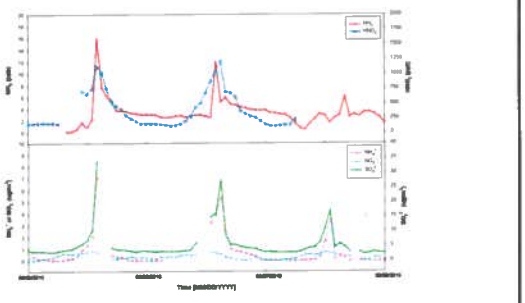
Results – simultaneous measurements



Weekday-weekend differences in NH_3 concentrations

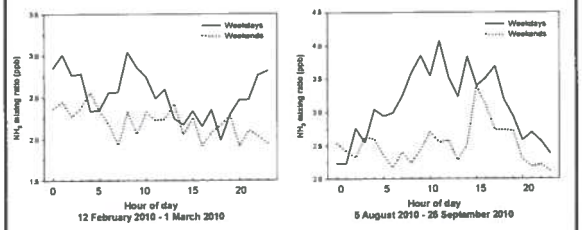


Photo of PAS based NH_3 sensor platform for atmospheric measurements