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Ammonia volatilization after application of urea to winter wheat over 3 years affected by novel urease and nitrification inhibitors

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A B S T R A C T

Ammonia emission from urea application negatively affects both environmental quality and human health, and so it is desirable to minimize nitrogen loss by ammonia volatilization and to improve nitrogen use efficiency. This field study aimed to assess the effects of recently introduced urease (N-(2 nitrophenyl) phosphoric triamide, 2-NPT) and nitrification inhibitors (mixture of dicyandiamide and 1H-1,2,4-triazol) on NH_3 emissions following urea application as compared to calcium ammonium nitrate (CAN) in Northern Germany. The measurements were carried out in winter wheat (Triticum aestivum) in the years 2011–2013 covering in total 12 urea application dates. Urea was applied as unamended granulated urea, or combined with urease or nitrification inhibitor or with both inhibitors. Fertilizers were applied in multi-plot field trials with four replications and ammonia losses were measured simultaneously by a combination of a calibrated dynamic chamber and passive samplers. Application date strongly affected relative NH₃ loss (% of applied N) due to seasonal variation of soil moisture, temperature, and rainfall. Initial soil moisture showed a strong effect on NH₃ emission. Averaged over the three vegetation periods, relative $NH₃$ losses from unamended urea amounted to 8%, with mean emissions of 5%, 4%, and 17% for split N applications in March, April, and early June, respectively. Compared with treatment without urease inhibitor, the urease inhibitor addition reduced emissions by 26–83%, resulting in emissions similar to that from CAN. Analyzing the total data set, no significant effect of the nitrification inhibitor on $NH₃$ emission was observed while at specific applications significantly higher as well as lower emissions compared to unamended urea were detected. The results highlight that NH₃ emissions after field application of urea are highly variable under north German climate conditions and simple emission factors should be reevaluated. Urease inhibitor and appropriate application timing are effective measures to reduce $NH₃$ emission from field applied urea.

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1. Introduction

Nitrogen fertilizer is essential for the high rate of food production delivered by modern agriculture. It contributes \in 20–80 billion of profit per year for EU farmers ([Sutton](#page--1-0) et al., 2011). Although calcium ammonium nitrate (CAN) is the principal N fertilizer in many

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European countries, the use of granular urea has increased and was second to CAN in Central and Western Europe in 2012 (IFA, [2014\)](#page--1-0). Urea is particularly popular in developing countries due to its advantages of a high N content, safety, and easy transportation ([Glibert](#page--1-0) et al., 2006). However, the increase of pH and surface soil NH4 + -concentrations resulting from urea hydrolysis can exacerbate $NH₃$ emission. This can cause low N use efficiency, especially in alkaline soil or soil with low sorption capacity, which limits the use of urea fertilizer in Europe [\(Sommer](#page--1-0) et al., 2004; Jensen et al., 2011). N $\log b$ NH₃ emission not only brings about economic loss to farmers, but also detrimental effects to ecosystems and human health (Bremner, 1995). It was estimated that NH₃ released into the air from agriculture, mostly from animal excreta, causes $\sim \epsilon$ 50 billion in annual damage in the EU ([Sutton](#page--1-0) et al., 2011).

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Many studies on $NH₃$ emission from organic and mineral fertilizer application and livestock housing have been performed in recent decades (Sommer and [Hutchings,](#page--1-0) 2001; Sommer et al., 2004). Nevertheless, the research related to NH₃ emissions after application of urea in many regions is still limited. For EU-27 countries, [EMEP/EEA](#page--1-0) (2013) provided a methodology with a $NH₃$ emission factor of 24% for urea N applied to arable soil. However, there are almost no published data on ammonia emissions from central Europe. [Schraml](#page--1-0) et al. (2009) reported maximum relative emissions from grassland in Southern Germany of 4–7%, which is much lower than the EMEP emission factor. Therefore, there is still uncertainty in the magnitude of ammonia emissions under practical conditions. Moreover, effects of soil and climate conditions on emission contribute additional variability not captured by a single emission factor.

Urease inhibitors have been proven to reduce $NH₃$ emission from urea applied in arable soil (Abalos et al., 2012; [Francisco](#page--1-0) et al., [2011\)](#page--1-0). They depress the rate of urea hydrolysis, which reduces the increase in NH_4^+ concentration in soil (Gill et al., [1999](#page--1-0)). However, the effectiveness of urease inhibitors is still uncertain, because soil properties, weather conditions, and the types of inhibitors varied in previous studies. For instance, the $NH₃$ reduction efficiency of urease inhibitor NBPT from the surface application of urea on a clay loam soil in the UK was 77–88% [\(Sanz-Cobena](#page--1-0) et al., 2011), while on forest soil in loblolly pine systems in the USA it decreases to only 25% [\(Zerpa](#page--1-0) and Fox, 2011).

To mitigate greenhouse gas emissions from agricultural land, nitrification inhibitors have become attractive for reducing $N₂O$ emissions from field applied fertilizers. They inhibit the production of nitrate, which is the electron acceptor for denitrification, the main process responsible for N_2O emission under temperate conditions (Pfab et al., 2012; [Weiske](#page--1-0) et al., 2001). However, the use of nitrification inhibitors prolongs the detention period of ammonium in soil, and therefore, could increase ammonia emissions. The application of the nitrification inhibitor dicyandiamide (DCD) has been found to increase $NH₃$ emissions by 18–29% (Soares et al., 2012; [Zaman](#page--1-0) et al., 2008). On the other hand, the use of urea fertilizer stabilized by nitrification inhibitors allows the reduction of split N applications from three to two doses due to reduced leaching risk of the stabilized ammonium. This may reduce management costs and intensity, thereby decreasing detrimental environmental effects as soil compaction and use of fossil fuels. For reduction of both $NH₃$ and $N₂O$ emissions, a combination of urease and nitrification inhibitors has been recommended for urea fertilization ([Chien](#page--1-0) et al., 2009). To test the effects of fertilizer and inhibitor type on ammonia emissions, the questions described above need to be studied under varying annual weather and realistic canopy conditions.

The principal objectives of this study were to investigate $NH₃$ emissions from winter wheat (Triticum aestivum) exclusively fertilized with urea (three split doses at different growth stages) over 3 years in Northern Germany and to quantify the reduction efficiency of a recently introduced urease inhibitor, N-(2-nitrophenyl) phosphoric triamide (2-NPT), and its interaction with a recently introduced nitrification inhibitor, a mixture of dicyandiamide (DCD) and $1H-1,2,4-triazol$, on $NH₃$ volatilization. As a benchmark, urea fertilization was compared to the most common N fertilizer in Germany, CAN. Ammonia losses were determined in replicated multi-plot field trials, which are the recommended approach in agricultural field studies (Shah et al., [2006\)](#page--1-0). Model analysis was applied to seek critical factors influencing NH3 volatilization in the study region. The guiding hypotheses of this study were (a) ammonia emissions are highly variable between split application dates strongly deviating from a single emission factor, (b) application of urease inhibitor is a robust approach for emission reduction, but its effectiveness is dependent on soil and weather conditions, and (c) applying urea with nitrification inhibitor increases $NH₃$ emissions as compared to unamended urea.

2. Materials and methods

2.1. Site description

The field experiment was conducted at the Experimental Station "Hohenschulen", property of Christian-Albrechts-University of Kiel in Northern Germany (54°18'N, 9°58'E). The soil is classified as Luvisol with a sandy loam texture (sand 58%, silt 29%, and clay 13%) and has the following properties: bulk density 1.37 g cm⁻³, pH 6.5, CEC 13 cmol kg^{-1} , total organic C 1.5%, total N 0.1%, water hold capacity (WHC) 37%, wilting point 10%. Due to regular liming, the soil is characterized by a well buffered pH to sustain high productivity.

2.2. Field experiment design

The field study was carried out during three winter wheat seasons, 2010/2011, 2011/2012, and 2012/2013. An unfertilized control and five different N fertilizers were tested ([Table](#page--1-0) 1): CAN, granular urea (U), a granular urea urease inhibitor formulation $(U+UI)$, a formulation of granular urea with nitrification inhibitor $(U + NI)$, and granular urea combined with both urease and nitrification inhibitors $(U+UI+NI)$. The urease inhibitor used in the study was N-(2-nitrophenyl) phosphoric triamide (2-NPT), and the nitrification inhibitor was a mixture of dicyandiamide (DCD) and 1H-1,2,4-triazol. These compounds were approved for use by the European authorities in 2003 and 2012 (EU regulations 2003/ 2003 and 223/2012). The concentrations of urease and nitrification inhibitors were 0.075% and 2% of the N content in the granular urea, respectively. Both inhibitors have similar migration behavior as urea. More than 95% of the granular fertilizer has a diameter ranging from 1.6 to 5.0 mm, with an average of 3.3 mm. The fertilizers were provided by the company SKW Stickstoffwerke Piesteritz GmbH, Germany.

The total nitrogen application rate for all applied fertilizers was 200 kg N ha⁻¹, based on the regional optimal N fertilization level. As typical for the regional N management in wheat, total N of all fertilizers without the nitrification inhibitor was applied in split doses at three different wheat growth stages: 70 kg N ha⁻¹ at EC 21 (begin vegetation period), 70 kg N ha⁻¹ at EC 32 (stem elongation) and 60 kg N ha⁻¹ at EC 49 (begin of heading). Here, the EC code describes the phenological development (growth stage) of cereal crops using a decimal code ranging from 0 (seeding) to 99 (harvested product) [\(BBCH-Monograh,](#page--1-0) 2001). Treatments with three applications are indicated by A3. The fertilizers which contain nitrification inhibitor $(U + NI)$ and $U + UI + NI)$ were applied in two doses, with 110 kg N ha⁻¹ at EC 21 and 90 kg N ha⁻¹ at EC 37 (begin of flag leaf expansion) indicated as A2. Due to this partitioning of urea applications for the different urea fertilizers, in 2011, simultaneous testing of all fertilizers was only done once at the stage of EC 21, but with different application rates. Since there are potential effects of the application rate and date on $NH₃$ emissions, in 2012 and 2013 two additional treatments with both urea fertilizers plus the nitrification inhibitor $(U + NI, U + NI + UI)$ applied in three doses were included. To indicate different measurement campaigns within a vegetation period, fertilization on EC 21, EC 32, EC 37, and EC 49 is coded by the month of fertilization (March–June, respectively). All N fertilizers were applied on the surface by tractor-driven fertilizing machinery for plot experiments (working width 3 m) which evenly applied the fertilizers vertically without horizontal throwing. The machine was adjusted to each fertilizer before application.

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