

# Effect of a new urease inhibitor on ammonia volatilization and nitrogen utilization in maize in North China Plain

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## Abstract

Maize field experiments were conducted over two years at Quzhou site (Hebei Province, North China Plain) to investigate ammonia (NH<sub>3</sub>) volatilization from urea and from urea amended with 0.12% (w/w) Limus<sup>®</sup> (a new urease inhibitor). Grain yields and nitrogen (N) budgets of all N treatments were evaluated to investigate the effects of urea-N application rates and Limus during two summer maize seasons. Cumulative NH<sub>3</sub> losses after two weeks for conventional urea ranged from 42 to 108 kg N ha<sup>-1</sup> (20-57% of applied N), while the new urease inhibitor Limus significantly reduced NH<sub>3</sub> losses by 65 to 90%. However, maize grain yields (9.5-10.1 t ha<sup>-1</sup>) were not significantly ( $P < 0.05$ ) increased by Limus compared to conventional urea without Limus (9.0-10.1 t ha<sup>-1</sup>). A clear increase in apparent N recovery efficiency (RE<sub>N</sub>) with Limus (ranging from 11 to 17 percentage points during two consecutive maize seasons) compared to equal amounts of optimized urea-N. A further 20% reduction in urea N rate amended with Limus led to the same maize yield but substantially decreased NH<sub>3</sub> losses and increased RE<sub>N</sub> compared with optimized urea treatment. Our study also demonstrates the role of Limus in reducing NH<sub>3</sub> losses and improving N use efficiency in maize production in the North China Plain.

## Key Words

Urea; Limus<sup>®</sup>, NH<sub>3</sub> losses, grain yields, N recovery efficiency, N budgets

## Introduction

China is the largest producer and consumer of nitrogen (N) fertilizer, and urea as a major N fertilizer accounts for over 50% of total N fertilizer consumption, due to its high N content (46% N), relatively low cost and its ease of use. Driven by an urgent need to maintain food security, farmers tend to apply excessive urea-N fertilizer as an “insurance” to meet crop needs. As a consequence, plant N use efficiency or recovery efficiency in China seldom exceeds 50%, while much of the rest is lost from plant-soil system causing numerous environmental problems (Zhang et al., 2013). Ammonia (NH<sub>3</sub>) volatilization is a significant urea-N loss pathway, in some cases amounting to more than 30% of total fertilizer N, in calcareous and alkaline soils (Bouwman et al., 1997). In China, the total NH<sub>3</sub> emission was estimated to be 9.8-20.4 Tg yr<sup>-1</sup>, 33-46% of which was derived from N fertilizer application (Huang et al., 2012; Gu et al., 2015). As one of the key reactive N components and the unique alkaline gas, NH<sub>3</sub> (together with its deposition) contributes to eutrophication of aquatic ecosystems, a decrease of biodiversity in terrestrial ecosystems and also the pollution of secondary aerosols or particles (e.g. PM<sub>2.5</sub>) with their associated human health risk (Sutton et al., 2011; Liu et al., 2013). Incorporation by tillage, deep point placement of urea fertilizer subsequently covered by soil, or surface broadcast followed by irrigation are key techniques to largely reduce NH<sub>3</sub> volatilization from croplands (Zhu, 1997). However, due to shortages of farm labors and decreased irrigation water resources in many agricultural regions of China, that are reducing practices such as soil covering immediately after fertilization and often delayed or no irrigation, NH<sub>3</sub> volatilization losses are expected to be high. Meanwhile, these above-mentioned NH<sub>3</sub> mitigation practices are even more difficult to carry out during top-dressing or split applications of N fertilizer at crop's later growing stage, which would be most recommended for increasing the N use efficiency. Thus a strong demand is required for alternative ways to decrease NH<sub>3</sub> losses while achieving higher N use efficiency and crop yields. Under this background, we believe that urease inhibitor can be an appropriate measure to achieve these goals, as it could delay the hydrolysis of urea and reduce the possible NH<sub>3</sub> losses and improve N use efficiency (Chien et al., 2009). A new urease inhibitor (trade named: Limus<sup>®</sup>) was developed by German chemical company, BASF SE. The Limus<sup>®</sup> product as chemical compound consists of 75% N-(n-butyl) thiophosphoric triamide (NBPT) and 25% NPPT (N-(n-propyl) thiophosphoric triamide). With the application of urea plus Limus, no extra irrigation or incorporation in soils by tillage is needed.

In this paper we report a two-year study conducted at Quzhou site (one typical calcareous soil in the North China Plain), to quantify the magnitude of NH<sub>3</sub> volatilization from maize field fertilized with urea and to evaluate the effect of urea amended with 0.12% (w/w) of the urease inhibitor Limus<sup>®</sup> on NH<sub>3</sub> losses. The main objective of our study is to develop a feasible recommendation to minimize NH<sub>3</sub> losses as well as to achieve high maize yield and N use efficiency in North China Plain.

## Methods

### *Field experimentation*

The two consecutive years' maize field experiments were conducted at Quzhou (QZ, 36°58'N and 115°12'E) in Hebei Province during 2012 and 2013. No winter wheat was sown in the intermittent winter season on the experimental plots. The soil is a calcareous alluvial soil, with initial soil pH 8.0, total N content 0.7 g kg<sup>-1</sup> and organic matter 12.0 g kg<sup>-1</sup>. Detailed fertilizer N treatments is listed in Table 1. All N treatments were surface applied in a randomized block design with four replications: Zero N fertilizer (N<sub>0</sub>), conventional farmers' N practice as plain urea (N<sub>con</sub>), optimized N treatments (an N reduction by 45% compared to N<sub>con</sub>) with plain urea (N<sub>opt</sub>) or urea amended with Limus (N<sub>opt/L</sub>) split into two doses, and one further reduced (by 20% N) treatment of urea amended with Limus applied only once (N<sub>80%opt/L-1</sub>) or two doses (N<sub>80%opt/L</sub>). The amount of optimized urea N was mainly based on local experts' previous research on N fertilizer recommendation.

### *NH<sub>3</sub> loss measurements*

The calibrated Dräger-Tube Method (DTM) was used to quantify NH<sub>3</sub> volatilization at QZ. This dynamic chamber method was introduced by Roelcke et al. (2002) for comparative NH<sub>3</sub> volatilization measurements. It detects minimum NH<sub>3</sub> fluxes of about 0.06 mg N m<sup>-2</sup> h<sup>-1</sup> or 0.6 g N ha<sup>-1</sup> h<sup>-1</sup>. Using multiple linear regression, Pacholski et al. (2006) calibrated the DTM with a micrometeorological Integrated Horizontal Flux (IHF) method over several seasons at the Fengqiu Experimental Station of Chinese Academy of Sciences (CAS) in Henan Province, belonging to the North China Plain. The calibration approach can be used under similar meteorological and field conditions irrespective of the soil characteristics or type of N fertilizer applied.

### *Statistical analysis*

Statistical analysis was conducted using the SPASS 17.0 software for the standard analysis of variance (ANOVA); the comparisons among different treatments were based on Duncan's test at the 0.05 probability level ( $P < 0.05$ ). Graphics were prepared using SigmaPlot 10.0 and Microsoft Excel 2007.

## Results

### *Cumulative NH<sub>3</sub> losses*

The cumulative absolute and relative NH<sub>3</sub> losses at QZ site of North China Plain in two years' maize growing seasons are given in Table 2. As a whole, cumulative NH<sub>3</sub> losses after two weeks for conventional urea ranged from 42 to 108 kg N ha<sup>-1</sup> (20-57% of applied N), while Limus addition clearly reduced total absolute losses by 38-55 kg N ha<sup>-1</sup> ( $P < 0.05$ ), corresponding to 65-90% reduction of NH<sub>3</sub> volatilization losses. Compared with farmers' plain urea-N practice (N<sub>con</sub>), optimized plain urea treatment (N<sub>opt</sub>) significantly ( $P < 0.05$ ) decreased total absolute NH<sub>3</sub> losses (by up to 13-23 kg N ha<sup>-1</sup>), although relative NH<sub>3</sub> losses were clearly higher than N<sub>con</sub> during past two years. Additionally, compared with optimized plain urea (N<sub>opt</sub>), urea amended with Limus (N<sub>opt/L</sub>) significantly reduced NH<sub>3</sub> losses by 70-83% at seedling stage, and 63-96% at trumpet stage, respectively. In contrast, no significant differences in NH<sub>3</sub> volatilization were observed among Limus addition treatments in first year. Only a clear reduction of total NH<sub>3</sub> losses by 14 kg N ha<sup>-1</sup> ( $P < 0.05$ ) was found on the further reduced treatment N<sub>80%opt/L-1</sub> compared to other Limus treatments (N<sub>opt/L</sub> & N<sub>80%opt/L</sub>) in the second year of maize trial.

### *Time courses of NH<sub>3</sub> fluxes*

The comparison of the dynamic time courses of measured NH<sub>3</sub> fluxes and relative weather conditions in the two study years at QZ site is shown in Fig.1. The NH<sub>3</sub> fluxes were higher in the treatments of N<sub>con</sub> and N<sub>opt</sub> practice, in which volatilization peaks of about 400-800 g N ha<sup>-1</sup> h<sup>-1</sup> and 200-700 g N ha<sup>-1</sup> h<sup>-1</sup> were recorded, respectively, during the first 3 days after surface application of urea N. Thereafter, NH<sub>3</sub> fluxes strongly decreased to about 0-200 g N ha<sup>-1</sup> h<sup>-1</sup> for N<sub>con</sub> and N<sub>opt</sub>. In contrast, NH<sub>3</sub> fluxes in the urea with Limus treatments (N<sub>opt/L</sub>, N<sub>80%opt/L</sub>, N<sub>80%opt/L-1</sub>) were only about 0-150 g N ha<sup>-1</sup> h<sup>-1</sup> after surface application. As a whole, similar maximum NH<sub>3</sub> fluxes (about 600-800 g N ha<sup>-1</sup> h<sup>-1</sup>) were monitored at each fertilization event although the pattern of NH<sub>3</sub> fluxes was slightly different during past two years. Following N fertilization at seedling and trumpet growth stages, NH<sub>3</sub> volatilization was only detected for 5-7 days after N fertilization during the first year (Fig. 1 a-b), while NH<sub>3</sub> losses occurred for up to 12 days after N fertilization in the second year (Fig. 1 c-d), respectively.

### *Grain yield, N uptake, and N recovery efficiency (RE<sub>N</sub>)*

The responses of maize grain yield and N uptake during the 2 years of repeated N application at QZ site of North China Plain are shown in Table 3. Compared to N<sub>0</sub>, the N fertilization significantly ( $P < 0.05$ ) increased grain yield of maize but no significant yield differences were found between any of the N application treatments. Even the treatment with a further 20% N reduction in optimized urea-N fertilizer rate with Limus

applied once ( $N_{80\%opt/L-1}$ ) preserved the same grain yields as all other N treatments during two consecutive years. The apparent N recovery efficiency ( $RE_N$ ) varied from 40% ( $N_{con}$ ) to 76% ( $N_{80\%opt/L}$ ) at first growing season, while 31% ( $N_{con}$ ) to 61% ( $N_{opt/L}$ ) at second growing season. Compared with  $N_{con}$ , most optimized N fertilization ( $\pm$  Limus) treatments significantly ( $P<0.05$ ) increased  $RE_N$  of maize, while no significant differences between optimized N fertilization ( $\pm$  Limus) were found in the 2<sup>nd</sup> year. The use of Limus ( $N_{opt/L}$ ) led to an average  $RE_N$  increase by 17 and 11 percentage points when comparing with the same urea treatment without Limus ( $N_{opt}$ ) in the first and second year, respectively. Moreover, the  $RE_N$  in treatment  $N_{80\%opt/L}$  was increased by 23 percentage points ( $P<0.05$ ) compared with the  $N_{opt}$  treatment in the first year. In contrast, the treatment  $N_{80\%opt/L-1}$  did not lead to significant difference in  $RE_N$  (ranging from 49 to 60%) compared with  $N_{opt}$  treatment (50-53%) in the second year.

**Table 1 Experimental treatments in maize season at QZ site (unit: kg N ha<sup>-1</sup>).**

Treatment	Seedling stage	13-leaf stage	Total N input
$N_0$	--	--	0
$N_{con}$	135	135	270
$N_{opt}$	75	75	150
$N_{opt/L}$	75	75	150
$N_{80\%opt/L}$	60	60	120
$N_{80\%opt/L-1}$	120	--	120

**Table 2 Cumulative absolute and relative NH<sub>3</sub> losses following fertilizer application in different treatments in two years' maize seasons at QZ site.**

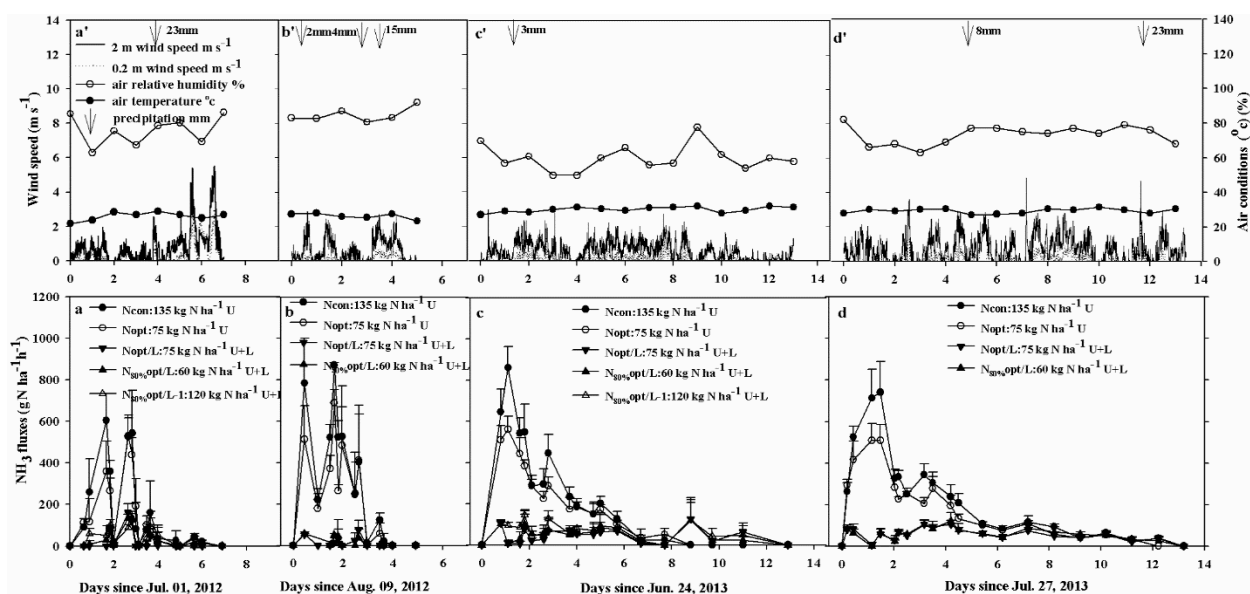
Year	Treatment	Seedling stage		13-leaf stage		Total NH <sub>3</sub> losses	
		kg N ha <sup>-1</sup>	%	kg N ha <sup>-1</sup>	%	kg N ha <sup>-1</sup>	%
1 <sup>st</sup> Year	$N_{con}$	24c	18b	31c	23b	55c	20b
	$N_{opt}$	18b	24c	24b	32c	42b	28c
	$N_{opt/L}$	3a	4a	1a	1a	4a	3a
	$N_{80\%opt/L}$	3a	5a	1a	2a	4a	3a
	$N_{80\%opt/L-1}$	5a	4a	--	--	5a	4a
2 <sup>nd</sup> Year	$N_{con}$	50c	37c	59c	44c	108d	40c
	$N_{opt}$	40b	53d	46b	61d	85c	57d
	$N_{opt/L}$	12a	16a	17a	23a	30b	20ab
	$N_{80\%opt/L}$	13a	22b	17a	28b	31b	26b
	$N_{80\%opt/L-1}$	17a	14a	--	--	17a	14a

Notes: values without same letters within the same column at each site are significantly different ( $P<0.05$ , Duncan's test), the same as the following.

**Table 3 Maize grain yield, N uptake, and apparent nitrogen recovery efficiency ( $RE_N$ ) in two study years.**

Year	Treatment	Grain yield (t DM ha <sup>-1</sup> )	Shoot biomass (t DM ha <sup>-1</sup> )	Grain N uptake (kg N ha <sup>-1</sup> )	Total N uptake (kg N ha <sup>-1</sup> )	$RE_N$ (%)
1 <sup>st</sup> Year	$N_0$	4.5a	9.9a	38a	64a	--
	$N_{con}$	10.1b	19.0b	118d	173c	40a
	$N_{opt}$	9.0b	17.3b	97bc	144b	53ab
	$N_{opt/L}$	9.6b	18.4b	108cd	169c	70cd
	$N_{80\%opt/L}$	10.0b	19.1b	107cd	155bc	76d
	$N_{80\%opt/L-1}$	9.5b	18.7b	92b	136b	60bc
2 <sup>nd</sup> Year	$N_0$	7.5a	13.7a	78a	102a	--
	$N_{con}$	9.9b	16.6ab	135b	185b	31a
	$N_{opt}$	10.0b	16.5ab	132b	177b	50ab
	$N_{opt/L}$	10.1b	19.3b	130b	193b	61b
	$N_{80\%opt/L}$	9.8b	16.2ab	131b	171b	58b
	$N_{80\%opt/L-1}$	9.8b	16.8ab	124b	161b	49ab

Notes:  $RE_N$  (%), apparent N recovery efficiency = (N uptake in fertilized treatment – N uptake in unfertilized treatment) / N applied in fertilized treatment × 100.



**Figure 1.** Time courses of  $\text{NH}_3$  fluxes following urea ( $\pm$ LIMUS) application at seedling and 13-leaf periods of N fertilization during two consecutive years in 2012 and 2013 at QZ (Fig.1 a-d), and corresponding period time courses of rainfall (mm), wind speed (2.0 m and 0.2m height), air temperature and relative humidity (Fig.1 a'-d').

## Conclusion

Cumulative  $\text{NH}_3$  losses after two weeks for conventional urea ranged from 42 to 108 kg N ha<sup>-1</sup> (20-57% of applied N), while Limus addition clearly reduced total  $\text{NH}_3$  losses by 38-55 kg N ha<sup>-1</sup> ( $P < 0.05$ ), corresponding to 65-90% reduction of  $\text{NH}_3$  volatilization losses during two growing periods at QZ in the North China Plain. Unexpectedly, adding Limus hardly increased the maize grain yield ( $P < 0.05$ ) during 2 consecutive summer maize seasons. However, compared to same N amount as plain urea-N fertilization, Limus addition clearly improved  $\text{RE}_N$  by 11-17 percentage points during two consecutive study years.

In addition, under a further reduced (by 20%) urea-N addition amended with Limus (an N reduction by about 55% compared to farmers' N practice), a single dose fertilizer application per season (thereby saving labors) maintained grain yield at QZ site, but requires further investigation under different soil and environmental conditions.

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