



# Influence of a nitrification inhibitor and of placed N-fertilization on N<sub>2</sub>O fluxes from a vegetable cropped loamy soil

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## ABSTRACT

Arable soils are a major source of the climate relevant trace gas nitrous oxide (N<sub>2</sub>O). Although N<sub>2</sub>O emissions from soils increase with the amount of N-fertilizer, there is still a lack of data for intensively fertilized systems, such as vegetable production. We investigated the effect of an ammonium sulfate nitrate (ASN) fertilization either placed or broadcast applied combined with a nitrification inhibitor (3,4-dimethylepyrazole phosphate (DMPP)) on soil surface N<sub>2</sub>O fluxes as compared to conventional broadcast ASN fertilization in a lettuce–cauliflower rotation over two years of measurement. Except for a lower cauliflower yield in the second experimental year with placed fertilization, no differences in yields between the fertilized treatments were observed. Annual cumulative N<sub>2</sub>O emissions of the conventionally fertilized treatment were 8.8 and 4.7 kg N<sub>2</sub>O-N ha<sup>-1</sup> yr<sup>-1</sup> for the first and second experimental year, respectively, indicating a high inter-annual variability.

The addition of the nitrification inhibitor significantly reduced N<sub>2</sub>O emissions during the cropping season and also during the winter period, resulting in an annual reduction of 45 and 40% as compared to the conventionally fertilized (CONV) treatment. The reason for the lower N<sub>2</sub>O release in the DMPP treatment as compared to the conventionally fertilized treatment remained unclear. Since we did not find any significant differences in the mineral N pools during periods with distinctive inhibition, this can be ruled out as reason for the lower N<sub>2</sub>O release in the DMPP treatment. We found lower soil respiration in the DMPP treatment during several months starting about six weeks after fertilizer application.

In contrast to the treatment with nitrification inhibitor, the placed fertilization as an N-depot (fertilizer bands inserted into the soil) did not reduce annual N<sub>2</sub>O emissions, although the ratio of ammonium (NH<sub>4</sub><sup>+</sup>) to nitrate (NO<sub>3</sub><sup>-</sup>) in the first weeks after N-application indicate inhibition of nitrification in the fertilizer depot. We assume that, even though NH<sub>4</sub><sup>+</sup> concentrations in the depots were high, toxicity was not sufficient for a complete inhibition of microbial activity in the surrounding of the depots, resulting in considerable N<sub>2</sub>O production. The emission factors calculated for CONV treatment were 1.6 and 0.8% for the first and second experimental year, respectively. For the treatment with nitrification inhibitor (NI), they were only 0.9 and 0.5%; for the treatment with placed fertilization as an N-depot (DEPOT) 2.0 and 0.8%. They were thus within the range proposed by the guidelines of the IPCC (2006).

However, although the N-input related N<sub>2</sub>O emission factors were within the range proposed by the guidelines of the IPCC, the absolute N<sub>2</sub>O emissions from the intensively fertilized vegetable field were high. For effective, but environmentally sound vegetable production, a deeper understanding of nitrification inhibitory strategies is necessary.

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## 1. Introduction

The concentration of the greenhouse gas nitrous oxide (N<sub>2</sub>O) has been continuously increasing over the last decades (Prather et al., 1995; IPCC, 2007). In soils, N<sub>2</sub>O is produced to a major part by the two microbial processes nitrification and denitrification (Bremner and Blackmer, 1981; Davidson, 1991). Intensive N-fertilization fuels these processes as it provides substrate for nitrifying and denitrifying microorganisms.

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Nitrification is the microbial oxidation of ammonium ( $\text{NH}_4^+$ ) to nitrite ( $\text{NO}_2^-$ ) which is further oxidized to nitrate ( $\text{NO}_3^-$ ) (Granli and Bockman, 1994). The provided  $\text{NO}_3^-$  serves as substrate for denitrification. N-fertilization with  $\text{NH}_4^+$ -rich fertilizers and the inhibition of nitrification is proposed as a potent measure to reduce  $\text{N}_2\text{O}$  losses from arable as well as from grassland soils (Bremner and Blackmer, 1981; Mosier et al., 1996; De Klein and Van Logtestijn, 1996; Akiyama et al., 2010). 3,4-Dimethylpyrazole phosphate (DMPP) is a relatively new nitrification inhibitor which has undergone standard toxicological and ecotoxicological tests (Roll, 1999). Zerulla et al. (2001) specified several advantageous properties such as high efficiency ( $0.5\text{--}1.5\text{ kg DMPP ha}^{-1}$ ) as compared to other inhibitors like dicyandiamide (DCD) and a low risk for translocation. The addition of the nitrification inhibitor DMPP is expected to reduce  $\text{N}_2\text{O}$  emissions during the vegetation period through the inhibition of the first reaction of nitrification that means by the inhibition of the enzyme ammonia monooxygenase (Vannelli and Hooper, 1992) which catalyzes the conversion of  $\text{NH}_4^+$  to hydroxylamine. The inhibition causes a stabilization of  $\text{NH}_4^+$  and a strong delay in the production of  $\text{NO}_3^-$  which was often shown to reduce leaching (Chaves et al., 2006; Diez et al., 2010). The stabilization of  $\text{NH}_4^+$  by nitrification inhibitors with lower risk of N-leaching allows for simplified fertilization strategies with reduced fertilizer application (Fettweis et al., 2001; Serna et al., 2000).

Several studies have been published on the reductive effect of DMPP on  $\text{N}_2\text{O}$  emissions: Weiske et al. (2001a) measured  $\text{N}_2\text{O}$  fluxes from arable soil for three years during the cropping season and found decreases in the cumulative  $\text{N}_2\text{O}$  emissions of up to 53% for this period. A decrease of  $\text{N}_2\text{O}$  emissions for DMPP was also reported for winter wheat by Linzmeier et al. (2001). They used fertilizer with DMPP in simplified fertilizer strategies (reduced number of applications) and compared it to conventional fertilization in two following years. However, these investigations were limited to the cropping seasons only. During four weeks after fertilizer application, fertilizer-derived  $\text{N}_2\text{O}$  losses were reduced by about 50% in the first year of their measurements. Menendez et al. (2006) found a reduction in  $\text{N}_2\text{O}$  emissions from grassland when adding DMPP to slurry, but not when adding DMPP to ammonium sulfate nitrate (ASN). In contrast, Belastegui Macadam et al. (2003) found a reductive effect of DMPP for both slurry and mineral fertilizer.

None of the published studies covered a continuous measuring period of a whole year. Nevertheless, the importance of annual datasets for the measurement of  $\text{N}_2\text{O}$  emissions is known and a contribution of up to 89% of winter emissions to total annual emissions has been reported for study sites with winter frost in Germany (Flessa et al., 1995; Kaiser and Ruser, 2000). Therefore, measures aiming at a reduction of the impact of agricultural activities on the earth's climate need to be verified on an annual base, at least in regions with distinctive freeze–thaw cycles during the winter season. In terms of nitrification inhibitors it could be assumed that lower  $\text{NO}_3^-$  leaching losses result in a higher fertilizer use efficiency which might decrease the C-to-N-ratio of plant residues thus stimulating their mineralization in fall. Kaiser et al. (1998) and Baggs et al. (2000) found increasing  $\text{N}_2\text{O}$  emissions during the winter period with decreasing C-to-N-ratio of crop residues. In addition, Ruser et al. (2001) found a strong correlation between the  $\text{NO}_3^-$  contents of the top soil and the  $\text{N}_2\text{O}$  emissions during the winter season. Up to now, no study has measured the effect of DMPP on  $\text{N}_2\text{O}$  emissions during a whole year including the winter season. Therefore it is still unclear whether the reduction of  $\text{N}_2\text{O}$  emissions by the use of nitrification inhibitors is also valid on an annual base.

Aside from the addition of synthetic nitrification inhibitors, nitrification can also be inhibited by the creation of unfavorable conditions for nitrifying organisms. Controlled Uptake Longterm

Ammonium Nutrition (CULTAN) is an N-placement fertilization strategy where N-fertilizer with a high  $\text{NH}_4^+$  portion is placed in the soil as a depot (Sommer, 2005). In the N-depots,  $\text{NH}_4^+$  concentrations are extremely high. It is known that high  $\text{NH}_4^+$  concentrations (e.g. in the soil solution  $>3000\text{ ppm}$ ) can completely inhibit nitrification (Wetselaar et al., 1972). This leads to a stabilization of  $\text{NH}_4^+$  similar to the use of nitrification inhibitors. To ensure an easily available N supply for vegetable crops with a short growing period, the CULTAN-method can be modified with additional  $\text{NO}_3^-$  covering this early N demand. These so-called pseudo-CULTAN strategies use fertilizer depots with up to 30% of the total N as  $\text{NO}_3^-$  (Sommer, 2005).

Vegetables like cauliflower are highly responsive to N-fertilization and are rarely negatively affected by excessive N applications (Thompson et al., 2000). The main reason for N surpluses in cauliflower production is that it is harvested in the vegetative growth stage with the main N-uptake in the late growing period. More than 90% of the N uptake in cauliflower occurred 50 days preceding harvest (Welch et al., 1987). The resulting high mineral N contents of the soil in combination with high soil moisture due to irrigation offer ideal conditions for denitrifying organisms. Therefore, comparably high  $\text{N}_2\text{O}$  flux rates can be expected for vegetable fields. Furthermore, only few datasets for vegetable production have been provided so far (Dobbie et al., 1999; Van Der Weerden et al., 2000). None of these investigations was carried out in a region with freeze–thaw cycles, which are known to contribute a major part of the total annual emissions (Flessa et al., 1995; Ruser et al., 2001). For these reasons, we chose a soil cropped with lettuce and cauliflower in a temperate region with strong winter frost (Southwest Germany) for our investigations.

Several studies have reported increasing yield or yield quality both for the use of nitrification inhibitors (Pasda et al., 2001) and for N-depot fertilization (Sommer, 2005) compared to broadcast fertilizer application. A higher plant N-uptake due to the nitrification inhibiting effect (either with an inhibiting compound or with the CULTAN-technique) during summer might result in lower C-to-N-ratios. The incorporation of residues with low C-to-N-ratio however could result in high  $\text{N}_2\text{O}$  emissions after harvest and during winter.

Therefore we expect reduced  $\text{N}_2\text{O}$  emissions during the vegetation period without any negative effects on yield, while an increase in  $\text{N}_2\text{O}$  emissions was expected for the winter season. Therefore, on an annual basis, no significant difference in  $\text{N}_2\text{O}$  emissions from conventionally fertilized soils is expected.

Thus, the aims of our study were: (1) to quantify the impact on  $\text{N}_2\text{O}$  emissions, yield and plant N by the addition of a nitrification inhibiting compound (DMPP) as compared to conventional N-fertilization; (2) to quantify the effect of N-fertilization according to the CULTAN-technique on  $\text{N}_2\text{O}$  emissions, yield and plant N as compared to conventional N-fertilization; and (3) to calculate emission factors for direct emissions (EF1) for all treatments according to the IPCC (IPCC, 2006).

## 2. Materials and methods

### 2.1. Study site

The field trial was established on the experimental farm “Heidfeldhof”, which belongs to the University Hohenheim, located 13 km south of Stuttgart, Germany ( $48^\circ43'00''\text{ N}$ ;  $9^\circ11'40''\text{ E}$ ) in an altitude of 410 m. The mean long-term annual precipitation is 686 mm, the long-term average air temperature  $8.8^\circ\text{C}$  (Henning-Müller, 2000). The soil type was a Haplic Luvisol derived from periglacial loess.  $\text{C}_{\text{org}}$  and  $\text{N}_t$  content of the top soil was 1.8% and 0.16%. Texture consisted of 2% sand, 68% silt and 30% clay, the initial soil pH was 5.5 and the gravel content was  $<1\%$  (Pfab et al., 2011).

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