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Calibration of a simple method for determining ammonia volatilization in the field – comparative measurements in Henan Province, China

Andreas Pacholski[1,]*, Guixin Cai[2], Rolf Nieder[3], Jörg Richter[3], Xiaohui Fan[2], Zhaoliang Zhu[2] and Marco Roelcke[3]

*[1]Institute of Crop Science and Plant Breeding, Agronomy and Crop Science Department, Christian-Albrechts-University of Kiel, Hermann-Rodewald-Str. 9, 24118, Kiel, Germany; [2]Institute of Soil Science, Chinese Academy of Sciences, Beijing East Road 71, 210008, Nanjing, P.R. China; [3]Institute of Geoecology, Braunschweig Technical University, Langer Kamp 19c, 38106, Braunschweig, Germany; *Author for correspondence (e-mail: Pacholski@pflanzenbau.uni-kiel.de; fax: +49-431-8801396)*

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Abstract

The determination of ammonia volatilization with sufficient spatial and temporal resolution requires a simple and versatile *in situ* measurement technique, particularly in developing countries. Therefore, a simple chamber method for determining ammonia (NH_3) volatilization in the field (Dräger-Tube Method; DTM) was calibrated by comparison with simultaneous measurements with a micrometeorological Integrated Horizontal Flux (IHF) method. Five field experiments were conducted following urea fertilization on summer maize and winter wheat plots (1998–1999) at Fengqiu Experimental Station, Central China. The simplicity of the chamber method allowed for measurements to be carried out by trained farmers. The measurements with both methods yielded very similar patterns of NH_3 fluxes and similar differences between fertilization treatments. Cumulative NH_3 losses determined by the IHF method ranged from 14.6 to 47.9% and from 0.6 to 17.9% of urea-N applied for surface broadcast and incorporated fertilization, respectively. As expected, cumulated NH_3 losses were underestimated by the DTM as compared to the IHF by about one order of magnitude. A calibration equation was calculated by multiple linear regression which included NH_3 flux data as well as temperature and wind speed values. The calibration model yielded a modelling efficiency c^2 of 0.86 resulting in an average estimation error of cumulative NH_3 losses of 17%. The equation was validated by comparison of IHF measurements and DTM fluxes not considered in the derivation of the calibration formula. The calibration approach can be used under similar meteorological and field conditions irrespective of the soil characteristics or type of N fertilizer applied.

Introduction

The anthropogenic emission of NH_3 entails several negative effects on the environment, such as direct damage to vegetation (Fangmeier et al. 1994; Krupa 2003), water and soil acidification and increased nitrogen (N) supply to natural areas (eutrophication) (ECETOC 1994). In the US, ammonium sulphate derived from emitted NH_3 is the major source of $PM_{2,5}$-particles (particulate matter that is 2.5 μm or smaller in size) in the atmosphere which are very harmful to the human respiratory system (Anderson et al. 2003). Ammonium sulphate particles are also transported over much greater distances than gaseous ammonia (Asman et al. 1998). Although first measures have been taken for the reduction of NH_3 losses, mainly from animal husbandry in Europe (Kirchmann et al. 1998; Sutton et al. 1998), NH_3 emissions are and will remain an important environmental issue for the future (Galloway et al. 2004), particularly in China (Bouwman et al. 2005).

Ammonia volatilization from soils and crop stands is usually measured by micrometeorological methods (Denmead 1983; McInnes et al. 1985; Denmead and Raupach 1993; Mannheim et al. 1995; Génermont et al. 1996; Cai 1997; Denmead et al. 1998). Simplified micrometeorological methods such as that by Leuning et al. (1985), which was also applied in this study, have been established as standard methods for the measurement of NH_3 losses in the field for agronomic purposes.

However, most of the micrometeorological methods require in-field current supply, adjacent laboratories and comparatively large homogeneous fields. All these preconditions cannot be fulfilled by most countryside situations, particularly in developing countries such as China. Recent NH_3 emission inventories showed the importance of determining emissions on a sub-annual level and a spatial resolution higher than the national level (Goebes et al. 2003). Although NH_3 losses after N fertilization have been determined in several Chinese agro-ecosystems (e.g. Cai et al. 1992, 1995, 1998; Roelcke et al. 2002), an investigation of NH_3 losses which copes with the variability of Chinese agroecosystems requires simple and versatile measurement methods such as chamber methods. This also applies to many other agricultural regions in developing countries.

Chamber methods have been mainly applied for carrying out systematic laboratory and *in situ* experiments. Because of their inherent properties, it is difficult to use them for the determination of NH_3 loss data under undisturbed conditions. Major restrictions comprise the controlling of air exchange rates in the chambers, temperature and plant cover effects. However, if applied carefully and if measurements can be calibrated by comparison with known true flux values, chamber methods can also provide reliable ammonia loss estimates (Svensson 1997; Vandré and Kaupenjohann 1998; Sommer et al. 2001).

The aim of this study is the calibration of the 'Dräger-Tube Method' (DTM) (Roelcke 1994; Roelcke et al. 2002) which was used as a chamber method for the *in situ* comparison of ammonia volatilization. The method consists of four connected conical chambers through which ambient air is drawn by means of a hand pump. Ammonia concentrations are instantly displayed by Dräger NH_3 indicator tubes. The main advantages of the DTM compared to other *in situ* chamber methods consist in its high simplicity requiring neither current supply nor laboratory equipment, and in its reduction of the disturbance of the study site and of environmental conditions to a minimum. However, due to low air exchange rates in the chambers actual volatilization losses are underestimated by about one order of magnitude.

Roelcke (1994) and Roelcke et al. (2002) have used the method for the comparison of NH_3 volatilization from N fertilizers in the Loess Plateau of China. Comparisons with laboratory measurements and ^{15}N field studies using the same treatments (Rees et al. 1997) showed that the DTM could be successfully used for the qualitative comparison of fertilization treatments and resulting NH_3 flux patterns, whereas the actual fluxes were strongly underestimated (Roelcke et al. 2002). This error could be corrected, e.g. by means of a calibration formula derived from simultaneous measurements with a valid micrometeorological method. In this study, a calibration formula sufficient for agronomic purposes shall be derived by relating the DTM measurement results to actual NH_3 fluxes approximated by micrometeorological measurements (Integrated Horizontal Flux (IHF) method, Leuning et al. 1985).

Materials and methods

Experimental site

The experiments were carried out on farmers' fields (Tunli village) adjacent to the Fengqiu Agro-ecological Experimental Station, Chinese Academy of Sciences, in Fengqiu County, Henan Province

(35°1′ N, 114°4′ E). It is located in the North China Alluvial Plain (Huang-Huai-Hai-Plain). The location is characterized by a sub-humid climate with a mean annual temperature of 14 °C and a mean annual precipitation of 615 mm. The groundwater table varies from 2 to 4 m below the soil surface.

Soil properties

The soil type is classified as an Ochric Aquic Cambisol (US Soil Taxonomy) or a Calcaric Fluvisol (FAO). The texture of the plough layer (0–0.2 m) is a sandy loam. The deeper soil layers consist of a multitude of clay and silt layers, some millimetres to several centimetres thick. Table 1 gives soil properties of the plough layers of the study sites. The top soils are low in C_{org}, and CEC_{pot} is also comparatively low. The mean pH (H_2O) of the soil is 8.5.

Agricultural management

The agriculture in the region is characterized by an annual double-cropping system of winter wheat (*Triticum aestivum* L.) – summer maize (*Zea mays* L.). Both main crops are irrigated by flood irrigation. In recent years on average 180–220 kg of chemical fertilizer N ha^{-1} have been applied to winter wheat and maize, respectively. Nitrogen fertilizer (as urea or ammonium bicarbonate) to winter wheat is applied either as basal dressing or topdressing. The fertilizer application method for basal dressing is uniformly mixing the fertilizer with the soil at ploughing, for topdressing fertilization is immediately followed by flood irrigation. Nitrogen fertilizer is applied to maize in one or two doses either by surface fertilization followed by irrigation or by 'deep point placement'. The latter method comprises the placement of about one spoonful of urea in a hole of about 5 cm depth to every second maize plant in the row which is subsequently covered with soil. Surface broadcasting of urea can be considered as an exception.

Experimental design

Five field experiments with urea application followed by measurements of NH_3 volatilization were undertaken altogether in the years 1998–1999 (Table 2). Each experiment included two treatments applied to two circular sample areas about 100 m apart from each other surrounded by unfertilized field. Each circular measurement area (radius 12.5 m, area 491 m^2) was equipped with an IHF measurement pole in the centre. The sample areas also contained two microplots of 4 m^2 (2 m × 2 m), for the measurements with the Dräger-Tube Method. Another microplot and measurement pole were set up in the surrounding unfertilized fields for the measurement of background NH_3 concentrations. The axis connecting the centres of both sampling areas was orthogonal to the main wind direction, in order to minimize the influence of the NH_3 emitted from one sampling area on the other (Figure 1). Fertilization rates and fertilizer application techniques were carried out in accordance with common practice in Fengqiu. In addition to these application methods each experiment also comprised a surface broadcast application treatment, using the same amounts of N fertilizer as in the incorporation treatment (Table 2). It has been shown in many field experiments that NH_3 volatilization losses from urea are higher following surface broadcasting as compared to other application methods. Thus a wider range of NH_3 fluxes would be available for the calibration of the DTM.

The experimental sites were irrigated by simple flood irrigation according to local practice, normally immediately after fertilizer application. In case of surface broadcast application of urea,

Table 1. Soil properties in Fengqiu study sites (surface soil 0–0.2 m).

Experimental site	pH(H_2O)	C_{org} (%)	P available (mg kg^{-1})	K available (mg kg^{-1})	N total (%)	CEC_{pot} ($mmol_c$ kg^{-1})
Maize (surface broadcast)	8.36	0.56	3.00	66.3	0.0601	73.3
Maize (deep point placement)	8.79	0.64	4.29	72.5	0.0659	80.3
Wheat (surface broadcast)	8.47	0.47	26.01	75.0	0.0520	80.9
Wheat (mixed incorporation)	8.69	0.48	3.29	62.5	0.0576	72.0

Table 2. Field experiments and treatments carried out at Fengqiu Agroecological Experimental Station, China (1998–1999) for the comparative measurement of NH_3 fluxes.

No.	Date	Crop/growth stage	Application rate (kg urea-N ha^{-1})	Application method	Irrigation (mm)
1	29 June–07 July 1998	Maize (seedling stage, 0.4 m)	75	a. Surface broadcast (SB) b. Fertilisation followed by irrigation (BI)	40–60
2	19–30 July 1998	Maize (10-leaf-stage, 1.2 m)	200	a. Surface broadcast (SB) b. Deep point placement (DP)	40–60
3	11–23 October 1998	Winter wheat (fertilization before/at sowing)	120	a. Surface broadcast (SB) b. Mixed fertilization (MF)	–
4	09–24 March 1999	Winter wheat (spring treatment)	100	a. Surface broadcast (SB) b. Fertilization followed by irrigation (BI)	40 – 60
5	12–24 July 1999	Maize (6-leaf-stage, 0.8 m)	150	a. Surface broadcast (SB) b. Deep point placement (DP)	–

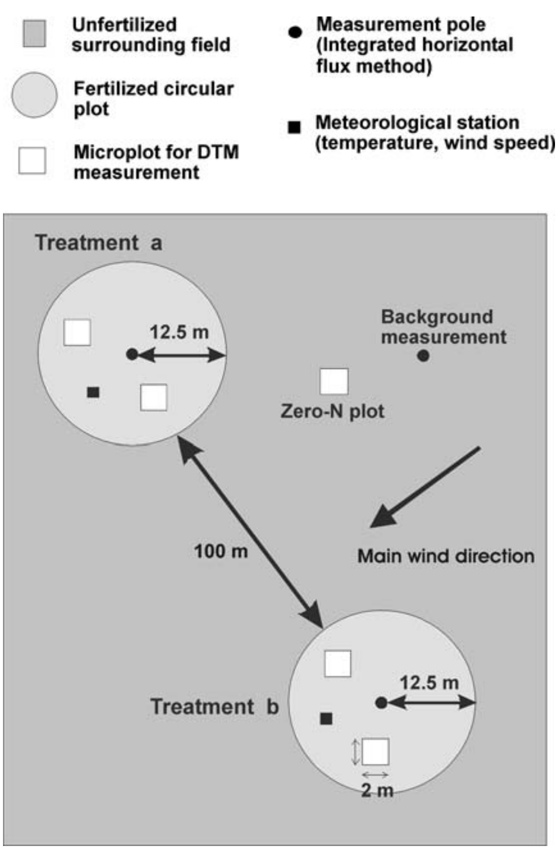

Figure 1. Set-up of field trials at Fengqiu Experimental Station, China (1998–1999).

irrigation water was applied 1 day before the start of the experiment, to avoid excessive moisture on the soil surface. Fertilizer was applied by hand.

Meteorological measurements

The instrumentation of the meteorological measurement poles consisted of two cup anemometers THIES optoelectronic (aluminium) and THIES compact (synthetic material, THIES, Germany) and two resistance temperature sensors (PT 1000 soil temperature sensor, PT 100 radiation protected temperature sensor). For the duration of the whole experiment the sensors were connected to a data logger (WILOG306, Wilmers Messtechnik Hamburg, Germany) which recorded 10-min average values as output data. The meteorological stations were put downwind of the IHF measurement poles – according to the main wind direction – in order to avoid perturbance of NH_3 measurement.

NH_3 measurements

Dräger-Tube Method (DTM)
The Dräger-Tube Method was developed by Richter (1972) for the measurement of CO_2 evolution from soil and was adapted for the measurement of NH_3 volatilization in arable soils following mineral N fertilization (Roelcke 1994; Roelcke et al. 2002). It can be described as a special variant of the dynamic chamber methods. Ambient air is sucked through four chambers (total area 415 cm^2, 104 cm^2 each) by means of a hand pump (Drägerwerk AG, Lübeck, Germany). The volume of each chamber is 370 cm^3. The air is enriched with NH_3 volatilizing from the soil surface. The

pump rate is about 1 l min^{-1}, corresponding to an air exchange rate of approximately 1 vol. min^{-1}. The air is then led through Teflon tubing to an NH_3 sensitive Dräger gas analysis detector tube (Drägerwerk AG, Lübeck, Germany) which immediately displays the NH_3 concentration (in volume ppm) (Figure 2). Ammonia fluxes were calculated according to Equation 1. The pumping rate was determined by the volume of pump strokes (100 ml $stroke^{-1}$) and the time period used for pumping measured with a stop watch. The NH_3 volume concentration values displayed on the Dräger-Tubes were corrected by a factor for the barometric air pressure and air temperature. Because of the way of NH_3 enrichment involved and the limited sensitivity of the Dräger NH_3 indicator tubes employed (>0.025 vol. ppm NH_3), only fluxes higher than the quasi-natural NH_3 efflux close to the soil surface can be detected using this method.

$$F_{N_g} = \text{volume} \cdot |\text{conc.}| \cdot 10^{-6} \cdot \rho_{NH_3} \cdot U_N \cdot U_F \cdot U_Z \quad (1)$$

where F_{N_g} is NH_3 flux (mg N m^{-2} h^{-1}); volume is air volume sucked through the chambers (l); | conc.|: value of NH_3 vol. concentration (volume-ppm); ρ_{NH_3} is temperature-dependent density of NH_3 (mg l^{-1}); U_N is molecular weight conversion factor of NH_3 to N; U_F is surface area conversion factor (m^{-2}); U_Z is time conversion factor (h^{-1}).

A single measurement took about 3 min. altogether. The timing of measurement was chosen taking into consideration the diurnal variation in NH_3 emissions, i.e. low NH_3 fluxes at night time and high fluxes at about noon. Cumulative NH_3 losses from the soils were calculated by linear interpolation between the NH_3 fluxes measured at two subsequent sampling events. According to the intensity of the NH_3 volatilization process, 2–5 measurements were carried out per day with 2–3 replicates on each measurement plot. Ammonia concentration values determined in ambient air and on zero-N plots were subtracted from measured NH_3 concentrations on the treatment plots before calculating the NH_3 fluxes. The readings of the NH_3 concentrations on the Dräger Indicator Tubes have a coefficient of variation between 10–15% as indicated by the manufacturer (Drägerwerk 1994).

Integrated Horizontal Flux Method (IHF)

The IHF method by Leuning et al. (1985), further modified by Sherlock et al. (1989), was used as the micrometeorological reference method for the calibration of the DTM. Passive NH_3 flux samplers, i.e. samplers through which the air is led by natural forces (wind) and without technical equipment (e.g. pumping), were mounted to a measurement pole 0.4 m, 0.8 m, 1.2 m, 1.6 m and 2 m above ground in the centre of the circular plots in the study site (Figure 1). Fins at the rear end

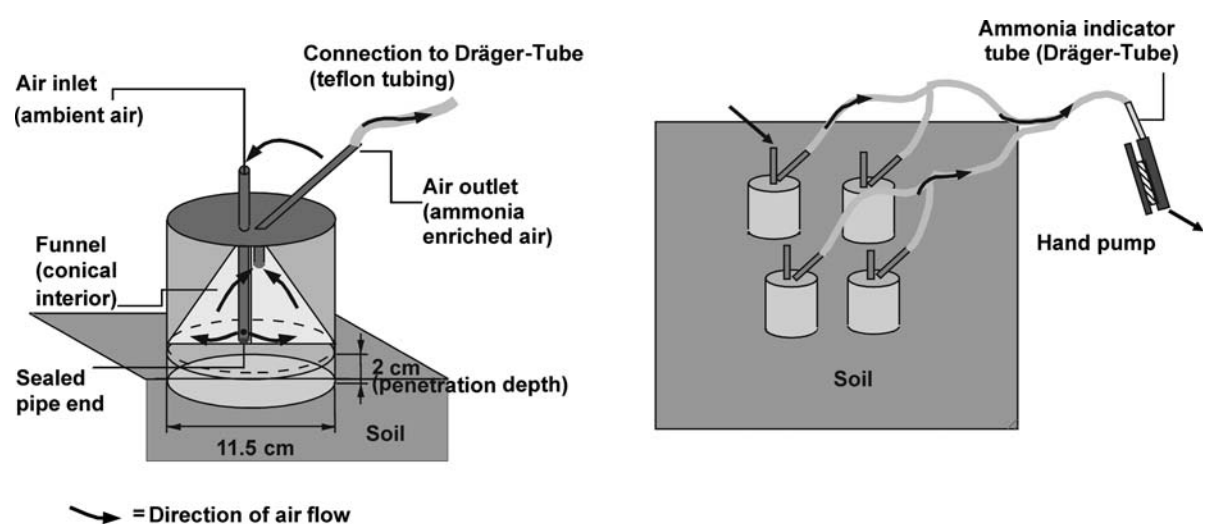

Figure 2. Experimental set-up of the Dräger-Tube Method applied with a hand pump.

kept the samplers aligned with the wind whenever the wind changed its direction. The duration of each sampling period depended on the intensity of the NH_3 volatilization process. In case of high NH_3 fluxes the samplers were exchanged 2–3 times a day. In line with decreasing NH_3 concentrations in the air sampling periods were extended to 1–2 days. After thoroughly rinsing the samplers with distilled water, ammonia concentrations in the extracts were measured with an ORION ammonia electrode (USA) and a millivolt meter.

Calibration approach

The low air exchange rate in the chambers (approx. 1 exchange vol. min^{-1}) was considered as the main reason for the underestimation of NH_3 losses by the DTM in previous studies (Roelcke et al. 2002). The air exchange rate in the DTM chambers is much lower than the air exchange rates at the soil surface induced by commonly prevailing ambient wind speeds. However, ambient wind speeds are quite variable in the course of an experimental period. Thus, constant high air exchange rates (15–20 vol. min^{-1}) in the chambers as used by other scientists (Kissel et al. 1977; Roelcke 1994) presumably lead to an overestimation of the NH_3 fluxes. Since it is much simpler to measure ambient wind speeds than to adapt the air exchange rate in a chamber to prevailing wind speeds with an appropriate accuracy, the DTM measurements were calibrated against the fluxes of the IHF method corrected by ambient factors as wind speed and temperature.

For each measuring event, mean fluxes measured by the DTM on both microplots were used. Several DTM NH_3 measurements were carried out during one IHF sampling interval. In order to compare the two different kinds of fluxes measured, time weighted means of the mean DTM fluxes were calculated on the basis of the single IHF sampling intervals. Average DTM fluxes were calculated according to Equation 2

$$\overline{F_{N_g}} = \sum_{i=1}^{i} w_i \cdot F_{\overline{N_g}} i, \qquad (2)$$

where

$$w_i = \frac{t_i}{t_{tot}};$$

$\overline{F_{N_g}}$ is DTM NH_3 flux time weighted average values for single IHF measurement interval (mg N m^{-2} h^{-1}); $F_{\overline{N_{g_i}}}$ is mean NH_3 flux of two DTM measurements for the time interval (i) between the two measurements (mg N m^{-2} h^{-1}); w_i is weighing factor ($0 < w_i \leq 1$, $\sum_{i=1}^{i} w_i = 1$); t_i is time interval (i) between two DTM measurements within the single IHF sampling interval t_{tot} (h); t_{tot} is time interval of single IHF sampling (h).

Mean values based on IHF sampling periods were also calculated for the meteorological data. The relationships between the fluxes measured with DTM and IHF as well as between NH_3 fluxes and field variables were examined by means of stepwise multiple linear regression (backward estimation). Weighted means of NH_3 fluxes from the DTM, fluxes from the IHF method, wind speeds at 2 m and 0.2 m height as well as soil and air temperatures were included for the derivation of the calibration formula. As a first step the multiple linear regression with intercept was applied for the estimation of the regression parameters. In cases when the regression analyses yielded no significant estimate for the *y*-axis intercept, a modified regression model without estimate for the intercept was applied. For this kind of model the coefficients of determination (R^2) are not comparable to the models estimated with intercept. Therefore the 'modelling efficiency c^2', (Equation 3) (Loage and Green 1991) was chosen for the comparison of the parameter estimates

$$c^2 = \frac{\left(\sum_{i=1}^{n}(O_i - \overline{O})^2 - \sum_{i=1}^{n}(P_i - O_i)^2\right)}{\sum_{i=1}^{n}(O_i - \overline{O})^2} \qquad (3)$$

where c^2 is modelling efficiency ($c^2 \leq 1$); P_i is i^{th} value predicted by the model; O_i is i^{th} observed value; $\overline{O}$ is mean value of observations.

The parameter c^2 reflects the portion of the variance of the observations which can be explained by the values predicted by the model. The values for R^2 and c^2 are identical when the model includes the intercept parameter.

Surface soil sampling and calculation of NH_3 partial pressure

As the DTM determines NH_3 fluxes at a constant, low air exchange rate close to the soil surface, hypothetically, NH_3 fluxes measured by the DTM should be closely related to the concentration of gaseous NH_3 in the atmospheric layer bordering the soil surface which is the driving force of NH_3 volatilization (Freney et al. 1983). The above given hypothesis can be tested by examining the relationship of NH_3 partial pressure at the soil surface and NH_3 fluxes determined by the DTM.

Surface soil samples (0–3 mm depth, diameter 10 mm) were taken with a micro-auger constructed at the Institute of Food and Land Resources, University of Melbourne, for the determination of mineral N contents, urea content, pH values and water contents. During each experiment, usually once a day before noon, hundreds of surface soil samples (0.25 cm^3 each) were taken randomly inside the circular plots and bulked to a mixed sample. Urea contents in the soil were determined after extraction with 1 M KCl (soil/solution ratio 1:4) solution containing 10 mg l^{-1} phenyl mercuric acetate (PMA) as urease inhibitor. NH_4^+-concentrations in the extracts were determined by continuous-flow analysis (SKALAR analytic, The Netherlands). In addition to mineral N contents, gravimetric water content (24 h at 105 °C) and pH (H_2O) (soil/solution ratio 1:2.5) were determined in the samples.

Ammonia partial pressure at the soil surface was calculated on the basis of soil pH, soil temperature and total ammoniacal nitrogen content (TAN, NH_3-N + NH_4^+-N) values (Denmead et al. 1982). An NH_4^+ adsorption isotherm was determined in the laboratory in order to be able to describe the partitioning of NH_4^+ between the sorbed phase on the soil matrix and the soil solution. Soil solution TAN concentrations were iteratively calculated on the basis of total NH_4^+ (sorbed and in liquid phase) and soil moisture contents. Soil temperatures (−0.05 m depth) were taken from continuous measurements in the study sites.

Statistical analysis

The data were tested for normal distribution applying the Kolmogorov–Smirnov test (significance level $P < 0.05$) (Lilliefors 1967). The experimental data were analysed with SPSS (10.0.7) statistics software for statistical testing (*t*-test), regression (linear regression, stepwise multiple linear regression) and correlation analysis (Pearson, Spearman–Rank). Fitting analyses were carried out using the Origin 4.1 software package. The numerical calculation of NH_4^+ contents in the aqueous solution from total NH_4^+ contents in soil was obtained from the Solver-routine included in the EXCEL software-package.

Results

Example experiments

Figure 3 (a–f) presents the results of experiment No. 5a, maize, July 1999, surface broadcast treatment (150 kg N ha^{-1}). As expected, the magnitude of the fluxes measured by the two methods differed by a factor of about 10, with total cumulative NH_3 losses determined by the IHF amounting to 38.2 kg N ha^{-1} while the DTM measured a total cumulative loss of 2.8 kg N ha^{-1} (Figure 3d, f). Ammonia fluxes measured by both IHF and DTM methods show that the start of NH_3 volatilization was slightly retarded due to 4.6 mm of rainfall on the first day of the experiment (Figure 3c, e). The highest fluxes were measured on the second day of the experiment and continuously decreased until the end of the measurements. The replicate DTM measurements showed a very good agreement (Figure 3f). The only striking difference between the flux patterns of the two methods lay in the stronger decrease of DTM NH_3 fluxes during the last days of the measurements compared to the IHF results (Figure 3d, f). In general the time courses and patterns of the fluxes determined by both methods agreed very well (Figure 3c, e). This was also proven by fitting a sigmoidal function to the time courses of the cumulated fluxes which yielded the same parameters for the rate constants and the time of maximum NH_3 loss for both methods (Pacholski 2003).

This experiment was similar to experiment No. 2a carried out in July 1998 with maize and surface broadcast treatment with a higher fertilization rate of 200 kg N ha^{-1} (Figure 4 a–f). As rainfall was very high prior to the beginning of experiment No. 5, the fields were not irrigated. During the beginning of the 1999 experiment temperatures were considerably lower than in 1998 (see Figures 3b and 4b). Therefore, environmental conditions with regard to NH_3 volatilization were not as

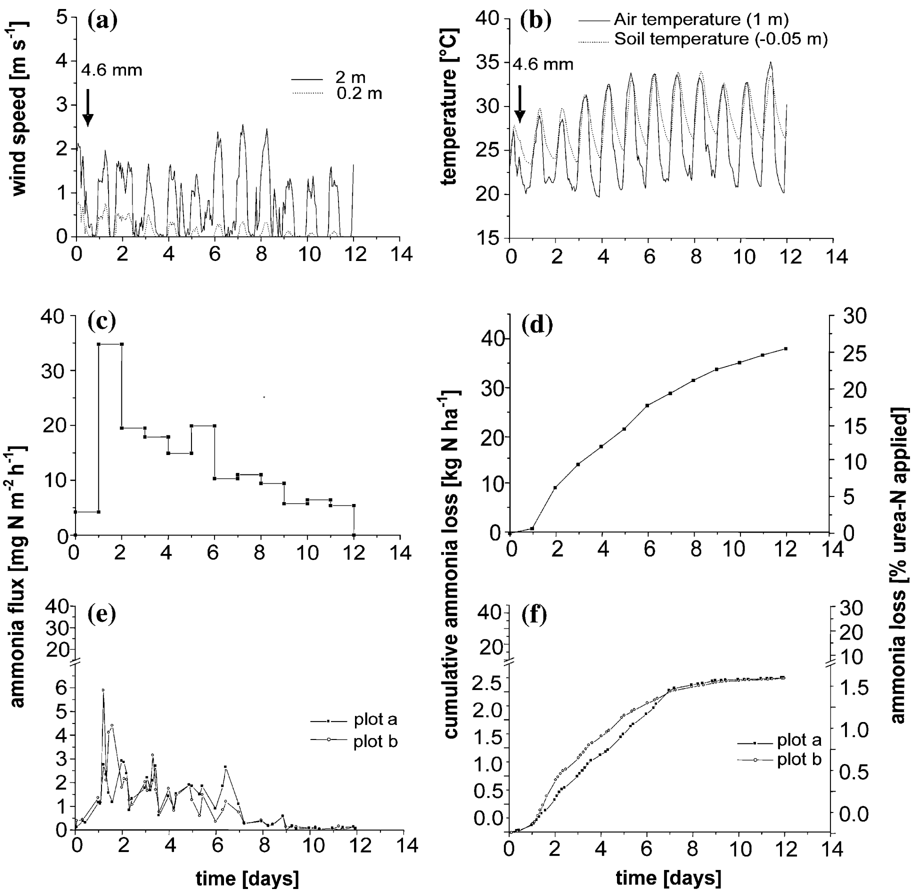

Figure 3. Comparison of Dräger-Tube Method and IHF NH_3 flux measurements at Fengqiu Experimental Station, China (1999), maize experiment 5a, surface broadcast treatment (150 kg N ha^{-1}): (a) wind speed measurements (0.2 and 2 m height), (b) air and soil temperatures (1 m and −0.05 m), (c) IHF NH_3 fluxes, (d) IHF cumulative NH_3 loss, (e) DTM NH_3 fluxes, (f) DTM cumulative NH_3 loss.

favourable in July 1999 as in July 1998. As a consequence and probably also due to the lower application rate, the percentage NH_3 loss in July 1999 was considerably lower than in July 1998. This difference was determined by both methods. While in 1998 a total cumulative NH_3 loss of 47.9 (% urea-N applied) was determined by the IHF method and 7.8 (% urea-N applied) by the DTM, the corresponding losses were only 25 (% urea-N applied) and 1.8 (% urea-N applied) in 1999, respectively (see Table 3).

General comparison of DTM and IHF results

An overview of the NH_3 loss measurement results is given in Table 3. Cumulative NH_3 losses determined by the IHF method ranged from 14.6 to 47.9% of the urea-N applied for surface broadcast application and from 0.6 to 17.9% for incorporated fertilization. The factor between the cumulative NH_3 losses at the end of the experimental periods measured with DTM and IHF given in Table 3 ranged from 6 (experiment 2a) to 27 (experiment 1a). Experiment 1b in June 1998 and experiment 2b in July 1998 were excluded from this comparison due to problems occurring during the experiment. The IHF and the DTM method showed the same qualitative differences between treatments in all experiments, i.e. treatments with higher and lower losses were distinguished by both methods alike. In all experiments NH_3 losses following surface broadcast of urea were several times higher than after incorporation of the fertilizer into the soil (either as deep point placement, fertilization followed by irrigation or mixed

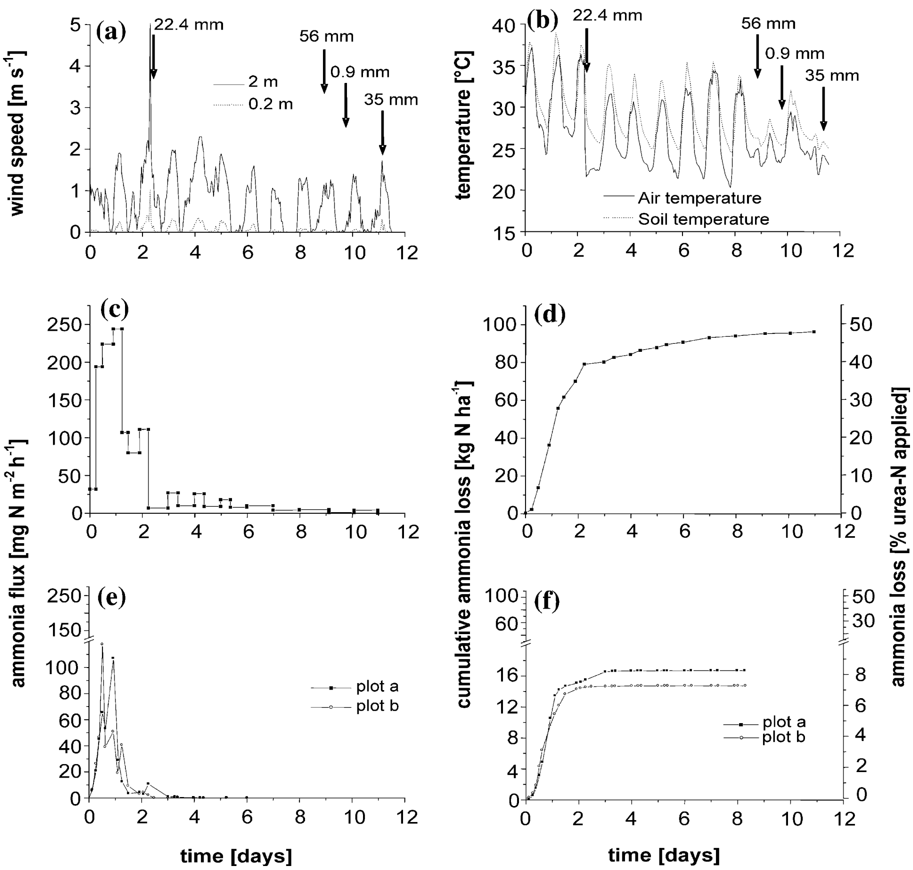

Figure 4. Comparison of Dräger-Tube Method and IHF NH_3 flux measurements at Fengqiu Experimental Station, China (1998), maize experiment 2a, surface broadcast treatment (200 kg N ha^{-1}): (a) wind speed measurements (0.2 and 2 m height), (b) air and soil temperatures (1 m and −0.05 m), (c) IHF NH_3 fluxes, (d) IHF cumulative NH_3 loss, (e) DTM NH_3 fluxes, (f) DTM cumulative NH_3 loss.

Table 3. Summary of cumulative NH_3 losses determined by Dräger-Tube and IHF methods and weather conditions during the 1998–1999 field experiments at Fengqiu Agroecological Experimental Station (DTM values with range of values).

No.	Date	rate (kg N ha^{-1})	Treatment*	Mean wind speed (2 m) (m s^{-1})	Mean wind speed (0.2 m) (m s^{-1})	Mean Air Temp. (°C)	Mean Soil Temp. (°C)	Cumulative ammonia loss (% urea-N applied)	
								DTM (± range)	IHF
1	29 June–07 July 1998	75	a. SB	2.00	0.52	27.0	27.8	1.60 ± 0.2	43.6
			b. FI	2.32	0.62	27.0	27.9	0.06 ± 0.02	17.9
2	19–30 July 1998	200	a. SB	0.76	0.05	26.9	29.0	7.80 ± 0.54	47.9
			b. DP	0.78	0.05	27.0	28.9	0.09 ± 0.02	10.8
3	11–23 October 1998	120	a. SB	1.68	0.95	15.3	17.6	0.80 ± 0.17	19.9
			b. MI	1.63	0.89	15.5	16.8	0.15 ± 0.01	2.3
4	09–24 March 1999	100	a. SB	2.79	0.64	4.7	6.7	1.10 ± 0.58	14.6
			b. FI	2.69	0.46	4.9	7.1	0.09 ± 0.04	0.6
5	12–24 July 1999	150	a. SB	0.76	0.12	25.8	28.3	1.80 ± 0.003	25.5
			b. DP	0.68	0.06	26.2	27.6	1.30 ± 0.38	12.5

*SB = Surface broadcast. FI = Fertilization followed by irrigation. DP = Deep point placement. MI = Mixed incorporation.

incorporation). Although the DTM measurements were carried out only in 2 replicates for statistical analysis, for most experiments the difference between the two treatments was statistically significant (experiments 1, 2, 3, 5, *t*-test, $P < 0.1$). Discrepancies in the qualitative results of DTM and IHF method can be attributed to the differing influence of the weather conditions on the two methods. However, considering all treatments, the DTM measurements gave a very similar ranking of all experiments including the different treatments as compared to the results of the IHF method (Spearman–Rank Correlation, $R^2 = 0.88$, $P < 0.01$).

Calibration of the DTM

Only the fluxes determined in the surface broadcast treatments (Experiments 1a–5a) were used for the derivation of the calibration formula. The whole range of NH_3 fluxes – from very low to very high NH_3 fluxes – was covered by the measurements during the surface broadcast treatments. The measurements not included in the calibration of the DTM, i.e. the treatments with fertilizer incorporation, were then applied as test data for the validation of the calibration formula.

Only the wind speed data (2 m and 0.2 m) fulfilled the normal distribution requirements. NH_3 fluxes measured with DTM and IHF were both log-normally distributed. Thus, natural logarithms of all variables were calculated for the calibration regressions. Several good fits between experimental data and different linear regressions were calculated. In addition, the regression approach was also applied to the unmodified data set. The best fit between the whole unmodified data set was calculated for the following regression Equation (4):

$$NH_3\ flux_{IHF} = 3.944 NH_3\ flux_{DTM} + 0.055 v_{2m} + 0.012 st - 0.241 \quad (4)$$

$$R^2 = 0.83,\ c^2 = 0.83$$

where $NH_3\ flux_{IHF}$ is NH_3 flux measured by IHF (kg N ha^{-1} h^{-1}); $NH_3\ flux_{DTM}$ is NH_3 flux measured by DTM (kg N ha^{-1} h^{-1}); v_{2m} is wind speed at 2 m height (m s^{-1}); st is soil temperature (°C).

The most successful model approach in the regression analysis, however, was determined using logarithmic values by forming two separate data sets for the maize (summer) and wheat (winter) seasons, containing data of three and two experiments, respectively. In this way the influence of the crops grown and of the specific seasonal conditions could be implicitly considered in the calculations. Both model estimates considered the DTM NH_3 fluxes and wind speeds for the approximation of IHF NH_3 fluxes. In case all treatments of both models were pooled, c^2 equalled 0.86. Thus the combined application of both formulas led to a satisfactory overall performance of the calibration formulas (Equations 5a and 5b).

Total model performance $c^2 = 0.86$

Winter season:

$$\ln(NH_3 flux_{IHF}) = 0.444 \cdot \ln(NH_3 flux_{DTM}) + 0.590 \cdot \ln(v_{2m})\ (c^2 = 0.64) \quad (5a)$$

Summer season:

$$\ln(NH_3\ flux_{IHF}) = 0.456 \cdot \ln(NH_3\ flux_{DTM}) + 0.745 \cdot \ln(v_{2m}) - 0.280 \cdot \ln(v_{0.2m}) \quad (c^2 = 0.72) \quad (5b)$$

$NH_3\ flux_{IHF}$ is NH_3 flux measured by IHF (kg N $ha^{-1}h^{-1}$); $NH_3\ flux_{DTM}$ is NH_3 flux measured by DTM (kg N ha^{-1} h^{-1}); v_{2m} wind speed at 2 m height (m s^{-1}); $v_{0.2m}$ wind speed at 0.2 m height (m s^{-1})

The observed vs. calibrated values shown in Figure 5 scatter symmetrically and closely to the line of equality.

The estimated calibration model (Equations 5a and 5b) was validated by comparing cumulative NH_3 losses calculated on the basis of NH_3 fluxes approximated by the calibration formulas with the NH_3 losses determined by the IHF method. The calibration formula was only applied in cases where NH_3 fluxes could be detected by the DTM, otherwise the flux was regarded as zero. Figure 6 (a and b) shows the results for the surface broadcast treatments and the treatments with fertilizer

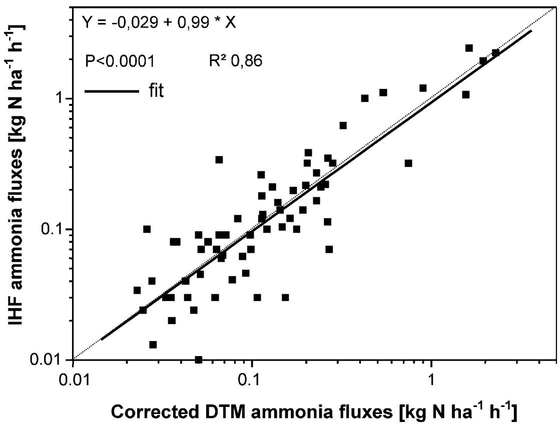

Figure 5. Observed (IHF) vs. calculated (calibrated DTM values) NH_3 fluxes determined at Fengqiu Experimental Station, China (1998–1999).

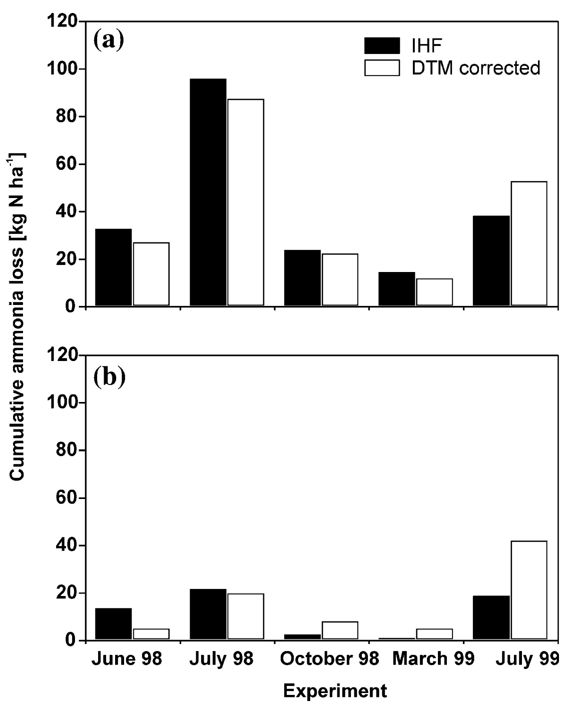

Figure 6. Comparison of cumulative NH_3 losses determined by the IHF method and corrected DTM NH_3 fluxes at Fengqiu Experimental Station, China (1998–1999), (a) surface broadcast treatments, (b) incorporation treatments.

incorporation. The comparison of the corrected DTM NH_3 loss estimates with the results determined with the IHF method for the surface broadcast treatment resulted in a mean absolute error of 6.5 ± 2.9 kg N ha^{-1} (mean relative error 17 ± 5 %).

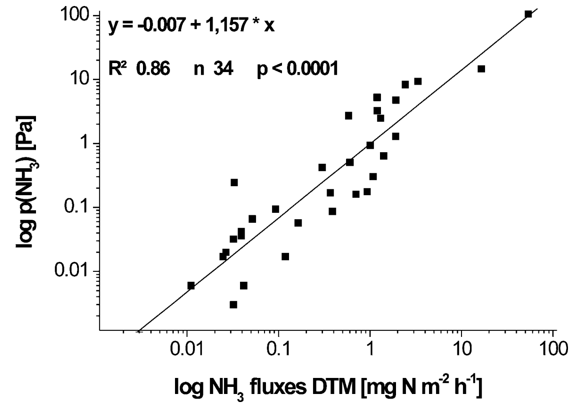

Figure 7. Linear regression for the whole data set between the logarithms of NH_3 fluxes measured by DTM (independent) and calculated surface soil (0–3 mm) NH_3 partial pressures (dependent) at Fengqiu Experimental Station, China (1998–1999).

Because the calibration formula was derived from DTM surface flux values only, the comparison with the corrected cumulative losses of the incorporation treatments (Figure 6b) could serve for the validation of the calculated calibration formula. Apart from experiment 5b in July 1999 the corrected cumulative NH_3 losses of the incorporated treatments matched the respective losses measured with the IHF method very well. The mean deviation from the losses determined by the IHF method was 8.6 kg N ha^{-1}, supporting the absolute error of the corrected DTM values given above.

NH_3 partial pressure at the soil surface

The calibration approach was also supported by the relationship determined between NH_3 partial pressure at the soil surface and the DTM NH_3 fluxes. The decadic logarithm of the data yielded a significant linear relationship (Figure 7, $R^2 = 0.86$). In contrast to the IHF method, DTM results were closely related to NH_3 partial pressure at the soil surface. This implies that the DTM does not sufficiently take into account the effect of wind speed on NH_3 volatilization which therefore had to be included in the calibration formula.

Discussion

Ammonia volatilization determined by the DTM and the IHF showed very similar NH_3 loss patterns in all experiments and for all treatments. The qualitative differences in NH_3 losses between urea fertilization methods, fertilization rates and growing seasons were well reflected in the results of both methods. However, as had been expected, uncorrected DTM results underestimated NH_3 losses measured by the IHF method by about one order of magnitude.

A general problem of the comparison of NH_3 losses by IHF method and DTM lies in the respective reference heights of NH_3 measurement. The DTM determines NH_3 emissions as NH_3 losses *from soil*, sampling the atmosphere at the soil surface, whereas IHF measures the whole profile in and above the plant canopy reflecting thus the net NH_3 fluxes from the site. However, NH_3 loss patterns determined by the two methods agreed quite well. Therefore, it was concluded that absorption or emission of NH_3 by the plant canopy did not markedly affect ammonia flux from the study sites or the comparison of the two methods.

The development and calibration of the DTM can be seen in line with recent developments in chamber methods. The DTM was designed to avoid the disturbance of environmental conditions by multiple short-term measurements which is a major advantage when compared with other chamber methods. The DTM is a simplified chamber method which has no demanding requirements with regard to gas sampling and analysis. During our field measurements in Fengqiu County, trained farmers of the village bordering the experimental sites could carry out the measurements all on their own. Calculations of the NH_3 losses could be done later on by accompanying technicians and scientists.

The crucial influence of wind speed on the measurement of NH_3 volatilization was supported by the comparison of NH_3 fluxes determined by the DTM and calculated NH_3 partial pressures at the soil surface. The data suggest that DTM NH_3 measurements can be regarded as an indicator for NH_3 partial pressure at the soil surface. As a consequence, the DTM measurements give NH_3 volatilization values based on NH_3 partial pressure at the soil surface without appropriately considering the influence of atmospheric exchange on the NH_3 volatilization process. The DTM had, thus, to be modified to include the effect of environmental conditions and atmospheric turbulence into the measurements by calculating corrected NH_3 fluxes on the basis of measured environmental variables. Ambient conditions were not directly reproduced by modifying the DTM measurement set-up but rather taken into account by including them in the calculations of corrected DTM NH_3 losses. The former approach was successfully applied for the optimisation of chamber methods by Svensson and Ferm (1993) and Sommer et al. (2001). The latter calibration approach was successfully applied in the present study. The indirect approach for the calibration of the DTM proved to be feasible and more elegant than a direct modification of the method.

As in comparable field studies, it was not possible to have replicate micrometeorological measurements during the Fengqiu field experiments. In general, micrometeorological methods exhibit a degree of measurement error, which according to Harper and Sharpe (1998) ranges from at least $\pm 15\%$ up to 50%. Similar values for the measurement error of micrometeorological measurements were presented by Denmead et al. (1977) and Sharpe and Harper (1995). Nevertheless, the IHF method applied in this study was also used in other experiments for the calibration of an improved method of field-scale measurement of NH_3 volatilization (Wood et al. 2000) and proved to be a robust method for determining NH_3 losses *in situ* (Misselbrook et al. 2005). The mean absolute error of the DTM NH_3 losses corrected by the calibration formula compared to the cumulative NH_3 losses measured with the IHF method was small, and its variation especially low (2.9 kg N ha^{-1}). The estimation error of 6.5 ± 2.9 kg N ha^{-1} is well within the accuracy required for agronomic purposes. According to the authors cited above a relative measurement error by the IHF method of at least ± 15 % for the five surface broadcast treatments with losses ranging from 14.6 to 95.8 kg N ha^{-1} would correspond to an absolute measurement error between 2.2 and 14.4 kg N ha^{-1}. Thus the use of this calibration approach would result in an estimation error of the same magnitude as compared to the error obtained by direct IHF measurements. Furthermore, this result of the calibration was supported by validating the formula using the DTM values of the incorporated treatments, yielding an average error of 8.6 kg N ha^{-1}.

The Dräger-Tube Method had previously been used in another region of China (Roelcke et al. 2002) as well as in several preliminary experiments in Germany (unpublished). It was now calibrated over a wide variety of seasonal, cropping and management conditions. The results of the experiments further confirmed the one order of magnitude between the fluxes measured with the Dräger-Tube Method and the IHF method. The authors are therefore convinced that their calibration approach is stable, not site specific, and also valid for regions outside the study area and China. The correction of the NH_3 fluxes determined by the DTM is based on measured fluxes and wind speeds only. The application of separate calibration equations for winter wheat and summer maize reflects the effect of season and crop stand on the correction of the DTM fluxes. Therefore, the winter wheat calibration equation should be applied in situations with comparatively low temperatures and crop heights, whereas measurements under high temperatures and in high crop stands should be corrected by applying the summer maize calibration equation. In addition, the geometry of the chamber system and of the hand pump applied (Drägerwerk AG, Lübeck, Germany) should be the same as in this study. Keeping these considerations in mind, the calibration approach can be used under similar meteorological and field conditions irrespective of the soil characteristics or type of N fertilizer applied.

The NH_3 losses determined by the IHF method in the Fengqiu experiments, ranging from a few percent to 50% of the urea-N applied to maize and wheat, depending on treatment, season and environmental conditions, are in good agreement with results by other authors and earlier experiments in China. Ammonia losses following urea fertilization of wheat and maize measured in China support the inference that NH_3 losses during maize growing seasons (Wang et al. 1991; Zhang et al. 1992; Cai 1997) are higher than during wheat seasons (Rees et al. 1997; Cai et al. 1998; Tian et al. 1998; Roelcke et al. 2002). This seems to be mainly due to seasonal factors (higher temperatures and higher rainfall in summer) and – to a lesser extent – higher fertilizer application rates for maize.

Conclusion

The Dräger-Tube Method was validated as a simple measurement tool for the qualitative and quantitative estimation of NH_3 losses under field conditions. The method is not as accurate as micrometeorological methods for determining total losses but is very useful for the determination of NH_3 losses *in situ* under limited technical facilities and remote conditions.

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References

Anderson N., Strader R. and Davidson C. 2003. Airborne reduced nitrogen: ammonia emissions from agriculture and other sources. Environ. Int. 29: 277–286.

Asman W.A.H., Sutton M.A. and Schjoerring J.K. 1998. Ammonia: emission, atmospheric transport and deposition. New Phytol. 139: 27–48.

Bouwman A.F., Van Drecht G. and Van der Hoek K.W. 2005. Global and regional surface nitrogen balances in intensive agricultural production systems for the period 1970–2030. Pedosphere 15: 137–155.

Cai G.X. 1997. Ammonia volatilization. In: Zhu Z.L., Wen Q.X. and Freney J.R. (eds) Nitrogen in Soils of China, Kluwer Academic Publishers, Dordrecht, pp. 193–215.

Cai G.X., Fan X.H., Yang Z. and Zhu Z.L. 1998. Gaseous loss of nitrogen from fertilizers applied to wheat on a calcareous soil in North China Plain. Pedosphere 8: 45–52.

Cai G.X., Peng G.H., Wu Y.W., Ma M.T., Gan S.W. and Men C.F. 1995. Fate of urea nitrogen applied to rape grown on red soil and efficiency of urea in raising rape yield. Pedosphere 5: 107–114.

Cai G.X., Yang N.C., Lu W.F., Chen W., Xia B.Q., Wang X.Z. and Zhu Z.L. 1992. Gaseous loss of nitrogen from fertilizers applied to paddy soil in southeastern China. Pedosphere 2: 209–217.

Denmead O.T. 1983. Micrometeorological methods for measuring gaseous losses of nitrogen in the field. In: Freney J.R. and Simpson J.R. (eds) Gaseous Loss of Nitrogen from Plant–Soil Systems, Martinus Nijhoff/Dr. W Junk, The Hague, The Netherlands, pp. 133–157.

Denmead O.T., Freney J.R. and Simpson J.R. 1982. Dynamics of ammonia volatilization during furrow irrigation of maize. Soil Sci. Soc. Am. J. 46: 149–155.

Denmead O.T., Harper L.A., Freney J.R., Griffith D.W.T., Leuning R. and Sharpe R.R. 1998. A mass balance method for non-intrusive measurements of surface-air trace gas exchange. Atmos. Environ. 32: 3679–3688.

Denmead O.T. and Raupach M.R. 1993. Methods for measuring atmospheric gas transport in agricultural and forest systems. In: Agricultural Ecosystem Effects on Trace Gases and Global Climate Change. ASA Special Publication, Madison/WI, USA, pp. 19–43.

Denmead O.T., Simpson J.R. and Freney J.R. 1977. A direct field measurement of ammonia emission after injection of anhydrous ammonia. Soil Sci. Soc. Am. J. 41: 1001–1004.

Drägerwerk A.G. 1994. Dräger-Tube Handbook: Soil, Water and Air Investigations as well as Technical Gas Analysis 9th ed. Drägerwerk Aktiengesellschaft, Lübeck, Germany.

ECETOC (European Center for Ecotoxicology and Toxicology of Chemicals) 1994. Ammonia Emissions to Air in Western Europe, ECETOC Technical Report No. 62, Brussels, Belgium.

Fangmeier A., Hadwiger-Fangmeier A., Van der Eerden L. and Jäger H.-J. 1994. Effects of atmospheric ammonia on vegetation – a review. Environ. Pollut. 86: 43–82.

Freney J.R., Simpson J.R. and Denmead O.T. 1983. Volatilization of ammonia. In: Freney J.R. and Simpson J.R. (eds) Gaseous Loss from Plant–Soil Systems, Martinus Nijhoff/ Dr. W. Junk, The Hague, The Netherlands, pp. 1–32.

Galloway J.N., Dentener F.J., Capone D.G., Boyer E.W., Howarth R.W., Seitzinger S.P., Asner G.P., Cleveland C.C., Green P.A., Holland E.A., Karl D.M., Michaels A.F., Porter J.H., Townsend A.R. and Vorosmarty C.J. 2004. Nitrogen cycles: past, present, and future. Biogeochemistry 70: 153–226.

Génermont S., Cellier P., Morvan T., Flura D. and Laville P. 1996. Measuring ammonia volatilization by the aerodynamic method under actual field conditions. C. R. Acad. Sci. IIA 319: 1145–1151.

Goebes M.D., Strader R. and Davidson C. 2003. An ammonia emission inventory for fertilizer application in the United States. Atmos. Environ. 37: 2539–2550.

Harper L.A. and Sharpe R.R. 1998. Atmospheric ammonia: issues on transport and nitrogen isotope measurement. Atmos. Environ. 32: 273–277.

Kirchmann H., Esala M., Morken J., Ferm M., Bussink W., Gustavsson J. and Jakobsson C. 1998. Ammonia emissions from agriculture. Nutr. Cycl. Agroecosyst. 51: 1–3.

Kissel D.E., Brewer H.L. and Arkin G.F. 1977. Design and test of a field sampler for ammonia volatilization. Soil. Sci. Soc. Am. J. 41: 1133–1138.

Krupa S.V. 2003. Effects of atmospheric ammonia (NH3) on terrestrial vegetation: a review. Environ. Pollut. 124: 179–221.

Leuning R., Freney J.R., Denmead O.T. and Simpson J.R. 1985. A sampler for measuring atmospheric ammonia flux. Atmos. Environ. 19: 1117–1124.

Lilliefors H.W. 1967. On the Kolmogorov–Smirnov test for normality with mean and variance unknown. J. Am. Stat. Assoc. 62: 399–402.

Loage K. and Green R.E. 1991. Statistical and graphical methods for evaluating solute transport models: overview and application. J. Contam. Hydrol. 7: 51–73.

Mannheim T., Braschkat J. and Marschner H. 1995. Measurement of ammonia emission after liquid manure application: II. Comparison of the wind tunnel and the IHF method under field conditions. J. Plant Nutr. Soil Sci. 158: 215–219.

McInnes M.J., Kissel D.E. and Kanemasu E.T. 1985. Estimating ammonia flux: a comparison between the integrated horizontal flux method and theoretical solutions of the diffusion profile. Agron. J. 77: 884–889.

Misselbrook T.H., Nicholson F.A., Chambers B.J. and Johnson R.A. 2005. Measuring ammonia emissions from land applied manure: an intercomparison of commonly used samplers and techniques. Environ. Pollut. 135: 389–97.

Pacholski A.S. 2003. Calibration of a simple method for determining ammonia volatilisation in the field – experiments in Henan Province, China, and modeling results. Landbauforschung Völkenrode – FAL Agricultural Research 249: 1–172.

Rees R.M., Roelcke M., Li S.X., Wang X.Q., Li S.Q., Stockdale E.A., McTaggart I.P., Smith K.A. and Richter J. 1997. The effect of fertilizer placement on nitrogen uptake and yield of wheat and maize in Chinese loess soils. Nutr. Cycl. Agroecosyst. 47: 81–91.

Richter J. 1972. Zur Methodik des Bodengashaushaltes: I. Ökologisches Modell II. Ergebnisse und Diskussion. J. Plant Nutr. Soil Sci. 132: 208–239.

Roelcke M. 1994. Die Ammoniak-Volatilisation nach Ausbringung von Mineraldünger-Stickstoff in carbonatreichen chinesischen Löß-Ackerböden. Ph.D. Thesis, Braunschweig Technical University, Braunschweig, Germany, pp. 194.

Roelcke M., Li S.X., Tian X.H., Gao Y.J. and Richter J. 2002. In situ comparisons of ammonia volatilization from N fertilizers in Chinese loess soils. Nutr. Cycl. Agroecosyst. 62: 73–88.

Sharpe R.R. and Harper L.A. 1995. Soil, plant and atmospheric conditions as they relate to ammonia volatilization. Fert. Res. 42: 149–158.

Sherlock R.R., Freney J.R., Smith N.P. and Cameron K.C. 1989. Evaluation of a sampler for assessing ammonia losses from fertilized fields. Fert. Res. 21: 61–66.

Sommer S.G., Soegaard H.T., Moeller H.B. and Morsing S. 2001. Ammonia volatilization from sows on grassland. Atmos. Environ. 35: 2023–2032.

Sutton M.A., Lee D.S., Dollard G.J. and Fowler D. 1998. Introduction atmospheric ammonia: emission, deposition and environmental impacts. Atmos. Environ. 32: 269–271.

Svensson L. 1997. A new micrometerological method for measuring ammonia emissions. International Workshop on Environmentally Friendly Management of Animal Farm Waste, Sapporo, 25 November, Japan, pp. 1–6.

Svensson L. and Ferm M. 1993. Mass transfer coefficient and equilibrium concentration as key factors in a new approach to estimate ammonia emission from livestock manure. J. Agric. Eng. Res. 56: 1–11.

Tian G.M., Cao J., Cai Z.C. and Ren L.T. 1998. Ammonia volatilization from winter wheat field top-dressed with urea. Pedosphere 8: 331–336.

Vandré R. and Kaupenjohann M. 1998. In situ measurement of ammonia emissions from organic fertilizers in plot experiments. Soil Sci. Soc. Am. J. 62: 467–473.

Wang X.Z., Zhang S.L., Xu Y.H. and Zhu Z.L. 1991. Fate of fertilizer nitrogen applied to crops grown on fluvo-aquic soil in Huang-Huai-Hai Plain. Pedosphere 1: 145–155.

Wood C.W., Marshall S.B. and Cabrera M.L. 2000. Improved method of field-scale measurement of ammonia volatilization. Commun. Soil Sci. Plant Anal. 31: 581–590.

Zhang S.L., Cai G.X., Wang X.Z., Xu Y.H., Zhu Z.L. and Freney J.R. 1992. Losses of urea–nitrogen applied to maize grown on a calcereous fluvo-aquic soil in North China Plain. Pedosphere 2: 171–178.