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Open-path, quantum cascade laser-based sensor for high resolution atmospheric ammonia measurements

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Abstract

We demonstrate a compact, open-path, quantum cascade laser-based atmospheric ammonia sensor operating at 9.06 μm for high sensitivity, high temporal resolution, ground-based measurements. Atmospheric ammonia (NH_3) is a gas-phase precursor to fine particulate matter, with implications for air quality and climate change. Currently, NH_3 sensing challenges have led to a lack of widespread in-situ measurements. Our open-path sensor configuration avoids sampling artifacts associated with NH_3 surface adsorption onto inlet tubing and reduced pressure sampling cells, as well as condensed-phase partitioning ambiguities. Multi-harmonic wavelength modulation spectroscopy allows for selective and sensitive detection of atmospheric-pressure broadened absorption features. An in-line ethylene reference cell provides real-time calibration ($\pm 20\%$ accuracy) and normalization for instrument drift under rapidly changing field conditions. The sensor has a sensitivity and minimum detection limit of 0.15 ppbv NH_3 at 10 Hz, a mass of ~ 5 kg and consumes ~ 50 W of electrical power. In-situ field performance of this open-path NH_3 sensor is demonstrated, with 10 Hz time resolution and a large dynamic response for in-situ NH_3 measurements. This sensor provides the capabilities for improved in-situ gas phase NH_3 sensing relevant for emission source characterization and flux measurements.

1 Introduction

Atmospheric ammonia (NH_3), the third most abundant nitrogen species and dominant atmospheric base, is an important precursor to ammoniated fine particulate matter (Nowak et al., 2007; Pinder et al., 2008). Total NH_3 , the sum of gas phase NH_3 and particulate ammonium, NH_4^+ , is an increasingly important component of the reactive nitrogen budget, with implications for human and ecosystem health (Bobbink et al., 2003; Galloway et al., 2003; Pinder et al., 2008). Ammoniated aerosols are a dominant component of inorganic aerosol mass in both clean and urban regions (Jimenez et al.,

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2009). Gas phase NH_3 measurements are crucial for understanding aerosol nucleation and new particle formation (Ball et al., 1999; Hanson and Eisele, 2002; McMurry et al., 2005; Benson et al., 2011), which facilitate long range transport of aerosol ammonium and nitrate (Nowak et al., 2007; Pinder et al., 2008). Ammoniated sulfate aerosols
5 also play an important role in cirrus cloud nucleation (Tabazadeh and Toon, 1998; Wang et al., 2008) and aerosol-cloud interactions have significant yet highly uncertain radiative effects on climate (Adams et al., 2001; Martin et al., 2004; Solomon et al., 2007).

Anthropogenic NH_3 emissions have more than doubled since pre-industrial times,
10 largely due to agricultural livestock and fertilizer emissions (Galloway et al., 2003; Battye et al., 2003; Anderson et al., 2003; Aneja et al., 2008). Uncertainties over 50 % exist in global NH_3 emission budgets due to the spatial and temporal variability of emissions and a lack of in-situ measurements for emission inventory validations (Battye et al., 2003; Clarisse et al., 2009). Recent comparisons between measured emissions
15 and concentrations with model inventories found significant discrepancies (Heald et al., 2012; Nowak et al., 2012; Walker et al., 2012).

Gas phase NH_3 has a short atmospheric lifetime of a few hours to a few days, which depends on ambient temperature, relative humidity and aerosol composition (Anderson et al., 2003). High spatial and temporal resolution observations are needed to fully char-
20 acterize NH_3 dynamics, including aerosol nucleation, gas phase uptake onto particles and volatilization of particulate ammonium (Battye et al., 2003; Nowak et al., 2007; Pinder et al., 2008). In-situ NH_3 instruments require high (sub-ppbv) sensitivity to measure low atmospheric mole fractions (pptv-ppbv), fast response time and large dynamic
25 range to capture atmospheric variability (von Bobruzki et al., 2010). Ammonia sensors must also account for gas phase NH_3 surface adsorption effects and condensed phase partitioning due to changes in temperature and relative humidity between the sampling volume and ambient atmosphere (Yokelson et al., 2003).

To date, the NH_3 measurement challenges have resulted in a variety of different approaches. Conventional off-line NH_3 sensors (passive filters, denuders and ion

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chromatographs) often have sufficient sensitivity (< 1 ppbv NH_3), but have long integration times, lack the requisite selectivity and are labor intensive to analyze (Fehsenfeld et al., 2002; von Bobruzki et al., 2010; Ellis et al., 2011). Chemical ionization mass spectrometry (CIMS) NH_3 instruments have high time resolution (seconds), selectivity
5 and extremely high sensitivity (< 100 pptv NH_3), but require large power consumption (kW) and space (multiple instrument racks) (Nowak et al., 2007; Benson et al., 2010; Spirig et al., 2011). Laser absorption spectrometers for gas phase NH_3 have been developed for real-time, high-sensitivity and selective detection. Near-infrared diode lasers have been used for NH_3 detection, but their sensitivity is limited due to the NH_3
10 overtone bands in the near-infrared (Claps et al., 2001; Kosterev et al., 2004).

More recently, advances in room temperature, continuous-wave, distributed feedback quantum cascade (QC) lasers have led to the development of QC laser-based NH_3 sensors using the strongest NH_3 absorption transitions located in the mid-infrared spectral region (Li et al., 2006; Manne et al., 2006, 2009; Whitehead et al., 2007;
15 McManus et al., 2008; Curl et al., 2010; Ellis et al., 2010; Gong et al., 2011). Although these closed-path systems are highly sensitive (ppbv or sub-ppbv), they suffer from sampling artifacts that limit precision and response time and complicate calibration methods (Whitehead et al., 2008; von Bobruzki et al., 2010). In addition, these systems are large (usually > 100 kg) and require pumps and temperature control systems
20 with high power consumption (usually hundreds of Watts).

In contrast to these closed-path systems, non-intrusive open-path designs address the sampling challenges and provide fast response times (Zondlo et al., 2010; McDermitt et al., 2011; Tao et al., 2012b). Peeters et al. (2000) demonstrated laboratory performance of an open-path cavity-enhanced absorption spectrometer for NH_3 ,
25 but the detection limit was not sufficient for atmospheric measurements. Open-path TDLAS and differential optical absorption spectroscopy (DOAS) systems in remote measurement configurations have been used to measure NH_3 with ppbv detection limits (Thoma et al., 2005; Volten et al., 2012). Mount et al. (2002) demonstrated open-path NH_3 measurements with a mid-ultraviolet DOAS system and achieved 1 ppbv NH_3

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sensitivity in 1 s. The high time resolution (> 1 Hz) of this approach illustrated the value of an open-path configuration. However, all of these sensors require long paths rather than compact sensor footprints. Currently, there are significant hurdles for compact, open-path, laser-based NH_3 sensing, including pressure-broadened absorption line-shapes sensitive to changes in environmental temperature and pressure and interferences from broad, overlapping absorption features from other atmospheric species.

To address the limitations of closed-path techniques and challenges for compact, open-path sensing, we demonstrate the performance of compact, open-path, high sensitivity, QC laser-based atmospheric NH_3 sensor. The sensor probes the fundamental mid-infrared NH_3 absorption transitions using a QC laser at $9.06\ \mu\text{m}$. Multi-harmonic wavelength modulation spectroscopy is used to isolate overlapping absorption features and an in-line ethylene reference cell is used for online calibration and normalization to account for sensor drift. The system is relatively compact, low power (~ 50 W), low mass (~ 5 kg), with a 10 Hz time resolution and high sensitivity (0.15 ppbv minimum detection limit at 10 Hz). The fast response time and dynamic range capabilities of the open-path system are illustrated. In-situ NH_3 measurements of emission sources are highlighted.

2 Instrument design

2.1 Sensor setup

The open-path, QC laser-based NH_3 sensor is shown schematically in Fig. 1. Overall, the open-path design is optimized for field portability with a $100\ \text{cm} \times 10\ \text{cm} \times 11\ \text{cm}$ sensor head, $35\ \text{cm} \times 33\ \text{cm} \times 15\ \text{cm}$ drive electronics unit and total mass of ~ 5 kg. The sensor uses a thermo-electrically (TE) cooled, continuous-wave, single mode, $9.06\ \mu\text{m}$ quantum cascade laser (Alpes Lasers) in a high heat load package, which is detected by a three-stage, TE-cooled, infrared HgCdTe photo-detector (Judson Teledyne). The opto-mechanical design consists of the laser, collimating lens, in-line

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ethylene reference cell, steering mirrors, multi-pass optical cell and detector. A Herriott multi-pass cell with spherical mirrors (Herriott et al., 1964) is used to achieve path lengths of 30–60 m in a 70 cm base path, depending on the spot pattern implemented. The laser beam is directed into the optical cell consisting of two protected silver-coated, 3 inch diameter spherical mirrors, both with a 6 mm diameter hole for laser beam entry and exit. The QC laser beam size is optimized with focusing mirrors to minimize clipping and distortion effects as the laser beam enters the input hole. A visible alignment laser (HeNe) is used to image the optical spot pattern on the mirrors and couple the QC laser beam into the optical cell. Custom anti-reflection coatings (reflectivity $< 0.5\%$) are applied to all transmissive optics, including laser and detector housing windows, to minimize signal baseline artifacts due to interference fringes that are unstable with ambient temperature changes.

The QC laser is driven by a low noise current driver (Wavelength Electronics, QCL500) and thermally controlled with a precise temperature controller (Wavelength Electronics, HTC3000). The QC laser current is modulated with a sawtooth ramp (50 Hz) and higher frequency (15 kHz) sinusoidal modulation. The detector signal is acquired with a National Instruments data acquisition board (NI-USB 6251) and processed in real-time. The 50 Hz raw signal is co-averaged to 2–10 Hz, depending on the field conditions and signal to noise ratio. Multi-harmonic wavelength modulation spectroscopy (WMS) detection is performed with a custom LabVIEW software algorithm, eliminating the need for a bench-top lock-in amplifier, as described in Tao et al. (2012b). The open-path configuration eliminates the need for large pumps that require high power consumption, resulting in low power consumption (~ 50 W excluding a laptop computer). The system requires no cryogenic cooling, allowing for autonomous field operation.

2.2 Spectroscopy

The strongest NH_3 absorption transitions occur in the mid-infrared spectral region near $10.3\ \mu\text{m}$ and are probed by other QC laser absorption spectrometers (McManus et al.,

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2008; Gong et al., 2011). However, this spectral region is not optimal for open-path detection, due to the carbon dioxide (CO₂) and water vapor (H₂O) pressure-broadened absorption lines that overlap with the NH₃ absorption lines. The most optimal absorption feature for open-path NH₃ detection is at 9.06 μm, a region between the strong absorption bands of N₂O below 8.9 μm and absorption bands of CO₂ and O₃ above 9.1 μm. The selected absorption feature is ~ 50 % weaker than the stronger NH₃ features near 9.5 μm, but the spectral clarity at 9.06 μm allows for higher sensitivity. Figure 2a shows HITRAN simulated spectra in the 9.06 μm region for 1 ppbv NH₃ and typical ambient concentrations of atmospheric absorbers at 296 K and 1013.25 hPa for a 60 m optical path length. The NH₃ absorption feature at 9.06 μm in Fig. 2a is a superposition of six overlapping absorption transitions. This feature overlaps with the minimum of a neighboring H₂O absorption feature, producing a direct absorption baseline. Owen et al. (2013) performed spectroscopic studies on relevant atmospheric absorbers in this region at reduced pressure to characterize the interferences. For open-path detection at ambient pressures, wavelength modulation spectroscopy is a well-suited detection technique for spectral resolution of these weak, overlapping absorption features (Schilt et al., 2003; Zondlo et al., 2010). As shown in Fig. 2b, second harmonic (2f) detection minimizes the water vapor absorption baseline and improves sensitivity and selectivity (Reid and Labrie, 1981). Other atmospheric species such as CO₂, O₃ and SO₂ also absorb in this region below ~ 5 × 10⁻⁵ fractional absorption. We note that polluted concentration conditions are illustrated in Fig. 2 (5 ppbv SO₂ and 80 ppbv O₃) to represent ambient conditions with possible interferences. However, the NH₃ absorption at 9.06 μm for 1 ppbv NH₃ is greater than five times the absorption of these species in this spectral region. As described in the following section, we use full spectral fitting routines to decrease the influence of adjacent and overlapping absorption features. Overall, the only significant interfering species for 2f detection at 9.06 μm is H₂O, which is addressed in the following section. The O₃ absorption baseline begins to interfere significantly for NH₃ concentrations below 100 pptv.

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2.3 Ammonia concentration retrieval

The ammonia concentration is retrieved with real-time spectral fitting at 10 Hz. We simulate the direct absorption signal recorded by the detector with multiple Voigt lineshape profiles for all relevant absorption transitions within the laser scan range as follows:

$$D(t) = \chi \cdot I(t) \cdot \exp \left(- \sum_i (x_i S_i L_i \psi_i(T, P, \nu(t))) \right) \quad (1)$$

where χ is the detector collection efficiency, $I(t)$ is the laser intensity function, x_i , S_i and L_i are the number density, absorption line strength and path-length respectively for different absorbing species i and $\psi_i(T, P, \nu(t))$ is the Voigt line shape function for absorption feature i and is a function of temperature, pressure and wavenumber $\nu(t)$. This signal is multiplied by a reference signal at the n th harmonic and passed through a virtual lock-in amplifier based on a numerical wavelength modulation spectroscopy model (Tao et al., 2012b). A least-square fitting routine is implemented to produce fitting coefficients for gas concentration, DC signal offset, linear and second order polynomial baselines. The spectroscopic parameters used in the fitting routine for the NH₃ absorption lines of interest have been measured experimentally by Sun et al. (2013), and generally agree to within 10 % of HITRAN. Ambient temperature, pressure and relative humidity (RH) are measured with a digital RH sensor (HYT 271, ±1.8 % RH, ±0.2 °C accuracy) and digital pressure sensor (MS5803-01BA, ±0.5 hPa accuracy) at 1 Hz and updated in real-time for the fitting routine. The H₂O mixing ratio value for spectral fitting is derived from these measurements. An in-line ethylene reference cell is inserted into the optical path as explained below.

The NH₃ and ethylene absorption features (centered at 1103.46 cm⁻¹ and 1103.36 cm⁻¹ respectively) are fit simultaneously in both second (2f) and eighth (8f) harmonics. The multi-harmonic approach separates the overlapping, broad ambient NH₃ absorption feature from the narrower ethylene reference signal as demonstrated by Sun et al. (2013). Figure 3 shows representative 2f and 8f spectra along with fitting

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results and residuals for an 8.0 ppbv ambient NH_3 signal. The 2f signal and fitting line-shape have two extra troughs, indicated by arrows, due to the ethylene absorption overlapped with the ambient NH_3 signal. The eighth harmonic (8f) is used for ethylene reference signal detection to achieve optimal separation between ambient NH_3 and ethylene reference signals. The 8f signal isolates the relatively narrow, reduced pressure ethylene reference signal, with negligible influence from ambient NH_3 absorption at 8f. We do not use harmonic orders higher than 8f due to limits of signal-to-noise ratio, since the signal intensity decreases as harmonic order increases. The even harmonic orders are advantageous since the maximum of the WMS function occurs at the spectral line-center, which is useful for line-locking procedures.

We implement an online spectroscopic calibration method using ethylene, which exhibits negligible adsorption artifacts compared with NH_3 . Calibration with an NH_3 reference cell would lead to artifacts associated with NH_3 reference cell concentration changes due to changes in cell temperature and pressure. In addition, when ambient and reference absorption features of the same species are overlapping, separating changes in concentration from changes in the reference signal becomes difficult. The in-line ethylene reference cell contains 1.5 % ethylene in nitrogen at 50 hPa total pressure in a 3 cm length. The concentration of ethylene was chosen to be comparable to NH_3 signals at ppbv levels. Spectroscopic parameters of both NH_3 and ethylene absorption features have been measured and compared with the HITRAN database to evaluate the calibration accuracy. Sun et al. (2013) has demonstrated this ethylene signal can serve as a reference of NH_3 concentration in real-time, with an overall calibration accuracy of $\pm 20\%$. In addition, we perform offline absolute calibration using NH_3 direct absorption measurements, as described in Sect. 3.1 below. These two calibration methods together can improve the accuracy to $\sim 10\%$.

The absolute accuracy of these combined calibration methods is comparable to existing sensors. However, the in-line ethylene reference signal is especially advantageous as it provides normalization for sources of instrument drift. Normalization for sensor drift is essential for open-path systems exposed directly to changing environmental

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conditions, which lead to undesirable or unknown opto-mechanical and electronic responses such as optical interference fringes, electrical component drift, laser and detector temperature instabilities and light attenuation due to precipitation. In addition, the sharp peaks and troughs of the 8f signal are used for line-locking via active control of the laser temperature to account for thermal drifts of the laser wavelength. This improves the drift during a typical $\sim 10^\circ\text{C}$ diurnal ambient temperature cycle from 0.04 cm^{-1} to $< 0.005\text{ cm}^{-1}$.

3 Instrument performance

3.1 Calibration

We perform absolute calibration off-line with direct absorption measurements for a range of NH_3 gas concentrations. The open-path optical cell is enclosed in a polyethylene calibration tube, into which a flow of 25 ppmv NH_3 in nitrogen (N_2) is introduced. Based on simulated sensitivity, the differences in HITRAN fitting parameters for N_2 compared with air result in a 5 % change in spectral fitting results. This effect is neglected here as this uncertainty (5 %) is within the uncertainty of our calibration method. The original NH_3 concentration is decreased incrementally by dilution with a dry N_2 gas flow and each calibration point is recorded in both 2f and direct absorption as shown in Fig. 4. The horizontal axis displays the retrieved NH_3 concentration based on 2f spectral fitting with the online spectroscopic calibration method described in Sect. 2.3. The vertical axis is the NH_3 standard concentration derived from direct absorption measurements. The concentration retrieval is derived from nonlinear Voigt lineshape fitting of the direction absorption spectra and assumes the number concentration is linearly proportional to the fractional absorption for typical (ppbv) atmospheric NH_3 concentrations. However, the retrieved concentration does not scale linearly with the standard concentration due to strong absorption non-linearity at concentrations > 100 ppbv NH_3 . Therefore, we fit a third-order polynomial to calibrate the retrieved concentration as

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shown in Fig. 4. The linearity of retrieved concentration is shown in the inset plot of Fig. 4 for concentrations below ~ 120 ppbv NH_3 . In this regime, we can assume absorption is linear with number concentration based on the Beer Lambert Law weak absorption limit. A linear best fit line in this range yields $R^2 = 0.99$, in agreement with the weak absorption limit. The uncertainty in NH_3 standard concentration derived from direct absorption is estimated to be $\sim 10\%$, based on the gas concentration and HI-TRAN parameter uncertainties for spectral fitting.

3.2 Precision

To investigate precision and stability of the open-path NH_3 sensor, Allan deviation analyses (Werle et al., 1993) are performed on NH_3 and ethylene reference signal time series. We compare the drift characteristics of the ambient and reference signals to determine the optimal integration time for normalization by the ethylene reference signal. For this analysis, we normalize both NH_3 and ethylene retrievals by the 1f DC value to account for changes in light intensity on the detector. The NH_3 concentration and air temperature are variable in the laboratory during the recorded time series, whereas the ethylene concentration in the reference cell is a constant. Ethylene signals were recorded at 1 Hz time resolution to optimize the signal quality for fitting and higher harmonic signal peak detection for line-locking.

Figure 5 shows the Allan deviation plot for NH_3 measurements, with a mean mixing ratio of 14.6 ppbv NH_3 recorded in the laboratory at 10 Hz time resolution. The precision is $\sim 1\%$ or 0.15 ppbv NH_3 at 10 Hz. The precision is similar at 1 Hz integration time. The minimum precision is ~ 15 pptv NH_3 for an integration time of ~ 200 s, beyond which drift dominates the Allan deviation. The 10 Hz precision is maintained out to time scales greater than 1 h. We note that while concentrations are fit in real time at 10 Hz, the data acquisition is synchronized to a GPS pulse per second (pps) signal at 1 Hz and current line-locking is implemented, which results in a transition from 100% to an effective 10% duty cycle from 0.1 s to 1 s integration time. We also note that the offset is consistent

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with a $\sqrt{10}$ decrease in Allan deviation resulting from a 10% duty cycle (Werle et al., 1993) at 1 Hz and longer time scales.

The Allan deviation plot for the ethylene reference signal recorded at 1 Hz time resolution is shown in Fig. 6. One second averaging is used for ethylene to improve the signal to noise ratio at the higher (8f) harmonics. The precision of the ethylene signal is $\sim 1\%$ at 1 Hz, comparable to that for NH_3 . The precision improves as integration time increases, but interference fringing at the higher harmonics (8f) and laser thermal drift limit this improvement for integration times > 100 s. The minimum of the NH_3 Allan deviation in Fig. 6 occurs at an integration time of ~ 200 s. Thus, a 200 s integration time is optimal for normalization by the ethylene reference signal to account for drift in the NH_3 signal. Note that the data in Figs. 5 and 6 show drift of $\sim 1\%$ or less at 3000 s integration time, which is much lower than the overall accuracy ($\pm 10\%$). In this case, the in-line ethylene reference signal is of marginal value under relatively constant laboratory conditions. However, the in-line ethylene signal is an important method to account for much larger system drifts expected under rapidly changing field conditions and over longer time scales (days).

3.3 Minimum detection limit

The minimum detection limit of the NH_3 sensor was determined by the measuring 1 σ of the concentration time series recorded under background (zero ammonia signal) conditions. The short term noise is expected to be the limiting factor for the minimum detection limit, as the Allan deviation plot shown in Fig. 5 indicates precision better than the 10 Hz precision on long time scales.

Background concentrations are difficult to determine for NH_3 in an open-path configuration, in large part due to the need to enclose the sensor, leading to adsorption and desorption effects with typical laboratory concentrations greater than 10 ppbv NH_3 . Figure 7 shows an ambient pressure background 2f ammonia spectrum recorded when the calibration tube was flushed with ammonia-free air and the calibration tube surface

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was coated with a concentrated (~ 20 wt%) citric acid solution to minimize NH_3 desorption effects. However, due to residual NH_3 in the tubing and large volume calibration cell, we can only achieve a background concentration of 0.70 ppbv NH_3 after flushing of the calibration cell. Based on the height of the 2f NH_3 signal and 1σ of the residuals in Fig. 7, the SNR for this spectrum is ~ 3.3 , equivalent to a minimum detection limit of 0.2 ppbv NH_3 at 1 Hz. Based on a HITRAN simulation, the influence of interfering absorption lines of O_3 and CO_2 is found to be $< 10\%$ of the 2f NH_3 signal height, both of which are smaller than the baseline noise sources (optical interference fringes) at $\sim 30\%$ of the signal level. We note that this estimate is derived from only one spectrum and may not be representative of the temporal variability of the background noise, which is expected to be dominated by optical interference fringing and electronic noise.

To achieve a zero NH_3 background signal and examine the time series characteristics of the noise and spectral fitting, we conducted additional experiments inside a pressure-regulated chamber. The calibration tube and the entire sensor head were placed inside a larger chamber with its inside walls coated with the citric acid solution. The larger chamber was pumped to a reduced pressure of 100 hPa. Even though the sensor was at 100 hPa, we maintained the same modulation amplitude as at ambient pressures. The absorption features of NH_3 and other relevant species are therefore over-modulated (effective modulation index > 5 for NH_3 at 100 hPa), effectively broadening and decreasing the 2f signal height by 67% compared to ambient pressures. Figure 8 shows the 2f spectrum recorded at 100 hPa under these conditions. The over-modulated 2f NH_3 signal magnitude is effectively at or near the noise floor. Thus, the resulting spectrum under these conditions is effectively representative of etalon and electrical noise. It is assumed here that etalons, determined by the free spectral range of various transmissive optics, are not affected by pressure changes since the whole sensing system is enclosed inside the chamber. We fit the residual signals to the ambient pressure lineshape function to examine how the spectral fit to the background (which should nominally be zero) changes over time. The minimum detection limit, defined as 1σ of the background signal time series, is 0.15 ppbv NH_3 at 10 Hz. This

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detection limit is also consistent with the measurement precision shown in Sect. 3.2. We also verified that there was negligible residual NH_3 concentration in the chamber by switching to lower modulation amplitude appropriate for 100 hPa.

3.4 Open-path time response

We demonstrate the dynamic response of the open-path configuration. Figure 9 shows the time series of NH_3 concentration measured in the field on a mobile vehicular platform at a dairy farm over the course of ~ 3 min at 5 Hz time resolution. During this time series, an order of magnitude decrease in concentration from ~ 2.0 ppmv NH_3 to 200 ppbv NH_3 is observed within 1 s. The inset plot of Fig. 9 shows a 5 s portion of this time series on a logarithmic y-scale to emphasize the two order of magnitude changes in concentration. During this time period, the sensor records an increase from ~ 200 to ~ 900 ppbv NH_3 in 1 s followed by a decrease in concentration (~ 900 to ~ 200 ppbv NH_3) in 0.8 s. The concentration decreases by two orders of magnitude to background concentrations (~ 10 ppbv NH_3) within 2 s following the ppmv maximum as the sensor left the farm and was no longer sampling the emission plume. This demonstrates the fast response time of the open-path sensor for two orders of magnitude change in concentration in a very short (2 s) timeframe.

We also demonstrate the time response for lower concentration levels. Figure 10 shows a time series of mobile measurements on the highway recorded at 2 Hz time resolution. There are two enhancements observed due to vehicle traffic emissions on the highway. For the first spike at 15:45:40 LT, the sensor recorded an increase of 10 ppbv NH_3 (13.0 to 23.0 ppbv) in 1 s. For the second maximum at 15:49:30 LT, the decrease in concentration from 16.0 to 10.0 ppbv following the transient spike is also recorded in 1 s. These measurements demonstrate similar fast response, but in a lower concentration range.

Ammonia surface adsorption and desorption effects in closed-path sensors typically limit the response time (for several hundred ppbv NH_3 changes) to a few seconds, resulting in attenuation of high frequency concentration fluctuations (Yokelson et al.,

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2003; Nowak et al., 2007; McManus et al., 2008; Whitehead et al., 2008; Ellis et al., 2010; Gong et al., 2011). The time response of closed-path sensors is often defined by the initial time constant for gas exchange and the slower surface adsorption time constant (e.g. ~ 0.4 s and ~ 15 s respectively for a QC-TDLAS instrument) (Ellis et al., 5 2010). For long-term stationary monitoring applications, this time response is sufficient since data is averaged to minutes or longer time scales. However, for mobile platform measurements of transient emissions with order of magnitude concentration changes, as well as eddy covariance flux measurements, a time response of at least 1 Hz, as demonstrated for this open-path sensor, is critical.

10 4 Field measurements

The open-path NH_3 sensor has been field deployed in a wide range of environments. These include hot, dusty, and dry conditions in the San Joaquin Valley, California; $> 40^\circ\text{C}$ ambient temperatures and high humidity (mid- 20°C dew-points) in Princeton, New Jersey; and cold, rain and dew conditions in Baltimore and Beltsville, Maryland. 15 The sensor has also operated on a mobile, battery-powered vehicular platform. These field deployments led to improvements in the opto-mechanical design to address temperature cycling effects on the alignment, laser thermal stability and detector temperature control. The optical cell structure and mirror mounting were custom designed with carbon fiber rods to minimize temperature cycling effects.

20 We performed high time resolution (5 Hz), mobile, open-path NH_3 measurements on the road and at a local animal farm (pigs, turkeys) in central New Jersey to measure vehicular and agricultural emissions. Simultaneous measurements of a vehicle emission tracer carbon monoxide (CO) by a separate QC laser-based sensor (Tao et al., 2012b) were used to identify these emission sources. Figure 11a shows the time series of 25 NH_3 measurements at the animal farm. High concentrations above 1 ppmv NH_3 are observed and do not correlate with CO, which remained at near background concentration at the animal farm. Figure 11b illustrates on-road vehicle NH_3 emission measurements,

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with maximum concentrations of ~ 60 – 120 ppbv NH_3 , depending on vehicle type and driving conditions. The enhancements in NH_3 concentration (Fig. 12b) correlate with on-road CO concentration measurements. These time series demonstrate the open-path NH_3 sensor is capable of performing high time resolution field measurements to 5 capture various emission sources.

5 Discussion

There are multiple limitations to the sensor capabilities presented in Sect. 3. The NH_3 sensor precision and detection limit presented here is equivalent to $\sim 10^{-5}$ fractional absorption, comparable to typical, field-deployable laser-based systems (Tittel et al., 10 2003). The detection limit and precision are limited by electrical noise and optical interference fringing, a dominant noise source in many laser absorption spectroscopy systems (Dharamsi et al., 1998; Werle, 2011). The dominant electrical noise sources are the power supplies used for the detector preamplifier and laser current driver. The dominant interference fringes in our system are due to the back reflections from trans- 15 missive optics (laser collimating lens and zinc selenide windows for laser, detector and reference cell packages) and QC laser beam quality for the multi-pass optical cell. Our current efforts focus on improving beam quality of QC laser high heat load packages and optimizing transmissive optics with custom anti-reflective coatings. We note that the ultimate detection sensitivity is also constrained by other uncertainties, including 20 the ability to isolate spectral interferences from CO_2 and O_3 absorption features near $9.06\ \mu\text{m}$ when approaching the detection limit.

The $2f$ signal baseline also affects concentration retrieval and calibration results. The background zero NH_3 signal is used for the zero calibration point and to assess the signal baselines shown in Figs. 7 and 8. This baseline is due to a combination of 25 detector non-linearity, intensity modulation, and optical fringing. Future investigations into the stability of this baseline under field conditions will be necessary to characterize the variability of the $2f$ signal baseline and decouple the baseline drift from the $2f$

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NH₃ signal for background subtraction. Signal baseline variability due to temperature changes is of particular concern for open-path systems, where the temperature cannot be controlled due to direct exposure of optical components and power limitations on field platforms.

5 Finally, the laser tuning capabilities also limit the desired sensitivity for open-path detection of the broad NH₃ absorption feature. The optimal modulation index cannot be reached with the current QC laser used in our system (Tao et al., 2012a). To address this issue, the integration of new QC lasers with twice the current tuning rate is an ongoing effort. Despite these limits, we demonstrate a sensor platform capable of high
10 sensitivity, high time resolution atmospheric NH₃ field measurements.

6 Summary

We present the instrument performance of a compact, low-power, field-deployable, open-path NH₃ sensor. The system uses a QC laser at 9.06 μm, Herriott multi-pass optical cell, multi-harmonic wavelength modulation spectroscopy and an in-line ethylene
15 reference cell. No cryogenics are required due to the capabilities of TE-cooled, continuous wave, distributed feedback QC lasers and HgCdTe photo-detectors. Our open-path NH₃ sensor has the requisite capabilities for ground-based atmospheric measurements, with a precision and minimum detection limit of 0.15 ppbv NH₃ at 10 Hz and calibration accuracy of ±10%. The sensor is capable of measuring a large dynamic
20 range of NH₃ concentrations due to in-situ emission sources. The fast (10 Hz) time resolution of the open-path system can be used to capture transient NH₃ sources with no surface adsorption time constant.

It is important to note that surface sampling artifacts in closed-path sensors are typically reduced by minimizing inlet length, optimizing inlet coatings, inlet heating and
25 maintaining high flow rates through small sampling volumes or other special sampling systems (Whitehead et al., 2008; Bianchi et al., 2012). Some of these measures increase power demands and limit portability for a variety of field platforms. In contrast,

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our open-path approach is advantageous in that it has negligible sampling artifacts and does not require pumps or heaters, allowing for a low power, portable design.

The compact, low-power design provides unique capabilities for stationary sensing and mobile platform spatial mapping of NH₃ concentrations. In addition, the open-path
5 sensor precision, stability and time resolution (10 Hz) makes it suitable for eddy covariance NH₃ flux measurements. Future investigations will focus on long-term inter-comparisons with existing commercial, atmospheric NH₃ sensors and demonstration of open-path eddy covariance NH₃ flux measurements. Future measurement applications for this open-path sensor include NH₃ emission measurements in agricultural and
10 urban regions to validate emission inventories.

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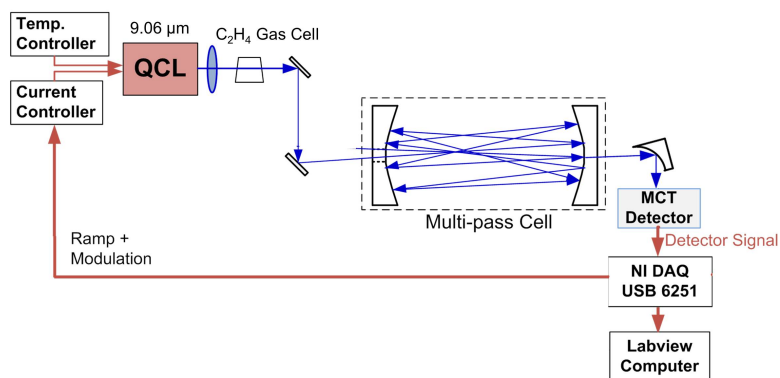
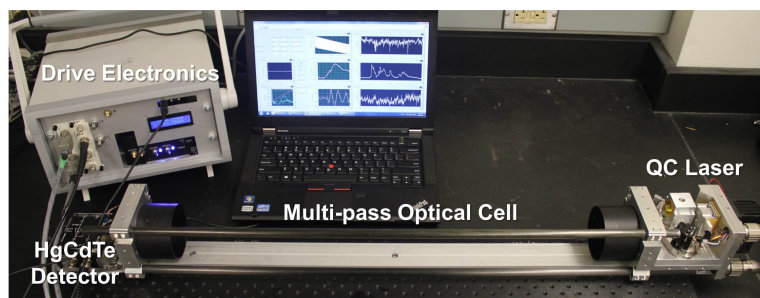


Fig. 1. Open-path atmospheric NH_3 sensor with drive electronics (top) and sensor schematic (bottom).

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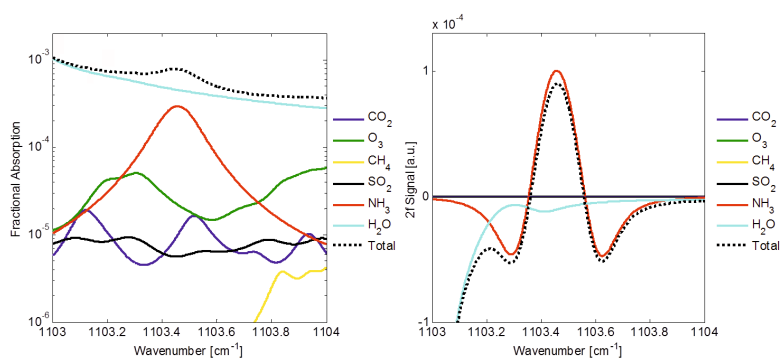


Fig. 2. (a) Direct absorption HITRAN simulation (Rothman et al., 2009) calculated based on 60 m path length, 296 K, 1013.25 hPa and the following atmospheric mixing ratios: 400 ppmv CO_2 , 80 ppbv O_3 , 1800 ppbv CH_4 , 5 ppbv SO_2 , 1 ppbv NH_3 and 2% H_2O ; **(b)** second harmonic spectrum calculated with same species showing elimination of water vapor baseline. Ozone and CH_4 do not appear in the second harmonic spectrum as they are flat baselines. The black dotted lines in **(a)** and **(b)** denote the total absorption of all species simulated.

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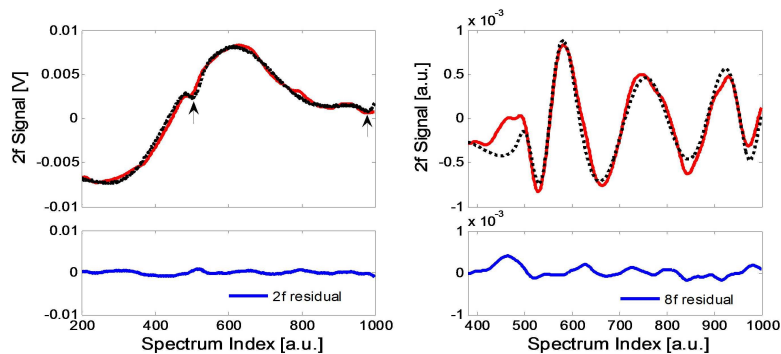


Fig. 3. Ammonia 2f (left) and ethylene 8f (right) spectra recorded at 10 Hz with real-time fitting results (dotted lines) and residuals. The 2f NH_3 signal was recorded for ambient laboratory conditions of 8.0 ppbv NH_3 . The two arrows in the 2f plot denote the locations of the two extra troughs due to the ethylene reference signal.

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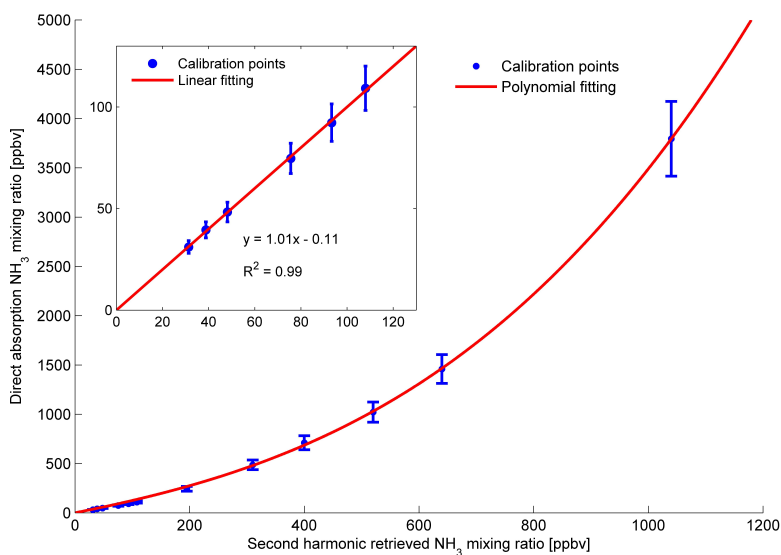


Fig. 4. Calibration curve derived from direct absorption measurements for various NH_3 gas standard concentrations at atmospheric pressure. Inset: linear fitting of calibration curve for concentrations < 120 ppbv NH_3 . Error bars for each calibration point are $\pm 10\%$ for each measurement method (direct absorption and 2f retrieval).

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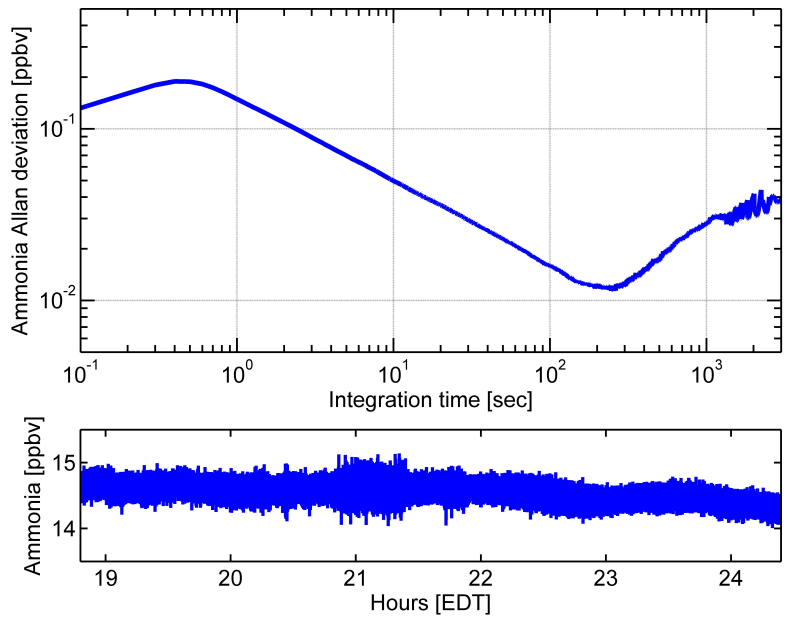


Fig. 5. Allan deviation plot of 14.6 ppbv NH_3 and the associated time series data recorded at 10 Hz over the course of 5.5 h.

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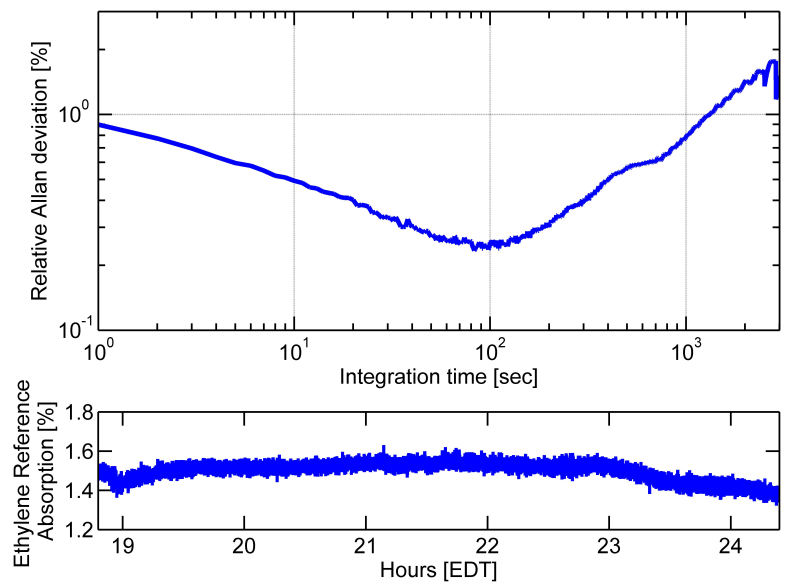


Fig. 6. Allan deviation plot of in-line ethylene reference cell signal and associated 5.5 h time series. The Allan deviation is expressed as a percent of the mean value of the reference signal time series (relative Allan deviation). Ethylene is recorded at 1 s time resolution.

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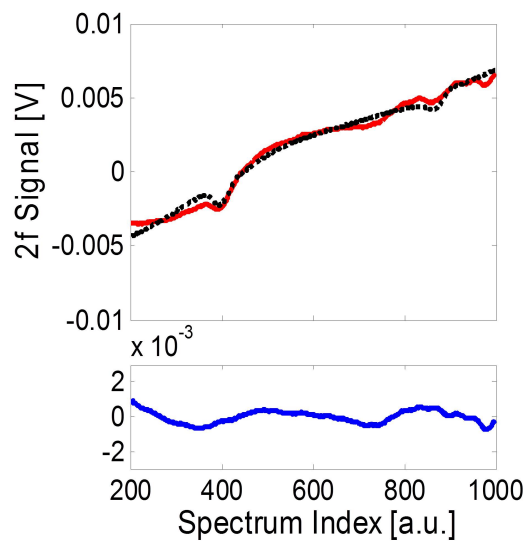


Fig. 7. Second harmonic spectrum of NH_3 background signal at ambient pressure with ammonia-free air and citric acid (0.7 ppbv NH_3) recorded at 1 Hz along with spectral fitting results and residuals.

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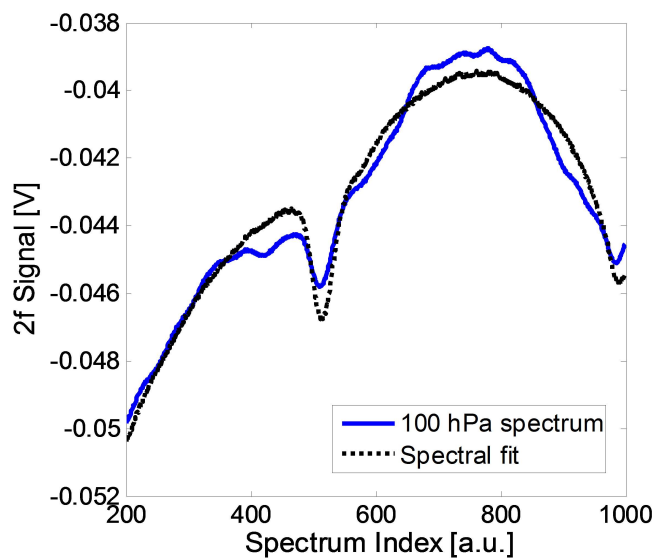


Fig. 8. Second harmonic spectrum at reduced pressure (100 hPa) with “zero” NH_3 signal recorded at 10 Hz time resolution.

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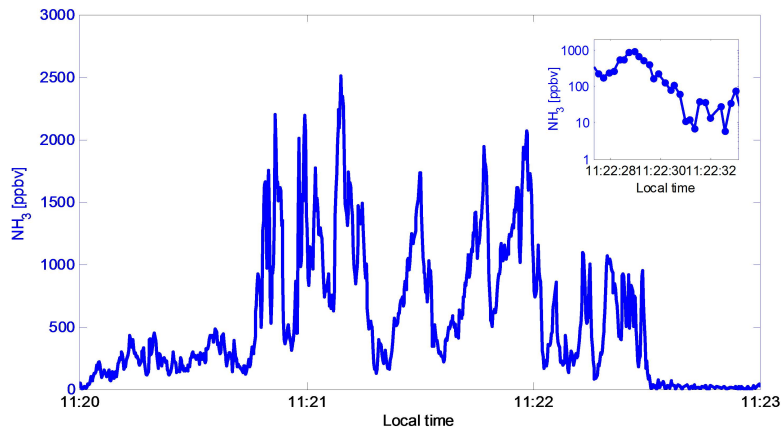


Fig. 9. Mobile, open-path NH_3 measurements of in-situ dairy farm sources recorded at 5 Hz. The inset plot shows a 5 s portion of this 5 Hz time series on a logarithmic y scale to emphasize the two order of magnitude change in NH_3 concentrations.

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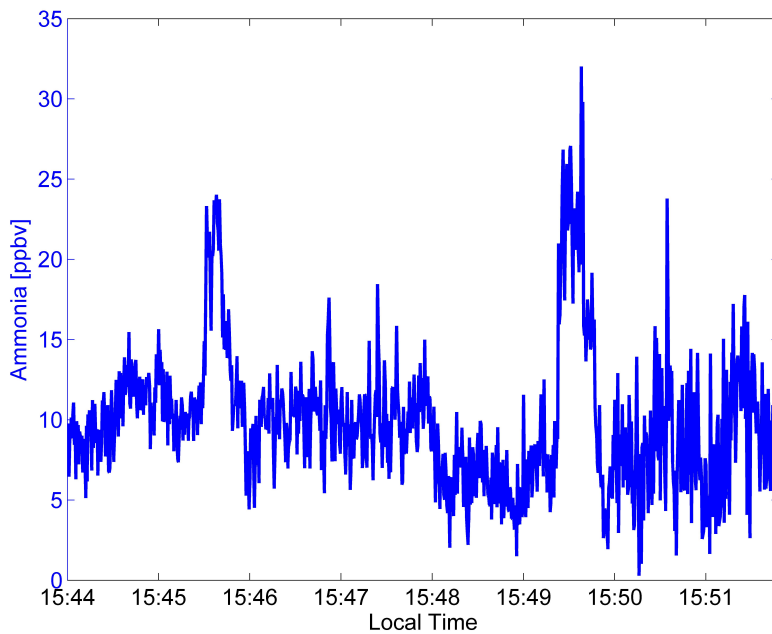


Fig. 10. On-road, mobile, open-path NH_3 measurements of highway vehicle emissions recorded at 2 Hz. The response time at ppbv NH_3 concentrations is demonstrated for the emission spikes at 15:45:40 and 15:49:30 LT.

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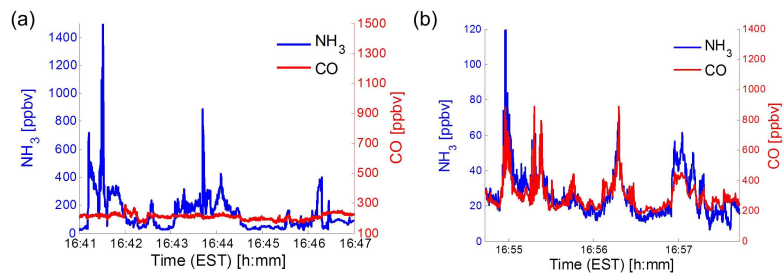


Fig. 11. (a) Time series of NH_3 measurements at an animal farm in central New Jersey; **(b)** on-road measurements in the Princeton, New Jersey area, with transient spikes correlated with CO emissions from vehicles.