Effects of the novel nitrification inhibitor DMPSA on yield, mineral N dynamics and N_2O emissions

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Abstract
Sustainable use of nitrogen (N) fertilizers is essential for agronomic efficiency and environmental stewardship. Nitrification inhibitors (NI) can play an important role in mitigating unwanted environmental impacts by N fertilization, i.e. nitrate leaching and greenhouse gas/N_2O emissions, while sustaining and increasing yields. A new nitrification inhibitor 3,4 dimethylpyrazol succinic acid (DMPSA) has been developed characterized by a slower reagent release curve and different physicochemical properties as compared to established inhibitors. In recent years, the new inhibitor was evaluated and tested in laboratory and field trials regarding yields, N uptake and N_2O emissions in different environments and combined with varying fertilizers (e.g. urea, CAN) and crops (arable crops, vegetables, fruits). DMPSA was proven applicable to reduce N_2O emissions form urea and CAN by 60-90% as compared to the untreated fertilizer. On the tested fertilization levels yields and N-uptake were mainly unaffected or slightly increased by application of DMPSA, on average +4% and +2% for yield and N-uptake, respectively. The effect of DMPSA appeared to be independent of the N fertilizer type combined with the compound and crop type. The application of the new compound could still be further improved by reducing fertilization levels sustaining the same yield and N uptake level and varying fertilizer management by reducing the number of split N applications. Additional options for an optimized fertilizer N management by use of DMPSA require further investigation.

Key Words
Nitrification inhibitor, DMPSA, incubation, N_2O, urea, CAN, yield

Introduction

Reactive nitrogen (N) is one of the key drivers with respect to agronomic productivity and global sustainability. According to the planetary boundary concept (Steffen et al. 2015) global fluxes of reactive N have already by far exceeded the estimated planetary boundary of sustainable and resilient use of natural resources. Agricultural practices, in particular animal husbandry and fertilization with synthetic N compounds, are together with fossil fuel combustion and organic wastes among the major sources of reactive N (Sutton et al. 2012). Reactive fertilizer N (NH_4^+, NH_3, N_2O, NO_3^-) not effectively used in agricultural production system cause environmental hazards as soils and water eutrophication, soil acidification, greenhouse gas (N_2O) emissions and fine dust (PM 2.5) formation (Erisman et al. 2008). It is thus a key challenge to the use of fertilizers to guarantee and even increase area based agronomic efficiency for global food supply while keeping N losses and unwanted environmental effects to a minimum. On this background novel active ingredients, namely nitrification and urease inhibitors, for the control of agronomic N dynamics have been developed. In particular the nitrification inhibitors diciandyamide (DCD) and 3,4 dimethylpyrazol phosphate (DMPP) have been widely used and tested in the last decades and have been proven as environmentally safe and to effectively sustain agronomic productivity while – even strongly – reducing nitrate leaching and N_2O emission (Weiske et al. 2001) from field applied fertilizers. However, the success in the development of this compounds calls for further improvements and extension of applicability of new NI reactive compounds. There is in particular a need for a broad applicability of an environmentally safe NI to all fertilizers irrespective of fertilizer chemistry and a modified kinetics of compound release and activity which may prolong and modulate the inhibitory effect as compared to already established NI. Such a compound could be combined with other novel technologies and inhibitors to further increase agronomic and environmental efficiency. In addition, the concentration of the reactive compound should be as low as possible to avoid costs and potential transfer to non-target systems.
The novel nitrification inhibitor 3,4 dimethylpyrazol succinic acid (DMPSA) shall combine the well-known inhibitory effect of DMP with the release behavior of succinic acid, an organic acid. The combination with succinic acid, which has to be microbially degraded for the release of the reactive compound, is aimed to result in a smoother and prolonged availability of DMP in soil. The non-polarity of DMPSA allows its combination with any mineral fertilizer (e.g. urea) and thereby increases the scope of applicability of NI. The specific release

kinetics of the compounds may also allow for lower compound requirement (concentration) to yield the same inhibitory effect as established NI.
In this contribution first experimental findings from the laboratory and field scale with respect to the agronomic effectiveness (yield, N-uptake) and environmental effects (N_2O) are presented. Key research questions of the studies were: a.) how do different fertilizers combined with DMPSA promote crop development as compared to the uninhibited fertilizer? b.) what effects do occur with respect to N losses particular N_2O emissions?

Methods

The new compound DMPSA was tested in a laboratory and a multi-plot field trial for both environmental efficacy and yield effects. Additional field trials were carried out to investigate the yield and N uptake effects of DMPSA combined with different synthetic N fertilizers.

Laboratory trial

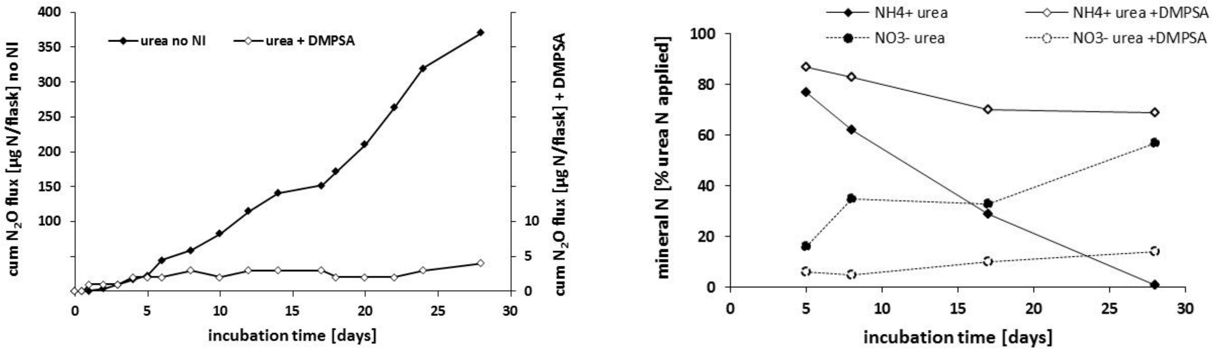
A replicated (n = 4) incubation trial (20 °C) was carried out at the University of Hohenheim, Germany. Soil(150 g) was weighted in glass bottles as part of a dynamic chamber array. Urea fertilizer at a rate of 200 kg N ha^{-1} (0.51 mg N g^{-1} soil) was applied to the soil surface (silt loam, pH 6.8) with and without DMPSA at a concentration level of 0.8% of the NH_4^+-N and unfertilized of the two compounds. Concentrations of different trace gases (N_2O, NH_3) evolving from soil were measured every second day by gas chromatography and cumulated emissions were calculated. For determination of mineral N dynamics (NO_3^-, NH_4^+) in soil, soil samples (5 g) were taken from each flask 5, 8, 17 and 28 days after start of incubation.

Field trials

A field trial in irrigated maize was set-up in 2014 and 2015 at the field station "El Encín", situated near Alcalá de Henares (Madrid, Spain), in the middle of the Henares river basin, (latitude 40°32´N, longitude 3°17'W). Experimental plots (56 m^2) were arranged in a complete randomized block design on a *Calcic Haploxerept* (Soil Survey Staff, 1999) with a clayey loam texture (28% clay, 17% silt, 55% sand, pH 7.6) in the plough layer. Fertilizer treatments (all at 180 kg N ha^{-1}) included a. Calcium Ammonium Nitrate (CAN), b.) CAN + DMPSA (0.8% of the NH_4^+-N) (CAN+NI) and c) Control with no N fertilizer (C). The N_2O-fluxes were measured using the closed chamber technique within the maize growing period (beginning April – end September). Concentrations of N_2O in the gas samples were determined using an HP-6890 GC (Agilent Technologies, Barcelona, Spain). Maize biomass and corn (at 14 % moisture level) yield were determined at black line stage by manual harvest in each plot consisting in 5 m.l.. Based on cumulated N_2O emissions over the whole vegetation period yield scaled N_2O emissions were calculated.
Additionally, the effect of DMPSA addition to different synthetic N fertilizers (CAN, DAP, AS, ASN) on yield and N-uptake was tested in recent years in a high number of replicated field trials in 16 different arable, fruit and vegetable crops in 9 European countries. Fertilizers with and without DMPSA were applied at the same dose in those trials while other agricultural management was identical. Generally yields were determined with additional investigation of crop N uptake in particular in grain crops.

Results

Nitrous oxide emissions were strongly reduced by the use of DMPSA (Fig. 1a) by >90% as compared to untreated urea fertilizer in the incubation trial. This reduction was closely related to modified soil urea, NO_3^- and NH_4^+-N dynamics. With addition of DMPSA, ammonium was sustained on a much higher level until the end of the trial, while nitrate remained at a considerably lower concentration (Fig. 1b). The very strong reduction of N_2O fluxes by application of DMPSA in this trial as compared to mean values for other NI in the literature (on average -37% Akiyama et al. 2010) may be explained by the small amount of soil used in the incubation trial resulting in high compound concentration per unit soil as compared to field applications.
Maize yields in the years 2014 and 2015 in Spain were unaffected or even significantly increased by CAN fertilization with DMPSA as compared to sole CAN application (Tab. 1). In both years, DMPSA decreased N_2O emissions from CAN by about 65%. This is higher as observed for other Nis reported by Akiyama et al. 2010, which mainly included measurement durations shorter than a whole year. However, reductions obtained by application of DMPSA may be smaller when measurements are continued after harvest which should be tested in future studies. Scaled to yield, N_2O emissions from CAN+DMPSA were not significantly different or even lower than those from the unfertilized control.



a.) **b.)**

Fig.1 a) effect of DMPSA addition on cumulated N_2O-emissions after application of urea to surface soil in incubation chambers and b.) ammonium and nitrate dynamics in soil during incubation

Table 1: Grain yields, cumulative emissions of N_2O during the experimental period, and yield scaled N_2O-emissions in irrigated maize grown in central Spain in 2014 and 2015

treatment	Grain yield (Mg ha^{-1})		N_2O (kg N ha^{-1})		Yield scaled N_2O emissions (mg N_2O-N kg grain^{-1})	
	2014	2015	2014	2015	2014	2015
C	3.54 a	5.97 a	0.11 a	0.10 a	49.92 ab	17.39 a
CAN	17.08 b	11.71 b	1.40 c	0.90 c	75.88 b	77.34 c
CAN+I	14.98 b	14.64 bc	0.52 b	0.33 b	33.15 a	22.34 a
S.E.	0.15	1.99	0.12	0.14	12.2	14.19

Different letters within columns indicate significant differences by applying the Least Significant Difference (LSD) test at $P< 0.05$. S.E. is the Standard Error of the mean. The variable "N_2O" was log-transformed.

In most cases combining DMPSA with different mineral N fertilizers resulted in yields and N-uptake (grain crops) on the same or higher level as compared to the uninhibited fertilizer (Fig. 2). In a small number of instances application of the new nitrification inhibitor resulted in a reduction in yield and N uptake, probably in environmental situations unfavourable for ammonium nutrition of crops. There were no specific differences in the efficacy of the inhibition depending on crop type (arable crop, vegetables, fruit) or inhibited mineral fertilizer (urea, CAN, di-ammonium phosphate, AS, ASN) (not shown). On average – though not significant – yields were increased by 4% and N-uptake by 2 %.

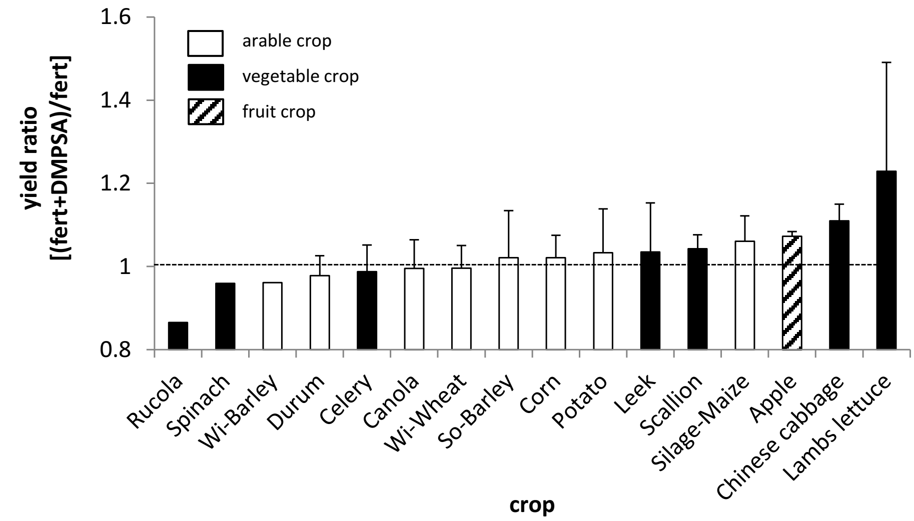


Fig.2) effect of addition of DMPSA to mineral N fertilizers on yield of arable, vegetable and fruit crops in overall 110 field trials and), error bars = standard deviation between independent field trials.

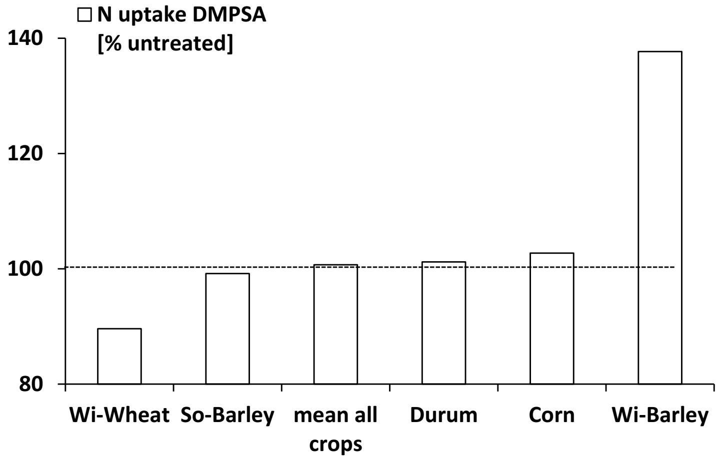


Fig.3) effect addition of DMPSA to mineral N fertilizers on N uptake by grain crops (9 trials)

Conclusions

The new nitrification inhibitor DMPSA was proven to reduce N_2O emissions from both urea and CAN fertilizer by 90% and 60%, respectively in an incubation and a field trial. This reduction is stronger than reported average values from other Nis but additional studies are needed to test the longevity of this effect. In more than 100 yield trials, DMPSA was effective in the combination with different mineral N fertilizers in sustaining or increasing yield and N uptake in a high variability of crops while reduced yields and N uptake were observed in only a small proportion of the field tests. Further investigations are needed to elucidate the environmental conditions fostering the latter effects and to derive application recommendations. As a result DMPSA can be considered a new promising versatile compound for the reduction of GHG emissions from agriculture while sustaining high yield levels. The wide applicability of the new compound calls for further investigation for its role in optimized crop N management systems in sustainable agronomy. These management options can include reducing N levels while sustaining high yields, reducing number of split N applications due to low risk of N losses when applying DMPSA and addition of DMPSA to organic fertilizers.

References

Akiyama H, Yan X, Yagi K (2010). Evaluation of effectiveness of enhanced-efficiency fertilizers as mitigation options for N_2O and NO emissions from agricultural soils: meta-analysis. Glob Change Biol. 16, 1837–1846

Erisman JW, Bleeker A, Hensen A, Vermeulen A (2008). Agricultural air quality in Europe and the future perspectives. Atmos. Environ. 42, 3209–3217, DOI: 10.1016/j.atmosenv.2007.04.004

Steffen W et al.(2015), Planetary boundaries: Guiding human development on a changing planet. Science 347, 1259855. DOI: 10.1126/science.1259855

Sutton MA, Oenema O, Erisman JW, Leip A, van Grinsven H, Winiwarter W. (2011). Too much of a good thing. Nature 472(7342):159-61. doi: 10.1038/472159a

Weiske A, Benckiser G, Herbert T, Ottow J (2001). Influence of the nitrification inhibitor 3,4-dimethylpyrazole phosphate (DMPP) in comparison to dicyandiamide (DCD) on nitrous oxide emissions, carbon dioxide fluxes and methane oxidation during 3 years of repeated application in field experiments. Biol Fertil Soils. 34, 109–117.