



## Evaluation of potassium thiosulfate as a nitrification inhibitor to reduce nitrous oxide emissions



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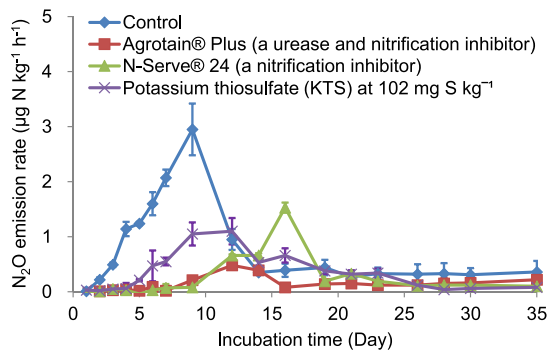
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### HIGHLIGHTS

- Potassium thiosulfate (KTS) showed the function of a nitrification inhibitor.
- KTS significantly reduced N<sub>2</sub>O emissions as application rate increased.
- KTS was as effective as a commercial nitrification inhibitor in reducing N<sub>2</sub>O emissions.
- KTS also resulted in less total N loss in comparison with commercial inhibitors.
- Using KTS as a nitrification inhibitor could reduce total chemical inputs.

### GRAPHICAL ABSTRACT



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### ABSTRACT

Potassium thiosulfate (KTS,  $K_2S_2O_3$ ) has been shown to function as a nitrification inhibitor, thus has the potential to reduce nitrous oxide (N<sub>2</sub>O) emissions and play an important role in effective N management. The objective of this research was to determine the potential effects of KTS on N<sub>2</sub>O emissions and N transformation processes in comparison with commercial N transformation inhibitors (stabilizers). A laboratory incubation experiment was conducted using urea and ammonium nitrate (UAN) applied at 150 mg N kg<sup>-1</sup> in a Hanford sandy loam soil (coarse-loamy, mixed, superactive, nonacid, thermic Typic Xerorthents). Treatments included three rates of KTS (26, 51, and 102 mg S<sub>2</sub>O<sub>3</sub><sup>2-</sup>-S kg<sup>-1</sup>), a urease and nitrification inhibitor (Agrotain® Plus), a nitrification inhibitor (N-Serve® 24), and an untreated control. Nitrous oxide emission, soil pH, and mineral N species were monitored for 35 days. Total N<sub>2</sub>O emissions were reduced significantly by all KTS treatments as a function of KTS rate. At 102 mg S<sub>2</sub>O<sub>3</sub><sup>2-</sup>-S kg<sup>-1</sup>, KTS reduced N<sub>2</sub>O emissions by 48% (0.18% of total inorganic N), which was statistically similar to the N-Serve® 24 treatment (60% reduction) although lower than Agrotain® Plus (78% reduction). The KTS resulted in significantly less unaccounted (total N) loss compared to the commercial inhibitors. If the N<sub>2</sub>O emissions reductions observed in this laboratory study are validated in the field, using KTS for this purpose can also provide a fertility benefit and may reduce total chemical inputs into agronomic systems. Future research needs to determine the effectiveness of thiosulfate for improving overall nutrient management while reducing N<sub>2</sub>O emissions under field conditions.

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## 1. Introduction

Nitrous oxide ( $\text{N}_2\text{O}$ ), a potent greenhouse gas, has received great attention due to its atmospheric longevity (about 120 years), global warming potential (310 times that of  $\text{CO}_2$  on a per molecule basis over a 100-year period), and its rapidly increasing concentration in the atmosphere (0.25% per year, IPCC, 2014). The foremost source of anthropogenic  $\text{N}_2\text{O}$  is agriculture, accounting for 60% of the global  $\text{N}_2\text{O}$  emission, and this has been accelerated by increasing use of synthetic nitrogen (N) fertilizers for food production (IPCC, 2014). In the U.S., agriculture emits about 79% of the total  $\text{N}_2\text{O}$  emissions (US Environmental Protection Agency, 2016).

Nitrous oxide is produced primarily via soil microbial activity through either nitrification or denitrification processes depending on whether oxygen is sufficient or limited (Khalil et al., 2004; Gillam et al., 2008; Wrage et al., 2005; Zhu et al., 2013). There are four proposed biological pathways for  $\text{N}_2\text{O}$  production: nitrifier nitrification, nitrifier denitrification, nitrification coupled denitrification by denitrifiers, and denitrification (Maharjan and Venterea, 2013; Wrage et al., 2001; Zhu et al., 2013). Although associated with N transformation processes,  $\text{N}_2\text{O}$  production was found to correlate with soil nitrite ( $\text{NO}_2^-$ , an intermediate product of nitrification) rather than ammonium ( $\text{NH}_4^+$ , produced from urea hydrolysis or ammonification) or nitrate ( $\text{NO}_3^-$ , the end product of nitrification) species (McGeough et al., 2012; Venterea et al., 2010; Zebarth et al., 2012). The positive correlation between  $\text{N}_2\text{O}$  emission and  $\text{NO}_2^-$  concentration has recently been clarified within two distinct soil water content ranges (above or below soil water holding capacity, WHC) with a much greater slope above WHC, i.e., in oxygen-deficient environment or dominated by nitrifier denitrification and/or denitrification processes (Cai et al., 2016).

Nitrogen fertilizer stabilizers (transformation inhibitors) that are commonly used for increasing N retention in soil and reducing losses due to run-off or leaching have been found to reduce  $\text{N}_2\text{O}$  formation and emissions. The most commonly used N fertilizer stabilizers are ammonification and nitrification inhibitors. Some of the inhibitors include *N*-(*n*-butyl) thiophosphoric triamide (NBPT, a urease inhibitor, the active ingredient in Agrotain®), and dicyandiamide (DCD, a nitrification inhibitor) that have been found to reduce  $\text{N}_2\text{O}$  emissions by over 70% in a laboratory study (Cai et al., 2016). These compounds have also been shown to reduce  $\text{N}_2\text{O}$  emissions under field conditions (Aulakh et al., 1984; McGeough et al., 2012; Misselbrook et al., 2014; Zaman et al., 2009).

Potassium thiosulfate (KTS), which is a common fertilizer source of potassium (K) and sulfur (S), is reported to function as a nitrification inhibitor at concentrations  $> 32 \text{ mg S kg}^{-1}$  in soil (Abbasi et al., 2011; Goos, 1985; Saad et al., 1996; Sallade and Sims, 1992). The inhibitory effects are reported as a direct toxic effect of thiosulfate or its oxidation products (tetrathionate or carbon disulfide) on nitrobacter and other  $\text{NO}_2^-$  oxidizing microorganisms (Janzen and Bettany, 1986) or indirect effects of volatile organic sulfur compounds produced from transformation of thiosulfate inhibiting on  $\text{NH}_3$  monooxygenase activity (Bremner and Bundy, 1974; Kelly and Smith, 1990; McCarty, 1990). We hypothesize that, as a nitrification inhibitor, KTS has the potential to reduce  $\text{N}_2\text{O}$  emissions. However, there have been no detailed investigations on the impact of KTS on  $\text{N}_2\text{O}$  emission, which limits our understanding of its potential in  $\text{N}_2\text{O}$  emissions mitigation and N management. If KTS is similarly effective as other commercial nitrification inhibitor products, it can also reduce total chemical input and associated costs in fertilized fields. The objective of this research was to determine the potential effects of KTS on  $\text{N}_2\text{O}$  emissions and N transformation processes in comparison with commercial N transformation inhibitors (stabilizers). A laboratory incubation experiment was conducted to examine the effects of different amounts of KTS on  $\text{N}_2\text{O}$  emissions, N transformation processes, and soil pH to evaluate its beneficial use in agricultural soils.

## 2. Material and methods

### 2.1. Soil and chemicals

The soil used in this study was a Hanford sandy loam (coarse-loamy, mixed, superactive, nonacid, thermic Typic Xerorthents) collected in a pomegranate orchard near Parlier, CA (36°36'42" N, 119°31'34" W). Detailed information on soil collection, characterization, and preparation for incubation experiments can be found in Cai et al. (2016). The soil has 0.4% total organic C (SOC), 0.04% total N, cation exchange capacity (CEC) of  $5.9 \text{ meq } 100 \text{ g}^{-1}$ , a water content of 12% (w/w) at  $-33.4 \text{ kPa}$  or 24% in saturated paste, and a particle size distribution of 59% sand, 32% silt, and 9% clay. The  $\text{EC}_{25}$  (saturation extract), pH (saturation extract), and  $\text{NO}_3^-$ -N content (2 M KCl extract) was  $171 \mu\text{S cm}^{-1}$ , 7.3, and  $8.4 \text{ mg kg}^{-1}$  soil, respectively.

Agrotain® Plus (a urease and nitrification inhibitor product containing active ingredients: 81.2% urease dicyandiamide, and 6.5% *N*-(*n*-butyl)thiophosphoric triamide; and 12.3% inactive ingredients) was obtained from Koch Agronomic Services, LLC (Wichita, KS, USA). The product was formulated for liquid N fertilizers and its detailed information is available online (<http://www.kochagronomicservices.com/us/products/agriculture/agrotainplus/>). N-Serve® 24 [a nitrification inhibitor containing 22.2% 2-chloro-6-(trichloromethyl)pyridine] was obtained from Dow AgroSciences LLC (Indianapolis, IN, USA) (<http://msdsdigital.com/n-serve%2%AE-24-nitrogen-stabilizer-msds>). KTS (a liquid fertilizer 0-0-25-17S containing 50% (w/w)  $\text{K}_2\text{S}_2\text{O}_3$ ) was obtained from Tessenderlo Kerley Inc. (Phoenix, Arizona, USA). UAN-32 (containing 16.5% urea-N, 7.75%  $\text{NO}_3^-$ -N and 7.75%  $\text{NH}_4^+$ -N) was from J.R. Simplot Company (Boise, ID, USA). UAN was selected in this study as the N source because it is widely used in drip irrigation or fertigation systems.

### 2.2. Incubation experiments

The incubation experiments followed a similar procedure described in Cai et al. (2016). Briefly, air dry soil (containing the equivalent of 3 kg oven-dry mass) was treated and placed into a 4 L high density polyethylene (PE) container (12.1 cm H  $\times$  22.2 cm D  $\times$  22.4 cm W) for incubation. During incubation, the containers were covered with perforated aluminum foil and closed with an air-tight lid during  $\text{N}_2\text{O}$  emission measurement. A UAN stock solution ( $70.31 \text{ g L}^{-1}$  or  $22.5 \text{ g N L}^{-1}$ ) was prepared with deionized (DI) water for N application. The procedures for preparing each treatment are described below:

1. KTS application rates. Potassium thiosulfate was applied to soil at rates of 0 (control), 26, 51, and  $102 \text{ mg S}_2\text{O}_3^{2-}\text{-S kg}^{-1}$ . Eighteen grams of the 50% (w/w) KTS product was first diluted in deionized (DI) water to a final volume of 200 mL ( $90 \text{ g KTS L}^{-1}$ ). Different amounts of the KTS solution (5, 10, and 20 mL) were well mixed in a spray bottle with 20 mL of the UAN stock solution and various amounts of DI water (200, 195, and 185 mL for the three KTS levels) for a total final solution volume of 225 mL. The solution was then sprayed onto the soil (with an initial water content of 2.5%) incrementally to achieve a final 10% soil water content (w/w), N application rate at  $150 \text{ mg kg}^{-1}$ , and KTS at 26, 51, and  $102 \text{ mg S}_2\text{O}_3^{2-}\text{-S kg}^{-1}$ , respectively. The KTS application resulted in addition of K at 31, 62, and  $125 \text{ mg kg}^{-1}$ .
2. Commercial N transformation inhibitors. Agrotain® Plus (Agrotain Plus) and N-Serve® 24 (N-Serve) were applied at the recommended rates (15 lbs/ton UAN, equivalent to  $23.4 \text{ g kg}^{-1}$  N for Agrotain® Plus, and 1 quart/100 lbs N, equivalent to  $20.9 \text{ mL kg}^{-1}$  N for N-Serve). For Agrotain® Plus, 1.05 g of the product was dissolved in 1000 mL of DI water first and 10 mL of the solution was pipetted into a spray bottle, mixed with 20 mL UAN stock solution and 195 mL of DI water before spraying onto soil. For the nitrification inhibitor treatment, 3 mL of N-Serve was diluted with DI water to

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