J9.4 DETERMINATION OF FIELD SCALE AMMONIA EMISSIONS BY EDDY COVARIANCE USING CHEMICAL IONIZATION MASS SPECTROMETRY

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1. INTRODUCTION

Emissions of ammonia (NH_3) into the atmosphere from agricultural sources strongly contribute to the effects of excess reactive nitrogen in the environment including causing degradation of biodiversity, detrimental effects on air, soil, and water quality, contributions to global warming, and impacts on human health (Galloway et al., 2003; Erisman et al., 2007; Erisman et al., 2011). Emissions from slurry applied to agricultural fields are accounted for about 30% to 50% of the agricultural NH_3 release (Reidy et al., 2008b,a; Jarvis et al., 2011; Leip et al., 2011).
Over the years a variety of methods has been applied for NH_3 flux measurements reflecting the instrumental state-of-the-art and/or constraints for methodological simplicity (Sintermann, 2011). Most common approaches include wind tunnel measurements, the Integrated Horizontal Flux (IHF) and ZINST methods, Dispersion Modelling (DiM), the Aerodynamic Gradient Method (AGM), and recently the Eddy Covariance technique (EC). The scales for which these flux measurements are representative differ for the various methods and characterise their applicability and experimental framework.

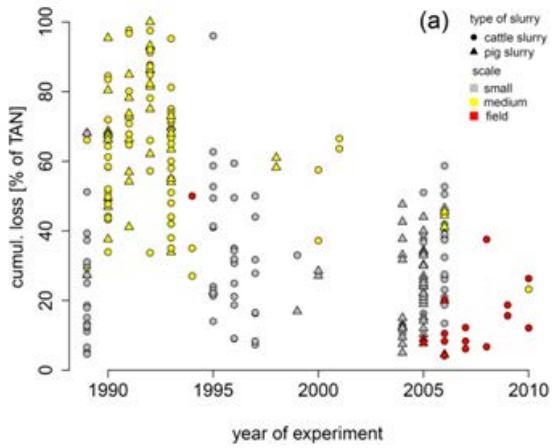

Figure 1: Reported NH_3 EFs for splash plate application plotted vs. the year of measurement. Circles show trials using cattle slurry and triangles represent pig slurry trials. A colour code is used for three classes of measurement plot scale (Sintermann et al., 2012).

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Wind tunnels apply to a small scale (square metre), IHF and ZINST to medium scale (mostly circles with radius ~25 m), and AGM and EC to the field scale, while DiM can be applied from medium to large scale (Sintermann et al., 2012).

2. PUBLISHED EMISSION VALUES

The volatilisation of NH_3 after slurry application may depend on environmental (e.g. soil, vegetation), meteorological (e.g. air temperature, horizontal transport and vertical mixing, humidity, rain), and slurry characteristics (e.g. TAN: total ammoniacal nitrogen, pH, DM: dry matter content). The total NH_3 loss to the atmosphere is usually quantified as the so-called emission factor (EF), i.e. the ratio (in %) of cumulated NH_3 emission to the applied TAN. Measured emission factors (for slurry spread by splash plate) collected from the literature scatter between almost zero and 100% loss (fig.1). Classifying these EFs shows a systematic difference in the emission levels determined by small, medium and large scale approaches, where medium scale techniques have measured largest EFs and field scale techniques have measured EFs in the lower range (Sintermann et al., 2012). Common empirical models for NH_3 emissions from slurry spreading (e.g. Menzi et al., 1998; Søgaard et al., 2002), mostly derived from the older medium scale experiments, can–to a certain degree–explain the variability introduced by environmental and slurry conditions but, compared to the recent (field scale) measure-ments, also exhibit a systematic overestimation (fig.2).

3. SOME ASPECTS OF EMISSION FLUX MEASUREMENTS

A major challenge in constraining representative emission values for distinct fertilised areas with methods theoretically relying on an infinite, homogeneous fetch (AGM, EC) is to account for flux divergence due to horizontal concentration gradients (fig.3). In contrast, IHF and ZINST make use of a limited upwind extent of the emission source (usually around 25 m) and dispersion modelling inherently relates measured concentrations to confined emission areas. Consequently, IHF and ZINST can only be applied to confined plots, while AGM and EC need to be corrected for the flux divergence by footprint analysis (Schmid, 2002; Neftel et al., 2008; Loubet et al., 2009).

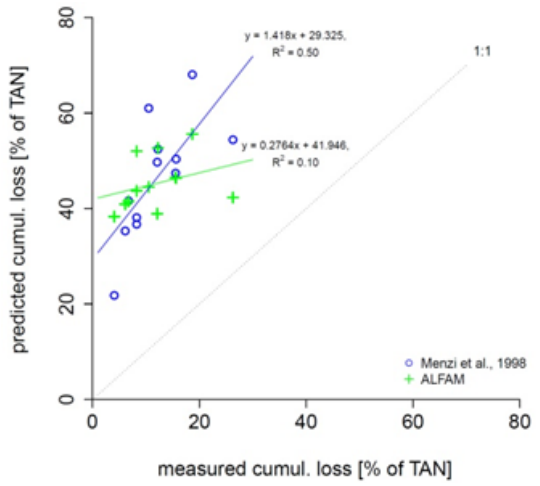

Figure 2: Predicted vs. measured cumulated NH_3 loss (emission factors) using the empirical models described by Søgaard et al. (2002: ALFAM) and by Menzi et al. (1998) for predictions (see Sintermann et al., 2012).

The EC approach (e.g. Baldocchi et al., 1988), the preferred micrometeorological flux measurement technique for measuring trace gas exchange, has been rarely conducted for NH_3 fluxes in the past. Because of the tendency of NH_3 molecules to strongly bind to surfaces of instrumentation and tubing used in their determination (Ellis et al., 2010, von Bobrutzki et al., 2010), EC flux measurements, usually requiring a high measurement time resolution of below 1 s, are very challenging (see Sintermann, 2011) and had not been satisfyingly validated for NH_3 emissions in the past (Whitehead et al., 2008).

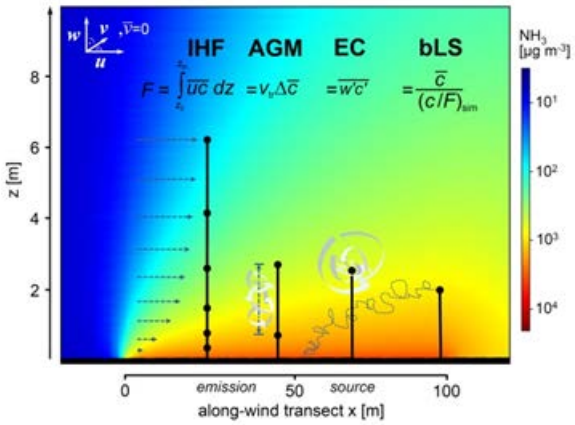

Figure 3: Vertical NH_3 concentration profile along-wind a transect through a strongly NH_3 emitting (200 µg m^{-2} s^{-1}) field (indicated by x-axis), surrounded by two non-emitting areas; different micrometeorological flux techniques; black circles represent NH_3 concentration measurements; for IHF and bLS, *c* denotes the measured concentration in excess of the upwind background concentration at *x*<0 m).
Displayed NH_3 concentrations were calculated using bLS (Flesch et al., 1995) with U = 3.5m s^{-1}, u_* = 0.4 m s^{-1}, z_0 = 0.023 m, L = −10 m (Sintermann, 2011).

4. DETERMINATION OF FIELD SCALE NH_3 EMISSIONS USING EDDY COVARIANCE

The potential for making fast NH_3 measurements by instrumental adaptation of Chemical Ionisation Mass Spectrometry (CIMS) in order to apply the EC technique for NH_3 has been shown by Sintermann et al. (2011b). Based on a commercial PTR-MS (Hansel et al., 1995; Lindinger et al., 1998), applied with electron transfer ionisation of sample gas compounds (Norman et al., 2007) and altered inlet- and drift tube versions (PEEK), the instrument can measure NH_3 on-line with, in principle, high time resolution. By strongly heating instrumental parts (hence: H(igh)T(emperature)-CIMS) and a long inlet tube to 180/150 °C NH_3 wall effects were decreased and a time response of ~1 s was achieved making EC measurements (termed EC/HT-CIMS) possible. With this approach, field scale NH_3 emissions following slurry spreading were determined by inclusion of detailed flux footprint analysis. The results were inter-compared to those of an independent micrometeorological backward Lagrangian Stochastic (bLS) dispersion method (Flesch et al., 1995) using open path Fourier Transform Infrared (FTIR) measurements.

In two experiments, NH_3 emissions from slurry applied to both an arable and a grassland site (details see Sintermann et al., 2011a) were determined by field scale flux measurements based on (i) EC/HT-CIMS with EC flux footprint analysis to account for the influence of advection from distinct slurry fertilisation tracks and unfertilised areas, and (ii) backward Lagrangian Stochastic dispersion modelling using Fourier Transform Infrared measurements (bLS/FTIR). This was accompanied by wet chemical impinger (acid trap) sampling coupled with off-line analysis, expected to represent a reliable NH_3 concentration determination.

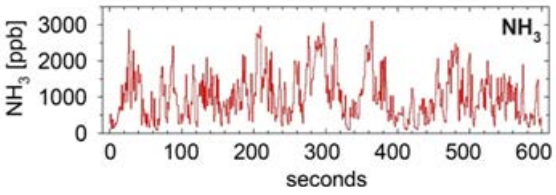

Figure 4: Exemplary 20 Hz time series NH_3 obtained by HT-CIMS measurements on 4 August 2009, 13:20–13:30 (Sintermann et al., 2011b).

After field-application of slurry, the HT-CIMS captured very high NH_3 concentration fluctuations over 3 orders of magnitude up to about 3 ppm (fig.4). The overall high-frequency EC flux attenuation (20% to 40%) was empirically quantified, based on comparison of the ogives (Ammann et al., 2006) of the raw NH_3 and sensible heat flux, and was parameterised by wind speed establishing proper EC/HT-CIMS flux correction. Detailed EC flux

footprint analysis (Neftel et al., 2002) enabled to parameterise NH_3 emissions (fig.5) from distinct fertilisation tracks using a bi-exponential time dependence. This yielded high spatial and temporal resolution of emissions from the entire field.

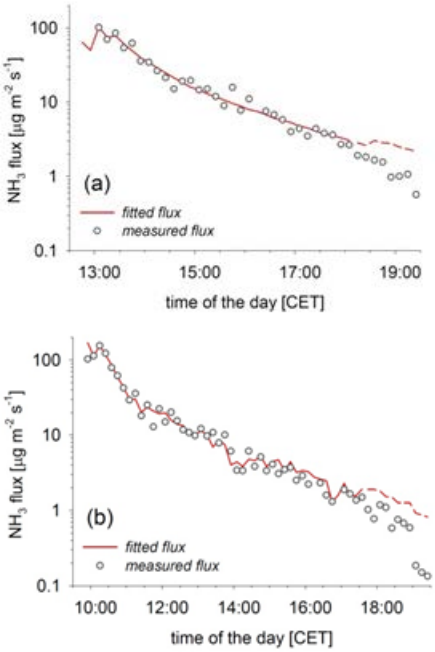

Figure 5: EC NH_3 fluxes measured and parameterised (fitted) on (a) 4 August 2009 and (b) 6 August 2009 (Sintermann et al., 2011a).

Results show that the first 2 to 3 hours after beginning fertilisation contributed to more than 3/4 of the overall NH_3 loss. Comparison of EC/HT-CIMS results with the impinger measurements suggested an accuracy of the EC/HT-CIMS measurement of ~10% for both experiments. Somewhat larger deviations were found for bLS/FTIR. Averaged over both approaches, 17±3% of applied TAN was volatised over the cropland and 16±3% over the grassland field (Sintermann et al., 2011a).

The presented EFs from recent field scale measurements are significantly lower (see also Spirig et al., 2010) than the general European EF proposed by EMEP/EEA (55%; EEA, 2009), as well as empirical model predictions, where the models are based on older measurements mainly over medium sized plots. An analysis (Monte-Carlo type, using meteorological and slurry parameter) of derived initial emissions suggests plausibility of the presented fluxes (Sintermann et al., 2011a). The same analysis indicates overestimation by at least some of the medium scale IHF and ZINST measurements (Menzi et al., 1998; Huijsman et al., 2001) although an assessment of the methodologies does not suggest any severe bias towards overestimation (Sintermann et al., 2012).

5. CONCLUSIONS

Validated EC measurements of NH_3 emissions from field application of slurry have, for the first time, given accurate emissions on the field scale. Recent EFs determined by field scale approaches (AGM and EC) seem to yield lower values than older medium plot scale results. Consequently, the EMEP/EEA EF of 55% possibly overestimates such emissions. Potential methodological biases in the earlier approaches might only partly explain the observed discrepancy, reflecting the ongoing need for more accurate, validated emission measurements under realistic conditions.

Acknowledgements

For funding our work we gratefully thank the Swiss Federal Office for the Environment (FOEN) for the support through the contract 09.0084.PJ / K233-1881, the Swiss National Science Foundation (TERMS, 200021-117686/1) and the EU project NitroEurope (Contract 017841) that is funded under the EC 6th Framework Programme for Research and Technological development.

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