

## ***Interactive comment on “Ammonia at Blodgett Forest, Sierra Nevada, USA” by M. L. Fischer and D. Littlejohn***

**M. Fischer**

mlfischer@lbl.gov

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Response to reviewer's comments:

We appreciate the useful comments from two anonymous reviewers. We have substantially revised the manuscript. In particular, we acknowledge that this represents preliminary work on NH<sub>3</sub> fluxes in the Sierra Nevada. We also agree that calculations of NH<sub>3</sub> emissions and transport from the central valley to Blodgett were too simplistic and have removed that analysis from the paper.

Here, we respond to the individual review comments in detail and identify and how where we have revised the manuscript. In this response, each the reviewer's comments

C10100

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Discussion Paper



is labeled R1 or R2 and our responses are labeled LBL.

General

Reviewer 1:

R1: The present manuscript includes a description of a fast response QCL NH<sub>3</sub> instrument, a method used to calculate the aerodynamic deposition velocity expected under different meteorological conditions, and a predictive model for NH<sub>3</sub> mixing ratios at the measurement site. In general this work falls into the scope of ACP.

The study site was not located as stated (Pg 14142, Ln 10) in the west but in the east of Sacramento adjacent to the Sacramento Valley. The predominant wind direction at the study site is from the west and the source area does not include areas with extensive cattle but rather crop production. In fact, the San Joaquin Valley (SJV) where dairy production takes place to a considerable extent is located much further south of BFRS and it is highly unlikely that SJV dairies contribute to the emissions measured at the study site.

The very low emission rates measured at the present study site using both measurement methods (denuder and QLC) confirm that the source region was low in NH<sub>3</sub> emissions. Measured emissions of 1-2 ppb NH<sub>3</sub> are not indicative of substantial contributions from animal agriculture.

LBL: We concur and have corrected the typographical error on location to state the site is actually “north-east” of Sacramento.

Previous back-trajectory analyses and measurements have shown that south-west winds often bring air masses from the valley to Blodgett Forest (Dillon et al., 2002). However, we agree with the reviewer that most of the NH<sub>3</sub> emitted from SJV sources likely deposit before reaching Blodgett forest.

However, as mentioned above, we concede our modeling approach is too simplistic and have removed this material from the manuscript.

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Interactive Discussion

Discussion Paper



R1: The instrument validation efforts show large data noise of the QLC instrument and poor agreement with the denuder technique. This item requires further discussion and additional investigation to establish the usefulness and precision of the QLC.

LBL: We have reexamined the question of QCL instrument noise and the comparison between the QCL and denuder measurements. First, the noise of NH<sub>3</sub> instrument was determined in the laboratory using standard air and during zero air additions in the field. Both the laboratory and initial field measurements showed the instrument noise was consistent with instrument specifications, yielding 0.3 ppb RMS noise at the 10 Hz data collection rate that integrates down as square-root of time to  $\sim 20$  ppt (at  $\sim 200$  seconds), and then increases to  $\sim 0.1$  ppb at 900 second (15 minutes), the time period chosen for the zero checks. The variations in NH<sub>3</sub> in ambient air obtained at the beginning of the experiment (e.g., June 11 & 12th) yield RMS noise between 0.05 to 0.1 ppb in 12 hr averages after zero subtractions. This level of performance is similar to the typical uncertainty in the denuder analysis.

However, examination of the QCL field measurements showed a gradual loss of optical signal and corresponding increase in instrument noise (as judged from periods with zero air additions) such that the 10 Hz instrument noise climbed to approximately 3 ppb at the time the comparison with the denuder measurements were performed. This increase in noise is apparent in Figure 4, and resulted in  $\sim 0.3$  ppb uncertainty in 12 hour mean NH<sub>3</sub> mixing ratios at the end of the field study when the denuder measurements were made. The difference between the four filter sample measurements and the corresponding time-averaged QCL spectrometer measurements is  $0.5 \pm 0.3$  ppb, consistent with the increased noise in the QCL measurements and not a detection of bias between the QCL and denuder observations. We have revised the discussion to clarify this point.

During field operations we tried minor adjustments to the optics but, because of the large logistical constraints, continued the measurements with increasing noise level. The reason for the degradation in performance was later identified. Upon return to

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the laboratory, we found that the spectrometer optical cell was contaminated with dust. Inspecting the field log, we now believe that the instrument was operated at BFRS for an extended period without the inlet filter, causing the dust contamination and resulting increase in noise. We have revised the results section of the paper to report this finding.

R1: The outlined simple NH<sub>3</sub> emission model assumes that NH<sub>3</sub> emissions are distributed evenly throughout the year. To the contrary, substantial diurnal and annual fluctuations are known to occur in the central valley of California. The estimated emissions factors (EF) of 185 g NH<sub>3</sub> per cow per day for dairy animals are biologically unreasonable and beyond the scope of this paper.

LBL: We appreciate the comment. We originally included the discussion of NH<sub>3</sub> transported to BFRS to examine whether the source of observed atmospheric NH<sub>3</sub> might be the large NH<sub>3</sub> sources known to exist in the Central Valley. We are not attempting to evaluate NH<sub>3</sub> emission factors or distant NH<sub>3</sub> emissions. The estimate of 185 g NH<sub>3</sub> per cow per day was drawn from the published literature. As mentioned above, we have removed this material from the manuscript.

R1: Figure 10 which is showing estimated surface NH<sub>3</sub> fluxes from cattle based on the above mentioned questionable EF. The indicated back trajectory seems highly improbable considering wind flow patterns and activity factors in this region.

LBL: The estimate of NH<sub>3</sub> fluxes is based on reported numbers of cows and an emission factor reported in the literature as noted above. The back-trajectory transport model is derived from NOAA's HYSPLIT model and driven by NCEP reanalysis weather that is reasonably consistent with observations at BFRS. There remains significant uncertainty in the NH<sub>3</sub> deposition rate in the model and we only use the model to examine whether NH<sub>3</sub> from the Central Valley might be expected produce the observed NH<sub>3</sub> at BFRS.

R1: The results from this short pilot study are not sufficient to support many of the interpretations and suggestions regarding contributions of animal agriculture on

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potential secondary particle formation in the Central Valley of California. Studies of the contributions of animal agriculture on NH<sub>3</sub> flux would require a longer term efforts at a different location (i.e. in the San Joaquin Valley where cattle actually contribute to real NH<sub>3</sub> emissions).

LBL: We concur with the reviewers comments that NH<sub>3</sub> emissions from livestock likely vary diurnally and seasonally and that the seasonal variations cannot be fully examined in a two-week field study. As noted above, we reported the simple model simulation to provide an order of magnitude estimate of how much NH<sub>3</sub> we might expect at BRFS and did not intend to address the more general questions of actual NH<sub>3</sub> emissions, deposition, or secondary particle formation in the Central Valley.

Given the reasonable objections of both reviewers, we have removed the section on modeling NH<sub>3</sub> transport to BRFS.

Anonymous Referee #2 Received and published: 18 December 2007 General Impression.

R2: The paper by Fischer and Littlejohn presents a short time series of measurements of NH<sub>3</sub> concentrations and fluxes made with a QCL absorption spectrometer at the Blodgett Forest Research Station. There are few direct measurements of ammonia fluxes over North American ecosystems, and thus any addition to the sparse database potentially makes a significant contribution to the literature. Unfortunately, both the measurement period and the data analysis are fairly short and do not provide the information needed to improve the description of dry deposition processes in atmospheric models. Instead, the authors focus in their conclusions on the controls of the ammonia concentrations by linking the measurements to a somewhat tentative modeling exercise. The application to such a clean site is pushing the detection limit of the QCL. There appears to be instrument issues with the QCL which are reflected in a different noise pattern during different periods and poor agreement between QCL and denuder sampler. It is therefore questionable whether the measurements support

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Interactive Discussion

Discussion Paper



the conclusions or further analysis of the fluxes suggested here.

LBL: We appreciate the reviewers comments and have revised the manuscript to reflect a simpler purpose, which is to report on an instrument for making eddy covariance fluxes of NH<sub>3</sub> based on the admittedly limited snapshot of measured NH<sub>3</sub> fluxes observed at the Blodgett forest site. We suggest that the revised paper is useful in these respects.

We completely agree that the measurements and analysis are not sufficient (or intended) to improve the description of deposition processes, particularly NH<sub>3</sub> fluxes driven by vegetation-atmosphere ammonium disequilibrium. We have revised the manuscript to only report the NH<sub>3</sub> fluxes and show they do not exceed the aerodynamic upper limit on deposition rate.

With respect to instrument performance, we investigated the source of increased noise in the QCL measurements and believe it was due to dust contamination and corresponding loss of optical signal in the spectrometer as described in the response to reviewer 1. We note that although the measurement noise degraded during the observation period, we believe the first week of measurements is sufficient for purpose of this paper.

As discussed above, we have removed the simplistic modeling of NH<sub>3</sub> emissions and atmospheric transport simulations.

Major Scientific Points:

R2: The description of the instrument setup is insufficient to judge whether it was suitable for flux measurements. For example, was the inlet sufficiently far away from the bluff body of the QCL and scissor lift? The measurement height (10 m) is certainly low compared with the tree height (10 - 12 m), and measurements were made well within the roughness sublayer, possibly within the canopy. Fig. 1 should be modified to illustrate the entire setup, not just the calibration manifold.

Full Screen / Esc

Printer-friendly Version

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Discussion Paper



LBL: We appreciate the comment. The instrument was designed so that the NH<sub>3</sub> inlet was located 3 m from the QCL housing, facing into the dominant wind direction. We have removed the map from Fig. 1, and replaced it with a photograph of the instrument mounted on the scissor lift near the top of the tree canopy. We agree the inlet was only slightly above the mean canopy height at BFRS, potentially within the roughness sublayer. However, the location of the lift was slightly higher than surrounding terrain and the local trees were slightly shorter than the mean. This provided an observation point above the local trees. We compared eddy covariance measurements of CO<sub>2</sub> flux made with a CO<sub>2</sub>/H<sub>2</sub>O gas analyzer (LI7500) co-located near the NH<sub>3</sub> gas inlet with the routine CO<sub>2</sub> flux measurements made by the long-term BFRS instruments (located well above the canopy). From the period covering our NH<sub>3</sub> observations, linear regression of CO<sub>2</sub> flux measurements near the NH<sub>3</sub> instrument on the CO<sub>2</sub> flux measurements on the BFRS tower yielded a linear regression slope of 0.79 ± 0.01 ( $R^2 = 0.82$ ) and no significant offset, suggesting that the NH<sub>3</sub> fluxes would not be expected to suffer from extreme (e.g, factor of 2) attenuation. We have added a comment to this effect.

R2: It sounds like the PTFE filter is subjected to 50 Torr. Surely, this would lead to evaporation of all available ammonium nitrate (and ammonium chloride) and subsequent detection as ammonia. Thus the measurement relates to the sum of gaseous ammonia and volatile ammonium aerosol. This needs to be discussed and considered throughout the manuscript.

LBL: We appreciate the comment. We did not discuss this aspect of the measurements in enough detail. The filter is in the sample stream at a relatively low pressure and this could lead to overestimates of gaseous NH<sub>3</sub> in a particulate rich environment. We have added a caution in this respect to the instrument description.

Also, while the gas phase NH<sub>3</sub> concentration measurements could be slightly overestimated, we do not expect that either NH<sub>4</sub>NO<sub>3</sub> or NH<sub>4</sub>Cl would vaporize rapidly enough to correlate with fluctuations in vertical wind and hence affect the flux measurements. We have added a sentence to this effect in section 3.2.

R2: It is not clear whether or how ammonia chemistry was considered in the back trajectory modeling and STILT. Having been developed for CO<sub>2</sub>, it is likely that chemistry is not considered. This would make the model inappropriate for NH<sub>3</sub>. Although there was no potential for aerosol formation at Blodgett, there may well have been potential for aerosol formation in the emission areas which would have changed the transport distance and atmospheric lifetime of total reduced nitrogen.

LBL: We concur that the transport modeling was too simple and have removed those sections.

R2: The difference between QCL and denuder samples could be due to problems with either method, but the authors need to resolve this problem to lend support to the remainder of the paper. What are the dimensions of the denuders that they are effective at 100 lpm? Have they been confirmed to be 100% efficient?

LBL: The filter measurements of NH<sub>3</sub> are indeed subject to errors but both the instrumentation and analysis of the denuder system and filters were the same as used for previously published work at the same flow rate. As described in our response to reviewer 1, further analysis showed that the instrument noise of the QCL system increased over time due to operation without the inlet filter. The resulting 0.5 +/- 0.3 ppb disagreement in mean NH<sub>3</sub> is not highly significant but does suggest that before the instrument malfunction, the QCL instrument was capable of measuring NH<sub>3</sub> in the 0-4 ppb range observed at BFRS.

R2: The comparison between measured and predicted equilibrium gas phase concentration products of NH<sub>3</sub> x HNO<sub>3</sub> adds little information to the paper as the concentration of HNO<sub>3</sub> was guessed (taken from a different measurement period).

LBL: We appreciate the comment. The comparison of equilibrium particulate matter formation was included to support the argument that it would be unlikely for particulate NH<sub>4</sub>NO<sub>3</sub> to be a significant source of error to the NH<sub>3</sub> measurements. However, given that the HNO<sub>3</sub> was measured in a previous campaign (though at the same time

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of year), we concede that the argument is circumstantial and have noted this in the discussion.

R2: It seems counterintuitive that the power spectrum of  $w'NH_3'$ ; shows a weaker slope than sensible heat. A damped signal should show a steeper slope. Hence, Fig. 7 raises more questions than it answers and provides little support that the frequency response of the system was sufficient. More discussion is needed. Are the unexpected slopes due to the effect of measuring well within the roughness layer (rather than the inertial sublayer)?

LBL: This is a good point and we wondered the same thing ourselves. We discussed this with colleagues who also observed spectra for  $w'C'$  that were flatter than the corresponding spectrum for  $w'T'$ . However, we have added some discussion indicating that the flatter spectrum might be explained by some combination of measurements within the roughness sublayer or the effective high pass filtering caused by time varying zero offset removal.

R2: The comparison of  $V_d$  and  $V_{dmax}$  (Fig. 9) only demonstrates that the measurements are not in contradiction with  $V_{dmax}$ . It would be more helpful to show a time-trace of  $R_c$  instead, which is a parameter that models can use. In general it would be helpful to see a table listing summary statistics (range, mean, median, standard deviation etc.) of concentrations,  $\dot{m}_{NH_3}$ ,  $V_d$  and  $R_c$ . In the analysis, the authors ignore the entire European literature on  $NH_3$  fluxes, in which this kind of analysis has been performed for 20+ years. The conclusions on the deposition rate (P14153, L2-5) are not clear and highly qualitative.

LBL: Yes, the comparison was only meant as a check the estimates of  $V_d$ . We have removed Fig. 9, and added the suggested table of summary statistics. We also reviewed the large body of recent European literature (to be honest only the recent papers) on  $NH_3$  fluxes and added some references to the discussion on deposition.

R2: In addition, there are references to TDL/QCL fluxes that should be included (e.g.

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper



Famulari et al., Water Air Soil Pollution Focus 1, 17-27, 2005; of interest is also the paper : Whitehead, J.D., Twigg, M., Famulari, D., Nemitz, E., Sutton, M.A., Gallagher, M.W. & Fowler, D.: Evaluation of laser absorption spectroscopic techniques for eddy covariance measurements of ammonia. Environmental Science & Technology, in press).

LBL: Thanks, we appreciate the suggestions.

Technical Comments: R2: P14143, L1: Should be: "... during a two-day period ... with a filter sampler " as the intercomparison has not previously been introduced. Also LBNL should be introduced on first use.

LBL: We have corrected the ambiguities.

R2: P14143, L17: incomplete sentence: "The mean ammonia flux ...".

LBL: Thank, we corrected the typo.

R2: P14147, L9: There seems to be a 'minus'; missing:  $V_d = - F/\text{conc}$ , judging by the sign convention used in the paper.

LBL: Done

R2: P14147, L13. It is well known that  $R_c$  is composed of two parallel pathways: stomatal uptake and cuticular uptake. In very dry conditions (probably dominating during this period),  $R_c$  may approach  $R_s$ .

LBL: We appreciate the comment and have added that clarification.

R2: P14148, L5. This equation needs a reference.

LBL: The references to the equation are mentioned above. We have emphasized that.

R2: P14148, L12. Delete 'and'.

LBL: This section was removed.

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R2: Figures. Please explain what the error bars represent in the figure captions, where appropriate. Why did the author decide not to connect the symbols of Figs. 4, 5 and 8?

L2: All error bars represent estimates of 1 sigma uncertainty in reported values. We have revised the text to clarify this point.

R2: Fig. 10. Additional 'of' in caption.

LBL: Figure was removed.

R2: Fig. 6. Mismatch between legend (with symbols) and trace (no symbols) of red trace.

LBL: Thanks, we have corrected the error.

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Interactive comment on Atmos. Chem. Phys. Discuss., 7, 14139, 2007.

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