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Fast in situ Airborne Measurement of Ammonia Using a Mid-Infrared Off-Axis ICOS Spectrometer

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Key words: ammonia; quantum cascade laser; ICOS; airborne; in situ measurement

ABSTRACT:
A new ammonia (NH$_3$) analyzer was developed based on off-axis integrated cavity output spectroscopy. Its feasibility was demonstrated by making tropospheric measurements in flights aboard the Department of Energy Gulfstream-1 aircraft. The ammonia analyzer consists of an optical cell, quantum-cascade laser, gas sampling system, control and data acquisition electronics, and analysis software. The NH$_3$ mixing ratio is determined from high-resolution absorption spectra obtained by tuning the laser wavelength over the NH$_3$ fundamental vibration band near 9.67 µm. Excellent linearity is obtained over a wide dynamic range (0 - 101 ppb$_v$) with a response rate (1/e) of 2 Hz and a precision of ±90 ppt$_v$ (1σ in 1 s). Two research flights were conducted over the Yakima Valley in Washington State. In the first flight, the ammonia analyzer was used to identify signatures of livestock from local dairy farms with high vertical and spatial resolution under low wind and calm atmospheric conditions. In the second flight, the analyzer captured livestock emission signals under windy conditions. Our results demonstrate that this new ammonia spectrometer is capable of providing fast, precise, and accurate in situ observations of ammonia aboard airborne platforms to advance our understanding of atmospheric compositions and aerosol formation.

1 INTRODUCTION

The accurate determination of trace gas species is critical in studying atmospheric composition and dynamics, as well as gauging their effect on global environmental change and air quality. Ammonia (NH$_3$), the most abundant gas-phase base in the Earth’s atmosphere, has natural, industrial, and agricultural sources. It plays an important role in atmospheric chemistry by coupling gaseous and particle interactions and aiding in aerosol production and cloud condensation.$^{1,2}$ Ammonia also plays a major role in the biogeochemical cycling of nitrogen.
Due to these critical atmospheric interactions, it is important to monitor ammonia concentrations accurately.

Ammonia emissions are known to have high spatial variability at a local scale.\textsuperscript{3–5} The ability to accurately quantify this spatial variability with rapid time resolution is important in improving and modeling the NH\textsubscript{3} emission inventory. The NH\textsubscript{3} spectrometer described in this article provides an excellent tool for airborne spatial characterization of NH\textsubscript{3} in the troposphere.

Conventional off-line methods for the detection of atmospheric ammonia include active and passive samplers,\textsuperscript{6,7} wet chemistry,\textsuperscript{8} and denuder-filter pack techniques.\textsuperscript{9–11} Additionally, a wide array of mobile techniques have also been used to measure ammonia fluxes emanating from dairy farms and other agriculture sources, including airborne Fourier transform infrared spectrometry (AFTIR),\textsuperscript{12,13} chemical ionization mass spectrometry (CIMS),\textsuperscript{14–17} and differential optical absorption spectroscopy (DOAS).\textsuperscript{18–20} Thorough discussion of ammonia measurement devices for different applications can be found in reviews elsewhere.\textsuperscript{21–23} Several recent studies also examine the differences among various ammonia measurement techniques.\textsuperscript{24–26}

Infrared (IR) spectroscopy is a powerful technique for trace gas detection that provides high sensitivity and selectivity.\textsuperscript{27–31} With the development of quantum cascade lasers (QCLs), IR spectroscopy has quickly met the demands of atmospheric trace gas monitoring for a broad range of species.\textsuperscript{32,33}

In this paper, we present a new NH\textsubscript{3} IR spectrometer that builds upon the earlier successful airborne deployments of off-axis integrated cavity output spectrometers (off-axis ICOS) measuring CO\textsuperscript{30} and H\textsubscript{2}O, CO\textsubscript{2} and CH\textsubscript{4},\textsuperscript{34}. We demonstrate the performance of the ammonia sensor during two test flights aboard the Department of Energy (DOE) Gulfstream-1 (G-1) research aircraft over the Yakima Valley, WA.
2 EXPERIMENTAL (MATERIALS AND METHODS)

2.1 Operation Principle, Calibration, and Data Analysis

A diagram of the NH$_3$ spectrometer is shown in Figure 1; it consists of a continuous-wave distributed feedback (DFB) QCL operating near 9.67 µm. The laser is mounted to a 2-stage thermoelectric cooler and actively held at 25 °C. The laser output beam is collimated and coupled into a high-finesse optical cavity. Light transmitted through the cavity is collected using a 2” diameter, ZnSe, f/0.85 meniscus lens and focused onto a liquid-nitrogen-cooled HgCdTe detector. The output of the detector is digitized, stored, and analyzed by an onboard computer. Gas temperature in the cell is monitored using a calibrated thermistor, and gas pressure is monitored using a strain gage bridge pressure transducer. The gas inlet is software switchable between external sample air and a reference gas cylinder using a Teflon solenoid valve. The sample inlet consists of a 120 cm long Teflon tube (½” OD, 3/8” ID). Gas is pulled through the analyzer using an external 4-head diaphragm pump, at a flow rate limited to 8.1 standard liters per minute (slpm) by a 900 µm critical orifice. The sample pressure in the cell is maintained at 135 Torr using a pressure control solenoid valve at the cell exhaust. Inlet air is filtered using a 47 mm diameter Teflon membrane filter with a mean pore size of 1.2 µm. Gas from a reference tank (1 L volume at 250 psi) is controlled using a miniature pressure regulator to produce a 230 standard cubic centimeters per minute (sccm) flow through a 150 µm critical orifice. To conserve reference gas during reference periods, the 4-head pump is deactivated and an internal, 2-head diaphragm pump is used to pull gas through the system. The entire instrument weighs 32 kg and consumes 170 W of electrical power, excluding the 4-head vacuum pump, which weighs 16 kg and consumes 115 W in steady state.
The NH$_3$ spectrometer utilizes off-axis ICOS, which has been described at length elsewhere.$^{35}$ Briefly, the QCL beam is injected into an optical cavity consisting of two spherical mirrors with a 1 m radius of curvature and very high reflectivity (total optical loss of 800 parts per million by volume (ppm$_v$)) (Figure 1). Light entering the cavity is reflected between the mirrors many times, thus increasing the effective absorption path length by a factor of:

$$G = \frac{R}{1 - R}$$

(1)

where $R$ is the cavity mirror reflectivity. The change in CW optical intensity transmitted through the cavity and incident on the detector due to absorbing species is described by:

$$\frac{\Delta I}{I} = \frac{GA}{1 + GA}$$

(2)

where $A$ is the single pass absorption according to Beer’s law ($A = 1 - e^{-\alpha(\nu)l}$, where $\alpha(\nu)$ is the gas absorption at wavelength $\nu$ and $l$ is the path length).

The laser is current tuned at a 1.2 kHz sweep rate over a frequency range of 14.5 GHz that includes the NH$_3$ absorption lines as well as areas that do not contain gas absorption. The areas without absorption are fit with a 2nd order polynomial to provide an estimate of the baseline laser intensity at each wavelength (i.e., $I$ in equation 2). $R$ of Eq. 1 can be determined by measuring the cavity ringdown time, $\tau = L/c(1 - R)$, where $L$ is the cavity length and $c$ is the speed of light, or by calibration with a gas sample of known concentration (thus determining $A$ of Eq. 2). By measuring $\Delta I$, $I$, and $G$ in Eq. 2, it is possible to calculate $A$ and thus the gas absorption at wavelength $\nu$. A sample, cavity-enhanced NH$_3$ spectrum measured during the test flight is shown in Figure 2. The area under the absorption features is obtained by fitting to Voigt line shapes with the Levenberg-Marquardt non-linear least-squares algorithm as shown in Figure 2. This
area, in conjunction with the measured gas temperature, gas pressure, and optical path length, provides a direct measure of the NH$_3$ mixing ratio.

Optical absorption from non-target trace gases can produce erroneous NH$_3$ readings if they are not properly included in the fit. Fortunately, because the shapes of NH$_3$ and O$_3$ absorption are heavily structured (e.g., they have a fixed separation and relative amplitude), any additional absorption peaks are poorly accounted for by the fit and are readily identifiable by examining the fit residual.\textsuperscript{36} During the deployment no interferences were found in flight, although during taxi engine exhaust was ingested resulting in significant interference from ethylene (corrupted data is not included in any of the results presented here).

## 2.2 Laboratory Performance

The instrument was calibrated using a permeation tube emitting 141.03±1.69 ng/min of NH$_3$ (VICI Metronics Dynacalibrator Model 150). Figure 3 depicts the calibrated instrument’s response to varying NH$_3$ concentrations obtained by diluting the permeation tube’s output with ultra-pure zero air and shows that the response is linear with a slope of 1.0079 and intercept of -0.0501 parts per billion by volume (ppb$_v$) and an R$^2$ of 0.99998. The instrument’s precision when measuring a constant NH$_3$ concentration was determined to be ±90 parts per trillion by volume (ppt$_v$), 1σ in 1 second (see Figure 4), indicating a 1-second detection limit of 270 ppt$_v$ at a 3σ signal-to-noise ratio.

NH$_3$ is notoriously “sticky”, typically having long equilibration times with instrument walls and adsorbed water. The walls constitute a reservoir from which NH$_3$ is exchanged at a rate dependent on temperature, humidity and partial pressure of the gas sample. Step changes in NH$_3$ concentration result in a response that is dual exponential where one time constant is determined by the bulk turnover of sample gas, and the other is determined by the exchange rate. Typically
the exchange time limits the instrument response rate and a common approach for improving performance is to increase the exchange rate by heating all of the wetted surfaces. Alternatively, it is possible to reduce the effect of wall exchange by flowing large quantities of sample gas through the system to continuously dilute the fixed flux of molecules emitted from the wall to a negligible level.

We have used the high flow approach, flowing 8.1 slpm of gas through the system. Figure 5 shows the instrument response to a step change in NH$_3$ under the high flow conditions. Sample gas is initially drawn from laboratory air with variable NH$_3$ added and having about 30% relative humidity at 23 °C. After the transition, gas is drawn from a tank containing 12 ppb, NH$_3$ in dry air. The response fits well to a single exponential decay, yielding a 1/e decay time of 0.492 seconds, corresponding to a response frequency of 2.03 Hz and has a flat response to within the instrument precision after the initial decay. The single exponential behavior is an indication that the contribution from wall flux is indeed negligible under the experimental flow conditions. Thus, NH$_3$ values were recorded at 2 Hz, which is suitable for *in situ* measurement on a fast-moving aircraft. With a larger, faster flow pump, response and sampling rates of up to 10 Hz are possible, albeit with an increased power requirement.

### 2.3 CO$_2$ Referencing

Because changes to optical alignment and mirror cleanliness can cause the instrument response to change, a reference gas was used to check instrument health before, during, and after the flights. Ideally, an NH$_3$ source of known concentration would be used as the reference. However, due to the difficulties involved in maintaining a stable NH$_3$ source in flight, weak CO$_2$ absorption lines that fall in the laser scan region were used to measure any changes in instrument response during the course of the deployment. Any changes to optical alignment or mirror cleanliness are
reflected in the measured CO₂ value allowing bounding or correction of the errors on the measured NH₃. During the flight deployment, the CO₂ reference (20.00 ± 0.02% CO₂ in synthetic air) was measured prior to takeoff, before and after the flight transects at each altitude (roughly every 30 minutes), and after landing. The CO₂ values measured in the laboratory before and after the flight were compared to the measured permeation tube NH₃ values to verify that CO₂ measurements track NH₃ response. The results depicted in Figure 6 show that variability in instrument response during flight is less than 5% of the expected value, providing an upper bound for variability on the NH₃ measurements during the deployment. The CO₂ measurements are expected to be significantly noisier than the NH₃ readings because the CO₂ absorption lines are highly temperature sensitive (E” >1,700 as derived from HITRAN[37]) and several of the lines appear at the edges of the laser scan range which can lead to errors in the baseline fit. The gas temperature ranged between 14 – 28 °C during the flights, likely leading to the larger than expected measured fluctuation of the CO₂ reference.

2.4 Instrument Configurations on G-1

The DOE G-1 research aircraft was used as the platform for the airborne worthiness study of the ammonia analyzer. The measurement capabilities of the G-1 are provided at the following on-line resource: [http://www.pnnl.gov/atmospheric/programs/raf.htm](http://www.pnnl.gov/atmospheric/programs/raf.htm). Specifically, for the two test flights, a series of aircraft state parameters was recorded with the SEA M300 data acquisition system. These parameters included measurements outside the aircraft (e.g., pressure, air temperature, air speed, relative humidity), measurements inside the aircraft (e.g., cabin pressure), aircraft attitude (e.g., roll, pitch, azimuth angles), and aircraft position (e.g., GPS coordinates, altitude above mean sea level). The coordinated universal time (UTC) time stamp was used
throughout the test flights, where Pacific daylight time (PDT) is seven hours behind UTC (\textit{i.e.}, PDT=UTC-7hr). During the test flights, the G-1 flew at a speed of 100 m/s.

To avoid potential contamination from the ingestion of large particles, a rear-facing inlet and outlet (separated from one another by approximately 30 cm; Figure 7) were integrated into the G-1 window panel. The ammonia sensor is installed immediately adjacent to the modified window panel to minimize the length of the Teflon sample tubing (1/2” OD, 3/8” ID, see Figure S1).

\section{2.5 Field Site Selection and Flight Plan}

Ammonia emissions from animal livestock sources including housing systems, manure storage, manure application, and outside grazing contribute significantly to environmental pollution\textsuperscript{21,38–40}. Earlier work conducted at Washington State University determined that sprinkler waste application emits 34 kg NH\textsubscript{3} cow\textsuperscript{-1} year\textsuperscript{-1} \textsuperscript{19} and that the total annual ammonia emission for a milking cow dairy is 40 kg NH\textsubscript{3} cow\textsuperscript{-1} year\textsuperscript{-1}.\textsuperscript{20} Emission inventories for dairy cows in the United States have also been studied.\textsuperscript{41} Due to these high emission rates, the ammonia sensor was flown near dairy cow housing facilities to quantify ammonia emitted from various point sources. The instrument was flown above the Yakima Valley, Washington (46°19’15”N, 120°0’44”W), an agricultural area with many local dairy farms. Transects over the study area were spaced approximately 2 km (1.2 mi) between legs and were flown at 2-3 different altitudes to demonstrate the instrument’s ability to spatially locate ammonia sources. Spirals were also flown to confirm that the instrument could operate under rapidly changing altitude and pressure conditions. The test flights were scheduled during late May because the temperature and relative humidity of the sampling environment affect the ammonia-ammonium
gas-particle phase transformation.\textsuperscript{42,43} Higher temperature promotes the dissociation of ammoniated salt particles to gas-phase ammonia.\textsuperscript{11}

Figure 10 and 11 show the flight paths executed on May 24, 2012 and May 25, 2012, respectively. The weather conditions were calm on May 24, 2012, with variable winds at an average speed of $3.8 \pm 1.5$ m/s. Conversely, on May 25, 2012, it was consistently windy from the NNE, with an average wind speed of $13.2 \pm 1.8$ m/s and a dominant wind direction of $25.1 \pm 7.6^\circ$. The first flight commenced from the Tri-Cities airport, then transited to Sunnyside in the afternoon on May 24, 2012. The survey flight pattern consisted of four parallel transects at each of the low (600 m), mid (1200 m) and high (1800) altitudes. After the high altitude mapping, the G-1 did a vertical spiral down and transited back to the Tri-Cities airport.

The weather conditions on May 25, 2012 were less favorable with high wind and turbulence. As a result, the flight plan was simplified to include transects at only two altitudes. Because the dominant wind direction was northeasterly, the flight transects were laid out perpendicular to the wind direction to resolve individual NH$_3$ plumes as they evolved downwind. The aircraft flew an initial spiral upon reaching the Yakima Valley and determined that the morning boundary layer height was approximately 2300 m. The G-1 then spiraled down to 670 m and followed four parallel transects to map out the ammonia emissions in the area. The aircraft then ascended to 1250 m and repeated the same flight pattern, after which the G-1 returned to the Tri-Cities airport.

3 RESULTS AND DISCUSSION

3.1 Temporal NH$_3$ Measurements

Temporal profiles of NH$_3$ mixing ratios acquired at 2 Hz on May 24, 2012 and May 25, 2012 are depicted in Figure 8. On May 24, 2012, the NH$_3$ plume was visible in the repeated flights
over the valley center with occasional spikes from direct flights over large dairies. The highest spike of 103 ppb\textsubscript{v} \(\text{NH}_3\) was observed during the low altitude transects while the lowest value of 1.6 ppb\textsubscript{v} was observed during the high altitude transects. On May 25, 2012, the baseline \(\text{NH}_3\) mixing ratio over the valley was much lower with narrow, individual spikes to 32 ppb\textsubscript{v} observed during flights over large dairies. Above the boundary layer, the average measured ammonia mixing ratio was 0.75 ppb\textsubscript{v}.

During both flights, the average measured mixing ratios decreased as the altitude increased; however, the \(\text{NH}_3\) mixing ratio and plume character differ. The May 24, 2012 afternoon flight occurred in a boundary layer with an estimated height of 1700 ± 200 m with little mixing. The boundary layer height was estimated based upon vertical profiles of virtual potential temperature and specific and relative humidity.\textsuperscript{44} In contrast, the boundary layer on May 25, 2012 was 2300 m as determined by the sounding spiral at the beginning of the flight. The boundary layer evolution over time has a known dilution effect on the mixing ratios reported in field observations.\textsuperscript{45} In addition, the wind was much stronger on May 25, 2012, making characteristic, narrow plume peaks corresponding to emissions from individual dairy farms readily discernible.

The observed airborne ammonia mixing ratios were within the expected range. Past research indicates that typical concentrations of ammonia in the boundary layer range from less than 1 ppb\textsubscript{v} in the free continental troposphere to ppm\textsubscript{v} levels over animal waste lagoons and near animal stalls.\textsuperscript{18}

### 3.2 Vertical NH\textsubscript{3} Distributions

Vertical distributions of ammonia vs. altitude during the two test flights are depicted in Figure 9. Specifically, the \(\text{NH}_3\) vertical distribution (excluding the large peaks from local emissions) ranged from 6.0 ppb\textsubscript{v} (4.2 \(\mu\text{g/m}^3\)) at 100 m to 2.3 ppb\textsubscript{v} (1.6 \(\mu\text{g/m}^3\)) at ~ 1750 m on May 24, 2012.
On May 25, 2012 the ammonia vertical distribution (excluding local emission peaks) ranged from 2.0 ppb, (1.4 µg/m$^3$) on the surface to 600 ppt, (0.4 µg/m$^3$) at ~ 2800 m. These values are in agreement with those observed in Bavaria,$^8$ in Germany,$^{17}$ at the NASA Langley Research Center in Hampton Virginia USA,$^9$ and over coastal Virginia and Maryland$^{10}$ using various aircraft and different detection techniques. These past observations reported the range of ammonia decreasing from several ppb, to tens of ppt, as the altitude increased to 2-3 kilometers.

3.3 Spatial NH$_3$ Distribution

Two-dimensional line plots of spatially resolved NH$_3$ measurements at different altitudes obtained on May 24, 2012 and May 25, 2012 are shown in Figure 10 and Figure 11, respectively. The data from May 24, 2012, when the winds were largely quiescent, show a relatively diffuse NH$_3$ plume over the feedlots (see also Figure S2). This observation is confined on both the east and west ends of the Yakima Valley by clear transitions in NH$_3$ mixing ratio to a baseline value of about 3 ppb. Although this plume of elevated NH$_3$ covers much of the area around Sunnyside, there are still localized peaks in the NH$_3$ concentration visible as the aircraft flew over large feedlots (see Figure 10(e)) demonstrating that the instrument is capable of locating individual sources in a highly variable background. In contrast, the data from May 25, 2012, when the winds were relatively strong and consistently from the NNE shows a much lower background value around Sunnyside. Consequently, large, but spatially narrow spikes in the NH$_3$ concentration were visible as the aircraft passed through plumes downwind of dairy feedlots and some plumes can be seen propagating downwind through several of the transects (see also Figure S3).

The differing wind conditions during the two flights provide an excellent demonstration of the instrument’s ability to quantify the complicated distribution of NH$_3$ in the troposphere. This data
may be combined with the work by Staebler et al.\textsuperscript{46} which illustrates that, with airborne NH\textsubscript{3} measurements, it is possible to reconstruct the ammonia plume in three-dimensions to advance our knowledge of ammonia’s role in the atmosphere.

4 ACKNOWLEDGMENTS

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5 Supporting Information Available

Additional figures as referred to in the text are located in the Supporting Information. This information is available free of charge via the Internet at http://pubs.acs.org/.

6 Notes

The authors declare no competing financial interest.

7 References


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8 Figures

**Figure 1.** The schematic of the ammonia gas analyzer. A thermo-electrically (TE) cooled QCL is collimated and injected off-axis into the ICOS cell. The transmitted signal is collected using a ZnSe lens and measured using a liquid nitrogen cooled, HgCdTe detector. Gas temperature is measured at the T port, and gas pressure is measured at the P port of the ICOS cell. The gas inlet configuration is shown at top and consists of a 3-way valve, switching between the sample branch and the reference gas branch. Depending on the state of the 3-way valve, gas is pulled through the cell using one of the two pumps: external (4-head diaphragm) and internal (2-head diaphragm). Pressure in the ICOS cell is maintained using a pressure controller at the cell exhaust to balance the inlet flow with the pump flow.
Figure 2. The measured cavity-enhanced absorption spectrum taken during the test-flight (see Eq. 2). The spectrum was fit to a multi-Voigt profile, yielding the residual shown atop the figure. The two large peaks are NH$_3$, while small peripheral peaks are O$_3$. The isolation of the NH$_3$ peak at -4.5 GHz allows the fit to easily differentiate between NH$_3$ and O$_3$. The NH$_3$ concentration for the displayed spectrum is about 100 ppb$_v$. 
**Figure 3.** Measured linearity curve. The instrument is highly linear ($R^2 = 0.99998$), having a slope differing from perfect agreement of only 0.79% and a zero offset of only 50 ppt$_v$. 

\[
y = -0.0501 + 1.0079x \\
R^2 = 0.99998
\]
Figure 4. The Allan deviation plot showing precision as a function of averaging time. The measured ammonia mixing ratio versus time is shown in the top panel. There is a slight upward drift with time associated with the stabilization of the NH$_3$ source. Also visible are oscillations due to air conditioning cycles caused by thermal shifting of etalons in the absorption spectrum and resulting in a peak in the Allan deviation at several hundred seconds. Precision remains better than 120 ppt, for all time scales.
Figure 5. A representative sample of the instrument response to a step change in NH$_3$ concentration. Initially sample gas is drawn from laboratory air with variable NH$_3$ added at about 30% relative humidity at 23 °C. After the transition, gas is drawn from a tank containing 12 ppb$_v$ NH$_3$ in dry air. The blue dashed line indicates the position of the step change. A single exponential fit to the data after the step yields a 1/e time constant of 0.492 seconds corresponding to a response frequency of 2.03 Hz. Data points are recorded at 10 Hz.
**Figure 6.** Measured NH$_3$ and CO$_2$ references before, during and after the flights. The CO$_2$ measurement varied by less than 5% during the flights and less than 7.5% after return shipment to the LGR laboratory.

**Figure 7.** A photo of the rear-facing inlet and outlet on the G-1 window panel outside the cabin. Flight direction is towards the left in the photo. The inlet is lined with $\frac{1}{2}$” OD Teflon tubing. The inlet and outlet are separated by approximately 30 cm.
Figure 8. Temporal profiles of the ammonia mixing ratios and altitude. (a) Data from the May 24, 2012 flight showing a diffuse NH$_3$ plume over the Yakima Valley. The inset shows a quiescent period with an average value of 3.31 ± 0.29 ppb$_v$ (at 2Hz). (b) Data from the May 25, 2012 flight showing highly localized NH$_3$ sources. The boundary layer sounding at the beginning of the flight shows the expected transition to very low NH$_3$ levels. The inset shows an isolated NH$_3$ spike demonstrating rapid response while airborne.

Figure 9. (a) Vertical profiles of NH$_3$ mixing ratios vs. altitude on May 24, 2012 and (b) May 25, 2012. The estimated boundary layer height is shown as a blue dashed line. Average NH$_3$ values at each transect altitude are shown as red dots and decrease with increasing altitude.
Figure 10. (a) A shaded relief map of the state of Washington highlighting the Yakima Valley
where flight measurements were taken. (b-d) Color coded flight paths showing the NH$_3$ mixing
ratio at three altitudes on May 24, 2012. The strong and isolated NH$_3$ plume is distributed
broadly over the feedlots because of the calm conditions in the shallow boundary layer. (e) A
satellite photo of an area with a high feedlot density. Feedlots are highlighted in blue and
correlate with high NH$_3$ concentrations along the flight path.
**Figure 11.** Color coded flight paths run perpendicular to the prevailing winds showing the NH$_3$ mixing ratio at two altitudes on May 25, 2012. (a) NH$_3$ Mixing ratios at 1270 m and (b) 670 m. Individual NH$_3$ plumes are visible across the flight paths because of the consistent NNE wind.
The schematic of the ammonia gas analyzer. A thermo-electrically (TE) cooled QCL is collimated and injected off-axis into the ICOS cell. The transmitted signal is collected using a ZnSe lens and measured using a liquid nitrogen cooled, HgCdTe detector. Gas temperature is measured at the T port, and gas pressure is measured at the P port of the ICOS cell. The gas inlet configuration is shown at top and consists of a 3-way valve, switching between the sample branch and the reference gas branch. Depending on the state of the 3-way valve, gas is pulled through the cell using one of the two pumps: external (4-head diaphragm) and internal (2-head diaphragm). Pressure in the ICOS cell is maintained using a pressure controller at the cell exhaust to balance the inlet flow with the pump flow.
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Measured linearity curve. The instrument is highly linear ($R^2 = 0.99998$), having a slope differing from perfect agreement of only 0.79% and a zero offset of only 50 ppt.
The Allan deviation plot showing precision as a function of averaging time. The measured ammonia mixing ratio versus time is shown in the top panel. There is a slight upward drift with time associated with the stabilization of the NH$_3$ source. Also visible are oscillations due to air conditioning cycles caused by thermal shifting of etalons in the absorption spectrum and resulting in a peak in the Allan deviation at several hundred seconds. Precision remains better than 120 ppt for all time scales.

234x204mm (300 x 300 DPI)
A representative sample of the instrument response to a step change in NH$_3$ concentration. Initially sample gas is drawn from laboratory air with variable NH$_3$ added (from the author’s hand) at about 30% relative humidity at 23 °C. After the transition, gas is drawn from a tank containing 12 ppb NH$_3$ in dry air. The blue dashed line indicates the position of the step change. A single exponential fit to the data after the step yields a 1/e time constant of 0.492 seconds corresponding to a response frequency of 2.03 Hz. Data points are recorded at 10 Hz.

$\tau = 0.492 \text{ sec}$

$= 2.03 \text{ Hz}$
Measured NH₃ and CO₂ references before, during and after the flights. The CO₂ measurement varied by less than 5% during the flights and less than 7.5% after return shipment to the LGR laboratory.
A photo of the rear-facing inlet and outlet on the G-1 window panel outside the cabin. Flight direction is towards the left in the photo. The inlet is lined with ½" OD Teflon tubing. The inlet and outlet are separated by approximately 30 cm.

130x101mm (96 x 96 DPI)
Temporal profiles of the ammonia mixing ratios and altitude. (a) Data from the May 24, 2012 flight showing a diffuse NH$_3$ plume over the Yakima Valley. The inset shows a quiescent period with an average value of $3.31 \pm 0.29$ ppb$_v$ (at 2Hz). (b) Data from the May 25, 2012 flight showing highly localized NH$_3$ sources. The boundary layer sounding at the beginning of the flight shows the expected transition to very low NH$_3$ levels. The inset shows an isolated NH$_3$ spike demonstrating rapid response while airborne.
(a) Vertical profiles of NH$_3$ mixing ratios vs. altitude on May 24, 2012 and (b) May 25, 2012. The estimated boundary layer height is shown as a blue dashed line. Average NH$_3$ values at each transect altitude are shown as red dots and decrease with increasing altitude.
(a) A shaded relief map of the state of Washington highlighting the Yakima Valley where flight measurements were taken. (b-d) Color coded flight paths showing the NH$_3$ mixing ratio at three altitudes on May 24, 2012. The strong and isolated NH$_3$ plume is distributed broadly over the feedlots because of the calm conditions in the shallow boundary layer. (e) A satellite photo of an area with a high feedlot density. Feedlots are highlighted in blue and correlate with high NH$_3$ concentrations along the flight path.
Color coded flight paths run perpendicular to the prevailing winds showing the NH$_3$ mixing ratio at two altitudes on May 25, 2012. (a) NH$_3$ Mixing ratios at 1270 m and (b) 670 m. Individual NH$_3$ plumes are visible across the flight paths because of the consistent NNE wind.

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