Comparison of different methods for the measurement of ammonia volatilization after urea application in Henan Province, China

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Abstract

Ammonia losses following urea fertilization of maize and winter wheat were determined in field trials carried out at Fengqiu Experimental Station in the North China Plain in 1998 and 1999. Four experiments were carried out using two simplified micrometeorological integrated horizontal flux methods [IHF(L) and IHF(S)], a chamber method (calibrated Dräger-Tube Method DTM) and the ^{15}N-balance method using ^{15}N-labeled urea. The IHF(L) was taken as the reference method. Both IHF methods showed good agreement in one experiment only, while the IHF(S) overestimated as well as underestimated cumulative ammonia losses compared to IHF(L) in the other experiments (deviation ranged from 12.5% to 64% based on cumulative ammonia losses). Regression analysis of the fluxes showed that in particular different sensitivities of the samplers to wind speed accounted for the discrepancies observed. The IHF(L) and the DTM flux curves were very similar in three experiments, while the values obtained with DTM considerably deviated from IHF(L) results in one experiment. A comparison with apparent fertilizer-N losses determined by the ^{15}N-labeling approach showed that ammonia volatilization was the major pathway of fertilizer-N loss in this study.

Key words: ammonia loss / integrated horizontal flux method / Dräger-Tube Method / ^{15}N

Accepted March 31, 2008

1 Introduction

A large variety of methods is available for the determination of ammonia volatilization after application of organic or mineral N fertilizers in the field (*McGinn* and *Janzen*, 1998; *Sommer* et al., 2004). Refined micrometeorological methods, in particular gradient diffusion, bowen ratio, relaxed eddy-covariance, or open-path laser-spectroscopy methods are available for high-precision measurement of ammonia fluxes. However, these methods are quite costly (eddy-covariance, open-path laser spectroscopy) or their application requires demanding preconditions such as large homogeneous fields, in-field current supply, and laboratory facilities close to the study site. Therefore, more simple methods such as integrated horizontal flux methods (IHF; *Wilson* et al., 1983; *Wilson* and *Shum*, 1992) and chamber methods are usually applied in agronomic studies. To a much greater extent, this also applies to NH_3-loss measurements carried out in rural areas of developing countries.

In a recent publication, *Misselbrook* et al. (2005) have shown the reliability of the samplers by *Leuning* et al. (1985) often used in such a simplified IHF method. Apart from this IHF approach, another simplified IHF method with different samplers developed by *Schjoerring* et al. (1992) was also frequently used for the determination of ammonia loss in agricultural studies (*e.g., Sommer* et al., 1996; *Schulz* and *Dämmgen*, 1999; *Schjoerring* and *Mattsson*, 2001; *Warren* et al., 2006). Due to the still demanding experimental requirements, these micrometeorological methods are usually applied without replication. For this reason, it is very hard to obtain an estimate of the measurement error or the spatial flux variability involved in the NH_3-flux measurements.

Chamber methods or small-scale micrometeorological methods (*e.g., Svensson*, 1994) are frequently used to gain information about the spatial variability of ammonia fluxes or when comparing different treatments. The results obtained by chamber methods, however, are often biased with regard to the absolute quantity of the measured fluxes because the air exchange in the chambers generally does not match the ambient wind speed and turbulence conditions. In addition, NH_3 can be absorbed by humid chamber surfaces which can also result in biased flux measurements.

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Studies on the comparison of different methods for the measurement of ammonia emission from agricultural soils and crop stands are scarce and were usually carried out for one experimental period only (*e.g., Marshall* and *Debell*, 1980; *Sherlock* et al., 2002; *Sommer* et al., 2005). More insight is needed in the relative sensitivity of the different measurement techniques which can be best obtained by repeated comparisons of the methods under differing experimental and environmental conditions. In order to acquire more data on the relative measurement accuracy of frequently used measurement methods, a measurement campaign of 4 field experiments was carried out for determining ammonia emissions following the application of urea on a calcareous soil in the North China Plain. Two IHF methods and one chamber method were applied for the *in situ* determination of ammonia volatilization. In addition, ^{15}N plots were used for the comparison of measured ammonia losses with total N recovery in the soil–plant system.

2 Material and methods

2.1 Study site

The experiments were carried out on farmers' fields 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 warm temperate, subhumid climate with a mean annual temperature of 14°C and a mean annual precipitation of 615 mm.

2.2 Soil properties

The soil type is classified as an Ochric Aquic Cambisol (US Soil Taxonomy) or as Calcaric Fluvisol (FAO). The texture of the plough layer (0–0.2m) is a sandy loam. The top soil is characterized by a pH(H_2O) of 8.5, a low soil organic-C content (0.5%), and a comparatively low cation-exchange capacity (75 $mmol_c$ kg^{-1}).

2.3 Experimental

Four field experiments with urea applied at different rates and application methods followed by measurements of NH_3 volatilization were undertaken in the years 1998–1999 (Tab. 1). For deep-point placement of urea, about one spoonful of urea was applied into a hole of approx. 5 cm depth to every second maize plant in a row and covered with soil (2.25 points per m^2). The study sites included a circular measurement plot (radius 12.5 m, area 491 m^2) which was equipped with an IHF measurement mast according to the method described by *Leuning* et al. (1985) in the center. According to the set-up of the IHF method by *Schjoerring* et al. (1992), four masts were placed perpendicularly to each other at the rim of the same circular experimental site (Fig. 1). The circular measurement plot also contained two microplots of 4 m^2 (2 m × 2 m), for the measurements with the Dräger-Tube Method (*Roelcke* et al., 2002; *Pacholski* et al., 2006), and a meteorological measurement mast for the determination of wind speed as well as soil and air temperature. According to the measurement principle of the IHF methods, the measurement plot was surrounded by an unfertilized area. A measurement mast of the IHF(L) method and another microplot were set up in the surrounding unfertilized area upwind of the treatment areas (> 50 m distance) for the measurement of background NH_3 concentrations.

The experimental sites were irrigated by simple flood irrigation according to local practice, normally immediately after fertilizer application.

Table 1: Comparative experiments for the measurement of NH_3 volatilization after urea application carried out at Fengqiu Experimental Station, Henan Province, P.R. China, and cumulative ammonia-N losses and apparent fertilizer-N loss determined by different measurement methods.

No.	Date	Crop (growth stage)	Application rate	Application method	Irrigation	IHF(L)	IHF(S)	DTM* (calibrated)	^{15}N apparent fert.-N loss	Difference [IHF(L), IHF(S)]
			[kg urea-N ha^{-1}][a]		[mm]	Cumulative NH_3 loss [kg N ha^{-1}] (% N applied)				[kg N ha^{-1}] (% loss IHF[L])
1	1998 06/29–07/07	maize (seedling stage, 0.4 m)	75	SB[b]	40–60	32.7 (43.6)	45.6 (60.8)	26.6 ± 3.8 (35.5)	_____	12.9 (39.4)
2	1998 07/19–07/30	maize (10-leaf stage, 1.2 m)	200	DP[c]	40–60	21.6 (10.8)	8.2 (4.1)	22.2 ± n.a. (11.1)	19.4 (9.7)	13.4 (62.0)
3	1998 10/11–10/23	winter wheat (fertilization at sowing)	120	SB	___	23.9 (19.9)	21 (17.5)	25.0 ± 4.8 (20.8)	_____	2.9 (12.1)
4	1999 07/12–07/24	maize (6-leaf stage, 0.8 m)	150	DP	___	18.8 (12.5)	8.6 (5.7)	51.0 ± 8.8 (34.0)	40.2 (26.8)	10.2 (54.3)
Mean										9.9 (42.0)

[a] Units in "( )" refer to values in parentheses, units in "[ ]" refer to values without parentheses.
[b] SB: surface broadcast
[c] DP: deep-point placement (about one spoonful of urea is applied into a hole of approx. 5 cm depth to every second maize plant in a row and covered with soil, 22,500 points per ha)
* mean values ± half range of the two replicates

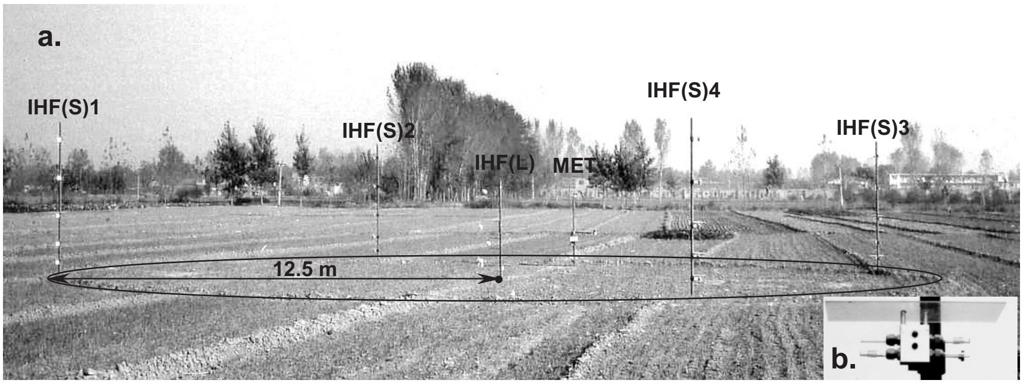

Figure 1: a) Experimental set-up of ammonia measurements during 1998 winter wheat season in Fengqiu Experimental Station [IHF(L) = IHF(L) measurement pole, MET = on-site meteorological station, IHF(S) = IHF(S) measurement poles]; b) set of IHF(S) sampling tubes for one measurement height.

2.4 NH_3 measurements

The studies included the application of two simplified integrated horizontal flux methods [IHF(L) and IHF(S)]. In these measurement approaches, the vertical flux of NH_3 from a defined treatment area surrounded by an untreated area is equated with the rate at which NH_3 is horizontally transported by the wind across a vertical plane downwind to the middle of the treated area (*Denmead*, 1983). Samplers were mounted in several heights in the center of the treatment area absorbing the ammonia of the air passing through them horizontally. Total ammonia losses were calculated by integration of the fluxes measured over the sampled measurement height layers (*e.g.*, 0–0.5 m, 0.5–1 m, *etc.*) corrected by subtraction of background values in the same sampling heights determined in the untreated area. For the measurement in high-crop stands, the sampling height of the two IHF methods was increased and only theoretically consistent NH_3-concentration profiles were used for the calculation of NH_3 losses.

2.4.1 IHF(L) method

The integrated horizontal flux method by *Leuning* et al. (1985) [IHF(L)], modified by *Sherlock* et al. (1989) was taken as the micrometeorological reference method for the comparison of the different measurement techniques applied in this study. Passive NH_3-flux samplers were mounted on a measurement mast 0.4 m, 0.8 m, 1.2 m, 1.6 m, and 2 m above ground (increased up to 3 m in higher maize-crop stands) in the center of the circular plot in the study site. Fins at the rear end kept the samplers aligned with the wind. In case of high NH_3 fluxes, the samplers were exchanged 2–3 times a day. With decreasing NH_3 concentrations in the air, sampling periods were extended to 1–2 d.

2.4.2 IHF(S) method

Using the IHF method by *Schjoerring* et al. [1992; IHF(S) method], the air profile in the boundary layer above the field was sampled at five heights (0.4 m, 0.8 m, 1.4 m, 2 m, 3 m). The samplers consisted of two pairs of glass tubes (7 × 10 mm, 100 mm length) coated with oxalic acid on the inside. For each measurement height, two sampler tubes were connected by means of a metal frame to another pair of tubes. A stainless-steel disc was connected to one tube of each pair. The two types of orifices were used to keep a balanced absorption of NH_3 in the tubes in spite of different impact angles of the wind. One pair of openings pointed towards the experimental site, the other pair to the opposite direction for taking up background ammonia fluxes from the unfertilized surrounding fields. Thus, ammonia fluxes to and from the fertilized experimental area were measured simultaneously. In contrast to the original, a plexiglas roof (0.35 m × 0.1 m, Fig. 1 b) was placed above the samplers as a shelter from heavy rain frequently occurring in summer months that could spoil the measurements as had been observed in previous studies (*Sommer* et al., 1996). As the IHF(S) samplers have a limited sensitivity with regard to varying wind directions, four masts had to be installed at the rim of the circular experimental area (Fig. 1). A sampling period of about one week was chosen for the measurements (*Schjoerring*, 1995; *Schjoerring* and *Mattson*, 2001).

For both IHF methods, following thorough rinsing of the samplers with distilled water, ammonia concentrations in the solutions were measured with an ORION ammonia electrode (USA) and a millivolt meter.

2.4.3 Dräger-Tube Method (DTM)

The Dräger-Tube Method (*Roelcke,* 1994; *Roelcke* et al., 2002) is a special type of the dynamic chamber methods. Ambient air was sucked through four soil chambers (height 0.105 m, diameter 0.115 m, surface area covered 0.01 m^2, insertion depth 0.02 m) by means of a hand pump. An NH_3-sensitive Dräger gas-analysis detector tube (Drägerwerk AG, Lübeck, Germany) immediately displayed the NH_3 concentration in the air led through the chambers. The four chambers were randomly placed onto the fertilized areas.

In case of urea deep-point placement, each measurement chamber was placed onto a fertilizer-amended spot. In contrast to surface application of urea, these data were extrapolated to a surface area of one hectare by multiplying the NH_3 fluxes in one chamber with the number of fertilizer-amended points per hectare.

Due to the low air-exchange rate in the chambers, the NH_3-flux values had to be corrected by means of a calibration approach which had been derived in five field trials in the framework of the same experimental campaign as that presented in this study (*Pacholski* et al., 2006). Two different calibration equations (Eq. 5a and 5b in *Pacholski* et al., 2006) were used for experiments in summer seasons (experiments No. 1, 2, 4; high-crop stands) and winter season (experiment No. 3; small-crop stands), respectively, for the correction of the raw DTM flux values. Flux values of DTM and wind speeds at 0.2 m and 2 m height were included in these formulas.

2.4.4 Nitrogen-15-balance studies

Urea fertilizer enriched with ^{15}N was applied to small microplots consisting of metal frames (0.5 m × 0.5 m, 0.6 m height, inserted to a depth of 0.55 m) located outside the circular plots in the surrounding unfertilized area. The ^{15}N enrichment was 7 atom% in 1998 and 6 atom% in 1999 (experiments No. 2 and No. 4, respectively). Fertilization rates, timing, and application method corresponded to those in the circular experimental plots. Each treatment was carried out in four replicates.

The soil was taken out of the frames in layers of 0–0.2 m, 0.2–0.5 m, and 0.5–0.8 m by means of a soil auger or as bulk soil at harvest time. The 0–0.2 m layer was taken as bulk soil in both experiments. In experiment No. 2, the two deeper layers were sampled by five cores with a soil auger (diameter 5 cm) for each layer, respectively. In experiment No. 4, soil was sampled as bulk soil down to a depth of 60 cm, the layer underneath was sampled with a soil auger as in experiment No. 2. Roots were removed by hand from the soil before determining the soil ^{15}N contents. Nitrogen-15 contents were also measured in above-ground plant material and roots. All ^{15}N contents were determined using a Finnigan mass spectrometer.

2.5 Meteorological measurements

The instrumentation of the meteorological measurement mast consisted of two cup anemometers (in 0.2 m and 2 m height), THIES optoelectronic (aluminum) and THIES compact (synthetic material, THIES, Germany), and two temperature sensors (PT 1000 soil temperature sensor, PT 100 radiation protected air temperature sensor). The optoelectronic anemometer with higher sensitivity was used at the height of 0.2 m because of lower wind speeds at that height. The sensors were connected to a data logger (WILOG306, Wilmers Messtechnik Hamburg, Germany) recording 10 min–average values. The meteorological stations were placed inside the circular plots downwind of the IHF(L) measurement mast—according to the main wind direction—to avoid perturbing the NH_3 measurements.

2.6 Statistics

For the regression analysis between the two IHF methods, time-averaged flux values for the IHF(L) as well as time-averaged meteorological values (temperature, wind speed) were calculated on the basis of the measurement intervals employed for the IHF(S). Data were analyzed by means of linear regression and nonlinear curve fitting with the R-Statistical Package (version 2.2.1, *R Development Core Team*, 2005).

The cumulative flux pattern of ammonia loss from urea is often characterized by a slow initial (lag) phase, a fast second phase, and a third phase with decreasing fluxes. This process can be best described by a sigmoidal logistic equation (*Demeyer* et al., 1995):

$$Y = a\,(1 - e^{(-ct)})^{i}, \quad (1)$$

Y = cumulative ammonia loss (kg N ha^{-1}),
a = asymptotic maximum ammonia loss (kg N ha^{-1}),
c = rate constant (process velocity; d^{-1}),
t = time (d),
i = parameter of sigmoidality (dimensionless).

Y, a, c, t, and *i* are positive values. If i is > 1, the process can be described by a sigmoidal curve, otherwise ($i \leq 1$), the curve has no turning point and thus no sigmoidal shape. The maximum flux rate and its point in time t_{max} (days after fertilizer application) was derived from this model by forming the first and second derivatives; t_{max} (d) was calculated from:

$$t_{max} = \ln i / c. \quad (2)$$

The logistic equation was fitted to the cumulative–ammonia loss curves over time for comparison of the cumulative ammonia losses measured with the IHF(L) and the DTM method. The IHF(S) was not considered in these calculations due to the low measurement frequency employed in this method.

3 Results

3.1 Comparison of the two integrated horizontal flux methods

The comparison of the two micrometeorological methods (Fig. 2 a–d) showed good agreement for the winter wheat experiment (No. 3) with a discrepancy between the methods of a cumulative loss of about 3 kg N ha^{-1} (Tab. 1), corresponding to a relative difference of 12.5% as compared to the loss determined by the IHF(L). However, the IHF(S) overestimated the cumulative losses determined by the IHF(L) in the first experiment (Tab. 1, 12.9 kg N ha^{-1} difference), while losses were underestimated in experiments No. 2 and 4 (Fig. 2b and 2d), both with incorporation of urea (Tab. 1, 13.4 and 10.2 kg N ha^{-1} difference, respectively). The highest relative deviation of the cumulative ammonia loss determined by the IHF(S) from the result of the IHF(L) was observed in experiment No. 2, where the cumulative NH_3 loss was underestimated by 62%. On the basis of cumulative losses determined at the end of each experiment, an average absolute difference of 9.9 kg N ha^{-1} between the two IHF methods was observed (Tab. 1).

Figure 3 shows the regression of the single fluxes obtained by the IHF(L) on the fluxes determined with the IHF(S). The regression in Fig. 3a is dominated by one pair of values with very high fluxes. For that reason, the same regression was also calculated without consideration of these values (Fig. 3b). Nevertheless, both regressions gave similar model parameters, *i.e.*, a y-axis intercept of about 1 kg N ha^{-1} d^{-1} and a slope of 0.6. The parameters indicate that in case of very low flux values, the IHF(S) underestimated the fluxes determined by the IHF(L), while with increasing fluxes, the IHF(S) determined increasingly higher values than the other method.

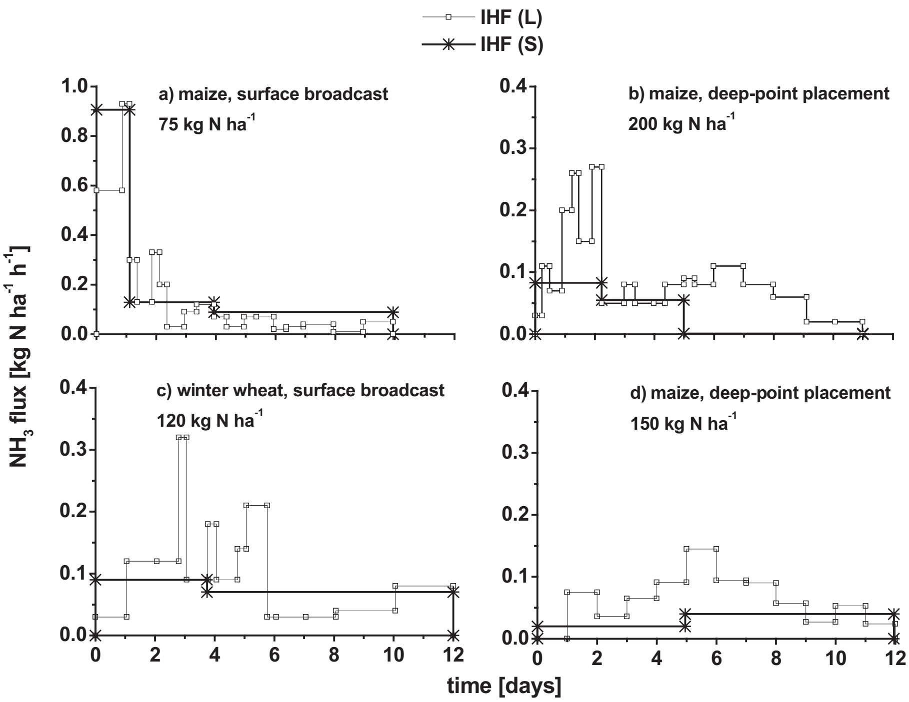

Figure 2: Ammonia fluxes following urea fertilization measured simultaneously with two integrated horizontal flux (IHF) methods in four field experiments (a-d) carried out at Fengqiu Experimental Station, Henan Province, P.R. China.

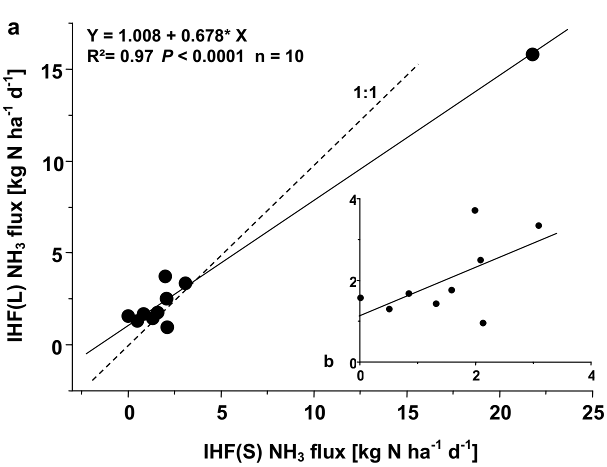

Figure 3: a) Regression of ammonia fluxes determined by two integrated–horizontal flux (IHF) methods [IHF(L) *vs.* IHF(S)] in four experiments carried out at Fengqiu Experimental station; b) without pair of highest flux values.

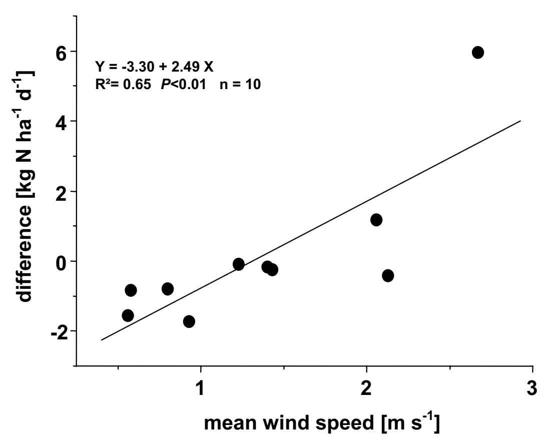

Figure 4: Regression of differences in ammonia fluxes measured by the IHF methods [IHF(S) values minus IHF(L) values] on wind speed (2 m height).

It was tested by regression analysis to which extent environmental and management factors (temperature, wind speed, crop height) accounted for the observed differences. Only the regression of the differences between the flux values obtained by both methods on wind speeds showed a significant result while the regressions on the other variables showed no significant relationship. Figure 4 shows the regression of the differences on the average wind speeds (2 m height) during the measurement intervals ($R^* = 0.65$, $p < 0.01$). Compared to the IHF(L), the IHF(S) underestimated the fluxes by about 2 kg N ha^{-1} d^{-1} at low wind speeds while higher fluxes were determined in cases with stronger wind. According to the regression model, a good agreement between the fluxes was determined at wind speeds of about 1.5 m s^{-1}. However, in general lower wind speeds occurred, so that in most situations, the IHF(S) resulted in lower flux rates than those determined by the IHF(L) method.

3.2 Qualitative comparison between NH_3 losses determined with IHF(L) and DTM

The calibration of the DTM had been carried out using part of the IHF(L) data given in the present study. Therefore, only a qualitative comparison of the methods is made, which is nevertheless possible as the calibration was based on single flux values and not on cumulated NH_3 losses.

Due to heavy rainfall at the beginning of the second experiment, fluxes from one DTM measurement plot were consider-

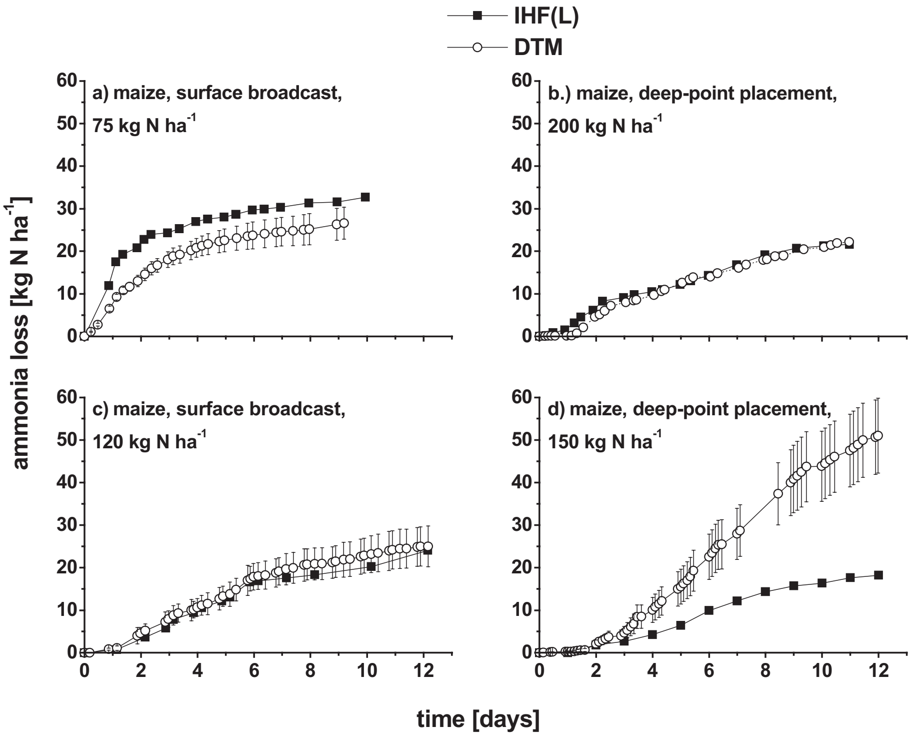

Figure 5: Cumulative ammonia losses following urea fertilization measured simultaneously with the integrated horizontal flux IHF(L) and a dynamic chamber method (calibrated DTM) in four field experiments (a-d) carried out at Fengqiu Experimental Station, Henan Province, P.R. China. Error bars depict the range of the DTM results (two replicates).

ably reduced and thus not included in the comparison of the two methods. Comparing the replicate DTM flux measurements on the two microplots, the average range of fluxes measured was about 40% of the momentary mean flux rate (experiment No. 1: 42%, No. 3: 43%, No. 4: 43%). Aggregated until the end of the experiment, this variability resulted in a deviation from the mean cumulative loss of ±14% (3.8 kg N ha^{-1}), ±19% (4.8 kg N ha^{-1}), and ±17% (8.8 kg N ha^{-1}) for experiments No. 1, 3, and 4, respectively.

There was a very good agreement between the time courses of the losses determined with the calibrated DTM compared to the IHF(L) in three of the four experiments (Fig. 5). However, in experiment No. 4, there was a greater discrepancy between the time courses obtained by both methods (Fig. 5 d).

Table 2 gives the parameters of the logistic equations fitted to the time curves of ammonia loss determined by the DTM and the IHF(L). Apart from the large difference in parameter *a* (asymptotic cumulative ammonia loss) between both methods for experiment No. 4, the parameters showed a good agreement. With respect to the parameters *c* (rate constant) and *i* (sigmoidality), both methods showed the same dynamics of the ammonia-loss process in the different experiments. The t_{max} values (Eq. 2), calculated from parameters *c* and *i*, were also very similar between the two methods compared for all experiments. This parameter could not be calculated for the IHF(L) method in experiment No.1 as the estimated parameter *i* was too small for the application of the equation. This indicates a very early attainment of the maximum flux rate and is in good agreement with the very low value (t_{max} = 0.24) for the calibrated DTM.

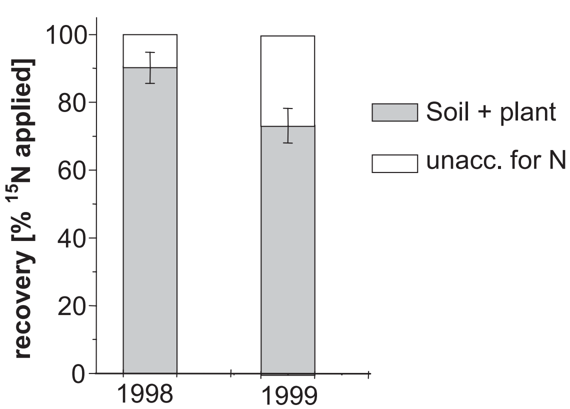

Figure 6: Nitrogen-15 recovery in soil and plant material and N not accounted for of ^{15}N-labeled urea (deep point–placement application) in two field trials with maize carried out at Fengqiu Experimental Station, Henan Province, P.R. China. Error bars depict standard error (n = 4).

3.3 Direct ammonia-loss measurements and ^{15}N results

The comparison of the ammonia fluxes determined directly by the two IHF methods and the DTM with the apparent total fertilizer-N loss by ^{15}N labeling was possible for experiments No. 2 and 4 (Tab. 1, Fig. 6). In experiment No. 2, ammonia losses determined by the IHF(L) (10.8% of fertilizer N applied) and the calibrated DTM (11.1%) were slightly higher than the amount of fertilizer ^{15}N not accounted for [(9.7 ± 5)%]. In contrast, the IHF(S) determined less than half of the IHF(L) losses (4.1% of fertilizer N).

Table 2: Parameters of the logistic equation (Eq. 1) fitted to the time curves of cumulative ammonia-N losses in the four experiments obtained by measurements with IHF(L) and the calibrated DTM (a = asymptotic cumulative ammonia loss, c = rate constant, i = position of the point of inflexion, t_{max} = point in time [d after fertilization] of maximum NH_3 flux). All parameters were estimated at a significance level of $p < 0.05$.

Experiment	Method	Parameter a (kg N ha^{-1})	c	i	t_{max} (d)
1	IHF(L)	32.5	0.3	0.6	—
	Calib. DTM	27.3	0.4	1.1	0.24
2	IHF(L)	32.4	0.1	1.1	0.95
	Calib. DTM	26.3	0.2	1.7	1.15
3	IHF(L)	24.2	0.3	2.5	3.1
	Calib. DTM	26.9	0.3	2.1	2.8
4	IHF(L)	20.6	0.3	4.2	4.8
	Calib. DTM	64.4	0.2	3.3	3.8

A total amount of 26.8% of fertilizer N applied was not accounted for by the ^{15}N technique in experiment No 4. While both IHF methods detected lower NH_3-N losses [IHF(L) 12.5% and IHF(S) 5.7% of fertilizer N applied] compared to this apparent total–N loss value, the measurements with the DTM resulted in considerably higher NH_3-loss values (34% of fertilizer N applied).

4 Discussion

Ammonia losses detected with the IHF(S) and IHF(L) methods were of the same order of magnitude, but results obtained by the IHF(S) measurements deviated by up to 60% from ammonia losses determined by the IHF(L). *Harper* and *Sharpe* (1998) reported that comparisons of replicate micrometeorological measurements suggested a variation of at least ±15% up to 50% of the cumulative losses measured for micrometeorological techniques. Some of our experiments were carried out under conditions not ideal for the application of IHF methods (No. 2 and No. 4 with high-crop stands). However, as both methods are based on the same measurement principle, they should have been affected in the same way and, thus, the comparison should not have been biased by the experimental conditions. In experiment No. 3 (wheat; urea surface-applied), the IHF(S) results showed a very good agreement to the losses determined by the IHF(L). A similar good agreement was observed in the comparison of both methods based on a single measurement campaign by *Sherlock* et al. (2002). However, in the other experiments, the IHF(S) measurements underestimated as well as overestimated ammonia losses compared to IHF(L) results. The regression analysis of the fluxes showed that different sensitivities of the samplers with respect to wind speed could account for the magnitude of the differences observed. As the IHF(L) samplers were successfully tested and re-evaluated in a recent study (*Misselbrook* et al., 2005), it can be hypothesized that the NH_3-absorption behavior of the IHF(S) samplers could mainly account for the observed differences. *Sommer* et al. (1996) reported that in situations of very low and high wind speeds bypass of the IHF(S) samplers can occur which could explain some of the deviation between the two IHF methods observed. *Schjoerring* (1995) corrected flux values obtained by the IHF(S) by weighting them based on average wind speeds in the respective measurement heights of the samplers for more precise ammonia-flux calculations. This agrees with the dependency of the accuracy of IHF(S) samplers on wind speed (Fig. 4). The modification of the IHF(S) samplers with rain-shelter roofs in our experiment might also offer an explanation for deviations of these samplers from the IHF(L) measurements in our study. The plastic-cover roof might have led to a considerable distortion of the turbulence of the air near the samplers. The deviations between the two micrometeorological methods could also be related to the radius of the circular experimental areas applied in this study. *Wilson* and *Shum* (1992) showed by model calculations that the IHF method yields emission rates accurate to within about 20% or better, when radii are >20 m and surface-roughness lengths are comparatively low. *Leuning* et al. (1985) used a 25 m radius in their original IHF(L) experiment, while *Sherlock* et al. (1989) had a 20 m radius. *Schjoerring* et al. (1992) used a 15 m radius for the original IHF(S) experiment. The radius chosen in this study was smaller (12.5 m) and the surface-roughness length higher due to high-crop stands in the maize experiments. However, *Sommer* et al. (1996) and *Warren* et al. (2006) applied even smaller experimental radii for determining NH_3 losses from manure-storage facilities with the IHF(S) with satisfactory accuracy, as compared to the losses obtained from a reference technique (NH_4^+-concentration change in NH_3 source).

The DTM loss values agreed very well with the ammonia fluxes determined by the IHF(L) with respect to the ammonia-loss kinetics, apart from experiment No. 4. Although the DTM gave reliable ammonia-loss estimates in the 1998 experiment with deep-point placement of urea (No. 2), it considerably deviated from the IHF(L) time curves in the 1999 experiment with the same treatment (No 4). The good agreement between the two methods in experiment No. 2 suggests that a deficiency in the calibration equations is not the major explanation for this difference. In the deep point–placement treatments, the DTM chambers were always placed onto the same spots. This presumably led to a severe disturbance of the soil structure entailing higher NH_3-diffusion rates through soil. In contrast to experiment No. 4, this effect was compensated by heavy rainfall in experiment No. 2 which led to a rewetting and recompaction of the soil. In future, DTM chambers should be placed onto PVC rings (soil collars) of the same diameter as the measurement chambers which are inserted in the soil prior to the experiment. This way soil disturbance can be reduced to a minimum. This approach is already used in soil-respiration measurements (*e.g.*, LICOR 6400-09 soil chamber, Li-Cor Inc., Lincoln, NE; *Pumpanen* et al., 2004). However, it still has to be tested whether such permanently installed soil collars would lead to major changes in the dynamics of the NH_3-volatilization process. Altogether, the calibration approach proved to give reliable NH_3-flux curves. *Pacholski* et al. (2006) showed that the calibration of the DTM is valid for a wide range of conditions as it was carried out over a 2 y period under a great variety of seasonal conditions, a wide range of temperatures (–2°C to +40°C) and experimental plots sown with winter wheat and maize. The reliability of the calibration was confirmed in a recent study which included the comparison of calibrated DTM measurements with measurements by the backwards Lagrangian stochastic dispersion technique (*Sommer* et al., 2005) for the determination of NH_3 losses following the application of biogas slurry in Northern Germany (*Pacholski* et al., 2007).

While in experiment No. 4, ammonia losses determined by IHF(L) and IHF(S) were considerably lower than the amounts of N not accounted for, ammonia losses determined by the IHF(L) (10.8%) were about the same as the amount of N not accounted for [(9.7 ± 5)%] of the ^{15}N-balance study in experiment No. 2. Nitrogen-15 not accounted for includes all kind of N losses which lead to nonrecovery of ^{15}N in the plant and soil material, *i.e.*, ammonia volatilization, nitrification/denitrification (N_2O and N_2 losses), nitrate leaching, or plant material omitted in the analysis (*e.g.*, debris). A proportion of ammonia volatilized from the soil surface can also be taken up by plant leaves (*Denmead* et al., 1976), depending on the ammonia-compensation point in the crop leaves (*Farquhar* et al., 1980; *Sutton* et al., 1995). As mineral-nitrogen concentrations in soil were very high after fertilization and plants were well supplied with ammonium, a priori, ammonia losses measured directly should be smaller than values of ^{15}N not accounted for. This consideration is also supported by findings of *Marshall* and *Debell* (1980) and *Reynolds* and *Wolf* (1988). Therefore, very close agreement between the measurement results of the IHF methods and the indirect ^{15}N method in experiment No. 2 indicates major measurement errors of at least one of the methods. The deeper layers (0.2–0.5 m, 0.5–0.8 m) of the ^{15}N microplots were sampled by five soil cores taken with a soil auger in this experiment. Remaining soil mineral N was possibly not evenly distributed, and samples were taken from the "hot spots" with high mineral-N contents. The deeper soil layers contributed about 50% of total recovered ^{15}N (data not shown). Thus, the use of the soil auger for soil sampling resulted in an overestimation of recovered ^{15}N and thus in an underestimation of ^{15}N not accounted for. This was an unexpected result as urea was applied to a soil depth of about 5 cm and soil samples were taken about 3 months after fertilizer application. These considerations are supported by the fact that, as expected, ammonia losses determined by both IHF methods were lower than apparent fertilizer-N loss obtained by the ^{15}N technique in experiment No. 4, where soil samples were mainly taken as bulk soil. The results of IHF(L) and ^{15}N measurements were in good agreement in the other experiments carried out on the same site in 1998 and 1999 (*Pacholski*, 2003). As a consequence, an underestimation of ammonia losses by the IHF(S) in case of low wind speeds and high plant canopy and an underestimation of total N losses by the ^{15}N-balance approach because of an inadequate soil-sampling procedure seem to be the appropriate explanations for the differences observed in experiment No. 2.

Ammonia losses determined by the micrometeorological methods and N not accounted for were of the same order of magnitude. Data from other studies at the Fengqiu Agroecological Station can be used for an additional assessment of the importance of other pathways of N loss. In 1994, N_2O losses following urea fertilization were determined by *Xing* (1998). Between 1% and 2% of urea N applied was lost as N_2O at a fertilization rate of 200 kg N ha^{-1}. These results did not include N losses *via* N_2 emission. *Cai* et al. (2002) undertook nitrification–denitrification experiments in 1998–2000 parallel to the experiments presented here and determined mean gaseous N_2O and N_2 losses of about 5% of the fertilizer N applied. Mineral-nitrogen profiles determined during the course of our experiments gave no evidence that major N losses occurred *via* nitrate translocation and leaching in the experimental periods (*Pacholski*, 2003). The direct measurements of ammonia loss and these findings suggest that ammonia volatilization was the main pathway of urea fertilizer–N loss in the study sites. This is in contrast to results of a study by *Liu* et al. (2003), in which nitrate leaching was the main process of fertilizer-N loss in a rotation of winter wheat and maize investigated in the North China Plain close to Beijing. However, besides differences in irrigation practice, fertilization rates were considerably higher, and the soil pH was slightly lower in their experiment than in our study.

5 Conclusions

Both simplified integrated horizontal flux methods were prone to measurement error depending on in-field and environmental conditions. The differences between the cumulative losses of the two methods in the four field experiments ranged from 12.5% to 62% of the cumulative losses as determined by the IHF(L) showing good agreement in only one experiment. This was in contrast to another study with a single experiment where both methods showed good agreement. As a consequence, the variability of cumulative losses determined by different methods and the effect of environmental conditions on their performance need to be tested in repeated field experiments in the future. The calibrated DTM yielded a good description of ammonia-flux curves. The cumulative NH_3 losses determined by the DTM on two microplots showed a similar variation (14%–19%) as the differences between the losses obtained by the two IHF methods. The application of the DTM is thus also advisable in situations where NH_3 losses could result in agronomically considerable losses of fertilizer N by ammonia volatilization. In particular, the method is useful for measurements in small, hilly, or remote experimental areas where the application of IHF methods is laborious or not possible. Nevertheless, modifications of the measurement procedure of the DTM should be undertaken in order to avoid disturbance of soil due to placement of the DTM measurement chambers.

Acknowledgments

This study was supported by the *Deutsche Forschungsgemeinschaft (DFG Ri 269/42, Ni 311/38)*, the *Gesellschaft für Technische Zusammenarbeit (GTZ VN 810 12 840)* and the *National Natural Science Foundation of China (NSFC).* We thank the farmers in *Tunli village* and the staff of the *Fengqiu Experimental Station* for their help in carrying out the field experiments.

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