available at www.sciencedirect.com journal homepage: www.elsevier.com/locate/agrformet

Short communication

Technical note: Laboratory evaluation of a tunable diode laser system for eddy covariance measurements of ammonia flux

J.J. Brodeur^b, J.S. Warland^{a,*}, R.M. Staebler^c, C. Wagner-Riddle^a

^a University of Guelph, Department of Land Resource Science, Guelph, ON N1G 2W1, Canada

^b McMaster University, School of Geography and Earth Sciences, Hamilton, ON L8S 4K1, Canada

^c Environment Canada, Processes Research, 4905 Dufferin Street, Downsview, ON M3H 5T4, Canada

ARTICLE INFO

Article history:

Received 19 May 2008

Received in revised form

12 August 2008

Accepted 13 August 2008

Keywords:

Ammonia

Trace gas analyzer

Eddy covariance

Tunable diode laser

Spectral response

ABSTRACT

A tunable diode laser trace gas analyzer (TGA 100, Campbell Scientific, Logan, Utah) was evaluated in the laboratory for its ability to measure ammonia fluxes using the eddy covariance technique. A random noise generator was used in the laboratory to switch sampling between high and low concentration air streams to simulate a range of eddy sizes with a known input. A mechanical switching system was developed to prevent pressure fluctuations during switching associated with valves. A half-power point of 0.4 Hz was found for 50 m of sampling tubing. Resolution, determined through laboratory tests, was conservatively estimated between 0.2 and 1 $\mu\text{g m}^{-2} \text{s}^{-1}$.

© 2008 Elsevier B.V. All rights reserved.

1. Introduction

Ammonia has many terrestrial sources such as agriculture (Yamulki and Harrison, 1996; Schjoerring and Mattsson, 2001), coal combustion (Silver et al., 1991) and biochemical processes in natural soils (Georgii and Lenhard, 1978). Agriculture is the major source of gaseous ammonia (NH_3), producing emissions through animal waste volatilization (Whitehead and Raistrick, 1990), fertilizer and manure application (Sommer et al., 1991; Hansen et al., 1998) and livestock grazing (Denmead et al., 1974; Jarvis and Pain, 1990). Natural and semi-natural systems were for a long time believed to be significant and continual sinks of atmospheric NH_3 (Sutton et al., 1993). However,

studies conducted over the past 10 years have shown that both agricultural and undisturbed ecosystems may demonstrate bi-directional fluxes between their surfaces and the atmosphere (Yamulki and Harrison, 1996; Zhu et al., 2000). The need to explain these differing directions of flux has spurred recent interest in the factors controlling NH_3 exchange in the soil-vegetation-atmosphere system, and necessitates the ability to monitor small fluxes on a continuous, high-resolution basis.

As an alternative to enclosure methods, such as chambers and windtunnels, micrometeorological approaches to NH_3 flux measurement afford the advantages of quantifying integrated fluxes over a large area (100–10,000 m^2), while being non-intrusive and non-destructive (Sutton et al., 1993).

* Corresponding author.

E-mail addresses: brodeujj@mcmaster.ca (J.J. Brodeur), jwarland@uoguelph.ca (J.S. Warland), ralf.staebler@ec.gc.ca (R.M. Staebler), cwagnerr@uoguelph.ca (C. Wagner-Riddle).

0168-1923/\$ – see front matter © 2008 Elsevier B.V. All rights reserved.

doi:10.1016/j.agrformet.2008.08.009

Due to the relatively low temporal resolution of most NH_3 concentration sensors, the majority of micrometeorological ammonia flux experiments have used flux-gradient or mass balance approaches, which allow for time-integrated measurements of gas concentration.

The eddy covariance (EC) method of estimating fluxes above a surface is based on direct measurement of the turbulent motions responsible for transport. In order to account for vertical transfer of scalars by eddies of all sizes found in the environment, it is necessary to use fast-response sensors capable of sampling at frequencies high enough to measure all natural fluctuations (Stull, 1988; Duyzer et al., 1992). This requirement is typically fulfilled through the use of a three-dimensional sonic anemometer and a fast-response temperature sensor or gas analyzer. This method offers the advantage of collecting direct and continuous fluxes, calculated at the height and location where the variables are measured (Stull, 1988). The EC method has been used to measure fluxes of many different atmospheric quantities, including energy (sensible heat, momentum) and gases (CO_2 , N_2O , H_2O). The use of this technique in research has greatly increased over the recent past, as more fast-response sensors have become commercially available and economical.

Tunable diode laser (TDL) absorption spectroscopy utilizes the highly specific mid-infrared (IR) absorption characteristics of trace gas molecules to measure the concentration of a desired species in a sample (Eng et al., 1980). TDLs emit monochromatic radiation that may be tuned at a high frequency and resolution. This allows for fast and sensitive measurement of trace gas concentrations using a highly focused absorption line (Eng et al., 1980). Most trace gas detection is accomplished using lead-salt diode lasers, which, as a group, can produce light in the wavelength region of 2.5–25 μm (Werle et al., 2002). Lead-salt TDLs have been used to measure concentrations of a large variety of gaseous species, including CH_4 , NO , NO_2 , N_2O , NH_3 , H_2O , HNO_3 , and SO_4 (Wagner-Riddle et al., 2005). More recently, quantum cascade lasers have been used for many of the same species which have lines from the first harmonic mode of the fundamental transition in the 1.4–1.9 μm region.

This paper evaluates the Campbell Scientific TDL trace gas analyzer (TGA100, Logan, Utah, referred to as TDLTGA), as described in Edwards et al. (2003), for ammonia concentration measurement. The TDL-based system operates at low pressures (~ 5 kPa), which decreases broadening of absorption lines from gas molecule collisions in the sample cells. This decrease in line broadening allows for more selective detection of NH_3 absorption lines by decreasing interference with other gases at nearby wavelengths (Eng et al., 1980). Low pressure within the TGA and sample tubing also lowers the partial pressure of water vapour in the system, greatly reducing the possibility of condensation. This reduces problems associated with NH_3 absorption and desorption from water present in the system (Dias, 1998). Previous studies have demonstrated the use of this system for micrometeorological measurements of NH_3 flux over multiple plots using the flux-gradient method (Warland et al., 2001).

Up to the present, the lack of reliable and readily available fast-response NH_3 concentration sensors has restricted the use of EC to quantify the flux of ammonia to a handful of

experiments (Sutton et al., 1993). This study examines the use of the TDLTGA for EC measurement of ammonia fluxes through the use of laboratory tests. The major focus of the study is on the performance of the system for EC measurements. The specific objective of the study is to design and use a laboratory system for characterizing the spectral response characteristics of the ammonia TDLTGA using a random noise generator. In addition to assessing the TDLTGA system for EC measurements, this note presents a new laboratory procedure for full evaluation of a trace gas analyzer system for micrometeorological use.

2. Methodology

2.1. Basic TDLTGA setup

The basic setup of the sampling system followed Dias (1998) and Warland et al. (2001) who showed that clear HDPE tubing combined with low pressure throughout the entire sampling system resulted in the most favourable response. For the sampling systems tested here, clear HDPE tubing with 6.25 mm i.d. was used. The main pressure drop was created by a 25 mm diameter, 1 μm pore size PTFE filter at the sample inlet. The system was run by a Busch RC-0040 vacuum pump and the pressure in the TDLTGA sample cell was 4.5 kPa, giving a flow rate of 36 SLPM through the analyzer. The sample cell was lined with clear HDPE.

2.2. Spectral response of the TDLTGA

To assess the response of the TDLTGA under controlled conditions, it was necessary to develop a system capable of simulating changes in ammonia concentrations over a wide range of time scales, analogous to the passing of different sized eddies across the sensor. To avoid pressure fluctuations associated with changing air streams by solenoid valves, a system was designed to physically move the sample intake between two air streams with different NH_3 concentrations. A lever system (schematically illustrated in Fig. 1) was constructed using a 42 cm section of 9.5 mm diameter stainless steel tubing, affixed to a plywood base at one end by a pivot pin. A pneumatic cylinder was mounted onto the plywood base, with its piston end attached perpendicular to the stainless steel tubing at a distance of 25.5 cm from the pivot. The position of the cylinder away from the pivot point allowed the unfixed end of the tubing to have a total travel distance of 13 cm. A filter intake was affixed to the unanchored end of stainless steel tubing and either a 2 or 50 m sample tube, running to the TDLTGA, was attached to the fixed end of the stainless steel. This allowed rapid lateral switching between two separate air streams that were supplied from below.

To deliver two separate, adjacent air streams of differing NH_3 concentration to the sample intake, two 3 m sections of 8.9 cm i.d. ventilation hose were used (Fig. 1). One end of each hose was mounted to an opening on a section of plywood. These two holes were spaced 13 cm apart to allow the filter intake to rest directly above the centre of each hole. The other ends of the hoses were equipped with a blower pushing ambient room air through the hose. A constant, high NH_3

Fig. 1 – Schematic illustration of experimental setup for testing TDLTGA frequency response. Tubing shown as dashed lines and cabling as solid lines. Direction of air flow indicated by arrows. Solenoid and needle valves indicated by SV and NV, respectively. 'A' and 'B' indicate ambient and 'high' concentration air streams, respectively. RNG indicates the random-noise generator. The compressed air tank was used to move the pneumatic valve.

concentration air stream was created in one of the hoses by mixing a 5.89% (by volume) ammonia mixture from a compressed cylinder with room air. The high- NH_3 mixture was leaked into the blower intake through a 2 mm copper hose attached to a needle valve. The consistent supply of ammonia coupled with the high flow rate of the blower through 3 m of hose provided ample time for thorough mixing to occur before it was exhausted at the sample intake. The concentration of ammonia exiting the hose could be precisely controlled and was maintained at approximately 500 ppb for all tests. A second, low NH_3 concentration air stream was produced in the other hose by simply exposing the blower end to ambient (room) air. This was reasoned to be superior to supplying 'zero' gas, as any change in the NH_3 concentration found in the room would be equally incorporated into the high and low concentration flows, thus preserving the difference between the streams. A small exhaust fan was positioned parallel to the mounting board and was operated to blow room air across the low NH_3 concentration air stream toward that of high NH_3 concentration. This ensured sampled ambient air was not contaminated by flow or diffusion from the high concentration stream.

Exact knowledge of the input signal, as determined by the switching of air streams, was required to examine the output of the sensor in comparison to the input. A random noise

generator (RNG)(3722A, Hewlett-Packard) was used to produce a binary signal which moved the air sample intake between a high and low concentration stream. The RNG produces a binary sequence with a line power spectrum with an envelope described by $(\sin(x)/x)^2$. The RNG was set to produce a spectrum with a fundamental frequency of 1.22×10^{-4} Hz with 'lobes' at 1 Hz and integral multiples. The random bit sequence generated by the RNG was output to the valve control box such that the sample tube switched between the two gas streams at frequencies of up to 10 Hz. This presented the TDLTGA with a sequence of pseudo-random step-changes in NH_3 concentrations at frequencies of up to 10 Hz. The power spectral density of the input signal is shown in Fig. 2A, along with the power spectral densities of the measured concentration signal. The TDLTGA concentration signal was recorded along with the analog input RNG signal at a frequency of 10 Hz by the TDLTGA computer.

Two separate evaluations were completed: (a) Using the minimal amount of tubing needed to mount the intake filter on the switching device (2 m) and (b) operation of the TDLTGA using 50 m of sample tubing between the filter intake and the TDLTGA inlet. Evaluation of frequency response at 2 m provided a representation of the spectral characteristics of the TDLTGA itself. Tests conducted with 50 m of tubing were used to predict the response of the system under field conditions.

Fig. 2 – (A) Power spectral densities normalized by variance for the random noise generator (input signal) and the measured TGA ammonia concentrations (output signals). (B) Ratio of power spectral densities of output (P_{cc}) to input (P_{mg}) signals with 2 and 50 m of tubing. Half-power points (HPP) indicated by dashed lines.

2.3. Resolution of TDLTGA

To test the resolution of the system for eddy covariance measurements, the noise of the instrument, measured with a constant-concentration input, is required. Noise data were collected by drawing air from an empty 200 L barrel with a loose fitting polyethylene cover. Though the barrel was unable to eliminate background changes in concentration due to the cycling of the building ventilation system, it served to minimize higher frequency fluctuations associated with turbulent motions. Changes in background ammonia concentration in the laboratory were generally of very low frequency, and data were not collected during times when the ventilation cycled. A small exhaust fan was suspended within the barrel to ensure adequate mixing inside the container. Tests were performed using 50 m of sample tubing to replicate field conditions.

3. Results of frequency response testing

Fig. 2B shows the ratio of the power spectral densities of the output to input signals shown in Fig. 2A for 2 and 50 m tubing

lengths. The gaps are due to the ‘lobes’ in the RNG signal. Both sampling configurations produce an increasing amount of power relative to the input signal at frequencies less than 0.17 Hz. A larger proportion of variance is produced at low frequencies with 50 m of sampling tubing. The production of output power at a magnitude greater than that found in the input signal indicates the presence of a low-frequency source of noise in the system. This additional variance is provided by low-frequency drift in the absolute concentration measured by the TDLTGA system, caused by small movements in the alignment of TDLTGA optics (optical fringing) or by changes in laser state. Coherence spectra (not shown) showed a decrease in correlation between the RNG and the concentration measurements at frequencies less than 0.02 Hz, indicating fringing at these longer periods.

At frequencies greater than 0.17 Hz, the power output from both tubing lengths decreases below that of the input signal, representing a loss of signal from the TDLTGA and/or the sampling system. The output signal produced using 50 m sample tubing experiences a steeper drop in output power at higher frequencies. Half-power points, indicated in Fig. 2, are 0.4 and 0.7 Hz for 50 and 2 m of tubing, respectively. Over 50% of the input signal is lost in the output at timescales less than 2.5 s for 50 m of sample tubing and 1.4 s with 2 m of sample tubing. The TDLTGA has a sample volume of 0.41 L and draws air using a pump with a flow rate of 11.1 L s^{-1} (at a pressure of 4.5 kPa) giving it a dynamic time constant $\tau = 0.004 \text{ s}$. This is a much faster response than shown by the spectral analysis, demonstrating that the signal losses are due to NH_3 adsorption on the sampling system walls.

4. Discussion

The ‘sticky’ nature of the ammonia molecule greatly influences the spectral response of the sensor. The polar configuration of NH_3 and its hydrophilic nature gives it the ability to bind and unbind from solid surfaces used in air sampling systems, as well as to absorb and disassociate in water. Such interactions result in attenuation of high-frequency concentration fluctuations within the sample tubing. This happens when high- NH_3 concentration air loses molecules to binding on tubing walls, while subsequent lower- NH_3 air samples are augmented by the molecules released from the same tubing walls in attempt to reach concentration equilibrium. In previous studies where NH_3 sampling techniques have been used, the influence of this sticky nature has been considered to be the largest contributor to high-frequency spectral power loss in NH_3 concentration measurements (Schiff and Mackay, 1987; Massman, 1991; Dias, 1998).

The approximate magnitude of the effect ammonia binding has on the spectral response of such a system can be estimated by comparing the results of Edwards et al. (2003), where frequency response tests were conducted on similar TDLTGA systems designed to measure N_2O and CH_4 . Completing similar tests at a TDLTGA pressure of 7.5 kPa with equal flow rates and minimal sample tubing, the half-power point was reported as 6.4 Hz. This demonstrates the large effect of NH_3 binding on frequency response characteristics of the TDLTGA system.

A half-power point of 0.4 Hz is at the lowest extent of the requirements for effective measurement using an eddy covariance approach. McBean (1972) discussed acceptable sensor response characteristics, stating that a half-power point of at least 1 Hz is typically required for most eddy covariance applications. However, the required frequency response of a sensor varies with measurement height above the surface and with the environmental conditions it is operated in. Therefore, sensors with slightly lower response may be used effectively in settings favourable for production of low-frequency concentration variation (e.g. above a tall forest during times of unstable atmospheric conditions).

4.1. Estimation of eddy covariance NH_3 flux losses

To evaluate the effect of spectral losses on eddy covariance measurements, ideal cospectra of ammonia concentration and vertical wind speed, S_{wc} , were created for specified environmental conditions using formulations presented in Moore (1986). A fifth-order polynomial was fit to the spectral loss curve (Fig. 2B). Integration of the ideal cospectra and the ideal cospectra multiplied by the fitted spectral loss curve allowed calculation of expected flux loss due to the response of the system. S_{wc} cospectra were produced over a range of u (1 – 6 m s^{-1}) for stable and unstable conditions and for short ($z - d = 1 \text{ m}$) and tall ($z - d = 21 \text{ m}$) tower scenarios (where z is measurement height and d is zero-plane displacement). This methodology makes several assumptions, most significantly that the cospectrum for ammonia flux is correctly represented by the ideal curve. Real-world cospectra will deviate from this shape, both due to differing correlations between vertical windspeed and the scalar in question and to turbulence conditions in each measurement period. However, this analysis provides a reasonable order-of-magnitude estimate and allows for a qualitative assessment of the system.

Results in Table 1 show that much greater underestimation of flux can be expected when the system is used at low heights, and in situations of increased wind speed and stable conditions. Each of these circumstances are responsible for reducing the timescale of movement of scalar-transporting eddies across the sensor. These trials show that over 80% of the real flux signal may be effectively lost during the application of the TDLTGA in near-ground measurements (e.g. above a short grass field). However, more than 90% of the

flux signal can be expected to be retained when measuring from a taller tower. This suggests that the TDLTGA is capable of eddy covariance measurement, provided a taller tower is used and some flux underestimation during stable, high-wind conditions is acceptable.

4.2. Estimation of flux resolution

The power spectral density of the zero-flux concentration time series (Fig. 3) shows little production of variance by the TDLTGA at frequencies greater than 0.015 Hz. However, as frequency decreases below 0.015 Hz, the spectral power produced by the TDLTGA concentration signal increases steadily. This enhancement of variance in the NH_3 concentration signal exemplifies the increased production of low-frequency noise by the TDLTGA system due to fringing effects and other influences such as fluctuations in laser power output.

Using the approach outlined in Wagner-Riddle et al. (2005), the minimum resolvable flux, F_{lim} , for the system can be estimated using the power spectral density calculation of the concentration time series measured under zero-flux. This variance spectrum is combined with a simulated ideal vertical wind velocity spectrum to calculate the expected standard error of the system, according to:

$$\text{S.E.} = \sum_{f=0}^{\text{inf}} \sqrt{\frac{S_w(f) \Delta f S_c(f) \Delta f}{4\pi f T}} \quad (1)$$

where T is the measurement period length (s), $S_w(f)$ and $S_c(f)$ are the variance spectra of vertical wind velocity and TDLTGA concentration signal at frequency f , respectively, and Δf is the frequency bandwidth (Hz). In this study, $S_w(f)$ was estimated following Kaimal and Finnigan (1994).

Since $S_c(f)$ solely represents the spectrum of noise produced by the TDLTGA system (as the deviation in concentration signal is assumed to be zero), S.E. is a measure of the standard error produced in the measured flux as a result of the contributions of TDLTGA noise under the specified environmental conditions. Therefore, it can be considered a

Table 1 – Estimated percentage of actual NH_3 flux magnitude measured using the TDLTGA system with eddy covariance in varying stability and wind speed conditions for application at heights $z - d = 1$ and 21 m

$u \text{ (m s}^{-1}\text{)}$	% flux measured			
	$z - d = 1 \text{ m}$		$z - d = 21 \text{ m}$	
	Stable	Unstable	Stable	Unstable
1	42.7	79.1	96.2	99.2
2	25.9	67.1	91.9	98.2
3	18.8	59.4	87.7	97.1
4	14.9	53.9	83.5	95.9
5	12.6	49.6	79.5	94.7
6	11.1	46.2	75.8	93.5

Fig. 3 – Power spectrum of TDLTGA-measured ammonia concentration time series collected during laboratory tests of ‘zero-flux’ conditions.

Fig. 4 – Minimum ammonia flux resolution (F_{lim}) for the TDLTGA system with eddy covariance measurement at 21 m height over conditions of (a) changing u^* with constant u , and (b) changing u values with constant u^* .

measure of F_{lim} when the sensor is used in an eddy covariance application (Wagner-Riddle et al., 2005).

To investigate changes in the value of F_{lim} at differing measurement heights and environmental conditions, $S_w(f)$ was estimated over a range of u^* (0.1–0.6 at increments of 0.1 m s^{-1}) and u (1–6 at increments of 1 m s^{-1}). This was done for measurement height $z - d = 21$ m. Fig. 4 displays the results over the range of conditions for a measurement height of 21 m and neutral stability. The lowest F_{lim} value obtained ($0.119 \mu\text{g m}^{-2} \text{s}^{-1}$) is under conditions of high u and low u^* , while the poorest resolution ($1.185 \mu\text{g m}^{-2} \text{s}^{-1}$) is observed during conditions of low u and high u^* . Note that newer TDLTGA have improved fringe-correction algorithms which should reduce F_{lim} , making these estimates conservative, worst-case scenarios.

5. Conclusions

A tunable diode laser trace gas analyzer was tested for use in micrometeorological measurements. The system operates at low pressure to reduce adsorption of ammonia to the walls. Laboratory tests using a random-noise generator demonstrated a half-power point at 0.4 Hz for 50 m of sample tubing. Though this is lower than recommended for high-frequency eddy covariance work, it is sufficient to capture more than 90% of the flux for a measurement height of 21 m under unstable conditions. Laboratory analysis of the system noise showed a flux resolution of about $0.2\text{--}1 \mu\text{g m}^{-2} \text{s}^{-1}$.

These results show that eddy covariance measurements will not be possible for ammonia flux except under very limited conditions. This is not due to limitations of the analyzer, which has been successfully applied to eddy covariance measurements of other trace gases, but to the

nature of ammonia. Though the assessment presented was negative, this note has also demonstrated a new procedure for full laboratory evaluation of a trace gas analyzer system for micrometeorological measurements.

Acknowledgments

We would like to acknowledge the support of the Natural Sciences and Engineering Research Council of Canada through a post-graduate scholarship and a Discovery Grant, as well as the assistance and support of Environment Canada. Steve Sargent of Campbell Scientific, Inc. was extremely generous with his time both in supporting the operation of the analyzer and in providing comments on this manuscript. We are very grateful for the constructive and insightful comments of the anonymous reviewers.

REFERENCES

- Denmead, O.T., Simpson, J.R., Freney, J.R., 1974. Ammonia flux into the atmosphere from a grazed pasture. *Science* 185, 609–610.
- Dias, G.M., 1998. Development of an Ammonia Measurement and Sampling System Based on Tunable Diode Laser Spectroscopy. Ph.D. thesis, University of Guelph.
- Duyzer, J.H., Verhagen, H.L.M., Westrate, J.H., Bosveld, F.C., 1992. Measurement of the dry deposition flux of NH_3 on to coniferous forest. *Environmental Pollution* 75, 3–13.
- Edwards, G.C., Thurtell, G.W., Kidd, G.E., Dias, G.M., Wagner-Riddle, C., 2003. A diode laser based gas monitor suitable for measurement of trace gas exchange using micrometeorological techniques. *Agricultural Forest Meteorology* 115, 71–89.

- Eng, R.S., Butler, J.F., Linden, K.J., 1980. Tuneable diode laser spectroscopy: an invited review. *Optical Engineering* 19 (6), 945–960.
- Georgii, H.W., Lenhard, U., 1978. Contribution to the atmospheric NH_3 budget. *Pure Applied Geophysics* 116, 385–392.
- Hansen, B., Nornberg, P., Rasmussen, K.R., 1998. Atmospheric ammonia exchange on a heathland in denmark. *Atmospheric Environment* 32 (3), 461–464.
- Jarvis, S.C., Pain, B.F., 1990. Ammonia volatilization from agricultural land. In: *The Fertilizer Society Proceedings*, No. 298, Peterborough, UK.
- Kaimal, J.C., Finnigan, J.J., 1994. *Atmospheric Boundary Layers: Their Structure and Measurement*. Oxford University Press, New York, NY, USA.
- Massman, W.J., 1991. The attenuation of concentration fluctuations in turbulent flow through a tube. *Journal of Applied Meteorology* 96 (D8), 15269–15273.
- McBean, G.A., 1972. Instrument requirements for eddy correlation measurements. *Journal of Applied Meteorology* 11, 1078–1084.
- Moore, C., 1986. Frequency response corrections for eddy correlation systems. *Boundary-Layer Meteorology* 37, 17–35.
- Schiff, H.I., Mackay, G.I., 1987. Measurement of atmospheric gases by laser absorption spectrometry. In: Johnson, R.W., Gordon, G.E. (Eds.), *The Chemistry of Acid Rain: Sources and Atmospheric Processes*. American Chemical Society, Washington, DC, (chapter 24), pp. 274–288.
- Schjoerring, M.K., Mattsson, M., 2001. Quantification of ammonia exchange between agricultural cropland and the atmosphere: measurements over two complete growth cycles of oilseed rape, wheat, barley and pea. *Plant and Soil* 228, 105–115.
- Silver, J.A., Bornse, D.S., Stanton, A.C., 1991. Diode laser measurements of trace concentrations of ammonia in an entrained-flow coal reactor. *Applied Optics* 30 (12), 1505–1511.
- Sommer, S.G., Olesen, J.E., Christiansen, B.T., 1991. Effects of temperature, wind speed and air humidity on ammonia volatilization from surface applied cattle slurry. *Journal of Agricultural Science* 117, 91–100.
- Stull, R.B., 1988. *An Introduction to Boundary Layer Meteorology*. Kluwer Academic Publishers, Dordrecht, The Netherlands.
- Sutton, M.A., Pitcairn, C.E.R., Fowler, D., 1993. The exchange of ammonia between the atmosphere and plant communities. *Advances in Ecological Research* 24, 301–391.
- Wagner-Riddle, C., Thurtell, G.W., Edwards, G.C., 2005. Trace gas concentration measurements for micrometeorological flux quantification. In: Hatfield, J.L., Baker, J.M. (Eds.), *Micrometeorology in Agricultural Systems*. American Society of Agronomy, Agronomy Monograph no. 47, Madison, WI, USA, pp. 321–344 (chapter 14).
- Warland, J.S., Dias, G.M., Thurtell, G.W., 2001. A tunable diode laser system for ammonia flux measurements over multiple plots. *Environmental Pollution* 114, 215–221.
- Werle, P., Maurer, K., Kormann, R., Mucke, R., D'Amato, F., Lancia, T., Popov, A., 2002. Spectroscopic gas analyzers based on indium-phosphide, antimonide and lead-salt diode lasers. *Spectrochimica Acta, Part A* 58, 2361–2373.
- Whitehead, D.C., Raistrick, N., 1990. Ammonia volatilization from five nitrogen compounds used as fertilizers following surface application to soils of differing characteristics. *Journal of Soil Science* 387–394.
- Yamulki, S., Harrison, R.M., 1996. Ammonia surface-exchange above an agricultural field in southeast England. *Atmospheric Environment* 30 (1), 109–118.
- Zhu, T., Pattey, E., Desjardins, R.L., 2000. Relaxed eddy-accumulation technique for measuring ammonia volatilization. *Environmental Science and Technology* 34, 199–203.