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Effects of ammonium thiosulfate and guanyl thiourea as calcium ammonium nitrate inhibitors on fertilization and plants

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ABSTRACT

The nitrate inhibition effects and decomposition of ammonium thiosulfate and guanyl thiourea, which are nitrification inhibitors, are discussed. When ammonium thiosulfate and guanyl thiourea are used as nitrification inhibitors, leaching of ammonium nitrate from calcium ammonium nitrate in soil is reduced, while the yields and nitrogen intake of the plant are increased. When ammonium thiosulfate and guanyl thiourea are used, labor costs are reduced without any loss of product yield or quality. The use of ammonium nitrate products containing ammonium thiosulfate and guanyl thiourea reduces the nitrogen requirement for maximum efficiency.

1. Introduction

In a past study, sodium sulfate (Na_2SO_4) was used as an inhibitor and its effect on nitrogen release was evaluated in order to decrease the release of ammonium nitrate (AN) in the presence of an inhibitor, and therefore, reduce the amount of fertilization in agricultural areas. The effect of Na_2SO_4 was lost at the end of the first three months when the nitrogen release was accelerated in the first month of application, but Na_2SO_4 subsequently decomposed from the AN fertilizer [1].

In order to better utilize the fertilizer nitrogen, other inhibitors were investigated for agricultural application, such as *N*-(n-butyl)thiophosphorictriamide (NBPT), dicyandiamide (DCD), DCD + NBPT, and a maleic and iconic acid polymer (MIP). In this case, the loss of ammonia concentration was up to 85% [2]. Another study to minimize nitrogen loss attempted the addition of dicyanamide (DCD) and NBPT as a nitrification inhibitor to calcium ammonium nitrate fertilizer. Nitrogen loss in the form of ammonia volatilization was different in each case, and the effect of DCD on N_2O emission was small [3].

The effect of nitrification inhibitors on emission release has been examined in various ways, and different inhibitors have been reported to cause 3% ammonia-induced nitrogen loss [4]. In another inhibitor trial, the effect of DCD and 3,4-dimethylpyrazole phosphate (DMPP) on calcium ammonium nitrate fertilizer was studied. The inhibitory effect on nitrogen loss was found to be 42.3 ± 2.2% for DCD and 40.2% for DMPP at the baseline [5]. In another inhibitor assay, a green algae species, Chlorella sp., was studied, and it was found that urea fertilizers maintain their initial nitrogen concentrations up to 6 months [6]. The mechanism underlying the inhibitor action is related to the numerous chemical reactions that occur when using inhibitors as additives for chemical fertilizers. One of these mechanisms involves the accumulation of excess oxalate as a result of such chemical reactions. Various studies have been conducted to prevent the accumulation of oxalate, as it influences coke development [7].

In another study, NBPT was investigated especially for ammonia volatilization and nitrate leakage inhibition

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from urea fertilizers. In this study, the use of nitrogen in the plant was investigated by monitoring the degradation time of 530, 850, 1500, and 2000 mg/kg NBPT in soil [8]. When using BrUrea as a urease inhibitor and urea AN supplement, ammonia volatilization was reduced by 60% [9]. Another inhibitor used to minimize nitrogen loss from urea solution is a mixture of NBPT and phenyl phosphorodiamidate (PPDA), which suppresses nitrogen loss by reducing the volatility of ammonia [10]. Ammonium sulfate was used together with DMPP as a nitrification inhibitor, and the CO_2, N_2O, NO, N_2 emissions in the cultivated area were investigated. Only N_2 emissions were observed to occur in moist soils [11]. A mixture of DMPP and 2- (N-3,4-dimethyl-1*H*-pyrazol-1-yl) succinic acid was also studied for use as an inhibitor. In this way, it was found that the fertilizer solution accelerates the reduction of N_2O in soil to N_2 [12]. As another inhibitor solution, DMPP was studied, and its possible toxic effects on soil and plants were investigated. The absence of any toxic effects other than nitrogen emissions has made DMPP a widely used inhibitor in agricultural fields [13]. Moreover, nitrification inhibitors were evaluated to reduce nitrate leakage and N_2O emissions, thereby controlling the release of N_2O and CO_2 [14]. Various nitrification inhibitors and mechanisms are being developed in order to use nitrogen sources for long-term application in a more healthy manner. The 3,4-dimethylpyrazole succinic acid (DMPSA) inhibitor assay provided a successful trial with a nitrogen release of 180 kg N/ha. In the agricultural field, studies have been performed using DMPSA inhibitor together with ammonium sulfate; the conversion of ammonium sulfate to nitrate is delayed by DMPSA, such that the plants can benefit more from the nitrogen of ammonium sulfate [15].

In this study, the effects of a mixture of ammonium thiosulfate and guanyl thiourea—which is predicted to be a nitrification inhibitor for calcium ammonium nitrate (CAN) fertilizers with 26% and 33% nitrogen content—on the growth of corn plants and nitrogen losses via nitrate leakage and ammonia volatilization were evaluated.

2. Materials and Methods

Materials used in this study, Ammonium thiosulfate (CAS No. 7783-18-8; purity, 98%, wt), guanyl thiourea (CAS No. 2114-2-5; purity, 98%, wt) CAN (26% nitrogen containing, Toros Agri, Turkey).

In this study, the nitrogen losses from a CAN fertilizer due to nitrate leaching and ammonia loss were investigated. The effect of temperature (20 °C) (Table 1) on the decomposition of both inhibitors and the trend in this decomposition under different pH conditions were analyzed. At the same time, the release of nitrogen dioxide at different concentrations of ammonium thiosulfate and guanyl thiourea inhibitor mixtures over time was examined (Figure 1). Accordingly, the addition of the ammonium thiosulfate and guanyl thiourea mixture at a low concentration led to more N_2O emission, and vice versa, within the same time. This implied that the CAN fertilizer without the inhibitor loses more nitrogen during the same period.

Table 1. Decomposition of ammonium thiosulfate and guanyl thiourea depending on temperature

Progress	% of added ammonium thiosulfate and guanyl thiourea remaining in soil			
Number of weeks	0	4	6	12
2	88	88	80	76
8	80	73	68	40
12	-	-	56	0
14	62	42	-	-
17	57	12	-	-

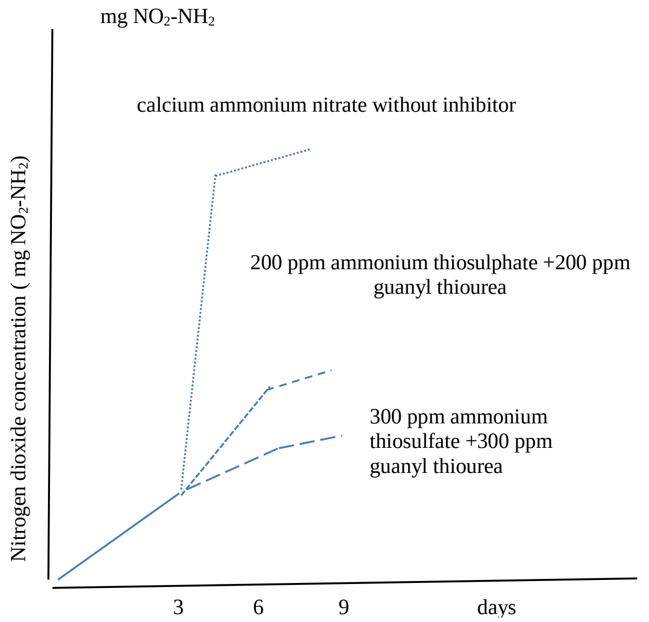

Figure 1. Effects of ammonium thiosulfate and guanyl thiourea on nitrite

In addition, nitrogen losses via nitrate leakage and ammonia volatilization under different pH conditions were evaluated in terms of total nitrogen content, and the effectiveness of each inhibitor at various pH levels was observed (Figure 2). At the end of the 17-week process, a CAN fertilizer in which ammonium thiosulfate and guanyl thiourea were employed together with the highest nitrogen concentration was used at pH 7.2. The combined use of these two inhibitors increased the soil pH and enhanced the utilization of the nitrogen from CAN fertilizer by the corn plant.

Ammonia emissions at different pH levels were measured with a Dräger MSI EM200-E system (TX, USA).

Nitrate loss was analyzed by using ion chromatography to monitor the concentration of nitrate (NO_3) in the samples collected from wastewater in the fertilized land. A Thermo Scientific Dionex ICS 2100 apparatus was used for ion chromatography.

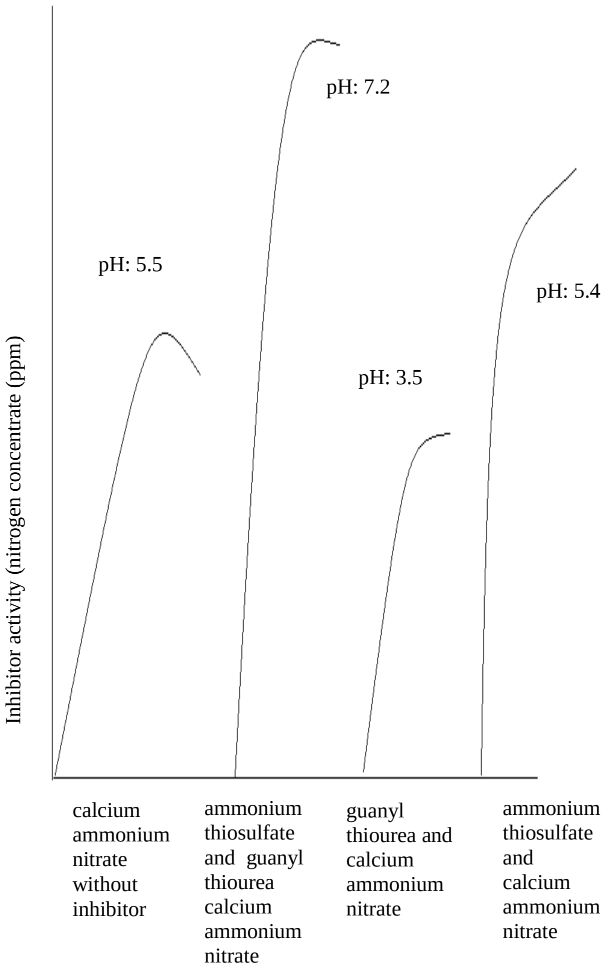

Figure 2. Inhibitor activity in terms of nitrogen concentration

As another parameter to evaluate the nitrogen loss from CAN fertilizers, the nitrogen concentration of fertilizers with and without the inhibitor was determined in terms of nitrate leakage (Figure 3). Similar to the total loss of nitrogen seen in Figure 2, an increase in the concentration of the ammonium thiosulfate/guanyl thiourea mixture in CAN nitrate manure during the same period minimizes nitrogen loss via nitrate leakage. Fertilization using CAN is carried out only at certain times of the year because differences in seasonal air temperature and soil pH hinder the effective utilization of the fertilizer nitrogen by the plant. In such cases, the effect of CAN fertilizer on nitrogen activity in different seasons can be analyzed by using an inhibitor. In Figure 4, nitrogen loss via nitrate leakage in a CAN fertilizer supplemented with different amounts of ammonium thiosulfate + guanyl thiourea mixture was monitored to investigate the effectiveness of the inhibitor at different air-soil temperatures. As the inhibitor concentration increases with increasing air and soil temperature, nitrogen losses via nitrate leakage decrease.

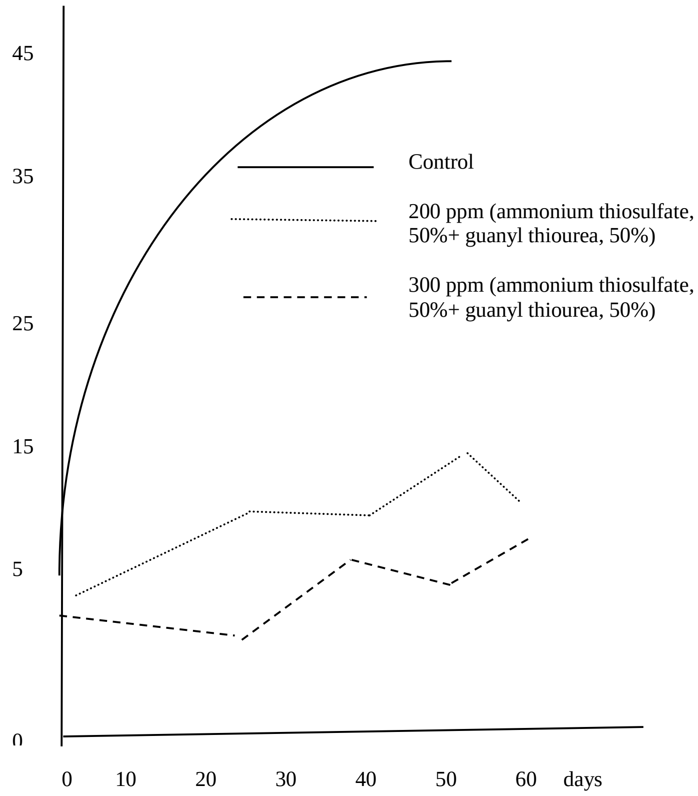

Figure 3. Inhibition of nitrification by ammonium thiosulfate and guanyl thiourea.

3. Results and Discussion

There are limited studies investigating the effect of inhibitors such as ammonium thiosulfate and guanyl thiourea on CAN fertilizers. In the present study, the performance of the aforementioned two inhibitors with CAN fertilizers was evaluated under different temperature and pH conditions. This study demonstrates that the use of nitrification and urease inhibitors is a potential solution to manage these losses. Some unsolved issues are also discussed herein. Studies have shown that the use of inhibitors to compensate for/minimize nitrogen losses by leaching or ammonia volatilization is a potential strategy.

During fertilizer applications, nitrogen from chemical fertilizers is mineralized by soil microorganisms, and this process is a feature of fertile soil. During fertilizer applications, nitrogen from chemical fertilizers is mineralized by soil microorganisms, and this process is a feature of fertile soil.

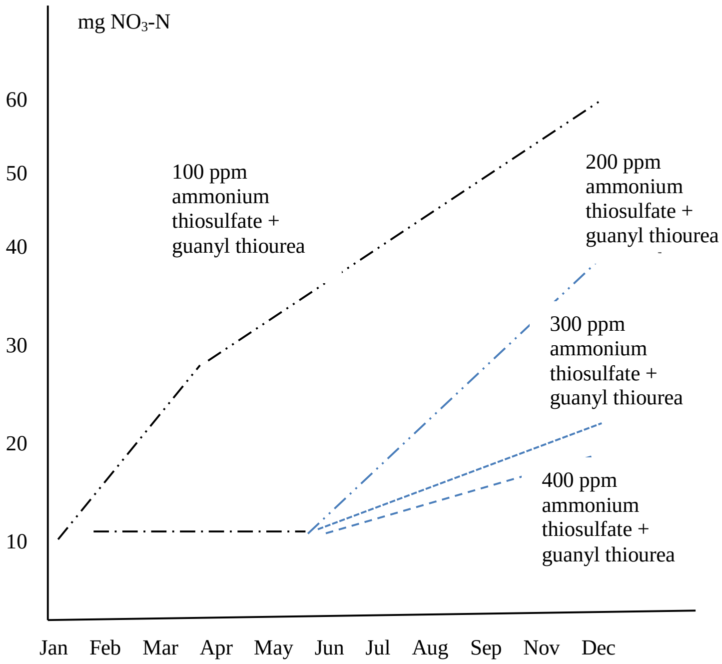

Figure 4. Nitrogen loss via nitrate leaching at various inhibitor concentrations due to seasonal differences.

During fertilization, the nitrogen chemicals in the fertilizer are converted to nitrate and taken up by the plant. The part that is not taken up by the plant is leached from the soil and mixes into the waste water. For this reason, fertilization is applied in periods where nitrogen loss is the maximum in the first spring period. The ammonium ions in the CAN fertilizer are converted to nitrate ions without the use of inhibitors. The conversion of ammonium ions to nitrate using inhibitors is delayed. Ammonium ions are more inert in the soil than are nitrate ions, but due to both soil pH and seasonal conditions, long-term adsorption of ammonium ions in the soil and plant roots is achieved through inhibitors.

Effects of ammonium thiosulfate and guanyl thiourea inhibitors on plant stress

Ammonium thiosulfate and guanyl thiourea inhibitors, together with CAN fertilizers, have adverse effects on various enzymes, especially when used at the initial stages of growth or in higher amounts as nutrient solutions [5]. The unused inhibitors are excreted mostly by sweating at the leaf edges of the plant [7]. Depending on the soil temperature, the nitrification rate is approximately 2 m^3 in autumn, 1 to 3 months in autumn, or 5 to 6 weeks in spring. Large amounts of nitrate present in the soil are exposed to leakage, and CAN might pose a problem representing a significant loss of nitrogen; this is because nitrate ions, which are released from the plant along with the leakage from the soil, mix with the groundwater. Hence, the CAN fertilizer does not benefit sufficiently from the high nitrogen content, and groundwater is contaminated by the nitrate ions. The highest nitrogen loss occurs under moderate climatic conditions between December and April, and the CAN amount reaches 60–100 kg N/ha after October/November. Ammonium thiosulfate and guanyl thiourea added to the CAN fertilizer at a rate of 10–20 ppm block nitrification at 14 °C for about 2 months. Ammonium thiosulphate and guanyl thiourea were doped at 20 kg/ha in the CAN fertilizer applied to the soil, and the following results were obtained. In November, 80% of NH_4-N in the CAN treated with ammonium thiosulfate and guanyl thiourea was nitrified even at soil temperatures of 1 °C, but nitrification with ammonium thiosulfate and guanyl thiourea was not successful even after a few weeks. With the addition of ammonium thiosulphate and guanyl thiourea, nitrification did not start until May, consistent with the increase in soil temperature. However, the addition of ammonium thiosulfate and guanyl thiourea to 50 m^3 /ha CAN fertilizer significantly reduced nitrate leakage, and NH_4-N was "protected" for use in the following crop.

Table 2. Nitrogen loss rates in inhibitor application

Inhibitor application (100 kg NH_4-N/ha)	Removal kg N/ha
calcium ammonium nitrate + ammonium thiosulfate + guanyl thiourea	55
calcium ammonium nitrate+ guanyl thiourea	75
calcium ammonium nitrate+ ammonium thiosulfate	90

Table 3. Nitrogen content lost via leaching and volatilization by inhibitors added to calcium ammonium nitrate fertilizer

Inhibitor application (100 kg NH_4-N/ ha)	Removal kg N/ha	Leaching kg N/ha
ammonium thiosulfate	90	80
guanyl thiourea	75	70
ammonium thiosulfate + guanyl thiourea	55	50

In a field study with corn, the addition of ammonium thiosulfate and guanyl thiourea to CAN fertilizers increased the yields by 23% to 45% and N uptake by 10% to 27%, depending on the air conditions and the time of application (Table 2). Various results were observed depending on seasonal differences. For example, in the CAN fertilization study with ammonium thiosulfate and guanyl thiourea, better corn yield was obtained in March than in October, implying that higher nitrogen leaching occurs in October. Likewise, although the yield of corn increased during fertilization in August, the leaching of nitrate was minimal. This means that the nitrogen taken up by the corn crop was not yet fully available for the next crop during early growth. Addition of ammonium thiosulfate and guanyl thiourea inhibitors to CAN fertilizers resulted in differences in seasonal nitrogen uptake and less nitrate leakage.

In particular, with the high rainfall in the growing season, the addition of ammonium thiosulfate and guanyl thiourea delays the conversion of ammonium to nitrate during fertilization and enables the plant to benefit from nitrogen in the fertilizer for a longer period [8]. Therefore, it is revealed that the addition of these two inhibitors with the CAN fertilizer results in 10% nitrogen contribution to the soil. A single application of these products instead of split applications might be labor-saving and economically advantageous. Nitrogen in CAN fertilizers can be protected or used more efficiently by crops. In intensive corn production, excessive nitrate supply prevents productive leaf growth and makes crops susceptible to diseases. However, high initial nitrogen application increases corn population density, while high nitrate application in spring results in excessive contamination. The rate of degradation of the inhibitor may vary depending on the temperature [9]. The rate of decomposition of ammonium thiosulfate and guanyl thiourea is strongly dependent on temperature [10]. Ammonium thiosulfate is a reductant with a nitrogen content of 19%, but CAN must be used as a nitrification inhibitor. Ammonium thiosulfate and guanyl thiourea have been studied as nitrification inhibitors to reduce the amount of fertilization. Ammonium thiosulphate and guanyl thiourea formulations may inhibit nitrification to a very small extent in different ways [11]. The use of nitrification inhibitors is a useful strategy for the efficient management of nitrogen fertilizers [12]. Increased productivity may still be possible in the near future via the use of inhibitors that enhance the nitrogen content of fertilizers by reducing loss as nitrates [16]. The ultimate aim is to increase the efficiency of nitrogen fertilizers and decrease nitrate losses, thus minimizing economic and environmental risks in agricultural production.

Based on the results of this study, it is possible to say that the mixture of ammonium thiosulfate and guanyl thiourea has the potential to reduce nitrate leakage and reduce nitrogen loss via ammonia volatilization. Therefore, inhibitors can be considered important potential tools for achieving agricultural objectives such as higher yields of higher-quality crops from agricultural areas with the use of CAN fertilizers.

4. Conclusion

Ammonium thiosulfate and guanyl thiourea have different inhibitory effects depending on the soil and climate structure, and the nitrate leakage and ammonia volatilization trends vary. Therefore, the effect of the soil structure was analyzed, and the effects of CAN fertilizers on soil and water quality were evaluated in field applications. Accordingly, the effects of ammonium thiosulfate used in combination with guanyl thiourea on CAN fertilizers were examined in terms of the degradation time of the inhibitors. In contrast to the individual use of ammonium thiosulfate and guanyl thiourea, the use of these inhibitors in combination with CAN fertilizers efficiently provided high-quality products, and smaller amounts of the CAN fertilizer could be used in a given season.

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