**Atmospheric
Measurement
Techniques**
Discussions

Interactive comment on "Open-path, quantum cascade laser-based sensor for high resolution atmospheric ammonia measurements" by D. J. Miller et al.

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Responses to Anonymous Referee #1:

Comment: The paper is well written, presents useful results and should be published with minor modifications. The requested modifications are mostly in the area of extrapolation of measurement capabilities.

Response: We are grateful for the constructive comments and useful suggestions of Anonymous Referee #1. Below are detailed explanations of the changes to improve the originally submitted manuscript in response to all comments and suggestions.

Comment: Mass and power: The open path configuration allows operation without a pump, the element that usually is the main power consumer in closed path systems. 50W power consumption is impressive. The laptop computer power is not included in the 50W. Is the laptop essential for operation? If so, what is its power requirement?

Response: The current laptop used in this system consumes $\sim$50 W of electrical power. The laptop computer provides LABVIEW-based data processing (lock-in detection), final retrieved mole fractions and diagnostics data recording. The same laptop has been used to control the NH3 sensor and another open-path, QCL-based sensor [Tao et al., 2012b] simultaneously. However, we are not limited to a standard laptop computer to perform these tasks. The algorithms and data recording can be accomplished with lower power computers (e.g. tablets or single board computers with single Watts power consumption) or compact embedded systems, which include drive electronics, data acquisition and processing with very low (single Watts) power consumption. These improvements make reductions in total system power quite feasible in future configurations. We add the following to the revised manuscript (section 2.1): "The laptop computer power consumption (currently $\sim$50 W) can be reduced further with alternative, lower power single-board computers or embedded systems."

Comment: The total mass of 5 kg also is impressive. The photograph in Figure 1 does not indicate that the instrument has been field hardened. How much would the authors expect the mass to change with such hardening?

Response: The sensor is a prototype that is not fully weather-proofed at this time. However, this sensor has operated under field conditions including rain, extreme temperatures and dust/insects. The mass of 5 kg includes basic aluminum shields for the laser and detector components (not shown in Figure 1), as well as lens tubes (shown in Figure 1) to protect the optical cell mirrors. Further field hardening of the sensor will not significantly increase the total mass (<10% expected). Specifically, the largest weight components of the sensor system are the electronics box and laptop computer. Miniaturization of these components into a more compact embedded system is ongo-

ing work, to allow for future deployments on platforms where weight is a limiting factor (e.g. drone).

Comment: Regarding 10 Hz measurements: [Abstract, Section 2.3, Section 6] Do the 10 Hz NH3 measurements use 10 Hz water vapor measurement? Water vapor introduces a significant interference, which is included in the retrieval [Section 2.3] via a separate (1 Hz) measurement. Please comment on how the measurement at 10 Hz for, e.g. eddy correlation, might be accomplished with water vapor measured separately, and somewhat remotely from the NH3 measurement volume.

Response: On short time-scales (10 Hz) for eddy covariance applications, the NH3 retrieval does not use a similarly fast water vapor measurement. According to field measurements with the LICOR LI-7500 CO2/H2O analyzer on our ground-based mobile measurement platform, the fluctuations of ambient water vapor mixing ratios recorded at 5 Hz time resolution are typically $\sim$ 100 ppmv H2O. According to a HITRAN simulation, these changes in ambient H2O have a negligible (0.2%) spectroscopic influence on the 2f NH3 retrieval at 1 ppbv NH3 mole fraction. Thus, for eddy covariance applications, a simultaneous water vapor measurement with an open-path commercial sensor (e.g. LICOR LI-7500A) is not necessary to include in the NH3 2f signal retrieval for spectroscopic interference on short-time scales. However, these fast H2O vapor measurements would be used for water vapor dilution and air density corrections in eddy covariance applications. Although eddy covariance measurements are possible with our open-path sensor, demonstration of this measurement application is beyond the scope of the current manuscript.

On long time-scales and for different regions (e.g. from the tropics to Arctic), H2O mixing ratios have a large dynamic range. To account for these variations, we use the average H2O mixing ratio for the region and time period of field deployment for our fitting routine. Again, variations around the mean do not significantly impact the retrieved concentration for our stated uncertainty. In short, we are not overly sensitive to water vapor at the percentage level. Finally, we note that the average H2O mixing

ratio is also used to calculate the overall NH3 absorption feature line-widths, including the effect of H2O broadening using the values measured by Owen et al. (2013).

The revised manuscript is corrected to clarify the current treatment of the water vapor effects as follows (section 2.3): "Water vapor introduces multiple, minor potential interferences for the 2f NH3 retrieval. The average ambient H2O mixing ratio for a given region and time period of sensor field deployment is used for spectral fitting of the H2O absorption baseline and used to calculate absorption line-widths to account for H2O broadening using the coefficients measured by Owen et al. (2013). On short time scales, the variability of ambient H2O vapor (a few hundred ppmv) has a negligible (<0.5%) impact on the 2f NH3 retrieval. For larger changes of water vapor, the mixing ratio of H2O is included in the fit from routine meteorology data."

Comment: Calibration and Zero Offset: An ingenious scheme for calibration is reported, wherein a low-pressure ethylene absorption line from an in-line absorption cell is monitored at the 8th harmonic of the modulation frequency, while the ammonia is measured at the 2nd harmonic. Could the authors remind us why the 8th harmonic is preferred? Higher harmonics seem somewhat "fragile".

Response: The preference for the 8th harmonic is explained in the original manuscript (section 2.3): "The eighth harmonic (8f) is used for ethylene reference signal detection to achieve optimal separation between ambient NH3 and ethylene reference signals. The 8f signal isolates the relatively narrow, reduced pressure ethylene reference signal, with negligible influence from ambient NH3 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."

Comment: The authors should say more about continuous baseline offset measurement. The "zero-level" stability is especially important in the measurement of a gas

with near zero background levels. Great pains were taken in laboratory measurements of zero levels. How can those techniques be transferred to continuous measurements?

Response: We add the following on baseline offset to the revised manuscript in section 3.1: "Calibration of the zero NH3 baseline offset is also important when retrieving NH3 mole fractions near the detection limit. The zero calibration point is obtained by flushing the calibration tube with dry air and coating the calibration tube surfaces with a concentrated (~20 wt %) citric acid solution to minimize NH3 desorption effects. We note that true zero NH3 conditions are very difficult to achieve for any NH3 instrument, due to surface adsorption and partitioning artifacts as well as residual NH3 found in dry air. We perform zero calibrations prior to, during, and following field deployments, along with the full calibration procedure described in section 2.4. Based on these zero calibrations, our absolute uncertainty in the zero calibration is 0.20 ppbv NH3. It is important to note that each time zero calibration is performed, there is additional uncertainty due to differences in the amount of residual NH3 in the calibration tube. Thus, 0.20 ppbv is an upper limit to our estimate of the zero calibration uncertainty. This metric defines an absolute accuracy at low NH3 mole fractions, due to uncertainty in the zero calibration point. Thus, the total estimated uncertainty is 0.20 ppbv NH3 $\pm$ 10%."

We also acknowledge the following in the revised manuscript (section 5): "Further investigations on the long-term stability of this baseline under field conditions will be necessary to characterize the variability of the zero calibration and ultimately improve uncertainties at low mole fractions. This uncertainty is currently the most significant limitation for our open-path NH3 sensor. 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."

We currently do not monitor the zero NH3 level in real-time during in-situ measurements, given the relative stability between different field deployments, slightly different optomechanical modifications between deployments, and different environmental con-

ditions. A potential future plan to understand how uncertainties can be improved better than 0.2 ppbv would be to flow "zero gas" during a measurement campaign for a long duration (e.g. diurnal cycles) and see how the sensor responds.

Comment: Autonomous field operation: Autonomous field operation is an attractive possibility, but has not yet been achieved [?]. What are some of the envisioned challenges to be overcome to achieve autonomous field operation?

Response: We have achieved >7000 km of mobile NH3 measurements with this open-path sensor in the Central Valley, California, Beijing, China and Houston, Texas and diurnal NH3 measurements in Beijing, China. The requirements for mobile operation are turning on the sensor and allowing a short time for sensor stabilization before driving. In general, the sensor system can be operated autonomously on a daily time-scale without maintenance. Challenges for long-term, (multi-day) stationary measurements include ensuring the optical cell mirrors are clean from dust, insects, precipitation deposits, etc., water-proofing and optimizing a solar panel/battery system to ensure uninterrupted power supply in remote field environments away from grid power. A sentence is added to the revised manuscript (end of section 5) describing these challenges.

Comment: Section 4, Field Measurements: How was sampled air delivered to the instrument in the mobile platform, and was there opportunity for losses at surfaces? Section 6, Summary: Line 11: No surface adsorption time constants? There are nearby surfaces, mirror supports and a baseplate in Figure 1. Line 17: The open path system has "negligible sampling artifacts". Are the authors certain? No adsorption/desorption from nearby cell structures?

Response: In our open-path sensor configuration, no air delivery system is needed. Ambient air flows across the optical cell region. For mobile measurements while in motion, the air is constantly flowing across the optical cell region, as explained in the revised manuscript in section 4. The only opportunity for losses at surfaces would be the surface of the sensor itself or nearby objects, such as the vehicle surface for mobile

measurements. We modify the manuscript to "minimal sampling artifacts" and "short adsorption time constant compared with existing closed-path sensors."

We compare the open-path sensor response with simultaneous measurements of non-sticky gases CO_2 and CO to assess surface adsorption effects in our open-path system in the attached figure. Herndon et al. (2005) reported on-road NH3 measurements performed by a closed-path QC-TDLAS sensor. We re-plot Fig. 4 from Herndon et al. (2005) (top frame in the following figure), which illustrated simultaneous closed-path NH3 and CO_2 measurements through a tunnel, with our open-path NH3 and CO_2 measurements also through a tunnel (bottom frame in the following figure). The vertical dashed lines in the figure indicate the time at which the sensor platform exited the tunnel. The CO_2 mixing ratio can serve as an indicator of the true decay of the tunnel plume, since CO_2 does not adsorb significantly. In both cases, CO_2 mixing ratio dropped rapidly when the mobile platforms exited the tunnels. In the closed-path measurements, NH3 mixing ratio showed a much longer decay and even did not reach background after more than 2 minutes. In contrast, the open-path NH3 measurements follow the CO_2 measurements closely. We also note that only the open-path NH3 measurements capture the rapid ($\sim$1 s) mixing ratio changes due to individual vehicle emissions (e.g. at 16:30:20 local time).

In addition, Figure 11b shows the response of the sensor with simultaneous response of an adjacent open-path sensor for the non-adsorbing gas CO. There is no delay between the spikes of these two species, which occur on time scales of seconds, due to vehicle exhaust emissions. This further supports our conclusion that the surface adsorption time constant for our open-path NH3 measurement is significantly reduced at these measurement time scales compared with previous closed-path sensors. We add this to the revised manuscript (section 4).

Figure caption in response: (Top) Tunnel measurements by closed-path NH3 sensor [Herndon et al., 2005]; (bottom) Tunnel measurements by the open-path NH3 sensor. Dashed line in both cases indicate the tunnel exit.

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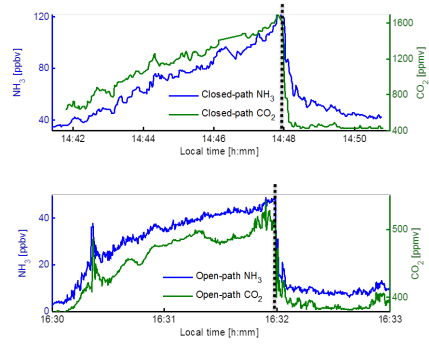Interactive comment on Atmos. Meas. Tech. Discuss., 6, 7005, 2013.

Fig. 1.

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