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Atmospheric Measurement Techniques Discussions

Interactive comment on "Characterizing a Quantum Cascade Tunable Infrared Laser Differential Absorption Spectrometer (QC-TILDAS) for measurements of atmospheric ammonia" *by* R. A. Ellis et al.

Anonymous Referee #1

Received and published: 12 January 2010

General Comments The manuscript by Ellis et al. describes both laboratory and field instrument intercomparisons of the QC-TILDAS for measurement of atmospheric ammonia. Special emphasis is placed on the design of the QC-TILDAS inlet. Accurate, near real-time measurement of ammonia is particularly arduous with mitigating factors introduced both by ammonia's physical properties and the environmental conditions of in-situ sampling. The authors highlight the analytical technique of the QC-TILDAS and their efforts to increase accuracy and response time with a novel inlet, sampling line

modifications, and varying background checks. The manuscript describes an interesting and relevant area of study in a well-organized manner.

Specific Comments Page 3312, Line 9: Specify the possible deposition surface, i.e. vegetation, land, etc. Page 3312, Lines12-13: Reword this sentence. Possibly: Ammonium particulates have a longer atmospheric lifetime than ammonia and therefore, can be transported over relatively long distances, which increases their potential to affect human health and influence radiative forcing. Page 3312, Line 16: A quite relevant reference for this sentence is Galloway et al. Galloway, J.N., Aber, J.D., Erisman, J.W., Seitzinger, S.P., Howarth, R.W., Cowling, E.B. and Cosby, B.J., 2003. The nitrogen cascade. Bioscience, 53(4): 341-356. DOI: 10.1641/0006-3568(2003)053. Page 3312, Lines 16-17: Chiefly North American policies have focused on the acidic species. Policies in the EU have traditionally been much more inclusive. For example, the Gothenburg Protocol specifically addresses ammonia. It may be prudent to specify the geopolitical area for the 'regulatory policies.' Page 3312, Lines 18-19: So as not to mislead readers, please quantify that the reduction is small, <1 ug/m3 as found by Makar et al. Page 3313, Line 19: Add a reference regarding the positive bias introduced by ammonium nitrate and ammonium chloride, possibly Chow et al. 1998. Chow J.C., Watson J.G., Lowenthal D.H., Egami R.T., Solomon P.A., Thuillier R.H., Magliano K., Ranzieri A., 1998. Spatial and temporal variations of particulate precursor gases and photochemical reaction products during SJVAQS/AUSPEX ozone episodes. Atmospheric Environment, 32 (16): 2835-2844. Page 3315, Line 6: Quantify precise spectral ranges for ethylene and methanol. Page 3315, Line 14: What's a typical flushing period? Page 3315, Line 24: Quantify 'moderately high above threshold.' Page 3317, Line 17: How was this 90% quantified with regard to flow separation? More explanation is needed for how flow successfully navigates the 90 degree right turn to enter the optical cell. Page 3318, Line 6: State the range of ammonia concentrations used in calibration. Page 3318, Line 11: What's the average time for stabilization of the signal during calibration? Also, state the frequency of calibration. Page 3319, Line 21: State the degree of accuracy of the difference. Page 3319, Line 25: While daily

replacement of the filter was probably sufficient, this reviewer wonders if any effects of such frequent changes were observed in the data. Is daily replacement recommended by the manufacturer or a practice adopted by the authors based on previous experience? Page 3320, Line 3: This reviewer assumes that met data were collected as hourly averages. Explicitly state if this is the case. Page 3322, Line 12: Are more concentrations available for comparison? Perhaps, step-wise changes of $\sim$50 ppb versus several hundred would be preferable. Even in agricultural systems, lower concentrations, especially with ammonia fluxes, can be present. Page 3322, Lines 14-16: A short paper by Mukhtar et al. addresses some of the physics and physical parameters influencing ammonia adsorption. It may provide some supporting information for this statement. Mukhtar, S., Rose, A., Capareda, S., Boriack, C., Lacey, R., Shaw, B. and Parnell, C., 2003. Assessment of ammonia adsorption onto Teflon and LDPE tubing used in pollutant stream conveyance. Agricultural Engineering International: The CIGR Journal of Scientific Research and Development: BC03012. Page 3322, Lines 24-26: Some reference to the physics involved, i.e. polarity, should be included. Page 3323, Line10: What about ammonia adsorption/desorption especially considering that the discrepancies occur at lower concentrations? It seems you address these later in the text when referring to Fig. 7b. This reviewer suggests the authors renumber figures so that Fig. 6 and Fig. 7b are Fig. 6a and Fig. 6b. Page 3323, Line 12: What's the evidence, anecdotal or otherwise, that fertilization caused these increased mixing ratios? Page 3323, Lines 19-20: This reviewer is not totally confident that your data fully support this statement. Based on simple statistical degrees of freedom, it is difficult to draw this conclusion. If other inlet-equipped devices were included in the study, then stronger evidence may have been possible. Page 3323, Line28: Was condensation visible in the lines? Were these sample lines heated to 40C as mentioned for the QC-TILDAS in Section 3.2? Norman et al. postulated that heated samples lines should have minimized this effect. Page 3324, Line 10: Again, Norman et al. only saw condensation during periods of precipitation, not during periods of high RH, even near 100%. Considering those findings, more weight should be placed on precipitation as

the mitigating factor instead of RH. Page 3324, Line 21: Specify how the background spectrum was assessed. Page 3334, Fig. 5: It would be helpful to have some quantifiable error associated with each D-factor shown as error bars.

Technical Corrections Throughout the manuscript, the authors use both the term 'ammonia' and the symbol NH3. Select one for consistency. Ensure that vendor names, cities, and countries (if applicable) are listed after the first mention of specific equipment used in the study. Page 3311, Line 5: Add a hyphen between 'thermoelectrically' and 'cooled.' Page 3311, Line 7: Id. Page 3312, Line 7: Add a comma after 'plants.' Page 3312, Line 9: Make 'reaction' plural. Page 3312, Line 14: Add the chemical symbol in parenthesis after 'ammonium.' Page 3312, Line 21: Add 'in-situ' after 'accurate.' Page 3313, Line 2: Replace 'often suffers from' with 'is prone to.' Page 3313, Line 6: Add 'in field conditions' after 'deploy.' Page 3313, Line 9: Delete 'both.' Page 3313, Lines13-14: Make 'surface' singular. Replace 'involved in the sampling intake' with 'in contact with the sample air flow.' Page 3313, Line 14: Make 'wall' plural. Delete 'in contact with the air flow.' Page 3313, Line 22: Add a comma after 'Research.' Add a period after 'Inc.' Page 3313, Line 27: Add 'and' after 'humidity.' Page 3314, Line 19: Add the chemical symbol for ethylene and delete later occurrence (Pg. 3315). Page 3315, Line 3: Define the acronym 'HITRAN.' Page 3315, Line 22: Change 'underestimates' to 'underestimation.' Page 3317, Line 15: Utilize consist units for pressure (kPa or Torr). Page 3318, Line 1: Replace 'experience' with 'encounter.' Page 3319, Line 19: Give full name of chemical, nitrogen oxide, in addition to symbol.

Interactive comment on Atmos. Meas. Tech. Discuss., 2, 3309, 2009.