8.2 FIELD SCALE MEASUREMENTS OF NH3 EMISSIONS AFTER ORGANIC FERTILIZER APPLICATION: COMPARISON OF DIFFERENT METHODS

Christoph Spirig[1,2,]*, Jörg Sintermann[1], Christof Ammann[1], Uwe Kuhn[1], and Albrecht Neftel[1]

1) Agroscope Reckenholz-Tänikon Research Station ART, Zurich, Switzerland
2) Federal Office for Meteorology and Climatology MeteoSwiss, Zurich, Switzerland

1. INTRODUCTION

As part of the EU 6th framework project NitroEurope (www.nitroeurope.eu), we aimed at measuring the complete set of nitrogen exchange above a managed grassland site in Switzerland. In this framework we monitored the ammonia (NH_3) exchange over two growing seasons with the aerodynamic gradient method using two AiRRmonia monitors (Spirig et al., 2010). The measurements covered also six applications of liquid cattle slurry by broad spreading, causing high NH_3 emissions which ultimately dominated the yearly ammonia exchange at this site (Flechard et al., 2010). Still, the cumulative emissions after slurry application (in the order of 15% of applied ammoniacal nitrogen) were roughly three times lower than the emission factors in the national emission inventory (Reidy et al., 2008).

A wide range (5-70% of applied nitrogen), of emission factors has been reported, depending on meteorological conditions, the characteristics of the manure, and the technique used for application (e.g. Pain et al., 1989, Søgaard et al. 2002, Misselbrook et al., 2005, Rochette et al., 2008). But even for similar conditions, a large range of emission factors can be found in the literature, reflecting a considerable uncertainty. Part of the uncertainty is related to the lack of NH_3 flux measurements after fertilization at the scale of whole agricultural fields. Such measurements still represent a challenge, mainly because of the sticky nature of the NH_3 molecule, which complicates measurements at high time resolution that are needed for observing the highly dynamic character of these emission events. Due to the difficulties of directly measuring these NH_3 fluxes at the scale of whole agricultural fields, previous emission studies are dominated by experiments on smaller plots using approaches requiring NH_3 measurements only at low time resolutions. However, it has been shown that the emissions from a fertilized surface scale with its extension, similar to evaporation being larger over an oasis as compared to that over larger water bodies (Génermont and Cellier, 1997). As a consequence, it is important to quantify NH3 emissions after fertilization on representative field sizes.

Here we report on an experiment performed in summer 2009, aiming at quantifying emissions of NH_3 after fertilization using different measurement approaches.

2. EXPERIMENTAL

2.1 Field site and fertilization

The experiments were performed in August 2009 at the NitroEurope site in Oensingen, Switzerland (Ammann et al., 2007). Liquid cattle slurry was applied on a previously harvested wheat field on 4.8. 2009 and on a grass field on 6.8. 2009 (also cut shortly before fertilizing). Six (wheat field) and three tanks(grass field) of slurry were spread with a splash plate device. The refilling and transport of the liquid manure trailer from the farm to the field took 15-20 minutes. Hence it took about 2.5 and a bit more than one hour, respectively, to completely fertilize the fields.

2.2 Eddy covariance measurements with eTR-MS

An electron transfer reaction mass spectrometer (eTR-MS) was used for fast measurements of NH_3. While it has previously been reported that this instrument is capable of accurately measuring NH_3 over a wide range of concentrations, it has also been noted that time resolution was limited and far away for applications in eddy covariance measurements

---

* *Corresponding author address*: Christoph Spirig, MeteoSwiss, Krähbühlstr. 58, CH-8044 Zurich, Switzerland; e-mail: christoph.spirig@meteoswiss.ch

due to absorptive effects of NH_3 within the instrument (Norman et al., 2007, 2009). A new variant of the instrument was used here, consisting of a drift tube with PEEK (polyetherethylketone) instead of PFA teflon, allowing the heating of all inner surfaces of the mass spectrometer to 180° C. Operating the instrument at this temperature significantly improved the time response for NH_3 measurements (Sintermann et al., 2010), potentially fast enough for eddy covariance (EC) applications. eTR-MS is also capable of measuring water vapor at sufficient time resolution for EC measurements, as demonstrated by Ammann et al. (2006).

The eTR-MS was operated in an air-conditioned trailer, thus requiring a more than 20m long tube for sampling air directly below a sonic anemometer (HS, Gill instruments, Lymington, UK). In order to reduce the attenuation of fast concentration changes, a ½" OD PFA Teflon tube with a flow of 100 STP l min^{-1} was used, and we equipped it with a custom made heater to control it at a temperature of 150°C.

Details about the calculation of fluxes from the eTR-MS measurements using the EC technique are described in Sintermann et al. (to be submitted to Atmos. Meas. Tech. Discuss.). In short, the data processing followed the methods applied by Spirig et al. (2005) and Ammann et al. (2006, 2010), allowing an integral quantification and correction of high frequency losses based on a comparison of the cospectra (ogive analysis) of vertical wind speed with temperature and NH_3, respectively.

2.3 Aerodynamic Gradient measurements

Two Airrmonia (Mechatronics, NL) monitors were operated in a gradient configuration for simultaneously measuring NH_3 at heights of 0.45 and 1.5 m at half hourly time resolution. These measurements were used to derive fluxes using the aerodynamic gradient method (AGM). Details about this system and the flux calculations are discussed in Spirig et al. (2010). The AGM system was operated on a small wagon that could be wheeled onto the field immediately after the passage of the slurry tank. Still, the measurement of initial fluxes was usually not possible with this instrument due to sensor saturation effects and violation of the homogenous footprint requirement during the slurry spreading.

2.4 Open path FTIR measurements

On a contractual basis an independent mass balance approach using three identically configured open-path FTIR-spectrometers (K300; Kayser-Threde) was applied to measure NH_3 concentrations at three heights (0,80 m, 1,85 m and 3,00 m) at the downwind side of the field. This system delivered line concentrations at a time resolution of 2 min., further details are described in Gärtner et al. (2008). Emissions from the fertilized field were calculated by multiplying concentration and wind profiles and adjusting geometrically for the part of the emissions passing beyond the measuring path.

3. RESULTS AND DISCUSSION

3.1 Eddy covariance measurements

After the spreading of slurry, NH_3 concentrations as recorded by eTR-MS immediately rose to more than 1 ppm. Short term variations between 100 ppb and more than 2 ppm were observed and clear fluxes could be detected as reflected in the covariance functions (Fig. 1). The integral damping losses (dominated by tube effects) as determined by ogive analysis were only about 10% higher for NH_3 as compared to water fluxes, suggesting that the sampling and measurement setup was successful. The emissions showed a fast decrease with time that could be described by an exponential decay.

$$E(t) = F_1 \cdot \exp\left(-\frac{t}{\tau_1}\right) + F_2 \cdot \exp\left(-\frac{t}{\tau_2}\right) \qquad \text{(Eq. 1)}$$

with two time constants (τ_1 and τ_2) and parameters F_1 and F_2 describing initial fluxes. Fig. 2 presents a comparison of EC fluxes with those obtained by the aerodynamic gradient, showing a good agreement.

3.2 Field Scale Emissions

Due to the sequential application of the manure (refilling of slurry tanks) and the fast decrease of NH_3 volatilization, detailed footprint calculations and corrections with a high temporal resolution were crucial for obtaining representative emission fluxes. Figure 3 illustrates the situation on the wheat field indicating the location of the EC sensors and the six slurry tracks that there were fertilized sequentially (refilling of the tanks after spreading).

For deriving the emission fluxes of the whole field, it was assumed that the emissions of each of the six tracks exhibited 1) the same initial emission flux and 2) the same temporal decay. Next, the contribution of each track to the footprint of the EC measurement was calculated with an analytical footprint model (Kormann and Meixner, 2001, Neftel et al., 2008). At any time, the flux as measured by the EC system is thus given by

$$F_{EC} = \sum_i FP_i \cdot E_i \qquad \text{(Eq. 2)}$$

with FP_i being the footprint fractions (details see Ammann et al., 2010) and E_i the emissions of each track. Using the measured time series of fluxes and the relationships described by Eq.1 and Eq.2 allowed finding best approximations for the constants in Eq.1 and thus deriving the integral emissions of the whole field. Figure 4 shows both the emissions from individual tracks (dashed lines) and the overall fluxes from the freshly fertilized field for the experiment on 4th of August. Also shown are the overall emissions as obtained from mass balance approach using the open path FTIR-measurements. The good agreement with this independent method supports the validity of the flux measurement and the footprint calculations. A detailed evaluation of this field intercomparison exercise will be given in a forthcoming paper.

4. CONCLUSIONS

An eTR-MS system was successfully applied for EC measurements of NH_3 emissions from agricultural fields following the application of liquid cattle slurry. The key for achieving a sufficiently fast time resolution was heating both the inner surfaces of the NH_3 instrument as well as the sampling line to at least 150°C.

The comparison of all applied methods showed good agreement on the magnitude of observed emission fluxes, confirming earlier measurements at this field site being rather at the low end of emission factors in the literature (15-20% losses of applied nitrogen).

ACKNOWLEDGEMENTS

Funding for this work was provided by the Swiss Federal Office for the Environment and the Swiss Federal Office of Agriculture (project “Validierung von Ammoniakverlusten nach Ausbringung von Gülle auf Feldebene“), the EU project NitroEurope (IP) (contract no. 017841-2), the Swiss National Science Foundation (project TERMS, 200021-117686/1) and the Marie Curie project CORN (PIEF-GA-2008-220842). We thank Andrea Gärtner (Landesamt für Natur, Umwelt und Verbraucherschutz NRW, D-45659 Recklinghausen) and Rainer Hirschberger (Ingenieurgesellschaft Niemann & Partner D-44799 Bochum) for providing the results of the Mass balance approach.

REFERENCES

Ammann, C., Brunner, A., Spirig, C., and Neftel, A.: Technical Note: Water vapour concentration and flux measurements with PTR-MS, Atmos. Chem. Phys., 6, 4643–4651, 2006.

Ammann, C., Flechard, C. R., Leifeld, J., Neftel, A., and Fuhrer, J.: The carbon budget of newly established temperate grassland depends on management intensity, Agr. Ecosyst. Environ., doi:10.1016/j.agee.2006.1012.1002, 2007.

Ammann, C., Spirig, C., Neftel, A: Validation of a simple footprint tool for trace gas flux measurements above agricultural fields. Proceedings of the 29th Conference on Agricultural and Forest Meteorology, Keystone CO, AMS, Boston.

Flechard, C. R., Spirig, C., Neftel, A., and Ammann, C.: The annual ammonia budget of fertilised cut grassland – Part 2: Seasonal variations and compensation point modeling, Biogeosciences, 7, 537–556, 2010.

Gaertner, A., Hirschberger, R., and Kotzian, F.: Estimation of diffuse NH3 emissions during and after slurry spreading, Gefahrstoffe Reinhaltung der Luft, 68, 149-155, 2008.

Génermont, S., and Cellier, P.: A mechanistic model for estimating ammonia volatilization from slurry applied to bare soil, Agr. Forest Meteorol., 88, 145-167, 1997.

Pain, B. F., Phillips, V. R., Clarkson, C. R., and Klarenbeek, J. V.: Loss of Nitrogen through Ammonia Volatilization During and Following the Application of Pig or Cattle Slurry to Grassland, J. Sci. Food Agr., 47, 1-12, 1989.

Misselbrook, T. H., Nicholson, F. A., and Chambers, B. J.: Predicting ammonia losses following the application of livestock manure to land, Bioresource Technology, 96, 159-168, 2005.

Neftel A., Spirig C. and Ammann C., Application and test of a simple tool for operational footprint evaluations, Environmental Pollution, 152, 3, 644-652, 2008.

Norman, M., Hansel, A., and Wisthaler, A.: O2+ as reagent ion in the PTR-MS instrument: Detection of gas-phase ammonia, Int. J. Mass Spectrom., 265, 382–387, 2007.

Norman, M., Spirig, C.,Wolff, V., Trebs, I., Flechard, C.,Wisthaler, A., Schnitzhofer, R., Hansel, A., and Neftel, A.: Intercomparison of ammonia measurement techniques at an intensively managed grassland site (Oensingen, Switzerland), Atmos. Chem. Phys., 9, 2635–2645, 2009.

Reidy, B., Rhimb, B., and Menzi, H.: A new Swiss inventory of ammonia emissions from agriculture based on a survey on farm and manure management and farm-specific model calculations, Atmos. Environ., 42, 3266–3276, 2008.

Rochette, P., Guilmette, D., Chantigny, M. H., Angers, D. A., MacDonald, J. D., Bertrand, N., Parent, L. E., Cote, D., and Gasser, M. O.: Ammonia volatilization following application of pig slurry increases with slurry interception by grass foliage, Can. J. Soil Sci., 88, 585-593, 2008.

Sintermann J., C. Spirig, A. Jordan, U. Kuhn, C. Ammann and A. Neftel, Eddy covariance flux measurements of ammonia by means of electron transfer reaction mass spectrometry, to be submitted to Atmos. Meas. Tech. Diss., 2010.

Søgaard, H. T., Sommer, S. G., Hutchings, N. J., Huijsmans, J. F. M., Bussink, D. W., and Nicholson, F.: Ammonia volatilization from field-applied animal slurry - the ALFAM model, Atmos. Environ., 36, 3309-3319, 2002.

Spirig, C., Neftel, A., Ammann, C., Dommen, J., Grabmer, W., Thielmann, A., Schaub, A., Beauchamp, J., Wisthaler, A., and Hansel, A.: Eddy covariance flux measurements of biogenic VOCs during ECHO 2003 using proton transfer reaction mass spectrometry, Atmos. Chem. Phys, 5, 465–481, 2005.

Spirig, C., Flechard, C.R., Ammann, C., and Neftel, A.: The annual ammonia budget of fertilised cut grassland – Part 1: Micrometeorological flux measurements and emissions after slurry application, Biogeosciences, 7, 521–536, 2010.

Figures

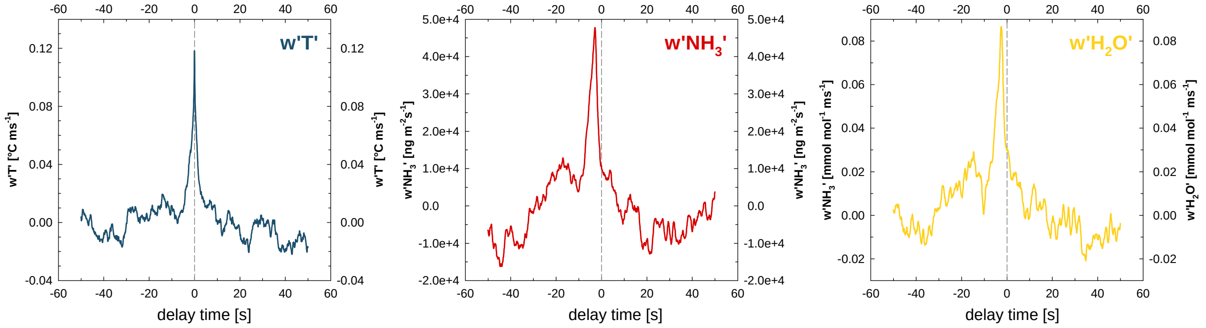

Fig. 1: Covariance functions of vertical wind speed with temperature, ammonia and water vapor.

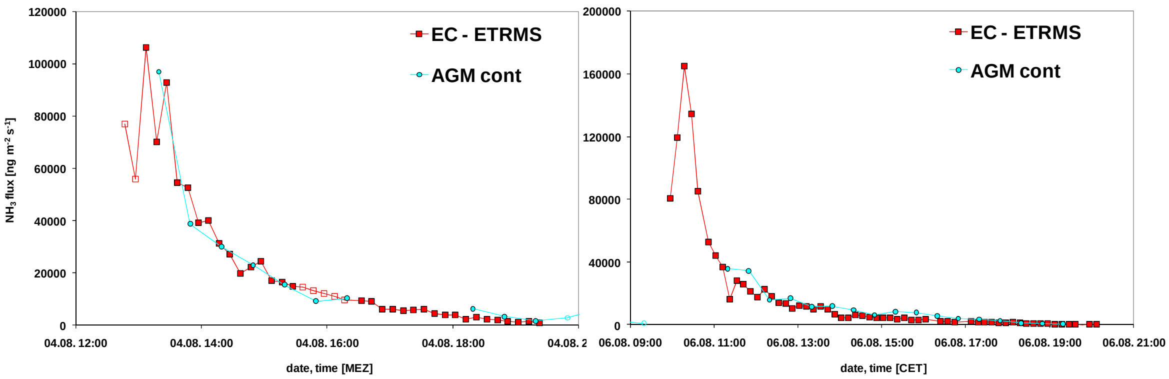

Fig. 2: Comparison of ammonia fluxes as measured by eddy covariance and aerodynamic gradient methods.

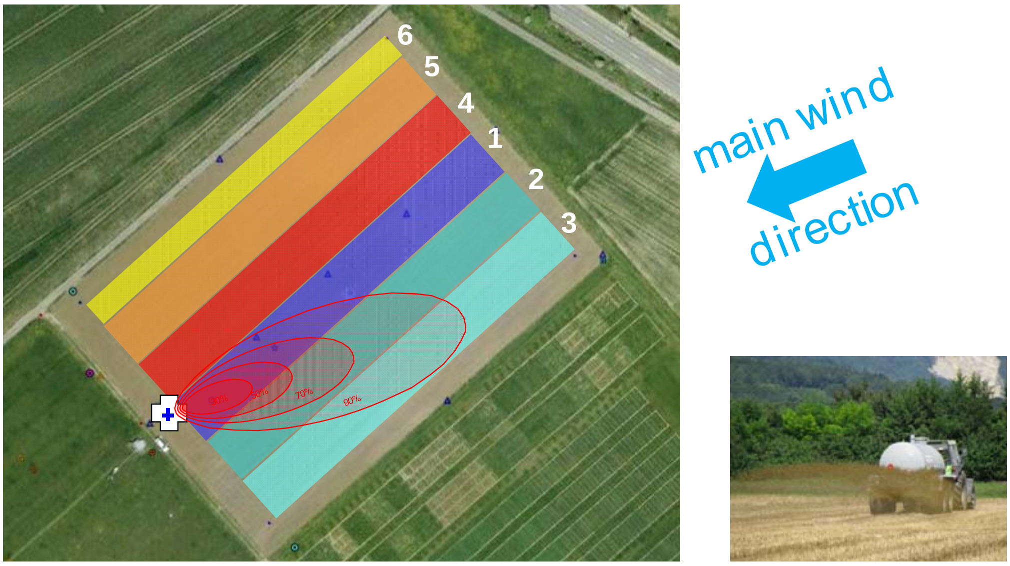

Fig. 3: Application of liquid cattle slurry on Aug-4 by sequential spreading of six tanks (tracks # 1-6) and position of EC system (cross).

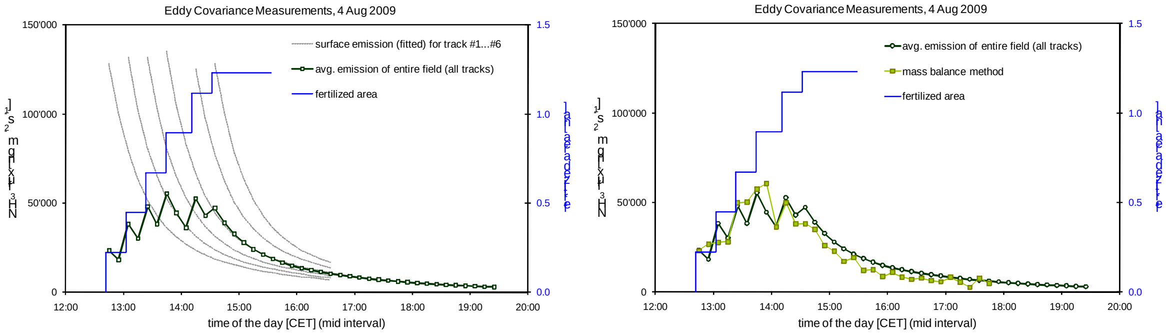

Fig. 4: Determination of the overall fluxes of the entire field; emissions of individual slurry tracks (left) and comparison to open path FTIR-results (right).