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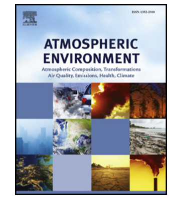

DMPSA and DMPP equally reduce N_2O emissions from a maize-ryegrass forage rotation under Atlantic climate conditions

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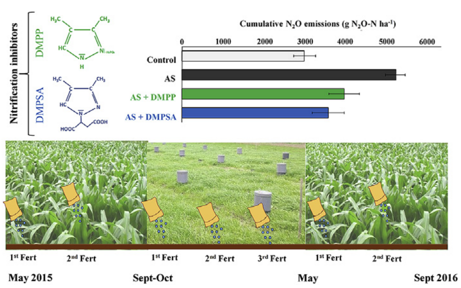
GRAPHICAL ABSTRACT



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ABSTRACT

The increase of the global demand for dairy products is reflected in a rise of animal feed and forage productivity. In the coastal Atlantic climate conditions of northern Spain the maize-ryegrass rotation is a common management used to satisfy this forage demand. With the aim of mitigating greenhouse gases (GHG) emissions associated with fertilization in this type of intensive management, the use of nitrification inhibitors (NI) such as 3,4-dimethylpyrazol phosphate (DMPP) or the isomeric mixture of 2-(3,4-dimethyl-1H-pyrazol-1-yl) succinic acid and 2-(4,5-dimethyl-1H-pyrazol-1-yl) succinic acid (DMPSA) could be a useful strategy. Until now, the new NI DMPSA has only been evaluated under Mediterranean conditions. The objective of this study was to compare the efficiency of DMPSA with respect to DMPP reducing GHG emissions when applied in a maize-ryegrass rotation under Atlantic climate conditions. Nitrogen fertilizer was applied as ammonium sulphate, with and without both NIs, split into two applications of 80 and 100 kg N ha^{-1} in the case of maize and in three applications of 80, 60 and 60 kg N ha^{-1} in the case of ryegrass. An unfertilized control treatment was also included. Nitrous oxide (N_2O) and methane (CH_4) fluxes were measured using the closed chamber technique. The new NI DMPSA showed a similar behaviour to DMPP, mitigating N_2O emissions down to the levels of the unfertilized soil. The effect of DMPSA reducing N_2O losses lasted for the same time as for DMPP (l $<$ four months). CH_4 fluxes were not affected by the application of any of both NIs. In terms of yield and quality, DMPSA and DMPP maintained the yield and the forage crude protein content of both maize and ryegrass.

1. Introduction

According to OECD/FAO (2015) the global demand for dairy products will increase by *ca.* 30% in 10 years. This will be reflected in an increase of animal feed and forage productivity. Unfortunately, cereal-based forages often contain less crude protein than silage grass,

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hence to achieve the correct balance between energy and protein for cattle, it is usual to combine both maize and grass in their diets. In the Basque Country (northern Spain) agriculture is associated with the production of forage crops at the farm scale to maintain dairy cattle systems, being the maize-ryegrass rotation one of the most common in this region (MAGRAMA, 2016).

Nitrous oxide (N_2O), carbon dioxide (CO_2) and methane (CH_4) are the most important greenhouse gases in climate forcing (IPCC, 2007). Considering a time horizon of 100 years N_2O and CH_4 present a global warming potential 265 and 28 times higher than CO_2 (IPCC, 2014). Agricultural soils are by far the main anthropogenic source of N_2O emissions, primarily as a result of the addition of synthetic nitrogen (N) fertilizers and animal manures to soil (Bouwman et al., 2002). The global contribution of agricultural soils to anthropogenic N_2O emissions is around 84% (Smith et al., 2008). In addition, N fertilization can also inhibit CH_4 oxidation (Tlustos et al., 1998) increasing soil CH_4 emissions as consequence of competition between NH_3 and CH_4 for methane monooxygenase enzymes (Holmes et al., 1995).

Soil N_2O emissions are mainly the result of the biological processes of nitrification and denitrification (Groffman, 1991; Conrad, 1996), being both processes strongly regulated by O_2 availability and therefore by soil water filled pore space (WFPS) (Davidson, 1991; Bateman and Bagss, 2005). Nitrification and denitrification occur simultaneously under most soil conditions and the net flux to the atmosphere is the result of both processes together (Fowler et al., 2009). CH_4 fluxes from soil are also mainly regulated by O_2 availability (*i.e.*, WFPS) (Le Mer and Roger, 2001; Maljanen et al., 2003). While under anaerobic conditions methanogenesis is the main process (Whitman et al., 2006), under aerobic conditions CH_4 oxidation occurs (Whalen and Reeburgh, 1996).

Intensive agricultural management is based on large inputs of N fertilizers, herbicides, pesticides, and fossil fuels (Jackson et al., 2007) which can cause undesirable environmental effects, such as, increased greenhouse gas (GHG) emissions (Mosier et al., 1991; IPCC, 1996). An intensive research effort over recent decades has enabled the identification of a number of fertilizer management options capable of reducing N_2O emissions (Millar et al., 2010). In order to mitigate N losses from agriculture the Intergovernmental Panel on Climate Change (IPPC) has proposed the use of ammonium-based fertilizers accompanied by nitrification inhibitors (NI) as a possible tool. Regarding NIs, DCD (dicyandiamide) has been widely researched and used commercially in the past. However, currently DMPP (3,4-dimethylpyrazole phosphate) is one of the most used NIs in Europe, reducing nitrate leaching and N_2O emissions (Dittert et al., 2001; Pfab et al., 2012; Huérfano et al., 2015, 2016). In addition to its ability to mitigate GHG emissions, several authors (Abalos et al., 2014; Huérfano et al., 2015; Linquist et al., 2013) have confirmed that the DMPP does not result in negative effects on the yield and/or quality of different crops.

The isomeric mixture of 2-(3,4-dimethyl-1H-pyrazol-1-yl) succinic acid and 2-(4,5-dimethyl-1H-pyrazol-1-yl) (DMPSA) (CA 2933591 A1 2015/06/18 Patent) is a new NI similar to DMPP based in the inhibitory effect of DMP and an organic acid. According to Pacholski et al. (2016), the non-polarity of DMPSA allows its combination with any mineral fertilizer (e.g. urea, CAN, DAP), which would not be possible with DMPP, as well as to improve the availability of DMP in the soil. DMPSA has already been tested in wheat crops under humid Mediterranean conditions, showing the same behaviour as DMPP in mitigating N_2O emissions, without affecting the crop yield (Huérfano et al., 2016). Also, it has been shown to mitigate N_2O losses from an irrigated maize crop in a semiarid Mediterranean climate (Guardia et al., 2017). However, in the Atlantic climate conditions of the coast of the Basque Country the climate is cool and damp with rainfall amounts up to almost 1200 mm yr^{-1} and average air temperatures in winter and in summer *ca.* 9.5 and 21 °C respectively. This generates a wide variability in the availability of water in the soil along the year together with permanent temperate soil temperatures whose combination provides interesting conditions in which to evaluate and to compare the efficiency of DMPP and DMPSA. In fact, laboratory studies have shown that the efficiency of DMPP and DMPSA is greatly influenced by water availability and soil temperature (Menéndez et al., 2012; Torralbo et al., 2017). So, the objective of this study was to evaluate the performance of the new NI DMPSA in comparison to DMPP when it is applied in a maize-ryegrass forage rotation under Atlantic climate conditions.

2. Materials and methods

The research was conducted in a maize-ryegrass forage rotation in the location of Zamudio in the Basque Country (northern Spain) in 2015–2016. Daily precipitation and mean air temperatures during the assayed period were measured in a weather station 350 m from the field experiment and are shown in Fig. 1. The soil (0–30 cm depth) presented a silt loam texture (33% sand, 52% silt, and 15% clay) with a pH (1:2 H_2O) of 7.0. The soil organic matter content was 1.8% and the C/N ratio was 8.0. Maize (*Zea mays* L. var. CisKo) was sown in spring 2015 after fallow at a density of 110,000 plants ha^{-1}. After maize harvest, ryegrass (*Lolium multiflorum* Lam. var. Westerwold starter) was sown in autumn 2015 at a density of 40 kg ha^{-1} and in spring 2016 maize was

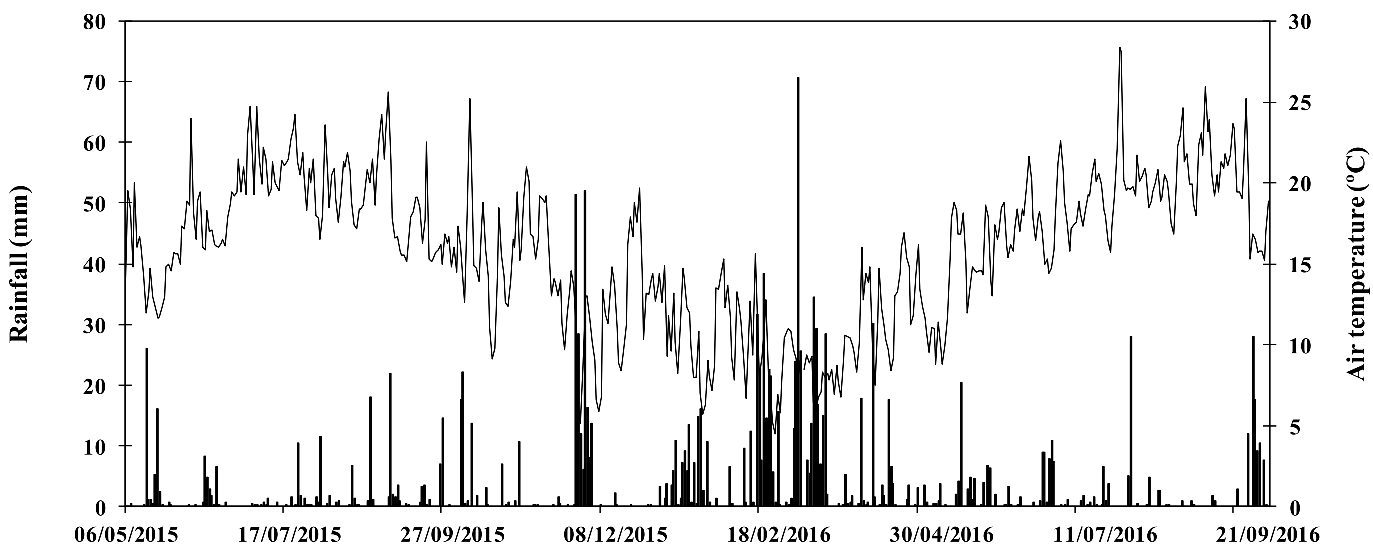

Fig. 1. Daily precipitation (bars) and mean air temperature (line) for the whole period of study in Zamudio.