Europ. J. Agronomy 80 (2016) 1–8

Contents lists available at ScienceDirect

European Journal of Agronomy

journal homepage: www.elsevier.com/locate/eja

Nitrogen use efficiency and residual effect of fertilizers with nitrification inhibitors

M. Alonso-Ayuso, J.L. Gabriel, M. Quemada*

Technical University of Madrid, Dpto. Producción Agraria, Avd. Complutense s/n, 28040 Madrid, Spain

ARTICLE INFO

Article history:
Received 1 February 2016
Received in revised form 11 June 2016
Accepted 16 June 2016
Available online 5 July 2016

Keywords:
Ammonium sulfate nitrate
DMPP
Fertilizer use efficiency
Nitrogen recovery

ABSTRACT

Blending fertilizers with nitrification inhibitors (NI) is a technology to reduce nitrogen (N) losses. The application of NI could increase the soil N supply capacity over time and contribute to an enhancement of N use efficiency (NUE) in some cropping systems. The objectives were to determine in a field experiment located in Central Spain (i) the effect of NI-fertilizers applied to maize (*Zea mays* L.) during two seasons on yield, N content and NUE compared to conventional fertilizers, (ii) the soil residual effect of NI-fertilizers in a non-fertilized sunflower (*Helianthus annuus* L.) planted during a third season, and (iii) the possible sources of residual N via laboratory determinations. The maize was fertilized with ammonium sulfate nitrate (ASN) and DMPP (3,4-dimethylpyrazole phosphate) blended ASN (ENTEC®) at two levels (130 and 170 kg N ha^{-1}). A control treatment with no added N fertilizer was included to calculate NUE. The second year, DMPP application allowed a 23% reduction of the fertilizer rate without decreasing crop yield or grain quality. In addition, the sunflower planted after the maize scavenged more N in treatments previously treated with ENTEC® than with traditional fertilizers, increasing NUE in the cropping systems. After DMPP application, N was conserved in non-ready soil available forms during at least one year and subsequently released to meet the sunflower crop demand. The potential N mineralization obtained from aerobic incubation under controlled conditions of soil samples collected before sunflower sowing was higher for ENTEC® than ASN or control treatments. A higher δ^{15}N in the soil indicated larger non-exchangeable NH_4^+ fixation in soils from the plots treated with ENTEC® or ASN-170 than from the ASN-130 or the control. These results open the opportunity to increase NUE by designing crop rotations able to profit from the effect of NI on the soil residual N.

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1. Introduction

The application of nitrification inhibitors (NI) is a strategy to increase the efficiency of nitrogen (N) in farming systems. These chemical compounds delay the conversion of ammonium to nitrate in soil by depressing the activity of nitrifiers bacteria. Consequently, when fertilizers pre-blended with NI are supplied the aim is to improve the synchronization between the N supply and crop demand, enhancing N use efficiency (NUE) and decreasing nitrate losses (Ladha et al., 2005). Evidence for the mitigation of nitrous oxides emissions has been reported in various studies (Ruser and Schulz, 2015) but for the increase of NUE is controversial. In a meta-analysis conducted by Quemada et al. (2013) in irrigated agricultural systems, the use of NI reduced nitrate leaching by 27% compared to conventional fertilizers but did not increase crop yield or NUE significantly. Whereas, Abalos et al. (2014) reported that NI increased crop productivity and NUE with varying degrees of success. Without underestimating the enormous importance of the environmental benefits, it is also crucial to consider the economic costs and profits of NI use. The opportunity of saving N-fertilizer, reducing the number of applications, or increasing the productivity are advantages that would justify the higher price of NI to farmers as a viable alternative over conventional fertilizers. Therefore, identification of cropping systems or environmental conditions in which NI enhances NUE and crop yield may contribute to the best practice of this fertilizer technology.

Among NI, the 3,4-dymethylpyrazole phospate (DMPP) has become very popular, particularly when added to ammonium sulfate nitrate (ASN), ammonium sulfate or urea (Trenkel, 2010). Several studies showed that the use of DMPP may reduce N_2O and NO emissions (Zerulla et al., 2001; Ruser and Schulz, 2015) and nitrate leaching losses (Weiske et al., 2001; Diez-Lopez et al., 2008; Li et al., 2008). In addition, increase of NUE was also observed in several studies (Diez-Lopez et al., 2008; Liu et al., 2013), but Arregui

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* Corresponding author.
E-mail address: miguel.quemada@upm.es (M. Quemada).

http://dx.doi.org/10.1016/j.eja.2016.06.008
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and Quemada (2008) did not observe an effect in a wheat/barley crop rotation under rainfed conditions. Results in terms of yield increase are also controversial. Pasda et al. (2001) observed an increase in yield and crop quality in cereals and vegetables when compared to conventional fertilizers; particularly pronounced at sites with risk of intensive rainfall or high application of irrigation water, and in light sandy soils. Liu et al. (2013) observed tendencies in crop yield, aboveground biomass and N uptake increase after application of DMPP blended with urea. As well, Martinez et al. (2015) observed a yield increase in strawberry plants. However, other authors did not observe significant response in yield when it was incorporated in the N-fertilizer applied over winter and summer cereals (Weiske et al., 2001; Arregui and Quemada, 2008; Ercoli et al., 2013) or applied pre-blended with urea over grasslands (Menendez et al., 2009). These apparent contradictory results in yield and NUE reinforce that the effectiveness of NI depends on the cropping system, management strategies and soil or environment conditions (Barth et al., 2001; Wu et al., 2007). Abalos et al. (2014) concluded in a meta-analysis that the NI mean effect in fine-texture and alkaline soils was lower than in medium or coarse texture and acidic soils, but the effects on the specific experiments were highly variable. Thus more field experiments are needed in order to clarify the optimal conditions for NI application.

Most researchers focused on the annual effect of NI on crop yield or NUE and only a few studied the residual effect in the years following the application. In a 2-year experiment, Sharma and Prasad (1996) observed a cumulative effect in wheat grown after maize where DCD blended urea was applied: wheat yield was higher in the maize plots previously treated with DCD-urea than with conventional urea or control plots (no N-fertilizer application). An effect on soil residual mineral N after harvest was more frequently reported. Wu et al. (2007) found that in a sandy loam soil, mineral N and NH_4^+-N concentration after harvest were greater in treatments where ammonium sulfate blended with DMPP was applied in comparison with conventional fertilizers. Wissemeier et al. (2001) observed that after an aerobic incubation in the laboratory, the NH_4^+ recovered in soils treated with DMPP was higher than in those treated with other NI or without NI. Therefore, an evaluation of the cumulative effect of NI in crop yield and the possible relationship with the soil residual N is necessary.

The cumulative effect could be explained through N immobilization by microorganisms and fixation by soil clay minerals in non-exchangeable forms. The capacity of soils to fix NH_4^+ is dependent mainly on soil characteristics and moisture conditions (Nieder et al., 2011). Fertilizer application increase NH_4^+ fixation in wedges of clay minerals (Liang et al., 1999). This pool of recently fixed NH_4^+ is more available to plants than native fixed NH_4^+, which is strongly retained and mostly not plant-available (Black and Waring, 1972). Regarding the use of NI, Juma and Paul (1983) noticed that NH_4^+ fixation was enhanced when 4-amino-1,3,4-triacole was applied. As well, Ma et al. (2015) noticed an increase of fixed NH_4^+ when DMPP was added to urea.

On the other hand, the microbial biomass has a major role regulating soil N availability through the mineralization/immobilization processes. Some authors found an increase in the soil N microbial biomass after NI application (Juma and Paul, 1983). Addition of DMPP enhanced the availability of NH_4^+ for microorganisms and increased N immobilization in a laboratory experiment (Ma et al., 2015). Moreover, the release of the immobilized N is closely related with the NH_4^+ fixation/defixation processes. Some laboratory studies in the last years (Ma et al., 2015) emphasized the relationship between biotic and abiotic processes regulating N availability, though results needs to be clarified under field conditions.

Therefore, we hypothesized that the application of NI could increase the soil N supply capacity over time and contribute to an enhancement of N-recovery in the cropping system. The objectives of the study were to determine: (i) the effect of NI-fertilizers applied over maize during two seasons on grain yield, N content and NUE compared to conventional fertilizers, (ii) the soil residual effect of NI-fertilizers, assessed in a non-fertilized sunflower planted during a third season, and (iii) the possible sources of residual N via laboratory determinations.

Table 1
Soil properties at the beginning of the experiment.

	Depth (cm)			
	0–23	23–40	40–70	70–120
pH (1:2.5)	8.2	8.1	8.0	7.8
Organic Matter ($g\,kg^{-1}$)	31.8	29.2	21.9	22.3
CO_3 ($g\,CO_3^{2-}\,kg^{-1}$)	198.0	201.3	159.0	181.0
Sand ($g\,kg^{-1}$)	260.0	250.0	250.0	250.0
Silt ($g\,kg^{-1}$)	490.0	510.0	520.0	460.0
Clay ($g\,kg^{-1}$)	250.0	240.0	230.0	290.0

2. Materials and methods

2.1. Field experiment

The field experiment was conducted from 2013 to 2015 at the Chimenea research station, located in Aranjuez, Spain (40°03′N, 03°31′W, 550 m a.s.l.). The soil type is silty clay loam (*Typic Calcixerept*) with pH value ~8 thorough the soil profile, and low stone content (Gabriel and Quemada, 2011). Main soil properties are presented in Table 1. The climate is Mediterranean semi-arid with an annual rainfall of 415 mm, mainly occurring in autumn and spring and almost negligible in summer, with mean annual temperature of 14.2 °C. Weather data were recorded by a climatic station located 100 m from the field plot.

Fifteen plots (12 m × 6 m) were randomly distributed in five treatments, with three replications in a 2600 m^2 field experiment. In two treatments, ASN (26% N) together with the nitrification inhibitor DMPP (3,4-dimethylpyrazole phosphate) was applied either at the recommended rate of 170 kg N ha^{-1} (ENTEC®-170), or with a reduced rate of 130 kg N ha^{-1} (ENTEC®-130). In two other treatments, ASN conventional fertilizer was applied with the same rates (ASN-170, ASN-130). A control treatment without N application was included. The recommended rate of 170 kg N ha^{-1} was based on previous N response trials conducted in the same research field (Quemada et al., 2014). Fertilizers were applied over a maize crop (*Zea mays* L., Pioneer P1574, cycle 700) in 2013 and 2014. In 2015, a sunflower crop (*Helianthus annuus* L.) was planted in the same plots but without the application of N fertilizers, in order to test the cumulative residual effect. In 2013 and 2014, before sowing the maize, 30 kg P ha^{-1} and 100 kg K ha^{-1} were applied to all plots to ensure P and K availability. In 2015, no pre-sowing fertilization was applied. The previous crop on the experimental site was non-fertilized sunflower in 2012.

Year after year, crops were established in the same plots. Maize was sown in April and harvested in late September or early October at a seeding rate of 80,000 seeds ha^{-1} (in rows separated 0.74 m and spaced 0.17 m within rows) with a no-till seeder. Fertilizer treatments were broadcast by hand over maize in one application at the end of May, when the crop had four fully unfolded leaves which correspond to the growth stage 14 (GS-14) of the decimal scale (Lancashire et al., 1991). Sunflower was planted in late April at the same seeding rate as maize, and harvested in early September. Irrigation water was delivered using a sprinkler system (12 × 12 m^2). The irrigation schedule and doses were estimated from the daily values of crop evapotranspiration (ETc). This was calculated as $ETc = Kc \times ET_0$, where ET_0 is the reference evapotran-

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