**Atmospheric
Measurement
Techniques**

Characterizing a Quantum Cascade Tunable Infrared Laser Differential Absorption Spectrometer (QC-TILDAS) for measurements of atmospheric ammonia

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Abstract. A compact, fast-response Quantum Cascade Tunable Infrared Laser Differential Absorption Spectrometer (QC-TILDAS) for measurements of ammonia (NH_3) has been evaluated under both laboratory and field conditions. Absorption of radiation from a pulsed, thermoelectrically cooled QC laser occurs at reduced pressure in a 0.5 L multiple pass absorption cell with an effective path length of 76 m. Detection is achieved using a thermoelectrically-cooled Mercury Cadmium Telluride (HgCdTe) infrared detector. A novel sampling inlet was used, consisting of a short, heated, quartz tube with a hydrophobic coating to minimize the adsorption of NH_3 to surfaces. The inlet contains a critical orifice that reduces the pressure, a virtual impactor for separation of particles, and additional ports for delivering NH_3-free background air and calibration gas standards. The level of noise in this instrument has been found to be 0.23 ppb at 1 Hz. The sampling technique has been compared to the results of a conventional lead salt Tunable Diode Laser Absorption Spectrometer (TDLAS) during a laboratory intercomparison. The effect of humidity and heat on the surface interaction of NH_3 with sample tubing was investigated at mixing ratios ranging from 30–1000 ppb. Humidity was seen to worsen the NH_3 time response and considerable improvement was observed when using a heated sampling line. A field intercomparison of the QC-TILDAS with a modified Thermo 42CTL chemiluminescence-based analyzer was also performed at Environment Canada's Centre for Atmospheric Research Experiments (CARE) in the rural town of Egbert, ON between May–July 2008. Background tests and calibrations using two different permeation tube sources and an NH_3 gas cylinder were regularly carried out throughout the study. Results indicate a very good correlation at 1 min time resolution ($R^2 = 0.93$) between the two instruments at the beginning of the study, when regular background subtraction was applied to the QC-TILDAS. An overall good correlation of $R^2 = 0.85$ was obtained over the entire two month data set, where the majority of the spread can be attributed to differences in inlet design and background subtraction methods.

1 Introduction

Ammonia (NH_3) is the most abundant alkaline gas in the atmosphere and plays an important role in many atmospheric processes. The majority of NH_3 emissions to the atmosphere arise from agricultural activities, such as application of fertilizer and volatilization from animal wastes (Pinder et al., 2006; Erisman et al., 2008). Other sources include light duty gasoline vehicles equipped with three-way catalytic converters, water and sewage treatment plants, and chemical production plants (Zhang et al., 2008; Livingston et al., 2009). Once in the atmosphere, NH_3 can either be deposited to land, vegetation or water bodies adjacent to the emission source areas or undergo atmospheric reactions with acids formed from the oxidation of sulfur dioxide (SO_2) and nitrogen oxides (NO_x). In the presence of these acids, NH_3 can contribute to the formation of fine particulate matter ($PM_{2.5}$) with strong implications for human health (Pope et al., 2002)

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and radiative forcing (IPCC, 2007). Particulate ammonium (NH_4) has a longer atmospheric lifetime than NH_3 and can therefore be transported over relatively long distances. Deposition of particulate phase NH_4 (and gas phase NH_3) can fertilize nitrogen-limited ecosystems or cause eutrophication in nitrogen-saturated ecosystems, as well as cause acidification of soils (Asman et al., 1998; Krupa, 2003; Galloway et al., 2003). North American regulatory policies put in place to control $PM_{2.5}$ levels have largely focused on reductions in emissions of SO_2 and NO_x. Recent modeling studies have explored the effectiveness of NH_3 emission reductions on the $PM_{2.5}$ mass loadings in North America. Pinder et al. (2007) found that a 10% reduction in NH_3 emissions decreased $PM_{2.5}$ by 1.4% in the summer and 5.7% in the winter in the Eastern US, and that NH_3 emission reductions are often more cost-effective than SO_2 and NO_x controls. North America wide reductions of agricultural NH_3 emissions by 30% were found to decrease average $PM_{2.5}$ by 0–7% but decreases in the 95th percentile could be up to a factor of six larger (Makar et al., 2009). Due to its environmental impacts, it is important to be able to predict the emissions and chemical transformations of NH_3 in the environment, but a lack of accurate in-situ measurements of NH_3 makes it difficult to constrain models and produce more precise emission factors for inventories.

One reason for the paucity of measurements in the past has been the absence of sampling and analytical techniques which are accurate, robust, and inexpensive. Traditional methods of measuring NH_3 involve the use of passive filters and denuders with long integration time and offline analysis, which often suffer from chemical interferences and are usually labour-intensive (Wiebe et al., 1990; Fehsenfeld et al., 2002). Chemiluminescence-based instruments offer higher time resolution, but this indirect method is prone to interferences and false positives (Winer et al., 1974; Dunlea et al., 2007; Steinbacher et al., 2007). More recent techniques involve the use of spectroscopic instruments and chemical ionization mass spectrometry (CIMS), which provide high time resolution and are both specific and sensitive to NH_3, but are often expensive and challenging to deploy in field conditions (Li et al., 2006; Nowak et al., 2007; Whitehead et al., 2007). A summary of instrument figures of merit for different NH_3 measurement techniques can be found in von Bobrutzki et al. (2010). Recent field intercomparisons involving NH_3 analyzers based on more traditional methods and newer analytical techniques indicate that many challenges remain in obtaining accurate NH_3 measurements (Norman et al., 2009; von Bobrutzki et al., 2010). The performance of any state of the art instrument is limited by the sampling efficiency. NH_3 is highly water soluble and can readily be adsorbed on any surface in contact with the sample air flow, such as filters, inner walls of inlet tubing, and analyzer parts. Thus, designing a sampling inlet that minimizes interactions of NH_3 with surfaces is essential in making accurate measurements. The sampling method should also be selective

against particles, especially for volatile salts such as ammonium nitrate (NH_4NO_3) and ammonium chloride (NH_4Cl) which may volatilize prior to detection and produce a positive bias for ambient NH_3 (Gras, 1984; Cheng and Tsai, 1997; Chow et al., 1998).

We present the results from two intercomparisons between a Quantum Cascade Tunable Infrared Laser Differential Absorption Spectrometer (QC-TILDAS, Aerodyne Research, Inc., Billerica, Massachusetts) and a Tunable Diode Laser Absorption Spectrometer (TDLAS, model TGA-100, Campbell Scientific, Logan, Utah) and between the QC-TILDAS and a chemiluminescence-based instrument (modified Thermo 42CTL, Thermo Scientific, Franklin, Massachusetts). The first analyzer intercomparison examines the impact of heating the sampling line and of changing ambient humidity on NH_3 adsorption. The second analyzer intercomparison examines environmental effects (ambient relative humidity and temperature) on the measurement of ambient NH_3.

2 Experimental methods

2.1 Quantum cascade laser absorption spectroscopy

Laser absorption spectroscopy is a powerful method of analysis for atmospheric trace gases with resolvable rotational-vibrational absorption features, especially in the mid-infrared region containing the stronger fundamental vibrational bands. The QC-TILDAS determines the mixing ratio of NH_3 by monitoring the molecule's absorption of radiation at $967\,cm^{-1}$. The system uses a thermoelectrically cooled quantum cascade (QC) laser (Alpes Lasers, Neuchatel, Switzerland) operating in the pulsed mode to provide high stability and increased power output over traditional lead-salt diode lasers (McManus et al., 2002). A layout of the optical table can be found in McManus et al. (2007). The laser output is directed into an astigmatic Herriott type multiple pass absorption cell (0.5 L, 76 m effective path length), the inside of which is coated with a hydrophobic fluorinated silane coating in order to limit the interactions of NH_3 with cell walls. The optical system also includes a reference path whose primary function is to serve as a pulse normalization leg in order to reduce the spectral noise from pulse-to-pulse amplitude variation. This is achieved by dividing the absorption spectrum (obtained from ∼150 individual laser pulses) by the pulse normalization reference spectrum. Periodically, the reference path is directed through a 5 cm cell containing ethylene (C_2H_4), a less surface reactive gas with a molecular line in the same region as NH_3, which can be used for absorption-line lock. If the laser line position drifts between reference locks, a small correction is applied to the laser temperature to bring the laser line back into position. Another role for the reference path is to measure the laser tuning rate by inserting a germanium etalon in the laser path.

Both the signal and reference paths are focused onto a thermoelectrically cooled HgCdTe infrared detector (Vigo Systems, Poland) and temporally separated by 250 ns, the time required to traverse the multiple pass absorption cell.

The software package TDLWintel, developed by Aerodyne Research Inc, drives the QC laser, retrieves, analyzes and stores spectra, and calculates and stores mixing ratios. The laser frequency is swept across the full molecular transition at 967.34 cm^{-1} and the resulting spectrum is fit by convolving the laser line shape with an absorption line shape calculated from the HITRAN (high-resolution transmission) molecular absorption database and the measured pressure, temperature and path length of the absorption cell (Herndon et al., 2007). Other trace gases that absorb in the same region as NH$_3$ are ethylene (at 967.33 cm^{-1}) and methanol (CH$_3$OH, at 967.36 cm^{-1}), which both have weak absorption lines and are not expected to be present in high quantities in the atmosphere. However, if these species were to cause interference with the NH$_3$ absorption spectrum, the TDLWintel software allows the operator to refit saved spectra for several different species. The software also controls the additions of calibration gas and background gas at user-defined time intervals through the use of two solenoid valves. One of the benefits of software-controlled background addition is the ability to perform automatic background subtractions. TDLWintel sends a signal to automatically open a solenoid valve, allowing NH$_3$-free air to flush the inlet, and measures the resulting spectrum for a specified period of time. The flushing period ranges from 30 s to several minutes and can be adjusted depending on the environmental conditions (ambient NH$_3$ mixing ratio, humidity). Only the last 1/3 of the measurements made during the flushing period are used for the background. The software then subtracts this background spectrum from all subsequent spectra, providing a flatter baseline for the fit. Further description of the optical design and data acquisition system of the QC-TILDAS can be found in Nelson et al. (2004).

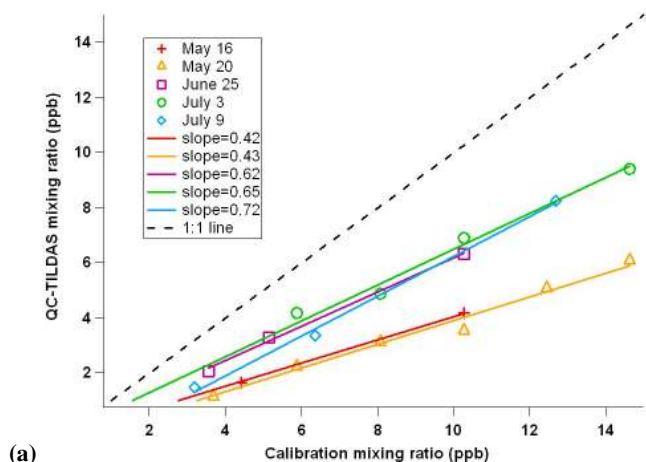## 2.2 Instrument figures of merit

2.2.1 Accuracy

While absorption spectroscopy is theoretically an absolute technique when the absorption cross section is known, external calibrations of the QC-TILDAS system indicated underestimation of the NH$_3$ mixing ratio that depended on the laser output voltage. When comparing to the TDLAS, the measurements obtained by the QC-TILDAS were approximately two times lower when the QC laser was being operated moderately high above threshold (by ~2 V). During the field intercomparison, we found about the same factor to hold true under similar laser parameters. It was also discovered that by tuning the laser output voltage down close to threshold, the QC-TILDAS would report mixing ratios closer to the calculated calibration values. Figure 1 shows
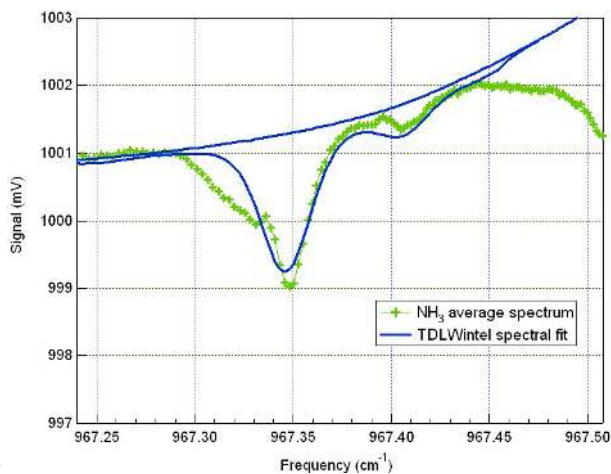
a series of multiple point calibrations performed throughout the two month field study at Egbert, ON. The calibrations can be separated into two groups, one with an average slope of 0.42 and one with an average slope of 0.66. The difference in slopes is due to changes in laser voltage, which in turn affects the retrieved NH$_3$ spectrum as shown in Fig. 1b and c. In these plots, the green spectrum is the average of 100 observed NH$_3$ spectra and the blue lines are the baseline and spectral fit calculated based on the HITRAN database and measured temperature, pressure and laser line width. In panel (b), a spectrum taken at high laser output voltage is shown to have considerable laser line shape distortion and increased laser line width, while the spectrum in panel (c), taken at low laser output voltage exhibits less distortion. The spectral fit shown in blue is based on a Voigt line shape which cannot duplicate the line shape distortion, thus resulting in an underestimation of the NH$_3$ calibration mixing ratio. It has been reported previously that laser line distortion occurs in QCLs that are operated high above threshold due to transient heating during the laser pulse (Nelson et al., 2002; Grouiez et al., 2009). The issue may be alleviated by keeping the laser near threshold, but it is done so at the expense of reduced signal to noise. However, since the distortion and underestimation is constant at any given laser output voltage, we can resolve the issue through frequent calibrations. Data from the two intercomparisons in the following sections has been corrected for line shape distortion in this manner.
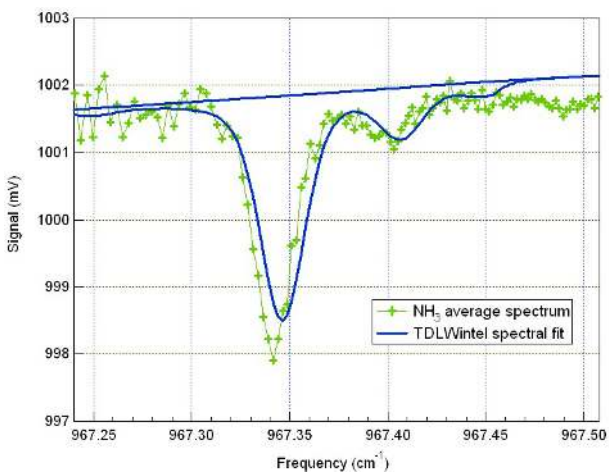
2.2.2 Precision

In systems that are mainly dominated by random instrument noise, the detection limit can be predicted by the Allan variance (Werle et al., 1993). Figure 2 displays 1 Hz measurements of 4.2 ppb NH$_3$ from a 1.9 ppm NH$_3$ gas cylinder diluted with zero air in the upper panel and the Allan variance plot for this data in the lower panel. This is a typical mixing ratio of NH$_3$ in ambient air away from major sources and was used to estimate the instrument detection limit at low mixing ratios. The amount of noise in a 1 Hz measurement is 230 ppt. Using the standard definition of detection limit (3σ of the signal) we estimate a detection limit of 690 ppt, where σ is the standard deviation retrieved from the Allan plot. The linearly decreasing part of the Allan plot is dominated by white noise, and further averaging of data in this region will result in a decrease in noise. With an averaging time of 60 s, the detection limit estimated from the Allan variance decreases to 100 ppt. The minimum point in the Allan plot is the optimum integration time (~300 s), which leads to a detection limit of 42 ppt. Instrumental drift begins to dominate beyond the optimum integration time, and further averaging of the data will not lead to a decrease in noise.
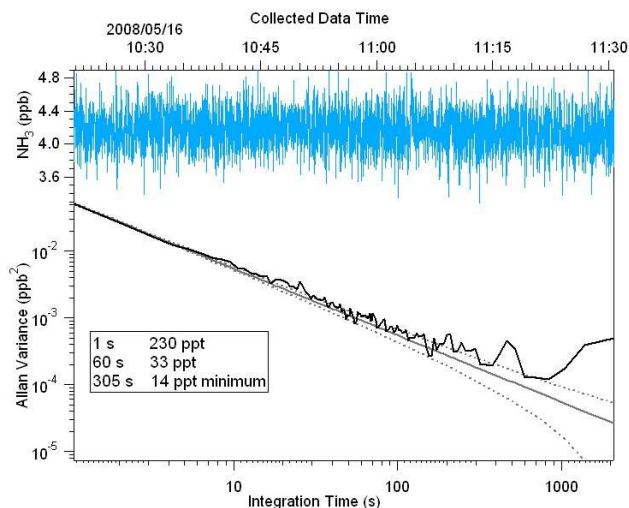
(a)

Fig. 2. Instrument noise and detection limit can be estimated using an Allan variance plot. Upper trace displays a one hour long measurement from an NH_3 gas cylinder at 1 Hz; lower trace shows the Allan variance for the data set with 230 ppt of noise in 1 s and a minimum of 14 ppt noise with approximately 5 min averaging. The detection limit can be defined as 3*noise and is equal to 690 ppt at 1 Hz.
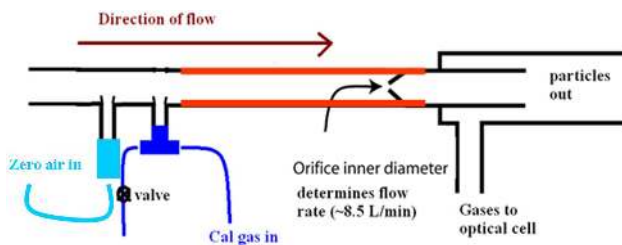

(b)

Fig. 3. Schematic of QC-TILDAS quartz inlet outlining the locations of background and calibration ports, critical orifice and virtual impactor. The red lines indicate heating of the inlet to 40 °C.

2.3 Inlet design

The first step in achieving accurate atmospheric measurements of NH_3 is using a sampling setup that reduces gas interactions with surfaces. Figure 3 illustrates the sample inlet used by the QC-TILDAS in this work. A short (10 cm), quartz inlet, originally designed by Aerodyne Research Inc., is internally coated with a fluorinated silane coating and heated to 40 ± 2 °C to limit condensation of water and the interaction of NH_3 with inlet surfaces. A critical orifice keeps a constant flow of ~ 9 L min^{-1} (measured upstream at 101.3 kPa and 298 K) and drops the pressure in the sampling line and optical cell to 5.3–8 kPa, which further minimizes NH_3 adsorption effects (Warland et al., 2001). Following the critical orifice, the flow is split into two branches with approximately 90% of the flow making a sharp turn and being pulled through the optical cell. The other 10% is pulled

(c)

Fig. 1. Multiple point calibrations **(a)** performed throughout the two month field study indicate QC-TILDAS is underestimating NH_3. Spectra retrieved at high laser output power **(b)** exhibit considerable laser line shape distortion resulting in calibration slope of ~ 0.42 and spectra exhibiting little distortion but increased noise **(c)** at low laser output power result in an average calibration slope of 0.66.

directly to the pump, relying on inertia to remove more than 50% of particles larger than 300 nm. Analytical techniques that do not separate the particulate and gas phase may suffer from a positive bias if ammonium produces an NH_3 signal (Gras, 1984; Cheng and Tsai, 1997; Chow et al., 1998). In the case of the QC-TILDAS, this could occur if NH_4NO_3 or NH_4Cl volatilized in the sampling line or optical cell prior to detection. However, the use of a filter to remove particles can also lead to volatilization of NH_4 particles from the filter surface along with loss of NH_3 to the filter surface, which can then be re-volatilized and lead to complicated results. The inlet design shown in Fig. 3 eliminates the use of filters and any interference they may cause while still protecting the optical cell mirrors. Two additional ports are used for the introduction of calibration gas and NH_3-free background gas, designed so that these flows encounter the inlet in the same way as ambient sampling. Background gas used for these experiments was either in the form of zero air or nitrogen from a cylinder. A solenoid valve in line between the background gas source and inlet is normally closed and opens automatically during the background cycle to slightly overflow the inlet with approximately $11 L min^{-1}$ of gas, ensuring that ambient air does not enter the inlet during that time. The QC-TILDAS calibration setup includes a NH_3 permeation tube source (KIN-TEK, La Marque, Texas) producing $\sim150 ng min^{-1}$ NH_3 that is kept continuously flowing at a low rate ($\sim0.5 L min^{-1}$) so that the surfaces on the inside of the calibration lines are sufficiently coated. A solenoid valve in line between the inlet and an external pump is kept normally open and will close automatically during the calibration cycle, causing the calibration gas to enter the inlet. This setup decreases the time required to reach stabilization during calibrations to 1 min or less. Calibration is usually performed every 2 h for 5 min, but is dependant on the stability of the system with regards to temperature and laser output voltage.

2.4 Inlet tests

In order to accurately measure NH_3 in the atmosphere, one needs to overcome the challenge of adsorption of this sticky gas to inlet walls and sampling lines. The sampling efficiency of the inlet described above was tested during an intercomparison between the QC-TILDAS and the TDLAS at the Ottawa Research Centre of Agriculture and Agri-Food Canada. Several experiments were carried out in a controlled laboratory environment in order to test the response of the instruments to a range of NH_3 mixing ratios using both humid ambient air and dry nitrogen and with the use of a heated sampling line. The TDLAS and QC-TILDAS have similar modes of operation, except that the TDLAS uses cryogenic cooling for both the laser and detector and a single-pass absorption cell. Both instruments were fitted with the quartz inlet described above and operated at a data acquisition rate of 10 Hz in order to capture fast time responses. Calibration

gas was produced using a 4 ppm NH_3 cylinder diluted with nitrogen resulting in a range of mixing ratios between 30 and 1000 ppb. Each mixing ratio was sampled for 15 minutes, followed by 15 min sampling of room air or nitrogen. Experiments were run using humid (RH $\sim$ 60–65%) and dry air with either a heated or unheated PFA-Teflon sampling line between the inlet and absorption cell.

The decrease in the mixing ratio of NH_3 was well-represented by a bi-exponential decay of the form:

$$y = y_0 + A_1 \exp\left(\frac{-(t-t_0)}{\tau_1}\right) + A_2 \exp\left(\frac{-(t-t_0)}{\tau_2}\right) \quad (1)$$

where A_1 and A_2 are constants and their sum is equal to the stable mixing ratio of NH_3 prior to the calibration flow being switched off; y_0 is equal to the NH_3 mixing ratio reached at the end of the decay; t is time and t_0 is the time at the start of the fit; τ_1 and τ_2 are time decay constants, the first of which is fast and corresponds to the gas exchange time of the system, and the second being much slower and corresponding to interactions of NH_3 with surfaces on the interior surfaces of the inlet, sampling lines and absorption cell.

2.5 Field intercomparison

Field measurements took place between May and July 2008 at Environment Canada's Centre for Atmospheric Research Experiments (CARE) in Egbert, Ontario ($44°13'57.00''$ N, $79°46'53.00''$ W, elevation 253 m). The facility is situated in a rural agricultural and forested region approximately 80 km northwest of Toronto, Ontario, Canada. The QC-TILDAS was operated alongside a modified Thermo 42CTL NO_y chemiluminescence-based analyzer for the duration of the study. The principle of operation of the Thermo 42CTL is based on the difference in the amount of reactive nitrogen species converted to nitrogen oxide (NO) over both a stainless steel converter at 750 °C and a molybdenum converter at 325 °C and the amount converted to NO 325 °C over just a molybdenum converter. This difference is attributed to the ambient NH_3 mixing ratio. The flow rate for the Thermo 42CTL was approximately $1 L min^{-1}$ through a short 15 cm inlet containing a filter to separate particles. In efforts to minimize any possible interference from NH_4NO_3 volatilization, the inlet filter for the Thermo 42CTL was changed daily. The QC-TILDAS sampled ambient air at $8.7 L min^{-1}$ through the quartz inlet described previously with a 3 m length of Teflon-PFA line between the inlet and the optical cell. The sampling frequencies were 1 s for the QC-TILDAS and a 1 min averaging time was reported for the Thermo 42CTL. Hourly averages of ambient temperature, relative humidity, wind direction, wind speed and precipitation data were also obtained at CARE.

Multiple point calibrations were carried out periodically using a 1.9 ppm NH_3 gas cylinder diluted with gas from a zero air generator to produce a range of mixing ratios between 1–15 ppb. One point calibrations were also performed

using two different permeation tube sources (KIN-TEK and VICI Metronics, Poulsbo, Washington). Backgrounds were measured by flushing the inlets with nitrogen gas or with air produced from a zero air generator (API, San Diego, California). The QC-TILDAS also performed periodic automatic backgrounds during the course of the study. The automatic background was set to flush the inlet with background gas for 1 min every 15 min. However, the cycle was changed to providing background gas to the inlet for 10 min every 2 h due to the suspicion that not all NH_3 was being flushed from the system using the shorter cycle duration. This was adopted as the best compromise between performing frequent backgrounds that capture changes in the spectral baseline and ensuring that air sampled during background checks is NH_3-free.

3   Results and discussion

3.1   Laboratory intercomparison of QC-TILDAS and TDLAS

The two laser absorption spectrometers were compared during a laboratory study at the Agriculture and Agri-Food Canada Ottawa Research Centre for one week in July 2008. Calibration of both instruments was performed simultaneously using a range of NH_3 mixing ratios from 30–1000 ppb. Very good correlation was obtained at 10 Hz between the QC-TILDAS and TDLAS with $R^2 = 0.91$ over the entire dataset from 0–1 ppm. Some of the spread can be explained by slight differences between the two instruments' computer clocks, making it difficult to exactly match the data at 10 Hz. In addition, optical fringing in the TDLAS caused a baseline interference of 50 ppb and fluctuations at mixing ratios lower than 100 ppb, which further contributed to the scatter. As TDLAS is mostly used to make NH_3 flux measurements in agricultural regions, where the NH_3 mixing ratios can reach ppm levels, we focused on the comparison of the two instruments at higher NH_3 levels. Figure 4a illustrates the response of both instruments to a step change from ambient to 350 ppb NH_3, a typical mixing ratio found close to sources such as recently fertilized fields and livestock farms. The majority ($>90\%$) of the increase occurs in a few seconds and both instruments reach a stable reading within the 15 min time period. A similar study by Schwab et al. (2007) that investigated the response to NH_3 step changes using mixing ratios between 5–40 ppb found that most instruments in the study required several hours to reach a stable reading. Allan variance analysis was performed on the time period indicated in red in Fig. 4a for both instruments and results are given in Fig. 4b. For a mixing ratio of 350 ppb, the amount of noise (1σ) in a 10 Hz measurement for the QC-TILDAS was 3.15 ppb and for the TDLAS was 7.30 ppb. For 1 s averaging of the 10 Hz data the QC-TILDAS standard deviation from the Allan variance analysis was 1.11 ppb and for the TDLAS 1.89 ppb. The optimum integration time for the QC-
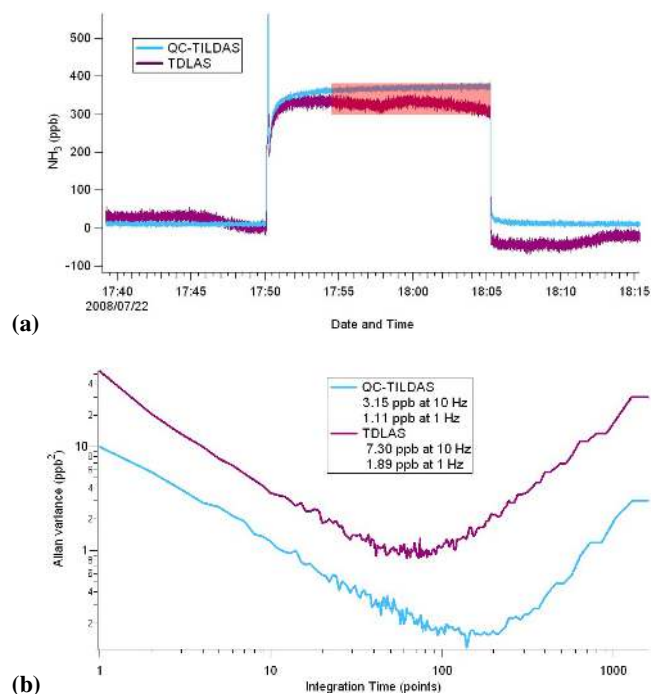

Fig. 4. (a) shows the time response at 10 Hz of the QC-TILDAS and TDLAS to a step change from ambient to 350 ppb NH_3. In **(b)**, the Allan variance for both instruments is displayed for the ten minute period highlighted in red in panel (a).

TILDAS ($\sim$130 s) yielded a minimum noise level of 0.34 ppb while the optimum integration time for the TDLAS ($\sim$60 s) resulted in a minimum of 0.92 ppb. Further averaging beyond the optimum integration time does not result in a decrease in noise due to the increase in instrumental drift. From the Allan variance plot, we observe that the QC-TILDAS achieves lower noise levels under these conditions and is less susceptible to instrument drifts.

3.2   Sampling line effects

Several studies have investigated the adsorption of NH_3 to different types of sample inlet materials at various temperatures (Yokelson et al., 2003; Shah et al., 2006; Whitehead et al., 2008). In our laboratory intercomparison between the QC-TILDAS and the TDLAS, we examined the effect of heat and humidity on NH_3 adsorption to sampling lines. The results from the bi-exponential decay analysis for the QC-TILDAS are presented in Fig. 5. Here we define a term D that refers to the fraction of the total loss of NH_3 that corresponds to the second (slow) exponential term in Eq. (1). It is described mathematically as:

$$D = \frac{A_2}{(A_1 + A_2)} \times 100 \qquad (2)$$

where A_1 and A_2 are the pre exponential constants described in Eq. (1). The relative contributions of surface interactions
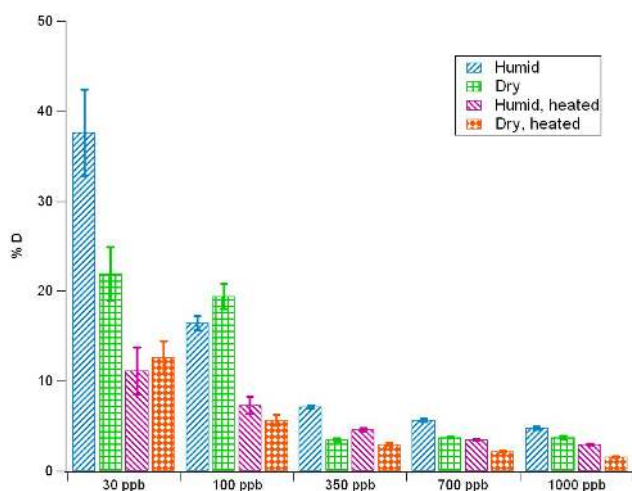
Fig. 5. D-factor illustrates the extent of NH_3 surface interaction at a range of NH_3 mixing ratios under conditions of dry and humidified air and using a heated line. The relative contribution of surface interactions is higher at lower mixing ratios, under humid conditions and without the use of a heated line. Error bars indicate one standard deviation.
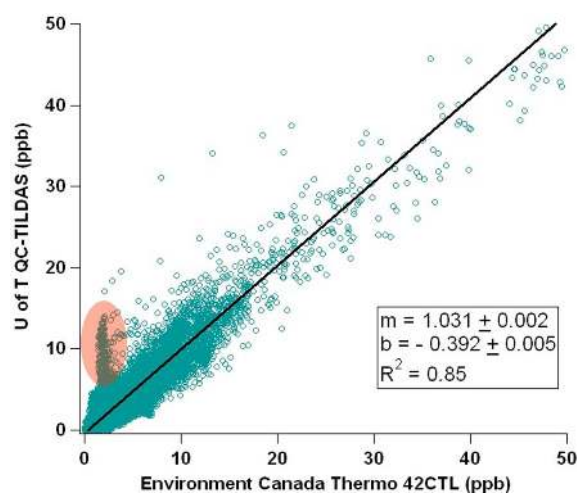

Fig. 6. Correlation plot of the QC-TILDAS and Thermo 42CTL. Most of the scatter can be explained by differences in inlet design and background subtraction methods. The time period outlined in red is shown in Fig. 7b.

are larger when the value of D is higher, since a higher D signifies that the second term in the bi-exponential decay given in Eq. (1), which is related to interaction of NH_3 with surfaces, is more prominent. For the QC-TILDAS, τ_1 was on the order of 0.4 s, and τ_2 was on the order of 15 s. In a similar study by Whitehead et al. (2008) where the time response of an older model quantum cascade laser absorption spectrometer was investigated, τ_1 was found to be on the order of 2 s.

Several deductions can be made from Fig. 5; first, there is a noticeable difference between the D factor at the lowest mixing ratio of 30 ppb to the highest (1000 ppb), indicating differences in the relative importance of NH_3 surface interactions at low and high mixing ratios. The PFA-Teflon polymer sampling line has a finite number of adsorption sites, which quickly fill up in the presence of high mixing ratios of NH_3, allowing subsequent molecules to pass freely with little to no surface interaction. At lower mixing ratios, with fewer molecules per any given surface area, a greater fraction of molecules will interact with the surface and undergo adsorption effects, increasing the D factor and thus the time required for all molecules to de-sorb from the polymer surface. Our observations are qualitatively consistent with Mukhtar et al. (2003), who examined NH_3 adsorption to PFA-Teflon and low density polyethylene (LDPE) at much higher mixing ratios. The second detail we observe from Fig. 5 is that the D factor is generally lower for experiments performed in dry nitrogen than in humid room air. This suggests that there is less interaction between NH_3 and inner tubing surfaces when those surfaces are dry. Since NH_3 is known to form strong hydrogen bonds with water, we expect increased adsorption

if a surface is coated with water, as observed. A significant improvement was observed when using a heated line held at a constant 40 °C between the inlet and the optical cell, reducing the relative contributions of surface interactions in the overall decay to ~10% at the lowest concentration of 30 ppb. Heating the line decreases the NH_3 adsorption to the surface, possibly by reducing the presence of condensed water inside the sampling line.

3.3 Field intercomparison

The QC-TILDAS was compared with a modified Thermo 42CTL chemiluminescence instrument at Environment Canada's Centre for Atmospheric Research Experiments (CARE) between 7 May and 18 July 2008. Ambient temperatures during this time were highly variable ranging from 0 °C to 32 °C. The relative humidity was approximately 40% during the day at the beginning of the study and close to 60% during the months of June and July. At night, the RH was very high, between 90–100%. Figure 6 displays a correlation plot between the QC-TILDAS and Thermo 42CTL. The correlation plot was obtained using an iterative bivariate least squares method that takes into account errors in both x and y, as described by Cantrell (2008). Overall good correlation was achieved for the study with a slope of 1.031 ± 0.002, R^2 of 0.85 and offset of -0.392 ± 0.005 using 1 min averaged data. Some of the scatter may be explained by differences in the NH_3 mixing ratio measured due the type of inlet used. Adsorption-desorption effects and differences in inlet time response can cause discrepancies between different NH_3 analyzers, especially at lower mixing ratios (von Bobrutzki et al., 2010). Figure 7a demonstrates one example of instrument time response to fast changes in
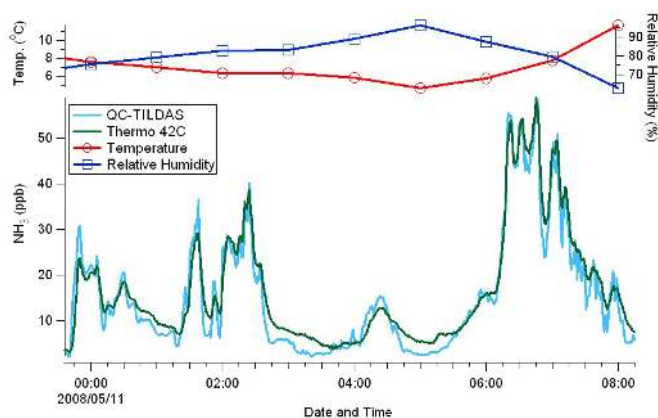
Fig. 7a. Time series of CARE observations of temperature and relative humidity and the response of the QC-TILDAS and Thermo 42CTL, both averaged to one minute. The inlet used for the QC-TILDAS results in a faster response to changes in ambient NH$_3$ mixing ratio.
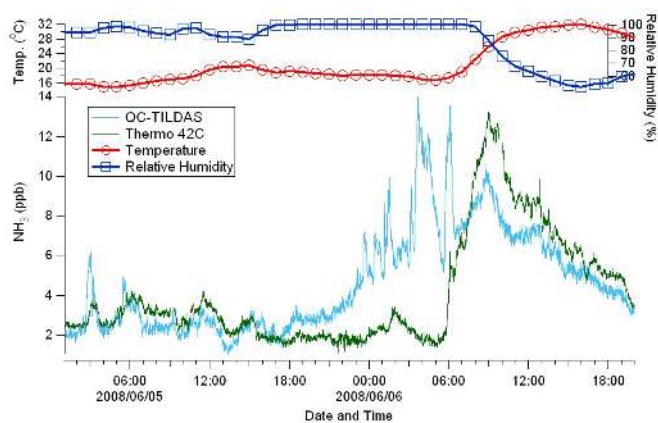

Fig. 7b. A period of rainfall and high relative humidity where the QC-TILDAS and Thermo 42CTL disagree for several hours may be due to condensation of water and uptake of NH$_3$ in the sampling lines of the Thermo 42CTL, followed by release of NH$_3$ the following morning when the temperature rose and the inlet dried.

NH$_3$ during a suspected fertilization event in the vicinity in the month of May, where the NH$_3$ mixing ratios were some of the highest seen during the study. Temperature and relative humidity during this time are also plotted in the upper trace. Although both instruments respond quickly to fluctuations at higher mixing ratios, the QC-TILDAS responds faster to changes at lower mixing ratios. The Thermo 42CTL seems to take longer to recover from higher inputs of NH$_3$, and we observe a time response lag where NH$_3$ is de-sorbing from the sampling lines. We have observed this effect in an intercomparison with several other instruments (von Bobrutzki et al., 2010), and believe that the faster time response of the QC-TILDAS can be attributed to the use of the quartz inlet and its ability to minimize gas-surface interactions. The differences in inlet design may also be the reason for the time
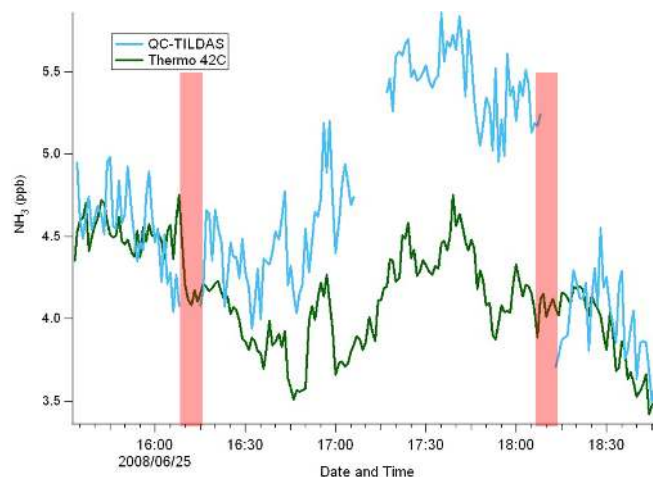

Fig. 7c. Time series of NH$_3$ from the QC-TILDAS and Thermo 42CTL indicate measurement drift for the QC-TILDAS due to changes in the background spectrum, which were not adequately captured with measurements of the background (indicated in red) every two hours.

period outlined in red in Fig. 6 and shown in Fig. 7b where the two instruments did not correlate very well. This period is marked by sporadic precipitation and very high relative humidity (RH>98%), which persisted for more than 24 h. The QC-TILDAS reports an increase in NH$_3$ on the evening of 5 June, but the Thermo 42CTL reports an increase in the mixing ratio the following morning when temperatures increase rapidly to 32 °C, the highest observed during the study. One of the reasons for this instrumental offset may be that the prolonged high humidity following rainfall on the previous day prevented evaporation of condensed water on the sampling intake of the Thermo 42CTL. However a visual inspection of the filter and sampling lines of the Thermo 42CTL for condensation was not performed. If condensation was present, when the temperature rose the following morning and the Thermo 42CTL inlet was dried, it may have released NH$_3$ trapped on the surface, leading to a delayed increase in mixing ratio. Norman et al. (2009) also observed losses due to condensation and uptake of NH$_3$ in the inlet during and after rainfall. The instruments' behaviour in Fig. 7b contrasts with that during drier conditions (RH = 70–85%) shown in Fig. 7a where both instruments respond to changes in NH$_3$ mixing ratios at approximately the same time. There may be other reasons for the apparent offset in Fig. 7b, since other shorter periods of rain during the study did not cause discrepancies in mixing ratios between the two instruments. Since this specific time period was the only time during the study when high relative humidity and rainfall persisted for more than several hours, we cannot conclude that every high relative humidity and rain event will lead to an offset.

Part of the scatter in the correlation plot may also be due to background effects in the QC-TILDAS. Figure 7c displays

a time period where both instruments are initially agreeing, but the QC-TILDAS measurement tends to drift upward over time. It is not until another background is performed, indicated in the plot by the red line, that the QC-TILDAS baseline is brought back down. This suggests that performing a background every 2 h is not sufficient to capture the changes in the background spectrum. Indeed, it is the case that when the QC-TILDAS was performing backgrounds every 15 min at the beginning of the study, the correlation was much higher ($R^2 = 0.93$). Longer, less frequent backgrounds were adopted to conserve zero air cylinder resources and maximize ambient data acquisition; however more frequent backgrounds appear to be necessary when the background spectrum is variable in time due to changing instrument conditions.

4   Conclusions

A Quantum Cascade Tunable Infrared Laser Differential Absorption Spectrometer (QC-TILDAS) was compared in a laboratory study with a Tunable Diode Laser Absorption Spectrometer (TDLAS) and during a two month field study with a Thermo 42CTL chemiluminescence based analyzer. The QC-TILDAS was found to underestimate the NH_3 mixing ratio when compared to both instruments due to significant laser line shape distortion when operating the QCL above threshold. As the distortion and underestimation is constant at a given laser output voltage, we can easily correct data using automatic in-field calibrations.

During the laboratory study, dry, humidified and heated lines were tested to determine what affects NH_3 adsorption to sample tubes. We observed an increase in the relative importance of NH_3 surface interactions at mixing ratios lower than 100 ppb, which further increased when sampling humid air as opposed to dry nitrogen. The NH_3 surface interactions were lessened by heating the line, where >95% of the NH_3 decay would occur during the time required for gas volume exchange in the system.

During the field intercomparison, inlet differences resulted in faster time response to changes in NH_3 mixing ratios for the QC-TILDAS when compared to the Thermo 42CTL. The Thermo 42CTL may be more susceptible to bias during rapid changes in relative humidity and temperature. The QC-TILDAS measurements were found to suffer from drift when less frequent backgrounds were applied. These differences contributed to the scatter observed in the correlation plot ($R^2 = 0.85$, slope $= 1.031 \pm 0.002$). Both studies indicate that backgrounds would be most optimally performed frequently, and by removing NH_3 from ambient air while keeping the humidity constant, rather than by overflowing the inlet with dry nitrogen or zero air.

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