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Urea-based fertilization strategies to reduce yield-scaled N oxides and enhance bread-making quality in a rainfed Mediterranean wheat crop

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ABSTRACT

Urea fertilizer applications to calcareous soils can result in significant nitrous oxide (N_2O) and nitric oxide (NO) emissions, predominantly via nitrification rather than denitrification. To address this, we explored several mitigation strategies based on improved urea management in a rainfed winter wheat (*Triticum aestivum* L.) crop during two consecutive cropping seasons with contrasting rainfall quantities and distribution. The strategies we investigated included the split application of urea at top dressing, the use of nitrification inhibitors (e.g. 2-(3,4-dimethyl-1H-pyrazol-1-yl) succinic acid isomeric mixture, DMPSA, and nitrapyrin), the urease inhibitor N-butyl thiophosphorictriamide (NBPT), or the double inhibitor DMPSA + NBPT. Emissions of N_2O, NO, methane (CH_4), as well as measurements of grain and straw yield and bread-making quality (protein content, reserve protein composition: glutenins and gliadins) were measured. Nitrogen (N) use efficiency (NUE) and N surplus were also calculated. Results were affected by rainfall, since the first cropping season experienced typical rainfall quantity and distribution, whilst the second cropping season was very dry, thus increasing significantly the yield-scaled emissions and N surplus, and markedly decreasing the NUE. In comparison to the single application of urea without inhibitors, all treatments generally decreased surface-scaled and yield-scaled emissions, with urea +DMPSA being the most effective and consistent mitigation option. Split urea and NBPT did not mitigate surface-scaled emissions in the dry cropping season, because of the marked peaks in N oxides after flowering, caused by inefficient crop N uptake. In the typical rainfall cropping season, the use of the double NBPT+DMPSA inhibitor led to the best balance between mitigation of yield-scaled N oxides emissions, N efficiency, crop yield and bread-making quality (i.e. increments in total protein, gliadins and glutenins). We did not observe any effect of nitrification inhibitors on grain yield (except in the dry cropping season) or the composition of gluten proteins. Our results suggest that the use of DMPSA with or without NBPT should be recommended to mitigate yield-scaled emissions of N oxides in rainfed semi-arid crops.

1. Introduction

Nitrogen (N) fertilization is essential to feed the increasing worldwide population through the enhancement of crop yields (Spiertz, 2010). On the other hand, N fertilizers can have a major impact on the environmental, e.g. through the release of gases such as ammonia (NH_3), nitric oxide (NO) or nitrous oxide (N_2O) to the atmosphere (Ussiri and Lal, 2013). Nitrous oxide is a powerful greenhouse gas (GHG) and an ozone-depleting substance (IPCC, 2014), while NO contributes to the formation of tropospheric ozone (O_3) and acid rain (Pilegaard, 2013). The main biochemical processes involved in the emissions of both N oxides are nitrification (i.e. the oxidation of ammonium, NH_4^+, to nitrate, NO_3^-, by autotrophic or heterotrophic microorganisms under aerobic conditions) and denitrification (i.e. the reduction of NO_3^- to N_2O/N_2 by heterotrophic microbiota under anaerobic conditions) (Caranto and Lancaster, 2017; Hallin et al., 2017).

Urea fertilizer is the most commonly used nitrogen (N) fertilizer used worldwide due to its low cost, high N content and ease of management during transport and storage (Glibert et al., 2006). After

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application to the soil, it rapidly hydrolyses to release NH_3 and carbon dioxide (CO_2). The use of this NH_4^+-N based fertilizer can result in lower N_2O emissions than NO_3^--based fertilisers (such as ammonium nitrate) in agro-ecosystems where denitrification is a dominant soil process (e.g. grasslands in humid areas) (Smith et al., 2012; Harty et al., 2016; Roche et al., 2016). However, greater N_2O emissions can occur from urea (compared to NO_3^--based fertilisers) under contrasting conditions, such as arable-crops in semi-arid areas (Zhang et al., 2016; Guardia et al., 2017; Volpi et al., 2017). This may be a result of the predominance of nitrification in semi-arid calcareous soils with low organic carbon (C) content (Aguilera et al., 2013) that causes NH_4^+ oxidation to be the main N_2O production pathway, even under irrigated conditions (Guardia et al., 2017, 2018). According to Tierling and Kuhlmann (2018), the accumulation of nitrite (NO_2^-) under non-denitrifying conditions plays a key role in the increase of N_2O production, and this is favored at high soil pH. Therefore, it is essential to find mitigation strategies for N oxides in semi-arid calcareous soils, where emissions from widespread urea fertilizer are significant.

One possible approach is the use of nitrification (NIs) and urease (UIs) inhibitors with urea. Dicyandiamide (DCD) has been one of the most widely used NIs worldwide, but its use is currently under discussion because traces of this inhibitor were found in New Zealand milk products (Chen et al., 2014). Plant interception and uptake, followed by grazing by dairy cows, were potential routes for this contamination of milk (Kim et al., 2012a; Marsden et al., 2015). There is therefore interest in other NIs, such as 2-(3,4-dimethyl-1H-pyrazol-1-yl) succinic acid isomeric mixture (DMPSA) or nitrapyrin (2-chloro-6-(trichloromethyl)-pyridine). Neither of these two NIs have been commercialized yet in Europe, although nitrapyrin was introduced as a NI to the US market in the 1960s (Goring, 1962). The efficacy of nitrapyrin has been demonstrated in other areas of the world under a range of management and environmental conditions (Thapa et al., 2016). DMPSA has been shown to reduce emissions of N oxides following calcium ammonium nitrate (Guardia et al., 2017, 2018) and ammonium sulphate (Huérfano et al., 2016) applications to soil, mainly under irrigated or humid rainfed conditions. However, the efficacy of DMPSA to reduce emissions of N oxides has not been tested with urea fertiliser in rainfed semi-arid conditions yet.

The use of NIs can result in negative trade-offs (pollution swapping), e.g. increased NH_3 volatilization (Qiao et al., 2015; Pan et al., 2016). Other possible mitigation strategies include the use of UIs such as N-butyl thiophosphorictriamide (NBPT), which delays the hydrolysis of urea thus reducing NH_3 emissions (Sanz-Cobena et al., 2008). Moreover, NBPT also has showed positive results in mitigating emissions of N oxides through the reduced availability of topsoil NH_4^+ and NO_3^- (Abalos et al., 2012). However, its N oxides mitigation efficacy may be more dependent on environmental conditions, thus leading to a lower average performance than NIs (Thapa et al., 2016). Therefore, it is important to evaluate the efficacy of NBPT in consecutive years in rainfed semi-arid areas, where high rainfall variability influences the effectiveness of N fertilizer mitigation strategies (Abalos et al., 2017). In this sense, the use of double NI-UI inhibitors may lead to mitigation of both N oxides and NH_3 emissions (Zaman and Nguyen, 2012). The potential for the double-inhibitor approach to improve the mitigation efficacy of N oxides (compared with NIs alone) has yet to be proved under rainfed semiarid conditions.

Since NIs and UIs are known to improve the synchronization of the N applied with crop demand (Abalos et al., 2014a), other strategies such as splitting N application should be compared against inhibitors. Previous studies have shown the potential of smaller more frequent doses of fertiliser to enhance N recovery efficiency and decrease N losses (Bell et al., 2015; Wang et al., 2016; Xia et al., 2017). Some of these mitigation strategies can increase farm costs and decrease net margins for farmers (Sanz-Cobena et al., 2017), in comparison to the single application of urea without inhibitors. Consequently, possible improvements of farm benefits through increments in crop yields and quality, or improvements in NUE, which can be affected by inhibitors or more split doses of fertilizer (Peltonen and Virtanen, 1994; López-Bellido et al., 2005; Grant et al., 2011; Abalos et al., 2014a) must be evaluated together with N oxides emissions.

A large number of previous studies have explored the use of NIs and UIs on gaseous emissions and crop yields, but a complete overview including crop quality (e.g. bread-making quality of wheat) is lacking. Previous studies have shown the potential of inhibitors and N application timing to increase plant N concentrations and/or influence N remobilization or protein composition of grain (Qiao et al., 2015; Thapa et al., 2016; Xue et al., 2016). In the case of bread-making wheat, an increase in grain protein content is closely linked to dough quality.

In this context, a field experiment was established to compare several strategies based on urea fertilization, including the use of NIs and/or UIs, and split dressings of urea. We hypothesized that all of these strategies would improve the balance between mitigation of yield-scaled N oxides emissions, NUE, crop yield and bread-making quality, compared to conventionally managed urea application. Although its contribution to GHG balance in semiarid croplands is generally low (Aguilera et al., 2015) methane (CH_4) emissions, which also affect the GHG balance of agro-ecosystems (Snyder et al., 2009), were also measured.

2. Materials and methods

2.1. Site description

The field experiment was located in the National Center of Irrigation Technology, “CENTER” (latitude 40°25′1.31″N, longitude 3°29′45.07″W) in the Madrid region of Spain. According to the Soil Taxonomy of USDA the soil is a *Typic xerofluvent* (Soil Survey Staff, 2014) with a silt loam texture (10% clay, 59.5% silt, and 30.5% sand) in the upper horizon (0–20 cm). The main physico-chemical properties of the topsoil were: bulk density, 1.27 Mg m^{-3}; water pH, 8.2; organic matter (Walkley-Black), 20.7 g kg^{-1}; total N, 1.64 g kg^{-1}; $CaCO_3$, 8.16 g kg^{-1}; extractable P (Olsen), 28.4 mg kg^{-1}; total K, 3.14 g kg^{-1}. The site’s mean annual average air temperature and annual rainfall during the last 10 years was 14.1 °C and 393 mm, respectively. The average rainfall from November to July (a typical winter cereal cropping period) was 296 mm (184 mm from February to July), while mean soil temperature (at 10 cm depth) for this period was 11.8 °C. Data for daily rainfall and daily air and soil temperatures were obtained from the meteorological station located at the field site.

2.2. Experimental design and management

A field experiment was carried out from October 2015 to October 2017, including two wheat cropping seasons: year 1 (2015/2016) and year 2 (2016/2017). The same plots were used in the two years. A complete randomized block design with three replicates was used, with each plot covering an area of 64 m^2 (8 m × 8 m). The application of fertilizers was adjusted to provide the equivalent of 120 kg total N ha^{-1} for all treatments during the cropping period. The different fertilizer treatments were: 1) Urea applied in one dose (U); 2) Urea + NBPT (U + NBPT); 3) Urea + DMPSA (U + DMPSA); 4) Urea + NBPT + DMPSA (U + DI); 5) Urea + Nitrapyrin (U + NIT) 6) Urea split (SU) in two applications (60 kg N ha^{-1} + 60 kg N ha^{-1}); and 7) Control with no N fertilization (control). The proportion of DMPSA in the fertilizers was 0.8% of the NH_4^+-N, whereas NBPT was applied at 0.13% of ureic N. NBPT and DMPSA based products were provided by EuroChem Agro in a granular form, and were homogeneously applied to the soil by hand. Nitrapyrin was applied was applied at a rate of 0.35% of the applied N (w/w). The mixture U + NIT was obtained by dissolving U and nitrapyrin in water. The solution was then sprayed with a manual applicator. All fertilizers were applied to the soil surface at tillering stage (26th February 2016 and 23rd February 2017). In the case of SU