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**EFFECT OF UREA COMPOUNDS AS FERTILIZER ON
DIFFERENT SOIL TYPES**

Doctoral Dissertation
Agricultural Sciences, Agronomy (A 001)

Kaunas, 2024

The dissertation was completed at the Agrobiological Laboratory, Lithuanian Research Centre for Agriculture and Forestry between 2019 and 2023. The authorization for doctoral studies was given to Vytautas Magnus University in collaboration with the Lithuanian Research Center for Agriculture and Forestry. On 22 February 2019, by decision No. V-160 of the Government of the Republic of Lithuania.

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The dissertation is available at Martynas Mazvydas National Library of Lithuania the Libraries of Lithuanian Research Center for Agriculture and Forestry, and Vytautas Magnus University.

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**KARBAMIDO JUNGINIŲ KAIP TRĄŠŲ POVEIKIS
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Mokslo daktaro disertacija
Žemės ūkio mokslai, Agronomija (A 001)

Kaunas, 2024

Mokslo daktaro disertacija rengta 2019–2023 m. Lietuvos agrarinių ir miškų mokslų centre pagal LR švietimo, mokslo ir sporto ministro 2019 m. vasario 22 d. įsakymu Nr. V-160 suteiktą doktorantūros teisę Vytauto Didžiojo universiteto su Lietuvos agrarinių ir miškų mokslų centru.

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Mokslo daktaro disertacija bus ginama viešame Agronomijos mokslo krypties gynimo tarybos posėdyje 2024 m. gegužės 21 d., 13 val. Lietuvos Agrarinių ir miškų mokslų centre adresu: Instituto al. 1, Akademija, Kėdainių r.

Disertacija galima peržiūrėti Lietuvos nacionalinėje Martyno Mažvydo bibliotekoje, Lietuvos agrarinių ir miškų mokslų centro ir Vytauto Didžiojo universiteto bibliotekose.

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LIST OF PUBLICATIONS AND PARTICIPATION IN CONFERENCES

The dissertation is prepared based on the publications listed below:

1. **Swify, S.;** Avizienyte, D.; Mazeika, R.; Braziene, Z. Comparative Study Effect of Urea-Sulfur Fertilizers on Nitrogen Uptake and Maize Productivity. *Plants* 2022, *11*, 3020. <https://doi.org/10.3390/plants11223020>
2. **Swify, S.;** Avizienyte, D.; Mazeika, R.; Braziene, Z. Influence of Modified Urea Compounds to Improve Nitrogen Use Efficiency under Corn Growth System. *Sustainability* **2022**, *14*, 14166. <https://doi.org/10.3390/su142114166>
3. **Swify, S.;** Mažeika, R.; Volungevičius, J. Mineral Nitrogen Release Patterns in Various Soil and Texture Types and the Impact of Urea and Coated Urea Potassium Humate on Barley Biomass. *Soil Syst.* **2023**, *7*, 102. <https://doi.org/10.3390/soilsystems7040102>
4. **Swify S.;** Mažeika, R.; Baltrusaitis, J.; Drapanauskaitė, D.; Barčauskaitė, K. Review: Modified Urea Fertilizers and Their Effects on Improving Nitrogen Use Efficiency (NUE). *Sustainability* 2024, *16*, 188. <https://doi.org/10.3390/su16010188>

Participation in national and international conferences on the topic of the dissertation:

1. **S. S. F. Swify**, R. Mazeika. 2020. Oral Presentation: “The release of Mineral Nitrogen from Urea granules in the Incubation Test in Sandy Soil”. The 9th conference of the young scientists of the Lithuanian Research Council.
2. **S. S. F. Swify**, R. Mazeika. 2021. Virtual-Oral Presentation: “Improve Urea Use efficiency by Using Urea Potassium humate in Soil Incubation Test”. The 17th International Conference of Young Scientists on Energy and Natural Sciences Issues (CYSENI 2021).
3. **S. S. F. Swify**, D. Avizienyte, R. Mazeika. 2021. Oral Presentation: “Use of Different Modified Urea Compounds as New Fertilizers to Improve Corn Growth and Nitrogen Use Efficiency”. 10th conference of young scientists of the Lithuanian Research Council.
4. **S. S. F. Swify**, R. Mazeika. 2022. Virtual-Oral Presentation: “Overview: New Approach To Use Modified Urea Fertilizers”. The 18th International Conference of Young Scientists on Energy and Natural Sciences Issues (CYSENI 2022).
5. **Swify, S.;** Avizienyte, D.; Mazeika, R.; Braziene, Z. Oral Presentation: “Comparative Study Effect of Urea-Sulfur Fertilizers on Nitrogen Uptake and Maize Productivity”. The 3rd International Conference/ Sustainable Management of Natural Resources, Green Economy & Technology Transfer, Istanbul, Turkey / 8 - 11 of March 2023.
6. **Swify S.,** R. Mazeika. 2023. Poster Presentation: “Acidic Soil Properties' and Its Effect On Mineral Nitrogen Release Process From Granulated Urea Fertilizers”. The 19th International Conference of Young Scientists on Energy and Natural Sciences Issues (CYSENI 2023).

LIST OF ABBREVIATIONS

Abbreviation	Definition
NH ₃	Ammonia
NH ₄	Ammonium
NO ₃	Nitrate
U100	100 kilogram N per hectare of urea
U200	200 kilogram N per hectare of urea
UPH	Urea coated with potassium humate
UPH100	100 kilogram N per hectare of urea coated with potassium humate
UPH200	200 kilogram N per hectare of urea coated with potassium humate
UAS	Urea+ammonium sulfate
UCS	Urea+calcium sulfate
UCSC	Urea cocrystals [CaSO ₄ ·4CO(NH ₂) ₂]
UC100	100 kilogram N per hectare of urea cocrystals [CaSO ₄ ·4CO(NH ₂) ₂]
UC200	200 kilogram N per hectare of urea cocrystals [CaSO ₄ ·4CO(NH ₂) ₂]
NUE	Nitrogen use efficiency
ANUE	Agronomic nitrogen use efficiency
ANR	Apparent nitrogen recovery
GNP	Gross National Product
POCU	Polyolefin-coated urea
SRN	Slow release nitrogen
CRN	Controlled release nitrogen
CRFs	Controlled-release nitrogen fertilizers
SRFs	Slow-release nitrogen fertilizers
2-yr	Two years
Kg N ha ⁻¹ yr ⁻¹	Kilogram nitrogen per hectare per year
Mg kg ⁻¹	Milligram per kilogram
r	Pearson correlation coefficient

INTRODUCTION

Urea stands out as one of the predominant nitrogen-based fertilizers, constituting roughly 43% of global sales [1], [2]. It finds widespread application within the agricultural sector because of its notable nitrogen concentration and cost-effectiveness [3], [4]. Nevertheless, the effectiveness of urea as a primary nitrogen source can be impacted by various factors, encompassing soil attributes, microbial activity, and environmental circumstances [5], [6], [7], [8]. The considerable solubility of urea fertilizers, once they are applied to the soil, can lead to nitrogen loss or hinder nutrient accessibility to plants within the soil-plant system. Urea nitrogen may be lost through various processes including volatilization via NH_3 , leaching, denitrification, immobilization, and fixation in soil [9].

In commonly used fertilizers like urea, the projected efficiency ranges between 30% to 70% for nitrogen application, yet typically falls below 50% [10], [11], [12]. This nitrogen loss could lead to significant worldwide environmental contamination, with nitrate leaching ($124\text{-}160 \text{ kg N ha}^{-1} \text{ yr}^{-1}$) potentially polluting groundwater, and the release of greenhouse gasses ($120\text{-}143 \text{ kg N ha}^{-1} \text{ yr}^{-1}$) into the atmosphere, which is a matter of substantial concern [11], [13], [14]. Consequently, the imperative lies in curbing nitrogen loss and seeking enhancements in the utilization efficiency of urea fertilizers [11], [15], [16]. Crops typically recover only around 30-40% of nitrogen from soluble nitrogenous fertilizers like urea, which can have significant environmental implications [17]. Therefore, understanding the factors that influence nitrogen loss from urea will enable urea users to select management practices that minimize volatilization and improve urea use efficiency [18].

Elevating the effectiveness of urea fertilizer utilization can be achieved by striking a balance between the nitrogen supply and crop nitrogen demand, while simultaneously minimizing nitrogen losses [11], [19]. Implementing a well-suited strategy will amplify the retrieval of applied nitrogen by crops, heighten production efficiency, and curtail the potential ecological repercussions associated with nitrogen usage [20], [21]. Frequent technological involvement, specifically those focused on utilizing diverse compounds derived from environmentally friendly sources [22], are instrumental in augmenting urea effectiveness as a primary nitrogen fertilizer, while simultaneously decreasing emissions into the environment [23]. A prevalent strategy involves creating nitrogenous fertilizer in a form that is either controlled or slow-released, and various approaches and materials have been outlined for this purpose [23], [24]. The products may be coated, chemically and biochemically modified, or granular [25]. Consequently, this nitrogen as controlled or slow release restricts the surplus nitrogen from transforming into ammonia, which would otherwise be released into the atmosphere, and nitrates that could enter water systems. As

a result, this approach mitigates both air and water pollution [23], [24], [26]. Thus, achieving a balance between profitable crop production and minimizing urea loss to the environment should be every producer's goal in managing urea inputs. The main aim of this study is to use different urea compounds coated or synthesized to improve urea use efficiency under different conditions in different soil types.

The aim of research.

This research work was carried out to study the effect of some urea compounds such as urea-sulfur, coated urea potassium humate, and urea cocrystals on mineral nitrogen release dynamics in different soil types to understand the interaction between soil characteristics and mineral nitrogen dynamics. Moreover, to investigate the effect of these compounds on maize growth and productivity under field conditions and in a glasshouse experiment to study their impact on barley biomass.

Formulation of a scientific problem.

Urea nitrogen loss is considered one of the most significant environmental problems facing specialists in studying nutrient management and soil fertility. Most studies on fertilization aim to minimize urea losses and enhance its efficacy in crop production. The optimal approach for managing urea, which maximizes its utilization and minimizes its detrimental environmental effects, is primarily by applying it as a blend of nutrients, as proposed in this research.

Study hypothesis:

Probably, the utilization of various urea compounds in different soil texture types can alter the transformation and release patterns of soil mineral nitrogen as a result of changing some soil properties. Moreover, modified urea compounds as new, and more stable compounds that can enhance the use efficiency of urea and increase the N uptake by plants.

Study objectives:

This study was carried out to use different urea compounds in different soil texture types to achieve these objectives:

1. Assess the use efficiency of urea as the main fertilizer.
2. Assess the behavior of different compounds of modified urea.
3. Improve the urea use efficiency and increase nitrogen uptake by the plants.
4. Assess the reduction of the environmental impact of urea nitrogen fertilizers loss.

Study tasks:

1. To investigate the effect of the application of urea and modified urea fertilizers on the mineral N transformation and its release dynamic patterns changing over time.
2. To evaluate modified urea compounds' influence (coated urea potassium humate and urea cocrystals) on improving maize growth and grain yield productivity in field trials.
3. To assess the effect of urea and coated urea potassium humate in different soil texture types on barley green biomass under glasshouse conditions.

Briefly statements of defense:

1. The soil mineral nitrogen concentration dynamics are significantly influenced by the soil texture class.
2. Modified urea fertilizers such as urea+ammonium sulfate, urea-gypsum cocrystals, and coated urea potassium humate can improve maize yield productivity and grain quality.
3. The use of modified urea had highly significant effects on N uptake compared to conventional urea and significantly affected the agronomic nitrogen use efficiency (ANUE), and Apparent Nitrogen Recovery Efficiency (ARN).
4. Coated urea potassium humate can mitigate nitrogen losses, thereby fulfilling the nitrogen necessities for barley growth.

Research Novelty.

The application of urea-modified compounds exhibits a positive effect on mineral nitrogen release patterns in soil under various soil conditions reflected positively on both plant growth and crop productivity. Urea slow-release fertilizer such as urea cocrystals, plays a crucial role in maintaining a balance between the plant's nitrogen requirements and the mineral nitrogen present in the soil. Coated urea potassium humate as a controlled urea fertilizer exhibits favorable effects by reducing urea nitrogen loss and increasing nitrogen uptake by plants.

Practical significance of the study.

The findings of this study revealed that the usage of modified urea fertilizers can serve as a beneficial tool to increase the N fertilizer availability leading to high use efficiency of the fertilizer to save the balance between the nitrogen stock and plant requirements, improve yields, increase crop productivity, and reduce the risk of nitrogen loss.

1. LITERATURE REVIEW

An extended literature review related to the dissertation topic was discussed in a review article (Article 4).

1.1. Soil Characteristics in Lithuania

Soils represent the primary natural asset of Lithuania; consequently, agriculture assumes a highly notable role as a contributor to the Gross National Product (GNP). Based on statistics provided by the State Land Cadastre since January 1999, the aggregate extent of agricultural land in Lithuania reached a total of 3,496,761.27 hectares. These figures encompass all territories utilized for agricultural purposes. Approximately 1,605,689 hectares are under private ownership [27]. Approximately 46.3% of the soils in Lithuania exhibit a pH level that is either in proximity to neutrality, ranging from 6.6 to 6.9, or precisely neutral with a pH = 7. Conversely, more than 16% of these soils display an acidic nature, necessitating the application of lime in agricultural contexts [27]. The Moraine highlands exhibit the largest proportions of slightly eroded soils, ranging from 12.4% in the Svencionys-Narocius highlands to 21.8% in the Suduva highlands. The sandy Southeastern plain also encompasses a significant extent (16.6%) of slightly eroded soils. Within certain regions of the Baltic highlands, moderately eroded soils constitute a considerable portion, ranging from 19.6% to 29.8% of soils utilized for agricultural purposes.

In the Central Zemaiciu highlands and Eastern Lithuanian plateau, eroded soils encompass approximately 5.7-7.2% of the total area. Conversely, severely eroded soils are more prevalent in the plateau and highlands of Eastern Lithuania, accounting for 1.6-7.7% of the land. The soils in Lithuania exhibit diverse characteristics in terms of age and origin, with Quaternary deposits being the most prevalent parent materials [27]. The thickness of these accumulations varies across the region, ranging from less than 10m in the northern part of Lithuania to 200-300 m in the Zemaiciai and Baltija Heights, with a significant number of deposits being 80-120m in thickness. The glacial accumulations can be classified into three types: morainic, glaciofluvial, and limnoglacial. Additionally, in certain locations, there are also alluvial, Eolian, and organic accumulations. These diverse deposits contribute to the development of a wide range of soils and a complex soil cover in Lithuania [27], [28]. Gleyic Albeluvisols (Retisols) and certain Dystric soils that originate from materials lacking in carbonate and deeply leached loamy deposits, predominate in the western regions of Lithuania.

In the eastern regions of Lithuania, Albeluvisols (Retisols) prevail on soil parent materials characterized by a light texture, where distinct erosion processes are prevalent. In the central regions of Lithuania, the soil parent material and the upper layers of soil contain a higher

proportion of carbonate and are less leached; hence, Calcaric Cambisols are commonly found. Calcaric Luvisols, Gleyic Luvisols, and, in select areas, Eutric Gleysols, which exist on loam, clay loam, and clay, are extensively distributed. Initial estimations indicate that Albeluvisols (Retisols) occupy approximately 30% of the country, while Luvisols account for 27%. Cambisols represent 13% of the soil composition, Arenosols encompass 12%, and Podzols make up 11%, primarily in forested areas. Gleysols and Histosols, totaling 5.3% of the soil composition, are found in the depressions [28], [29].

1.2. Conventional urea as a main nitrogen fertilizer

Regularly, farmers require nitrogen fertilizer to provide the specific nutrients required for the most advantageous development of plants in their agricultural fields and horticultural areas. Urea is particularly noteworthy as the prevailing type of solid nitrogen fertilizer, particularly in developing areas of the globe [30]. Roughly 80-85% of urea production is utilized specifically as a crop fertilizer [30], [31]. Noteworthy is the fact that more than 40% of the total worldwide food production is dependent on the utilization of urea fertilization [31]. Urea adoption covers about 57% of global agricultural nitrogen usage, and the demand for urea is expected to rise annually by 1.5% [30].

The commercial production of urea fertilizer entails the amalgamation of gaseous carbon dioxide (CO_2) and liquid ammonia under conditions of elevated compression and temperature. Subsequently, after the removal of water, ammonium carbamate is introduced, and the resultant mixture is conveyed through a granulator or prilling tower to yield either prills or pellets. Additionally, on a global scale, urea represents the most widely utilized solid nitrogenous fertilizer owing to its elevated nitrogen content (46%) and its exceptional solubility in water.

Compared to alternative nitrogen fertilizers, urea offers a higher nitrogen concentration, providing both plants and soil with a greater quantity of nitrogen. The versatility in application methods of conventional urea is one of the primary advantages of using urea. It can be broadcast over large areas, utilized near the roots of the plant in a band, or incorporated into the soil via tillage. This endows it with a commendable suitability for both diminutive and extensive agricultural endeavors. Nonetheless, there exist a few potential disadvantages associated with the utilization of customary urea.

The nitrogen transformation as urea fertilizer in the soil-plant system is presented in Figure 1. Upon application of urea into the soil, the urease enzyme catalyzes the hydrolysis of urea, necessitating its conversion into ammonium before its utilization by plants [32], [33]. Ammonia (NH_3) represents the highest nitrogen content nearly 82%, and plants can directly use it [33].

Nevertheless, before the use of ammonia (NH_3), the plant must transform ammonia into ammonium (NH_4) and nitrates (NO_3).

Hence, the widespread acceptance of urea as a primary nitrogen fertilizer has been impeded by substantial nitrogen loss pathways, shown in Figure 1, attributable to its relatively low nitrogen use efficiency (NUE) of only 50% [10]. The main factor contributing to this challenge is urea's heightened vulnerability to nitrogen loss through NH_3 volatilization, with rates of 2-20% [33], [34]. Moreover, the interaction of urea with organic components in the soil triggers a loss ranging from 15-25%, while leaching into water systems results in a further loss of 2-10% [10]. The hydrolysis process of urea raises the soil pH in the vicinity of the granules, leading to significant global ammonia losses, which typically amount to around 16% of the applied nitrogen. In warmer and more humid conditions, these losses can escalate to 40% or even higher [32], [33]. While urea and urea-containing fluids exhibit the highest potential for volatilization, it is important to note the surface application of ammonia and ammonium-based nitrogen fertilizers can undergo this process. Volatilization alone accounts for a substantial loss, ranging from 20–50% of the nitrogen introduced to the soil [33]. These losses pose considerable environmental concerns [35], [36].

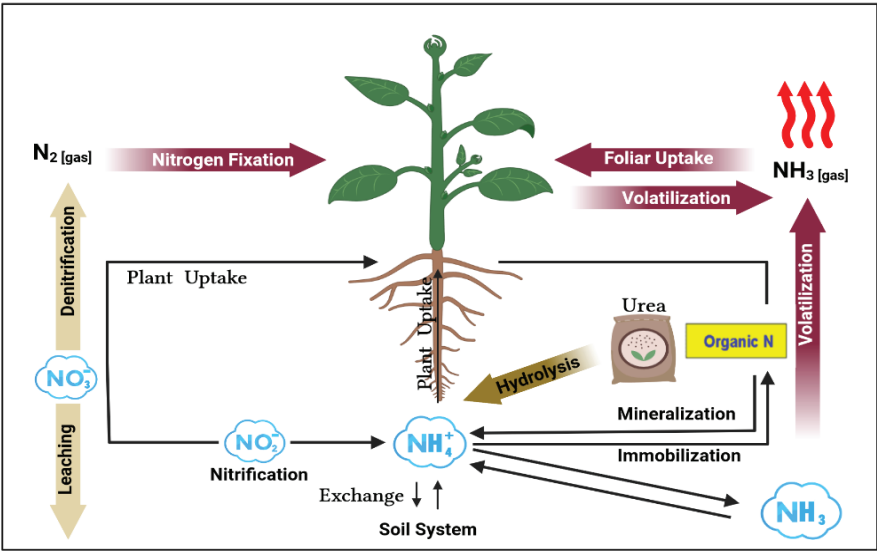


Figure 1. Urea transformation in the soil system

1.3. The strategy of modifying urea and the resulting fertilizers

Mineral nitrogen (N) fertilizers were first introduced in the 1950s, following the World Second War, to enhance agricultural output and satisfy the world's expanding population's growing food demands. The "Green Revolution," which began in the 1960s with the introduction of high-yielding crop varieties that responded well to fertilizers, was made possible by this

innovation. Notably, a seven-fold rise in the use of N fertilizer worldwide has been intimately connected to the doubling of agricultural yields over the previous 50 years [37]. In 40 years, the amount of nitrogen fertilizer used increased from 10.8 million metric tons to 82 million metric tons, and by 2050, it is predicted to reach 249 million metric tons. Significantly, it is estimated that approximately half of global food production derives substantial benefits from the application of nitrogen (N) fertilizers. This practice facilitates rapid crop growth and contributes to increased yields [38].

Moreover, the pursuit of bolstering food security has exerted a substantial influence on global fertilizer consumption in recent decades. Anticipated future demand is likely to be shaped by a broader spectrum of factors, including efforts to mitigate the environmental consequences associated with nutrient losses. In addition, the available area of arable farmland is diminishing due to excessive economic expansion, the conversion of arable land into residential areas, and the impacts of global climate change [39]. Meeting these challenges necessitates meticulous planning and proactive measures are essential for evaluating global food shortages and future requirements. Particular, including adaptations in the agricultural sector, are already being implemented to tackle these concerns. Several of these challenges could potentially be addressed by implementing measures such as coating urea fertilizer and controlling its release rate. At this juncture, slow and controlled-release fertilizers hold promise not just for boosting agricultural productivity but also for mitigating environmental harm [40], [41].

The proliferation of slow and controlled-release fertilizers, along with stabilized fertilizers, significantly aligns with the characteristics of an ideal fertilizer. Nevertheless, it is crucial to bear in mind that while controlled or slow-release and stabilized fertilizers offer advantages, they cannot compensate for errors in field and crop management. However, they can lessen any detrimental effects on the environment and increase NUE. Therefore, these special types of fertilizers must be consistently integrated into a robust agricultural strategy or best management practices approach [30], [42]. The process of urea modification involves reacting a substance with urea to improve its qualities.

Urea is a mixture of nitrogen, carbon, and oxygen that is frequently used to improve the durability of materials, especially in hot and humid environments. This process is effective in rendering materials more resistant to corrosion, UV radiation, and various environmental factors. Urea modification serves as an efficient means to augment the durability and performance of a diverse array of materials. Chissoasahi notably spearheaded the development of Polyolefin coated urea (POCU), which features a sigmoid release. This innovative design allows for a single basal application and simultaneous placement of the fertilizer [42].

The common types of modified urea fertilizers are two main categories described as “slow-release nitrogen” (SRN) and “controlled-release nitrogen” (CRN) [24], [26], [43]. Despite their frequent interchange, these phrases have different meanings. The terms controlled-release nitrogen and slow-release nitrogen are interchangeable and belong to the same general category, "Enhanced Efficiency Nitrogen." It is important to note that Trenkel (1997) has distinguished the two words clearly and emphasized their minor variations [42]. Synthetic-modified urea compounds can be categorized into two main groups. Urea-formaldehyde which is produced by chemical reaction, falls under the first category, which results in slow-release nitrogen (SRN) as a by-product. The fertilizer prills in the second group were coated with materials such as resin, wax, or sulfur to provide controlled-release nitrogen (CRN) [44].

The mechanism of nutrient release from slow-release fertilizers can be influenced by various factors, including soil type and properties, as well as meteorological conditions [42], [45]. The slow-release fertilizer operates randomly mechanism. Conversely, controlled-release nitrogen fertilizers offer a more predictable mechanism, ensuring comprehensive predictability in terms of both the quantity and nutrient release rate [41], [42], [45], [46]. The mechanisms underlying controlled-release nitrogen and slow-release fertilizers differ greatly, even though both release nitrogen more gradually than standard urea. Furthermore, the most basic characteristic that separates SRN and CRN sources is whether they are coated or uncoated [10]. SRN doesn't rely on coatings to achieve extended release of nitrogen, while CRN depends entirely on coatings to delay the nitrogen release. The primary distinction between these two types of modified nitrogen lies in the presence or absence of these coatings. Several studies have indicated that both slow-release and controlled-release fertilizers can enhance nutrient use efficiency, boost crop yields, and minimize the environmental impact due to their eco-friendly nature and minimal pollution to the environment. [35], [36], [47]–[51].

1.4. The benefits and drawbacks of SRN and CRN application

While controlled-release nitrogen fertilizers supply nitrogen to plants at a regulated rate, slow-release fertilizers supply nitrogen to plants over a prolonged period. The advantages and disadvantages of applying slow-release and controlled-release nitrogen fertilizers will be covered in the following paragraphs. The long-lasting impact on the soil is one of the primary benefits of slow-release or controlled-release nitrogen fertilizers. The nitrogen is gradually liberated at a regulated pace, thereby ensuring that the plants are supplied with the necessary amount of nitrogen precisely when it is required. As a result, the plants can ingest this nutrient over a longer period.

Consequently, the necessity for frequent application of fertilizers is mitigated, thereby leading to reduced costs, time, and energy expenditure, thereby conferring an economic advantage

[52]–[54]. Moreover, the application of slow or controlled-release nitrogen fertilizers has been demonstrated to enhance nitrogen use efficiency and reduce nitrogen loss [18], [54], primarily by reducing nitrate leaching, volatilization, and nitrous oxide emissions, thus leading to a decreased environmental impact in comparison to conventional nitrogen fertilizers [55]. A steady supply of nitrogen can be provided to the plants by slow and controlled-release nitrogen fertilizers to help them raise their profits [56] – [59]. The utilization of controlled or slow-release nitrogen fertilizers presents an additional benefit, as they facilitate the stimulation of robust root development [60], [61]. The gradual liberation of nitrogen supports the elongation of roots into the soil, aiding the plant in accessing essential nutrients. This process enhances overall plant health and strengthens its resilience to challenges like drought.

Furthermore, the controlled and gradual release of nutrients at an optimal pace contributes to agronomic security by mitigating potential toxicity levels that plants may face, particularly in their early developmental stages. This stands in contrast to the conventional application of chemical fertilizers, which can lead to a localized accumulation of ions, creating high concentrations that result in osmotic stress and harm to plants [10], [62]. On the flip side, controlled or slow-release nitrogen fertilizers come with drawbacks, as they can be less adaptable compared to traditional nitrogen fertilizers. Once applied, adjusting the release rate becomes challenging in response to changing environmental conditions, such as heavy rainfall [42]. These limitations include the potential for nitrogen loss from the soil or over-fertilization due to the difficulty in adjusting release rates. Additionally, controlled or slow-release nitrogen fertilizers tend to be more costly than traditional options, posing a significant challenge for farmers on a tight budget.

These fertilizers take a longer time to impact plant growth compared to conventional nitrogenous fertilizers, requiring farmers to be patient to gain the results of this fertilization. Controlled-release nitrogen fertilizers, if not utilized properly, can contribute to over-fertilization [63]. Therefore, it is critical to understand that a variety of factors, in particular crop species, soil features, and environmental circumstances, influence the choice between controlled-release and slow-release nitrogen fertilizers. For example, crops with constant nitrogen needs during the growing season are better served by slow-release nitrogen fertilizers, while crops with distinct nitrogen requirements at different growth stages are better served by controlled-release nitrogen fertilizers. It is critical to assess the overall sustainability of applying nitrogen fertilizers in agriculture in addition to the benefits and drawbacks. Excessive use of nitrogenous fertilizers can lead to environmental issues such as soil deterioration, gas emissions, and water pollution. Therefore, using nitrogen fertilizers sparingly and combining them with other sustainable agriculture techniques like crop rotation, cover crops, and conservation tillage are essential.

1.5. Influence of modified urea fertilizers on crop yield and NUE

Multiple studies have consistently highlighted the positive impact of controlled or slow-release fertilizers on N use efficiency, taking into account factors in particular crop species and soil conditions. The noted improvement in crop output serves as the main motivator for producers to use these fertilizers. Various researchers have delved into the exploration of controlled or slow-release fertilizers, aiming to enhance both crop yield and nitrogen use efficiency, as documented in Table 1 (Article 4).

The crucial role of fertilizer utilization efficiency in crop production is evident as it enhances yields, optimizes crop management, and minimizes nitrogen loss. Urea, a widely employed nitrogenous fertilizer, has been effectively employed in agricultural practices for more than a hundred years. On the other hand, conventional urea fertilizer application is proven to have detrimental effects on the ecosystem [35], [36]. Many investigations have documented that urea exhibits diminished efficacy and its nitrogen use efficiency stands at merely approximately 50%. A significant portion, ranging from 2% to 20%, is lost due to the process of ammonia volatilization. Another noteworthy proportion, estimated at roughly 15% to 25%, reacts with organic constituents present in the soil, while approximately 2% to 10% leaches into water systems [10], [35], [64].

Hence, it became imperative to augment the efficiency of urea nitrogen utilization to mitigate its detrimental ecological effects. In recent times, the majority of studies about fertilization have inclined towards advancing and adapting urea compounds to amplify nitrogen utilization and diminish nitrogen losses [52]. In the following discussion, we will focus on the variables that affect nitrogen use efficiency and how changed urea compounds affect yields and agronomic nitrogen use efficiency (ANUE). Fertilizers with controlled or slow-release nitrogen can greatly increase crop output and nitrogen use efficiency at the same time [65].

Moreover, controlled or slow-release nitrogen can facilitate an exceptionally efficient nitrogen source for grain crops, leading to increased yields. The use of controlled or slow-release fertilizers may allow for a reduction in the recommended application rate by 20-30% or more compared to conventional fertilizers [42].

Several factors affect the efficiency of nutrient utilization, with a specific focus on the loss of nitrogen. This entails improving the absorption of nutrients by plants, consequently reducing the quantity that remains in the soil and is susceptible to environmental depletion [42]. The selection of controlled or slow-release fertilizers could potentially be impacted by various direct economic aspects, such as the potential losses of nutrients and the expenses associated with fertilizer applications [66]. The agronomic use efficiency of controlled or slow-release fertilizers

(CRFs or SRFs) is significantly impacted by these factors. The most significant aspect is the possibility of losing nutrients due to a variety of physical, biological, and chemical processes, such as leaching, immobilization, surface runoff, volatilization, denitrification, or fixing [67]. The utilization of slow-release fertilizers (SRFs), controlled-release fertilizers (CRFs), and bio-amended ammonium fertilizers has been demonstrated to mitigate nutrient losses, resulting in improved nutrient recovery and increased crop yield [67], [68], [69]. Another important economic consideration is the cost of applying fertilizer [52], [70].

The adoption of slow-release fertilizers (SRFs) or controlled-release fertilizers (CRFs) can lead to substantial cost savings. A single application can supply nutrients for the entire growing season, diminishing the necessity for multiple applications and thereby reducing overall expenses [52], [67]. SRFs or CRFs with delayed release characteristics can be applied during periods of less restricted trafficability. This involves applying in the fall for crops grown in the spring or winter or before the yearly spring rush. The practical benefits of employing such fertilizers are increased by the flexibility in application scheduling. This flexibility in application timing adds to the practical advantages of using such fertilizers [7], [71].

Moreover, slow-release fertilizers (SRFs) or controlled-release fertilizers (CRFs) may reduce the demand for short-season and manual labor for top-dressing, especially during peak periods such as in rice paddies [36]. Additionally, the application of controlled or slow-release fertilizers could yield significant advantages in terms of improving plant nutrition and physiological functions [42], [67]. Unlike conventional soluble fertilizers, which can contribute to an excess nutrient supply, the use of SRFs/CRFs helps prevent an increase in the concentration of soluble salts in the root area [72], [73]. Accordingly, this leads to a multitude of challenges, such as osmotic stress, specific harm to plants at various growth stages, and negative occurrences such as lodging. These challenges represent only a limited selection of the potential issues that may arise [74], [75]. The utilization of slow or controlled-release fertilizers is, in contrast, linked to diminished levels of stress and targeted toxicity. This is due to the gradual release of nutrients over an extended duration, thereby mitigating the potential hazards associated with excessive fertilization [76], [77]. The slow-release mechanism of these fertilizers enables plants to absorb nutrients as required, preventing hazardous nutrient concentrations from building up in the soil. This controlled nutrient release contributes to a more balanced and sustainable approach to plant nutrition [40], [77].

Research has additionally demonstrated that the utilization of SRFs and CRFs is correlated with elevated levels of germination, agricultural yield, reduced incidence of leaf burns, stalk fractures, and disease infestation [57], [73], [78], [79]. To summarize, the utilization of slow-release fertilizers (SRFs) can enhance plant growth, increase yield, and improve crop quality.

Furthermore, supplying nutrients in the preferred chemical forms for plants stands out as one of the factors influencing fertilizer use efficiency [67]. Over the past 20 years, there has been a lot of focus on providing plant nutrients in the chemical forms that they like, especially when it comes to combined ammonium-nitrate feeding [50]. Numerous research efforts have revealed significant advancements in grain production and protein density through the utilization of mixed-nitrogen nutrition, surpassing the outcomes of relying solely on nitrate or ammonium consumption alone [6], [52], [67], [80] – [82]. The observed positive results in grain production and protein content were evident exclusively in experiments where the ammonium/nitrate ratio appropriately regulated in the soil was maintained.

Achieving an enhancement in ammonium nutrition can be accomplished through various methods, including the use of nitrification inhibitors, controlled or slow fertigation, or the elevation of local concentrations of ammonium or ammonia [83], [84]. In conclusion, there is accumulating evidence that various nutrients can synergistically interact, particularly when supplied simultaneously or positioned in proximity to the absorption sites near the root surface. The management of the pattern and chemical form of nutrient release from flow-release fertilizers (SRFs) or controlled-release fertilizers (CRFs) can enhance the advantageous physiological effects provided by these treatments [85]. Nevertheless, the mentioned effects necessitate heightened attention, especially at the field level, to thoroughly evaluate their real contribution, beyond just the reduction of nutrient losses. Practical field assessments are crucial to understanding the overall impact and effectiveness of these approaches in real-world agricultural settings [67].

1.6. Summary

The modified urea fertilizers application has emerged as an essential component in enhancing the availability of nutrient nitrogen in the soil. The nitrogen content in these fertilizers is enhanced, but they also reduce the rate at which it is released, resulting in a greater effectiveness of these substances in crop cultivation. Furthermore, numerous research studies have demonstrated the beneficial effects of urea-controlled or slow-release substances on plant growth. Even with these developments, more research is still required to fully understand these drugs' impacts. Researchers are working to refine the urea-modified fertilizer formulations and combine them with effective agronomic techniques in order to reduce nitrogen losses and increase nitrogen use efficiency in the farming industry.

2. MATERIAL AND METHODS

The major goal of this study is to improve the mineral nitrogen release patterns by using modified urea compounds and their management in different soil types.

2.1. Fertilizer sources

This study was performed to contrast two further modified urea compound fertilizers such as coated urea potassium humate as CRFs and urea-gypsum cocrystals as SRFs with conventional urea fertilizer (Figure 2). These material's characteristics are as follows:

1. Urea (Total N 46.2%).
2. Urea potassium humate (coated form): contains 40% N and 1% Potassium Humate. Provided by AB Achema Company in Kaunas city.
3. Urea cocrystals [$\text{CaSO}_4 \cdot 4\text{CO}(\text{NH}_2)_2$] contents: 29.8% N; 8.5% S; 10.6% Ca. The fertilizer is produced mechanochemically by chemists from the Faculty of Chemical Technology, KTU.

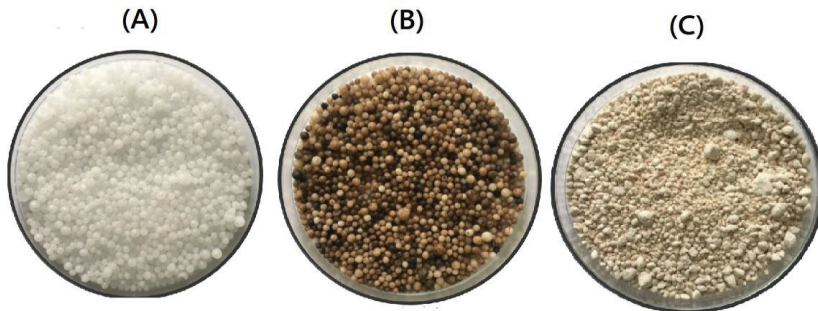


Figure 2. The study fertilizers sources: urea (A), coated urea potassium humate (B), and urea cocrystals (C)

2.2. Study area description and soil characteristics

The experimental work was conducted in both fields and under glasshouse conditions. The Lithuanian Research Center for Agriculture and Forestry's Rumokai Experimental Station (54°43'15.7044" N, 22°58'36.667" E) served as the site of two years trial conducted there in 2018 and 2019 and one season there in 2020. The field soil type was *Hapli-Epihyogleyic Luvisol* with a loamy texture [86]. The purpose of the first field experiment was to compare the benefits of applying urea+ammonium sulfate, urea+calcium sulfate, and urea cocrystals to conventional urea as nitrogen fertilizers to maize. Table 1, (Article 1) displayed the chemical characteristics of the soil at a depth of 0–20 cm, except for available mineral nitrogen and sulfur at the soil depth (0–

30 cm). In the second trial, which used corn as the test crop, several modified urea, such as coated urea potassium humate and urea cocrystals, were investigated for their effects on mineral nitrogen release and their use efficiency. Table 1 displays the chemical characteristics of the soil at 20 cm as well as the concentrations of nitrogen forms at the soil's surface (0–30 cm) and subsurface (0–60 cm) layers (Article 2).

The glasshouse experiment was conducted by using four soil types with different soil textures and the samples were collected from Lithuanian agricultural soils. To fill the pots, soil samples representing the four different soil types with different texture types were taken from the surface layer (0–30 cm) of four profiles. The soils are formed and developed under cold (6.0–7.5 °C) and wet (600–820 mm) climate conditions [87], [88]. The soil profiles are classified and named according to the WRB 2022 classification, [89]. The identified soil types included *Endogleyic Haplic Luvisol (Loamic, Aric)* [89]; *Endogleyic Epistagnic Endocalcaric Cambisol (Loamic, Aric, Drainic)* [89], the third type was formed in limnoglacial sands and named *Dystric Arenosol (Aric)* [89]; and *Glossic Epigleyic Dystric Retisol (Clayic, Aric, Cutanic, Drainic)* [89] was the fourth type. The soil typological units of the study sites were not determined by excavation and description of soil profiles, but it was based on other literature and previous studies [28], [90], [91], The soil types and their corresponding physio-chemical characteristics are detailed in Table 1.

Table 1. The soil types and their physio-chemical characteristics at soil depth 0–30 cm

Soil Characteristics	Rumokai	Dotnuva	Kazlu Ruda	Vezaiciai
Soil Type	<i>Endogleyic Haplic Luvisol (Loamic, Aric)</i>	<i>Endogleyic Epistagnic Endocalcaric Cambisol (Loamic, Aric, Drainic)</i>	<i>Dystric Arenosol (Aric)</i>	<i>Glossic Epigleyic Dystric Retisol (Clayic, Aric, Cutanic, Drainic)</i>
Texture	Loam (L)	Sandy Loam (SL)	Sand (S)	Sandy Clay (SC)
% Sand	51.7	58.8	96.4	60.3
% Silt	31.6	37.3	2.9	4.2
% Clay	16.7	3.9	0.7	35.5
pH _{KCl} mol/L	7.4	6.9	5.3	4.5
P ₂ O ₅ mg·kg ⁻¹	244	266	102	139
K ₂ O mg·kg ⁻¹	201	308	40	240
SOM* (%)	1.04	1.26	0.79	1.25
SOC** (%)	0.60	0.73	0.46	0.72
Ece mS/m	14.4	12.7	2.31	6.10
Total N (%)	0.148	0.151	0.013	0.120
N _{min} mg·kg ⁻¹	23.99	37.32	1.74	41.60
NH ₄ -N mg·kg ⁻¹	2.06	1.33	0.98	3.68
NO ₃ -N mg·kg ⁻¹	21.93	35.99	0.76	37.92

* SOM = Soil organic matter, ** SOC = Soil organic carbon.

2.3. Research scheme and experimental design

The general scheme of the investigation is presented in Figure 3. This study included two field trials and a one-pot experiment. The initial field experiment spanned a duration of two years (2018–2019) and was organized in a randomized complete block design (RCBD) with a total of 20 experimental plots with a total plot area of 4 m² (2 m × 2 m). Five treatments were applied and arranged in four replicates, comprising of a control, urea, urea combined with ammonium sulfate, urea combined with calcium sulfate, and [CaSO₄·4CO(NH₂)₂]. The field preparation and maize cultivation dates for 2018 and 2019 are detailed in Table 2 (Article 1). The second experiment, conducted in 2020, followed the same design but included seven treatments with four replicates and a total of 28 experimental plots. Treatments consisted of control, (100 and 200) kg N ha⁻¹ of urea, (100 and 200) kg N ha⁻¹ of coated urea potassium humate (UPH), and (100 and 200) kg N ha⁻¹ urea cocrystals [CaSO₄·4CO(NH₂)₂].

Maize (*Ramirez*, characterized as *FAO 160*) seeds were sown manually one day after fertilization for both two field experiments during 2018–2019 and 2020. Row spacing was set at 50 cm, with a plant spacing of 20 cm and a maize density of 10 plants/m² (equivalent to 100,000 plants ha⁻¹). No pesticides were applied in the cultivation process. Manual measurements of corn productivity and biometrics were carried out at the physiological maturity phase of corn (BBCH 88-89). Following the harvest, the residual plant remains were plowed to a depth of 22 cm.

The pot experiment was performed in the glasshouse specifically in the Agrobiological Laboratory, Lithuanian Research Center for Agriculture and Forestry in 2021. The primary aim was to investigate the impact of different soil types on nitrogen mineral release patterns, utilizing both conventional urea and coated urea potassium humate. The experiment spanned a duration of 45 days, focusing on the growth of the spring barley (*Hordeum vulgare L.*) cultivar ‘*Ema DS*’. Five treatments were identified as control without fertilizer, (100, 200) kg N ha⁻¹ urea, (100, and 200) kg N ha⁻¹ coated urea potassium humate, as presented in Figure 2 (Article 3). The treatments were applied in three replicates. The experimental design involved arranging 60 pots into four groups (A, B, C, and D), as presented in Figure 1 (Article 3). The dimensions of each pot were 25 cm in height and 25 cm in diameter, filled with 10 kg of soil.

2.4. Soil sampling and analytical procedures

In the field experiments conducted in the Rumokai field from 2018 to 2019, soil samples were collected at a depth of 0–30 cm from both non-treated and treated plots. During the 2020 season, samples were collected in three replicates at soil depths of (0–30) cm and (30–60) cm. Samples for soil mineral nitrogen analyses were taken before sowing, then every two weeks

throughout the growing season (7 times), and again after harvesting. A stainless-steel push probe was used to obtain samples, to create one sample three subsamples per plot were combined. Soil sampling was collected from the pots at different time intervals in the pot experiment. These intervals included one day, as well as days 4, 7, 14, 21, 28, and 45.

The Agrochemical Research Laboratory at the Lithuanian Research Center for Agriculture and Forestry conducted a comprehensive analysis of soil properties and mineral nitrogen content throughout the study. This analysis was documented in articles 1, 2, and 3. According to ISO 10390:2005, the soil pH was determined [92], [93]. According to LVP D-07:2019, soil-available K_2O was measured by using a JENWAY PFP7 flame photometer and P_2O_5 was determined by using ammonium molybdate (Olsen method) via the spectrometric method with a Shimadzu UV 1800 spectrophotometer [94]. Soil electrical conductivity (E_c) determination was according to ISO 11265:1994 [95]. Total nitrogen was measured based on ISO 11261-1995 [96], [97]. The soil mineral nitrogen was determined by the method developed by the laboratory and the use of a spectrometric flow injection analysis (FIA) [18]. According to ISO 10694:1995, the soil organic carbon content was determined [18], [98]. The particle size distribution of the soil samples was determined according to ISO 11277-2020 [99].

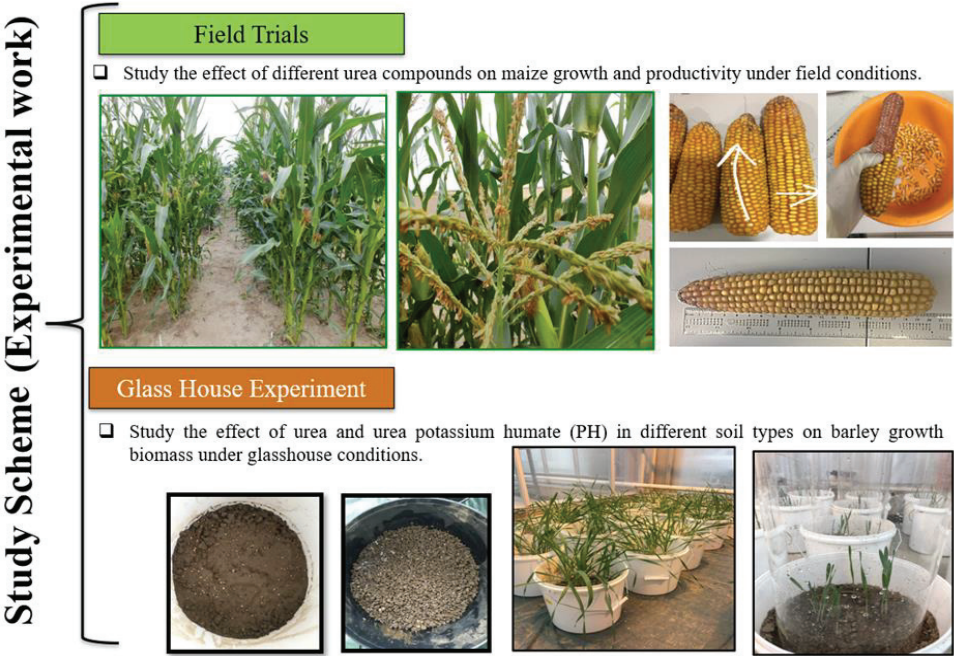


Figure 3. General scheme of the investigation

2.5. Maize biometric parameters and yields and grain quality

The maize biometric measurements were evaluated by harvesting the central portion of the plots, specifically the inner area measuring 2×2 m, at the physiological maturity stage. Twenty randomly selected plants were utilized for the determination of grain yield and grain biomass quality. Samples were collected from all the replicates and subjected to oven-drying at 65 ± 5 °C until a constant weight was achieved to obtain dry biomass and yield weight. The grain quality characteristics, including total nitrogen, carbohydrates, and starch, were analyzed by the Agrochemical Research Laboratory at the Lithuanian Research Center for Agriculture and Forestry according to 72/199/EEC methods [100].

2.6. The field experiment meteorological conditions

Figure 4 shows the significant variations in the seasonal weather conditions during the study for 3 years. The region has a moderate climate, with high temperatures reported from June to August and with an average temperature of 16 °C. The average air temperature in 2018 was warmer than the other two seasons, except for June. Therefore, in 2018 the harvest occurred a month earlier than the typical schedule. In contrast to 2018, the other two seasons experienced drier conditions in April, leading to a delay in maize cultivation and an early onset of crop development.

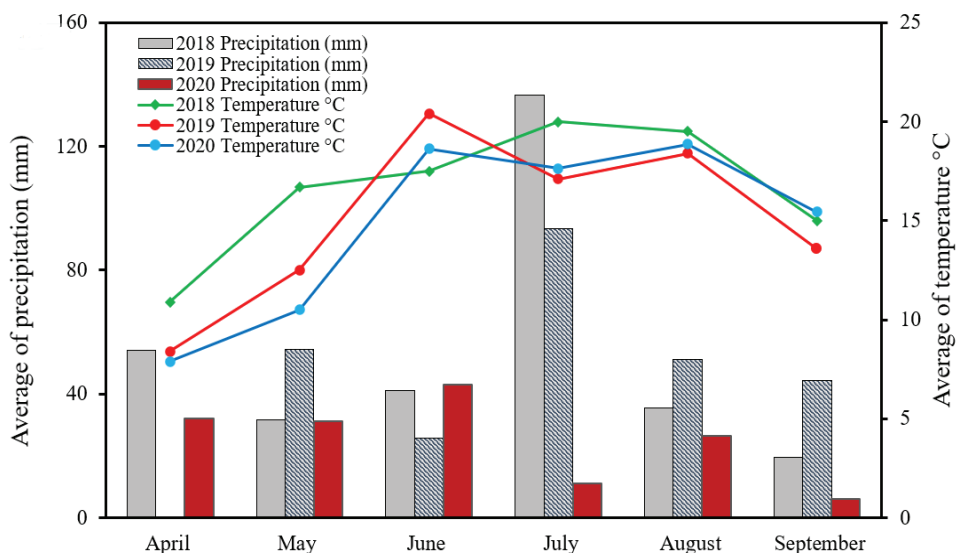


Figure 4. Monthly means of the temperatures °C and precipitation (mm) during the maize growing seasons in 2018–2020

2.7. Statistical analysis

To determine the statistical significance of the differences, analysis of variance (ANOVA) was used. Pearson's correlation analysis was used to ascertain the link between time (days or weeks) and soil mineral nitrogen concentration, including its forms. IBM SPSS 25.0 was utilized as the statistical analysis program (Armonk, NY, USA). To differentiate means based on the ANOVA results, Duncan's test was used at level ($p < 0.05$).

3. RESULTS AND DISCUSSION

3.1. Mineral nitrogen release patterns in the soil

3.1.1. Mineral nitrogen release in the grown maize soil from urea-sulfur fertilizers

Two years of field trials (2018–2019) were carried out at the Rumokai experimental station. The objective of applying urea-sulfur fertilizer to maize plants was to investigate the effect of these fertilizers on maize productivity, as well as the soil nitrogen accumulation and its uptake, as detailed in Article 1. The current findings indicated a noteworthy impact of the participatory urea-sulfur fertilizers application on the soil mineral nitrogen release in comparison to the use of conventional urea alone. The application of sulfur in the soil significantly amplified the soil mineral nitrogen release from the urea granules, as anticipated [101] – [103]. The results showed that the soil mineral nitrogen content, formed by nitrate NO_3 and ammonium NH_4 , was higher in 2019 than it was in 2018, owing to the cumulative application effect [104]. Additionally, the findings illustrated that in both years 2018 and 2019, the soil ammonium concentration was comparatively lower when compared to nitrate levels. Moreover, the ammonium NH_4 concentration accounted for approximately 9% and 17% of the total mineral nitrogen present in the soil during the years 2018 and 2019, respectively.

A significant ($p \leq 0.01$) negative correlation between the concentration of nitrate NO_3 in the soil and the duration of maize growth (weeks) in both the years 2018 ($r = -0.66^{**}$) and 2019 ($r = -0.46^{**}$) was exhibited. Notably, the concentration of ammonium did not exhibit a significant correlation with either the duration of time (weeks) or the fertilization treatments during 2 years (2018–2019). The mineral nitrogen concentration in the soil throughout the maize growth exhibited a significant correlation ($p \leq 0.01$) with time (weeks). There was a notable negative linear relationship in 2018 ($r = -0.65^{**}$) and in 2019 ($r = -0.45^{**}$) between soil mineral N and time (weeks), indicating a decrease in concentration over time. Further details of these results are elaborated in Article 1.

3.1.2. Mineral nitrogen release from different modified urea fertilizers

A field trial in 2020 was carried out to study the impact of various modified urea fertilizers including synthesized urea cocrystals and coated urea potassium humate with different two doses on soil mineral nitrogen release at soil depths (0–30 cm and 30–60 cm) to maximize nitrogen uptake and its use efficiency and minimize nitrogen loss, under the maize growth system (Article 2). Throughout the release process of the soil mineral nitrogen, the various urea compounds underwent conversion into ammonium (NH_4) and nitrate (NO_3). Across all treatments, the

concentration of ammonium was consistently lower than that of nitrate. The soil surface layer (0–30 cm) demonstrated a greater concentration of ammonium and nitrate compared to the subsurface layer (30–60 cm). In Table 2, the results demonstrate that the soil mineral nitrogen release at soil depths 0–30 and 30–60 cm during the corn's growth had a negative significant correlation with the time (weeks) for all the treatments except U200 and UPH100 in the surface layer 0–30 cm.

Furthermore, as observed in Table 2, the fertilization treatments had higher mineral nitrogen concentrations in the soil surface layer (0–30 cm) than in the subsurface layer (30–60 cm). Approximately 40–65% of the mineral nitrogen was discovered in the subsurface layer (30–60 cm), according to a comparison of the means of the mineral nitrogen at the soil's surface layer (0–30 cm) and subsurface layer (30–60 cm). The explanation for that could be due to the leaching of nitrogen to the subsurface layers [105].

Table 2. Correlation among soil mineral nitrogen concentration ($\text{mg}\cdot\text{kg}^{-1}$) and the time (weeks) in soil surface 0-30 cm and subsurface 30-60 cm layers during the corn's growth in 2020

Treatments	Mean	Pearson Coefficient (r)	P-value
<i>Soil depth (0-30) cm</i>			
C	16.05	-0.82**	0.007
U100	23.80	-0.73*	0.025
U200	27.59	-0.67	0.050
UPH100	25.25	-0.59	0.097
UPH200	26.13	-0.73*	0.026
UC100	21.72	-0.71*	0.032
UC200	29.34	-0.70*	0.035
<i>Soil depth (30-60) cm</i>			
C	10.72	-0.81**	0.008
U100	13.59	-0.83**	0.005
U200	13.50	-0.81**	0.008
UPH100	12.11	-0.87**	0.002
UPH200	12.52	-0.89**	0.001
UC100	11.81	-0.87**	0.002
UC200	13.74	-0.72*	0.028

** . Correlation is significant at ($p<0.01$).

* . Correlation is significant at ($p<0.05$).

Among the treatments, the control (without fertilization) exhibited the most minimal values of mineral nitrogen concentration in both the soil surface (0–30 cm) and subsurface (30–60 cm) layers followed by UC100 (Table 2). Conversely, the treatment of urea cocrystals (UC200) displayed the highest concentration in both soil depths 0–30 cm and 30–60 cm. At the soil depth of 0–30 cm, the treatment of UC200 obtained mineral nitrogen $13.29 \text{ mg}\cdot\text{kg}^{-1}$ more than the control, $3.21 \text{ mg}\cdot\text{kg}^{-1}$ more than UPH200, and $1.75 \text{ mg}\cdot\text{kg}^{-1}$ more than U200. Interestingly, at the soil depth of 30–60 cm, urea treatments (U100 and U200) means were higher than other

comparative treatments which explains that the urea fertilizer had high solubility and can be leached easily [106]. Additional findings can be found in Article 2.

3.1.3. Mineral nitrogen patterns in different soil texture types

A vegetative experiment was conducted in pots under controlled glasshouse conditions (20 ± 2 °C and 60% humidity) aimed to investigate the dynamic release of mineral nitrogen in different soil types including Arenosols, Cambisols, Luvisols, and Retisols with varying textures such as sandy, sandy loam, loamy, and sandy clay, respectively. The primary objectives of this work were to comprehend the interaction between soil characteristics especially soil texture and mineral nitrogen release, as well as to evaluate the impact of coated urea potassium humate compared to conventional urea on the production of barley green biomass. More information about this investigation can be found in Article 3.

The mineral nitrogen (N_{\min}) release dynamics, along with its primary forms ammonium (NH_4) and nitrate (NO_3), were affected by the soil characteristics and presented different patterns as presented in Figure 5. This suggests that the chemical and physical characteristics of the soil receiving the fertilizer can have a substantial impact on the efficacy and release rate of the fertilizers [5], [107]. Moreover, the results indicated that the utilization of urea and coated urea potassium humate significantly ($p\leq 0.01$) influenced the soil mineral nitrogen release and its primary forms (NH_4 and NO_3).

The lowest values of mineral nitrogen were obtained by the treatments in sandy texture soil (Figure 5). Coated urea potassium humate treatments (UPH200 and UPH100) recorded higher mineral nitrogen than urea treatments (U200 and U100), UPH200 recorded the highest values of mineral nitrogen with increases of $47.87\text{ mg}\cdot\text{kg}^{-1}$, $27.71\text{ mg}\cdot\text{kg}^{-1}$, and $6.55\text{ mg}\cdot\text{kg}^{-1}$ compared to control, U100, and U200, respectively (Table 2, Article 3). Moreover, the treatments of coated urea potassium humate (UPH200 and UPH100) obtained higher means of mineral nitrogen compared to urea treatments (U200 and U100) in loamy texture soil (Table 2, Article 3).

In sandy loam soils, U200 recorded the highest mean at $271.25\text{ mg}\cdot\text{kg}^{-1}$ with $58.47\text{ mg}\cdot\text{kg}^{-1}$ higher than UHP200. Otherwise, there is no difference observed between U100 and UPH100. Urea fertilizer treatments (U200 and U100) in sandy clay texture recorded higher means of mineral nitrogen in comparison to coated urea potassium humate treatments (UPH200 and UPH100), U200 obtained the highest mean of mineral nitrogen at $425.08\text{ mg}\cdot\text{kg}^{-1}$, with an increase of $93.39\text{ mg}\cdot\text{kg}^{-1}$, higher than UPH200, and U100 recorded $44.05\text{ mg}\cdot\text{kg}^{-1}$ higher than UPH100 (Table 2, Article 3).

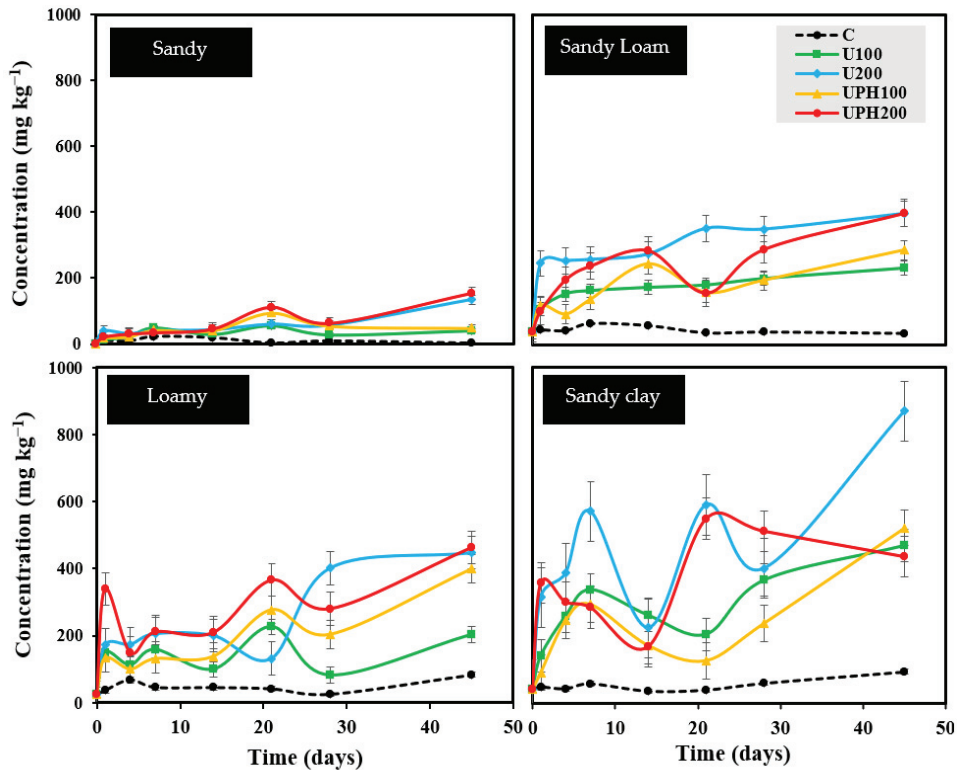


Figure 5. Dynamic patterns of mineral nitrogen release regarding the concentration ($\text{mg}\cdot\text{kg}^{-1}$) and time (days) in different soil textures during 45 days in a pot experiment

The fertilization treatments affected the soil mineral nitrogen and its forms (ammonium and nitrate) accumulation significantly compared to the control as shown in (Table 3). The highest significant ($p < 0.01$) accumulative concentration of N_{min} was observed after 45 days by the end of the experimentation for all the soil texture types under the treatment of U200 with a mean of $241.89 \text{ mg}\cdot\text{kg}^{-1}$. Followed by UPH200 with a mean of $214.54 \text{ mg}\cdot\text{kg}^{-1}$ and UPH100 at $147.69 \text{ mg}\cdot\text{kg}^{-1}$.

Among the four soil texture types, it has been observed that sandy soil (Arenosol) consistently exhibited the lowest significant ($p < 0.01$) concentration of mineral nitrogen with a mean of $38.22 \text{ mg}\cdot\text{kg}^{-1}$ (Table 3). This may be attributed to its poor nature, and low fertility (i.e., low cation exchange capacity) [32], [107], [108]. On the other hand, mineral nitrogen content in sandy loam (Cambisol) and loamy (Luvisol) soils did not show significant differences from each other. Otherwise, their mineral nitrogen content was significantly higher than sandy texture soil. The sandy clay (Retisol) soil displayed the highest significant ($p < 0.01$) concentration of mineral nitrogen compared to the other comparative soil types as shown in Table 3. These soil types with

higher mineral nitrogen content are predominantly found in the central and western regions of Lithuania, which are known to be more fertile than the eastern soils [107], [109].

Table 3. The effect of the soil texture type and urea fertilizers application on accumulative mineral nitrogen and its forms (NH_4 and NO_3) in the surface layer 0–30 cm depth after 45 days.

Soil Texture Type	NH_4	NO_3	N_{min}
	$\text{mg}\cdot\text{kg}^{-1}$		
Sand	16.33 ^a	21.89 ^a	38.22 ^a
Sandy loam	43.03 ^a	133.49 ^c	168.31 ^b
Loam	37.92 ^a	127.74 ^{bc}	165.66 ^b
Sandy clay	137.55 ^b	105.12 ^{bc}	257.52 ^c
<i>p-value</i>	$p < 0.003$	$p < 0.002$	$p < 0.001$
Treatments	$\text{mg}\cdot\text{kg}^{-1}$		
Control (C)	9.87 ^a	29.97 ^a	38.26 ^a
U100	56.60 ^{abc}	89.29 ^b	144.75 ^b
U200	94.84 ^c	132.00 ^d	241.89 ^d
UPH100	45.71 ^{abc}	102.91 ^{bcd}	147.69 ^b
UPH200	86.51 ^{bc}	131.14 ^{cd}	214.54 ^{bcd}
<i>p-value</i>	$p < 0.021$	$p < 0.003$	$p < 0.001$

Numbers followed by the same letter in the same column are not significantly different ($p < 0.05$) by Duncan's test.

3.2. Influence of modified urea application on crop productivity, yields, and biomass

3.2.1. The impact of urea-sulfur fertilizers on plants' density, green matter, dry matter yield, grain yields, and grain quality (Article 1)

The plant density and green and dry matter yield data after using urea-sulfur fertilizers compared to conventional urea are presented in Table 4. In the year 2018, it was observed that the treatments had a significant ($p \leq 0.01$) impact on the plant density and green matter yields when compared to the control. Urea+ammonium sulfate displayed the highest significant ($p < 0.01$) plant density and green matter yield compared to the control (Table 2). There were no significant differences observed between the other comparative treatments for the plant density, and urea treatment obtained lower green matter than the other comparative treatments.

Moreover, a noteworthy effect was observed between the treatments on the plant density and green matter yields in 2019. Urea cocrystals [$\text{CaSO}_4\cdot 4\text{CO}(\text{NH}_2)_2$] exhibited higher density and higher significant ($p < 0.05$) green matter yield than urea and control, as illustrated in Table 4. The analysis for both years (2018 and 2019) revealed that the treatments did not yield any significant impact on dry matter yields. Nevertheless, urea cocrystals [$\text{CaSO}_4\cdot 4\text{CO}(\text{NH}_2)_2$] consistently demonstrated the highest dry matter yields for both seasons in 2018 and 2019, respectively, as indicated in Table 4.

Table 4. Means of plants' density, total fresh and dry matter yields after using urea-sulfur fertilizers for the 2-year study (2018-2019).

Treatments	Plants' Density	Green matter yield	Dry matter yield	% Moisture
	1000 plants ha ⁻¹		t / ha ⁻¹	
2018				
<i>Control</i>	92.50 a	17.90 a	6.29 a	64.86
<i>Urea</i>	97.50 b	20.00 b	7.52 a	62.40
<i>Urea + (NH₄)₂SO₄</i>	100.00 b	22.33 c	7.59 a	66.00
<i>Urea + CaSO₄</i>	98.75 b	21.88 c	7.84 a	64.16
<i>CaSO₄·4urea</i>	97.50 b	22.05 c	8.43 a	61.77
<i>SE±</i>	1.21	0.38	0.53	-
<i>P-value</i>	0.009	0.000	ns*	-
2019				
<i>Control</i>	92.83 a	17.47 a	8.92 a	48.94
<i>Urea</i>	93.98 a	18.93 a	9.83 a	48.07
<i>Urea + (NH₄)₂SO₄</i>	97.60 ab	18.79 a	9.85 a	47.58
<i>Urea + CaSO₄</i>	95.55 ab	18.22 a	9.66 a	46.98
<i>CaSO₄·4urea</i>	100.00 b	22.12 b	11.41 a	48.42
<i>SE±</i>	1.59	0.85	0.92	-
<i>P-value</i>	0.049	0.020	ns*	-

Note. values in the same column followed by the same letter are not different ($p < 0.05$) according to Duncan's multiple range test at the 5% level. *ns= not significant.

Furthermore, the fertilizer treatments significantly impacted corn biometric measurements, including the developed corn cobs, fresh and dry cob yields, and grain yields compared to the control. The two-year study's results (2018–2019) were presented in Table 4 (Article 1), with superior outcomes noted in 2019 compared to 2018. Otherwise, there were no significant differences observed between the tested fertilizers in 2018, while urea+ammonium sulfate (UAS) treatment obtained a higher effect for all productivity parameters except the developed corn cobs yield. In 2019, urea cocrystal [$\text{CaSO}_4 \cdot 4\text{CO}(\text{NH}_2)_2$] exhibited significantly ($p < 0.01$) higher productivity parameters, in terms of developed corn cobs, dry cob yields, and grain yields compared to the other comparative treatments. The grain yields during both the 2018 and 2019 seasons, was detailed in Figure 6.

However, when comparing yields between the two seasons (2018–2019), no significant differences were observed. The utilization of fertilizers such as urea+ammonium sulfate (UAS), urea+calcium sulfate (UCS), and urea cocrystals [$\text{CaSO}_4 \cdot 4\text{CO}(\text{NH}_2)_2$] resulted in a noteworthy improvement in grain yields during both 2018 and 2019. This improvement was linked to the higher sulfur content present in these treatments compared to both urea and the control [110] – [112]. Specifically, in 2018, the treatments of urea+ammonium sulfate and urea cocrystals produced an increase in grain yields by 47.8% and 43.73%, respectively, more than the control by these respective percentages and also outperforming urea by 10.5% and 7.50%. Moving to 2019, urea cocrystals treatment exhibited a substantial increase in grain yields, recording 41.17% and

23.07% higher yields than the control and urea, respectively, Following closely UCS demonstrated a 26.70% and 10.46% increase higher than the control and urea, as presented in Table 4 (Article 1). UAS ranked third, providing a 23.52% increase surpassing the control and urea by 7.60%, respectively.

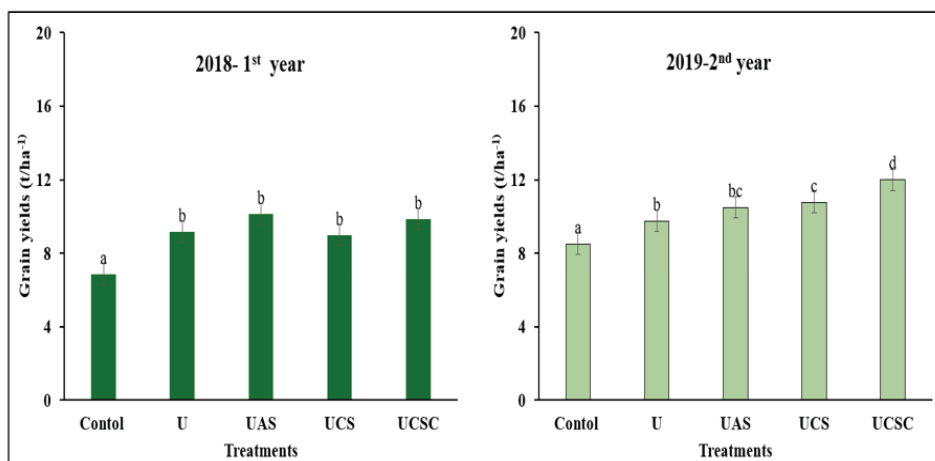


Figure 6. The corn grain yield means (t/ha^{-1}) of the field experiment 2018-2019 after using different urea-sulfur compound fertilizers. Control U = urea, UAS = urea + ammonium sulfate, UCS = urea + calcium sulfate, and UCSC = urea cocrystal ($CaSO_4 \cdot 4urea$). Note. Different lowercase letters indicate the significant difference according to Duncan's multiple range test at ($p < 0.05$).

The combined application of urea and sulfur-based fertilizers demonstrated a sustainable impact on gradually enhancing soil mineral nitrogen accumulation and promoting increased nitrogen uptake in grains over time, resulting in elevated grain yields [110], [113] – [115]. It is noteworthy that the positive response to nitrogen and sulfur fertilization was particularly evident in maximizing grain yield, especially in the year 2019. Moreover, the fertilizer treatments had a significant impact on various grain quality attributes, including the grain total nitro, and crude protein, during both 2018 and 2019 compared to the control, with no significant differences between the tested comparative treatments as outlined in Table 5 (Article 1).

Moreover, the application of fertilizers did not result in a significant effect on starch content in either of the two years (2018 and 2019). Urea cocrystals demonstrated the highest total nitrogen levels in grains, surpassing other treatments by 1.42% in 2018 and 1.47% in 2019. Additionally, urea cocrystals exhibited the highest crude protein content in grains in both years.

3.2.2. The impact of synthesized and coated urea on plants' density, fresh leaves and stems, and dry matter yields (Article 2)

The application of modified urea, whether as a cocrystal or coated with urea potassium humate, had a significant impact on corn plant density, fresh leaves and stems, and dry matter. The corresponding plant density, fresh leaves and stems, and dry matter yields are presented in Table 2 (Article 2). Figure 7 shows that UC200>UPH200 treatments recorded significantly ($p < 0.01$) higher fresh leaves and stems yield compared to the control and urea treatments, followed by UC100>UPH100 treatments. Furthermore, the same treatments significantly ($p < 0.01$) affected the dry matter yields compared to the control. While, urea treatments (U100 and U200), exhibited nonsignificant effects in comparison to the control for the fresh leaves and stems and dry matter.

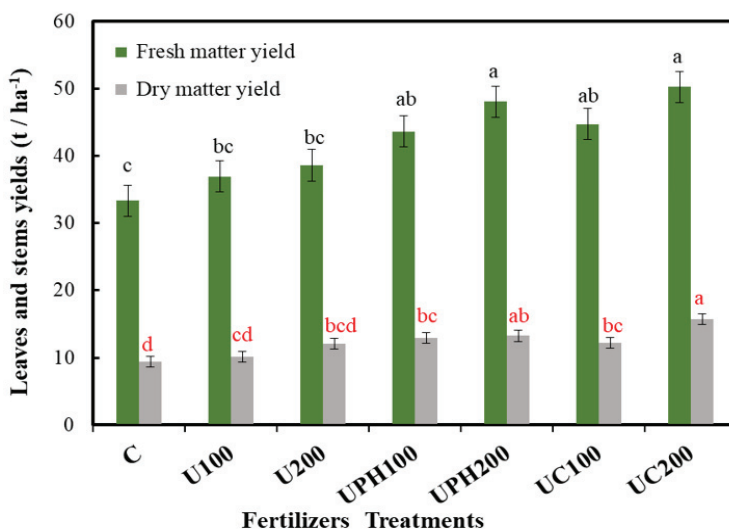


Figure 7. The effect of different urea fertilizers on plant fresh and dry matter yields followed by Duncan's multiple range test letters at $p < 0.05$. The letters with the same color have the same significance level. Note. Control (C) = non-treated, U100 = 100 kg N ha⁻¹ urea, U200 = 200 kg N ha⁻¹ urea, UPH100 = 100 kg N ha⁻¹ urea+potassium humate (UPH), UPH200 = 200 kg N ha⁻¹ urea+potassium humate (UPH), UC100 = 100 kg N ha⁻¹ urea cocrystals, and UC200 = 200 kg N ha⁻¹, urea cocrystals.

Furthermore, the application of urea as a cocrystal and coated urea potassium humate significantly influenced grain yields ($p \leq 0.01$) as represented in Figure 8. U100 treatment had a nonsignificant difference from the control but increased the grain yields by 7.1%. U200 treatment significantly ($p < 0.01$) obtained a higher grain yield than the control and U100 with increases of 30.53% and 21.89%, respectively. In contrast, urea + potassium humate (UPH100, UPH200) and urea cocrystals treatments (UC100, UC200) exhibited significant ($p < 0.01$) substantial increases

of 30.53%, 50.47%, 39.25%, and 56.62% in grain yields, respectively, compared to the control. Additionally, the treatments of UC200>UPH200 recorded a higher significant grain yield than U200, also UC100>UPH100 had a significantly higher grain yield than U100 as presented in Table 3, Article 2.

In comparison to the control, the cob yields including fresh and dry cob matter yields were affected significantly by the modified urea treatments. Table 3 (Article 2) provided the means of fresh and dry cob yields for different modified urea compound fertilizers, following Duncan's test letters.

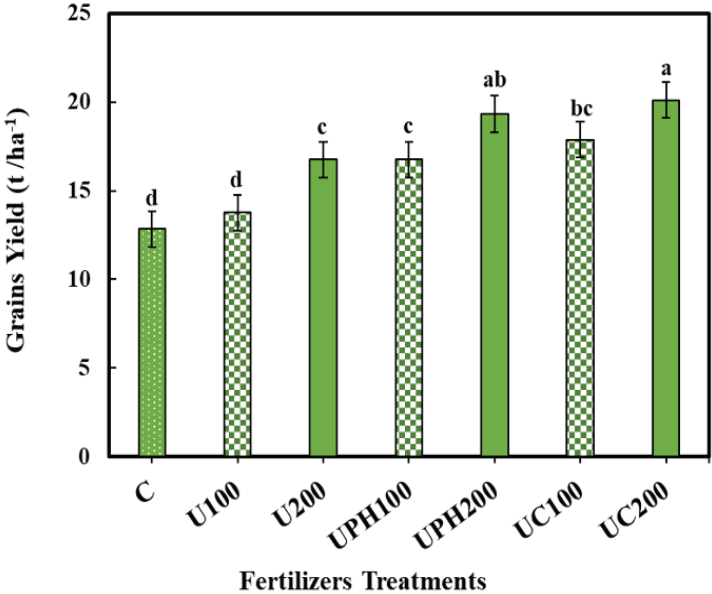


Figure 8. The corn grain yield means (t/ha⁻¹) of the field experiment (2020) after using different urea compounds fertilizers followed by Duncan's multiple range test letters at 5% level. Note. Control (C) = non-treated, U100 = 100 kg N ha⁻¹ urea, U200 = 200 kg N ha⁻¹ urea, UPH100 = 100 kg N ha⁻¹ urea+potassium humate (UPH), UPH200 = 200 kg N ha⁻¹ urea+potassium humate (UPH), UC100 = 100 kg N ha⁻¹ urea cocryystals, and UC200 = 200 kg N ha⁻¹, urea cocryystals.

Additionally, the modified urea treatments significantly impacted grain characteristics, including grain protein, total nitrogen, and carbohydrate content, as detailed in Table 4, Article 2. The grain dry matter did not exhibit a significant effect. The control yielded the lowest significant ($p < 0.01$) mean of total nitrogen in the grain and grain protein compared to the other tested treatments, but no significant differences were observed between the other treatments. In contrast, UC200 exhibited the highest total nitrogen concentration at 1.23% and total grain protein at 7.67 %. Grain dry matter ranged from 93.68% to 95.13% in UPH200 and UPH100, respectively with no significant differences between the comparative treatments. The treatments affected

highly significant the grain carbohydrate content, urea cocrystal treatments (UC200 and UC100) obtained the higher significant ($p < 0.01$) contents of the carbohydrate at 76.69 and 73.43% compared to the other comparative treatments, and that explained due to their content from sulfur which plays an important role in enhancing the carbohydrate accumulation [115].

3.2.3. Effect of urea compounds on germination and barley biomass (Article 3)

The germination in the pots started on the fourth day after applying fertilizers with 70–90%. The application of modified urea fertilizers significantly influenced barley germination ($p \leq 0.01$). Across all soil textures, UPH200 and U200 demonstrated significantly lower germination rates compared to the control. Conversely, no significant differences were observed between UPH100 and U100 in comparison to the control as presented in Table 5.

Table 5. The effect of urea and coated urea potassium humate fertilizers application on germination, green biomass, and dry matter of barley

Treatments	Germination	Green biomass	Dry matter
	%	(g)	(g)
Control (C)	88 ^c	20.47 ^a	69.68 ^a
U100	83 ^{abc}	25.05 ^{abc}	70.84 ^a
U200	75 ^{abc}	31.25 ^{bc}	74.96 ^c
UPH100	85 ^{bc}	25.91 ^{abc}	71.42 ^{abc}
UPH200	70 ^a	31.44 ^c	73.11 ^{abc}
<i>p-value</i>	<i>p < 0.01</i>	<i>p < 0.001</i>	<i>p < 0.05</i>

Numbers followed by the same letter in the same column are not significantly different by Duncan's test.

Moreover, applying urea and urea potassium humate treatments had a significant effect ($p < 0.05$) on the green biomass of barley in different soil texture types compared to the control. Within the tested treatments, no significant differences were recorded, However, UPH200 and U200 had the higher biomass at 31.44 g and 31.25 grams, respectively. There was no difference between U100 and UPH100 when compared to the control group, which had the lowest biomass with a mean of 20.47 g. When examining the treatments within soil texture types, clear differences were observed as presented in Figure 9. Particularly, within the sandy soil, the application of the fertilizer treatments had a noteworthy effect on barley's green biomass ($p \leq 0.01$) compared to the control. The UPH200 and UHP100 treatments yielded a higher significant biomass than U100 and control, with no significant difference observed with U200 as shown in Figure 9. In sandy clay soil, the impact of urea compounds on green biomass was statistically significant ($p \leq 0.05$). The treatment of UPH200 exhibited the most significant biomass in comparison to the other comparative treatments. The U200 treatment followed, which displayed a significant decrease of

around 42% of the biomass. There were no significant differences in biomass between the U100 and UPH100 treatments in contrast to the control.

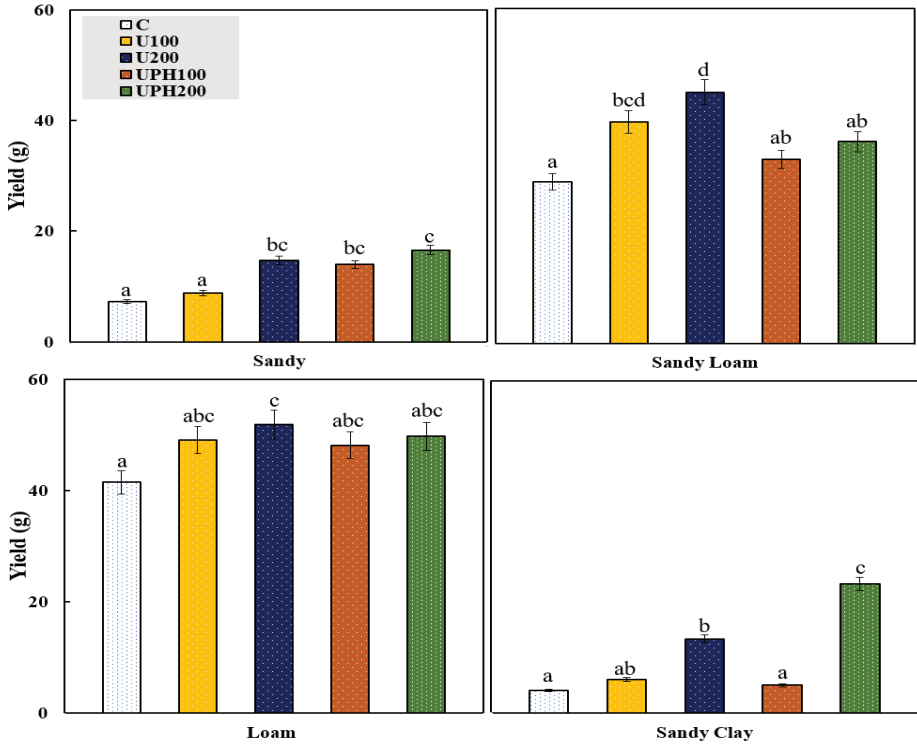


Figure 9. The green barley biomasses after being treated with urea and coated urea potassium humate in four soil types with different soil textures: sandy, sandy loam, loamy, and sandy clay. The columns with the same letter are not significantly different by Duncan’s test at ($p < 0.05$).

Furthermore, the influence extended to sandy loam soil, where both U200 and U100 treatments exhibited a significantly ($p < 0.05$) heightened effect on biomass compared to the control. Conversely, UPH200 and UPH100 had no discernible impact on biomass relative to each other or the control group (Figure 9). Although the treatments resulted in the highest barley biomass in loamy soil, values compared to other soil types, these differences did not achieve statistical significance. U200 exhibited the highest significant biomass at 51.8 g, followed by UPH200 at 49.7 g, as depicted in Figure 9.

Additionally, dry matter was significantly influenced ($p \leq 0.05$) by soil texture types. For each type of soil texture, the average dry matter values were as follows: sandy loam had the highest dry matter, followed by sandy clay. Lower dry matter values were found in sandy and loamy soil, at 70.15 g and 71.03 g, respectively. However, the treatments had no significant impact on dry matter. The following are the average dry matter values for each treatment, listed in

chronological order: U200 weighed 74.96 g, UPH200 weighed 73.11 g, UPH100 weighed 71.42 g, U100 weighed 70.84 g, and the control weighed 69.68 g.

3.3. Nitrogen uptake and nitrogen recovery and use efficiency

3.3.1. Nitrogen uptake and apparent nitrogen recovery efficiency in grains (Article 1)

The values for grain nitrogen (N) uptake and apparent nitrogen recovery (ANR) are provided in Table 6. The fertilizer treatments had a significant impact ($p < 0.01$) on both N uptake and ANR, compared to the control, during the 2 years (2018–2019). In 2018, there were no notable differences in N uptake and ANR among the tested fertilizer treatments. However, the urea+ammonium sulfate treatment exhibited the highest N uptake of 142.45 kg ha⁻¹ and the highest nitrogen recovery value in the grains at 43.44%. In 2019, the statistical analysis demonstrated significant disparities in N uptake and ANR among the fertilizer treatments, as indicated in Table 6. The urea cocrystals [CaSO₄·4CO(NH₂)₂] treatment demonstrated the highest significant ($p < 0.01$) N uptake and agronomic nitrogen recovery (ANR) at 173.31 kg ha⁻¹ and 37.34%, respectively compared to the other comparative treatments.

Table 6. Analysis of variance for grain N uptake and ANR in 2 years (2018–2019).

Treatments	N Uptake in grains (kg ha ⁻¹)		ANR (%) in grains	
	2018	2019	2018	2019
Control	77.24 a	117.30 a	0.00 a	0.00 a
Urea	123.13 b	136.76 b	30.66 b	12.98 b
Urea + (NH ₄) ₂ SO ₄	142.45 b	168.47 cd	43.44 b	34.12 cd
Urea + CaSO ₄	123.68 b	153.86 bc	30.94 b	24.38 bc
CaSO ₄ ·4 CO(NH ₂) ₂	139.90 b	173.31 d	41.79 b	37.34 d
<i>p</i> -value	<.000	<.000	<.000	<.000

Numbers followed by the same letter in the same column are not significantly different ($p < 0.01$) by Duncan's test.

In 2018–2019, soil mineral nitrogen at soil depth (0–30 cm) exhibited a significant correlation ($p < 0.01$) with grain N uptake as presented in Figure 10. The increase in grain N uptake significantly ($p < 0.01$) contributed to the elevation of total N in grains and grain yield in both study years (2018 and 2019). In 2018, a strong positive linear relationship was observed between soil mineral nitrogen and N uptake in grains. Similarly, in 2019, the correlation coefficient (r) indicated a positive linear relationship between soil mineral nitrogen and N uptake in grains. Moreover, the grain yield in both study years correlated significantly with the soil mineral nitrogen content as shown in Figure 10. Additionally, the correlation provided a strong positive linear relationship between the N uptake and the grain yields in 2018–2019, respectively as presented in Table 5, Article 1.

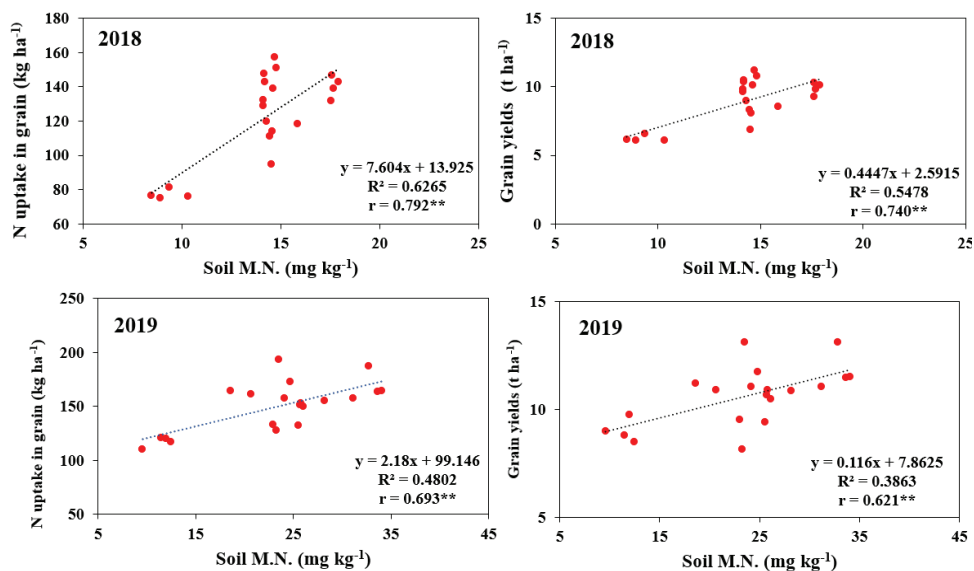


Figure 10. The correlation between the soil mineral nitrogen and N uptake in the grains, and the grain yield during 2018-2019.

In addition, the soil available sulfur correlated significantly ($p < 0.01$) in both 2 years with the soil mineral nitrogen content and the grains N uptake in a positive linear relationship as presented in Figure 11. Whereas, the grain yields significantly ($p < 0.05$) correlated with the soil sulfur in a medium positive linear relationship in 2018 and a significant ($p < 0.01$) strong positive linear relationship in 2019 as shown in Figure 11. These relations can be evidence to prove that the application of the urea combined with the sulfur can enhance the soil mineral release and improve the N uptake to obtain good grain yields [101], [110].

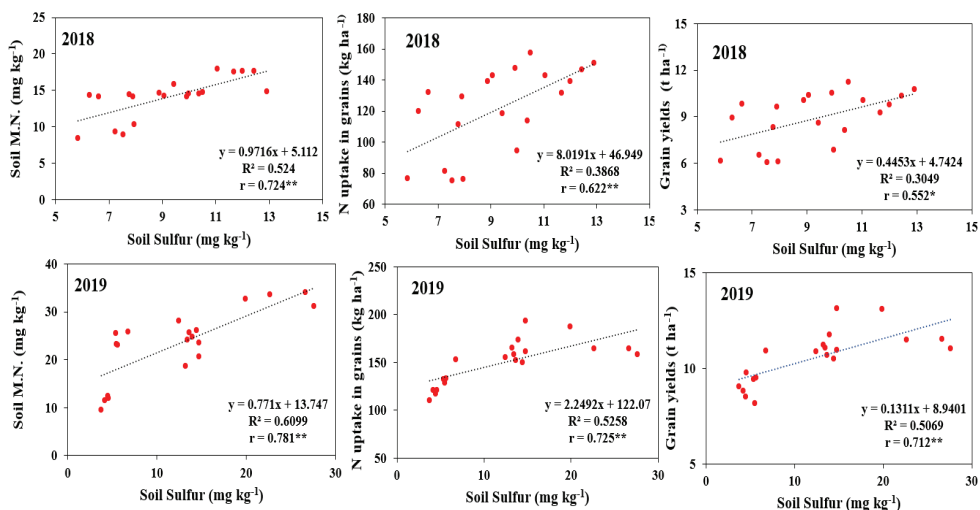


Figure 11. The correlation between the soil available sulfur and the soil mineral content, N uptake in the grains, and the grain yield during 2018-2019

3.3.2. Nitrogen uptake and Agronomic nitrogen use efficiency (Article 2)

The statistics presented in Table 8, Article 2, indicated that applying coated urea potassium humate and urea cocrystals at high rates of 200 kg N ha⁻¹ had a remarkably significant impact on nitrogen uptake in both grains and stems. As well as the overall nitrogen uptake by Maize crop, as compared to the control and conventional urea alone (Figure 12).

Moreover, the UPH200 and UC200 treatments exhibited an increase of 79.15% and 93.677%, respectively, in grain nitrogen uptake in comparison to the control, registering the highest N uptake in the stems with means of 133.58 and 168.49 kg ha⁻¹, respectively. Additionally, these treatments significantly influenced agronomic nitrogen use efficiency (ANUE), as depicted in Figure 12. Urea cocrystals and coated urea potassium humate enhanced nitrogen use efficiency, particularly at the 100 kg N ha⁻¹ rate. UC100 showed the highest nitrogen use efficiency, followed by UPH100. This suggests that higher fertilizer rates of 200 kg N ha⁻¹ may achieve higher yields but are less efficient compared to the economic dose of 100 kg N ha⁻¹ [116].

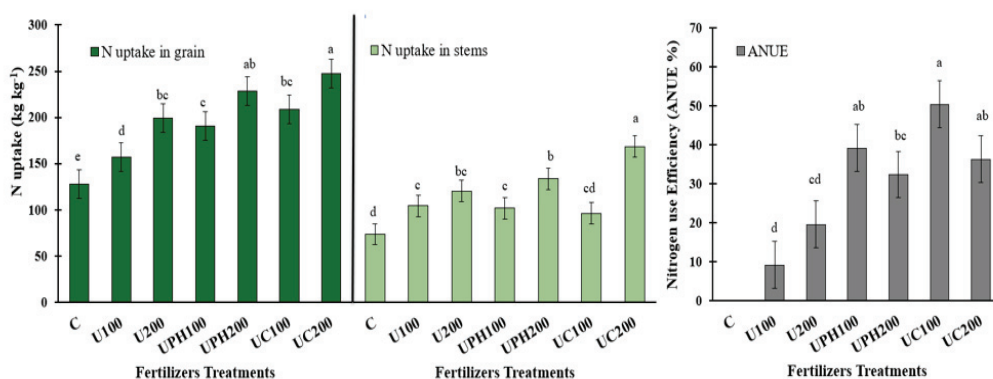


Figure 12. The effect of urea compounds treatments on N uptake (kg ha⁻¹) in maize grains and straw, and ANUE (kg kg⁻¹) followed by Duncan's multiple range test letters at 95% level. The letters with the same color have the same significance level test. Note. Control = non-treated, U100 = 100 kg N ha⁻¹ urea, U200 = 200 kg N ha⁻¹ urea, UPH100 = 100 kg N ha⁻¹ coated urea potassium humate (UPH), UPH200 = 200 kg N ha⁻¹ coated urea potassium humate (UPH), UC100 = 100 kg N ha⁻¹ urea cocrystal [CaSO₄·4CO(NH₂)₂], and UC200 = 200 kg N ha⁻¹, urea cocrystal [CaSO₄·4CO(NH₂)₂].

3.4. Assessment of mineral nitrogen availability in the soil (Article 3)

The descriptive statistics reveal noteworthy fluctuations in the levels of mineral nitrogen present in the soil at depth (10 cm) (Table 7). The levels of N_{min} available in the soil can be classified as follows: Low <40 (mg kg^{-1}), moderate 40-80 (mg kg^{-1}), and high >80 (mg kg^{-1}) [117]. Following this classification, the sandy soil exhibited a low level of mineral nitrogen availability at 38.22 mg kg^{-1} . Conversely, the sandy loam, loamy, and sandy clay soils demonstrated a high level of mineral nitrogen availability at $168.31 \text{ mg kg}^{-1}$, $165.66 \text{ mg kg}^{-1}$, and $257.52 \text{ mg kg}^{-1}$, respectively. This disparity can be attributed to various physicochemical properties of the soils, including soil texture, organic matter content, exchange cation capacity, and pH. These soil properties play a crucial role in determining the abundance and availability of nutrients within the soil [118], [119]. For example, sandy soil is loose and poor thus it always its content of nutrients has been low [99], [108]. Whereas, the loamy soil or sandy loam had more fertility and its properties were better so the nutrient contents were more available [109], [120].

Table 7: Descriptive statistics ($n=8$) of soil mineral nitrogen (N_{min}), ammonium, and nitrate of the study soil texture types at 10 cm depth.

	Soil texture type	Min.	Max.	Mean	SD	CV (%)
N_{min} (mg kg^{-1})	Sand	10.36	58.23	38.22	18.85	23.41
	Sandy loam	43.57	271.25	168.31	84.25	104.61
	Loam	45.95	255.47	165.66	81.46	101.15
	Sandy clay	53.15	425.08	257.52	138.76	172.29
NH_4 (mg kg^{-1})	Sand	8.14	23.70	16.33	5.77	7.17
	Sandy loam	6.69	80.96	43.03	35.26	43.78
	Loam	8.15	77.24	37.92	27.45	34.08
	Sandy clay	16.53	221.70	137.55	76.24	94.66
NO_3 (mg kg^{-1})	Sand	2.22	40.24	21.89	14.03	17.43
	Sandy loam	36.88	194.21	133.49	59.01	73.28
	Loam	37.80	178.23	127.74	57.57	71.48
	Sandy clay	42.99	144.67	105.12	41.24	51.21

Additionally, the coefficient of variation (CV) serves as a valuable statistical measure for assessing the level of variability among distinct data sets, even when the means exhibit significant disparities [117], [121]. The degree of variability in soil properties can be determined based on their CV values, CV of less than 10% signifies a state of limited variability, while a range of 10%-100% indicates a moderate level of variability [121]. Conversely, a CV exceeding 100% denotes a high degree of variability [121]. In the scope of this investigation, the sandy soil samples displayed a CV of 23.41 for the soil N_{min} , thereby reflecting a moderate level of variability (Table 4). In contrast, the sandy loam, loamy, and sandy clay soils exhibited a CV greater than 100%, signifying a high level of variability in terms of mineral nitrogen within these soil samples. Hence, the substantial variability observed suggests that crop plants may potentially access fertilizer nitrogen over prolonged periods.

CONCLUSIONS

1. The comprehensive results of this study, which include fresh and dry matter yields, grain yields, grain characteristics, nitrogen uptake in grain and stems, total nitrogen uptake, and nitrogen use efficiency, all confirm that modified urea fertilizers (such as urea potassium humate and urea cocrystals) perform better than conventional urea at increasing corn yield productivity and nitrogen use efficiency.
2. Utilization of urea-sulfur fertilizers indicated a positive correlation between the accumulation of mineral sulfur-nitrogen (MSN) in soil over time and increased nitrogen uptake significantly, particularly when utilizing synthesized urea as the nitrogen source. Therefore, this methodology introduces a pioneering framework and technique for attaining high yields and superior maize quality. This strategy can be the optimal utilization of nitrogen in crops and has the potential to mitigate the risk of environmental issues such as nitrate leaching and ammonia volatilization.
3. The nitrogen release rate plays a pivotal role in mitigating nitrogen loss and enhancing the nitrogen use efficiency of fertilizers. Conventional urea's rapid release at the onset of fertilization elevates the risk of nitrogen loss. Therefore, the use of urea cocrystals as slow-release fertilizer played a leading role in maintaining a balance between the plant's nitrogen requirements and the mineral nitrogen stock in the soil. Furthermore, coating urea with potassium humate as a controlled urea fertilizer exhibits positive effects by reducing urea nitrogen loss and increasing nitrogen uptake by plants.
4. The efficiency of modified urea fertilizers depends significantly on their chemical characteristics, application rates, and the physicochemical properties of the soil to which they are applied. Therefore, the application of tested fertilizers has demonstrated diverse responses from soils. Notably, the coated urea potassium humate efficiency outperformed conventional urea in sandy and loamy soil textures. Whereas, conventional urea had notable efficiency in the sandy loam and sandy clay textures, regarding increased nitrogen levels.

Practical importance / Recommendation

The role of modified urea fertilizers on crop productivity has been discussed in this investigation and it is posited that the outcomes of this research will be advantageous to scholars who are engaged in exploring the nexus between the fertilizers industry and the agriculture sector, to augment crop productivity. Therefore, when it comes to the application of urea compounds as fertilizer on different soil texture types, here are some recommendations:

Firstly, it is advised to adjust the application rate of urea fertilizer based on the soil texture type. For instance, coarse-textured soils such as sandy soils typically require higher application rates, whereas fine-textured soils may necessitate lower rates due to their greater nutrient-holding capacity.

Moreover, as indicated by this study, the lower or economic dose of urea is more effective compared to the high nitrogen rates. Additionally, it was found that for soils with lower organic matter content or high pH levels, it is beneficial to incorporate urea into the soil rather than applying it on the surface. This approach can aid in reducing nitrogen losses through volatilization.

Finally, to mitigate losses this study recommends the use of modifying urea fertilizers by coating or synthesizing can be added to decelerate the conversion of urea to ammonia, thereby reducing nitrogen loss. Therefore, this study recommended modified urea compounds as a useful and effective fertilizer in comparison to conventional urea.

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Article

Comparative Study Effect of Urea-Sulfur Fertilizers on Nitrogen Uptake and Maize Productivity

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Abstract: Combined nitrogen (N) and sulfur (S) fertilization is a good management strategy to reduce N loss and increase the efficiency of N fertilizers to achieve high grain yields and quality. Field trials for 2 yrs. (2018–2019) were conducted to evaluate the comparative advantage of conventional urea (150 N kg ha⁻¹) compared to urea+ ammonium sulfate (150 N kg ha⁻¹), urea+ calcium sulfate (150 N kg ha⁻¹), and urea cocrystals (CaSO₄·urea) (150 N kg ha⁻¹) when applied as nitrogen fertilizers to the maize. The statistics show a significant treatments effect on developed corn cobs, fresh and dry cob yields and grain yield, with 1000 grains with better results in 2019 than in 2018. The fertilization treatments affected grain yields significantly for 2018 and 2019, respectively. Urea+ ammonium sulfate and urea cocrystal provided a significant increase in grain yields by 10.5% and 7.50%, respectively, compared to urea in 2018, whereas, in 2019, urea cocrystal supplied the grain yields with a significant increase of 23.07% compared to urea, followed by urea + calcium sulfate which provided a 10.46% increase compared to urea. The study highlights that using urea-sulfur fertilizers enhanced the release of mineral nitrogen in the soil, improved the grain's N uptake by the plant and increased maize grain yields.

Keywords: urea; sulfur; ammonium sulfate; urea cocrystal; nitrogen uptake; maize productivity



Citation: Swify, S.; Avizienyte, D.; Mazeika, R.; Braziene, Z. Comparative Study Effect of Urea-Sulfur Fertilizers on Nitrogen Uptake and Maize Productivity. *Plants* **2022**, *11*, 3020. <https://doi.org/10.3390/plants11223020>

Academic Editor: Dimitris L. Bouranis

Received: 24 September 2022
Accepted: 6 November 2022
Published: 9 November 2022

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1. Introduction

Recently, the use of urea nitrogen (N) fertilizers varies between conventional urea and modified-urea fertilizers. Due to the economic advantage of solid urea production compared to other nitrogenous fertilizers, urea has been increasingly used in some regions of the world since 1980 [1,2]. Moreover, urea is the only rich (45–46%) source of primary solid nitrogen and accounts for 35% of the world's production [3]. Several nitrogen fertilizers were produced and developed, beginning with ammonium sulfate in 1923 and ending with sulfur-coated urea in the 1960s. However, N loss is still the main problem especially in urea fertilizers as some of the nitrogen may be lost as ammonia gas when applying urea on the soil surface layers [4,5], or as surface runoff, leaching to the ground and surface water [6].

Most fertilization research tries to reduce the nitrogen losses resulting from using urea as the primary nitrogen source and to improve its effectiveness for crop production [7–11]. Therefore, the best management practices for nitrogen fertilizers such as urea to maximize profit and reduce negative environmental impacts strongly depend on the input of fertilizers, which are mostly applied as a mixture of nutrients [12]. The use of N and S fertilizer mixing to meet crop requirements is a possible option to improve crop N and S use efficiencies, but this requires a good understanding of crop responses to N and S application.

Many studies report that urea use efficiency can be increased by mixing it with other materials such as sulfur [13–20] or organic acids [10,11,21–30], synthesizing and coating it with inert materials [21,31–37] or N stabilizers [2,8,38–43]. The coating delays the dissolving of N, while acid amendments lower the pH of the fertilizer strip, preventing or minimizing

rapid hydrolysis and volatilization of ammonia, which may increase N use efficiency and reduce the potential for N losses [34,40,44].

Furthermore, various studies with a long series of fertilization trials have shown that N and S fertilization combinations showed positive interactions, greatly enhancing yield and quality in different crops [13,18,20,37,45–48]. Sulfur additions can improve nitrogen use efficiency (NUE) [13–16,18,20,48,49]. Integration of nitrogen (N) and sulfur (S) fertilization appears to be of particular importance and is among the successful strategies that have substantially enhanced the productivity of cereal crops [13,15,16,18,20,45,48]. Similarly, when S was applied at the highest N rate, N uptake increased, indicating harmony between both nutrients. Furthermore, concurrent N and S management is critical for lowering the potential contamination of residual soil nitrate by enhancing N recovery from the soil while maintaining high nitrogen use efficiency [35,50–52].

Thus, the main objectives of this study were (1) to evaluate the efficiency of conventional urea compared to urea-sulfur fertilization, (2) to reduce nitrogen losses and improve N uptake and (3) to improve corn's yield production and grain quality. This study hypothesized that urea-sulfur fertilizers, especially synthesized urea (urea cocrystals), as modified urea fertilizers would significantly improve maize production because their slow release would meet the nutrient demands of maize during the whole growing period. Moreover, sulfur will improve nitrogen uptake by plants.

2. Materials and Methods

2.1. Experiment Location and Soil Characteristics

Field trials for 2 years (2018–2019) were carried out at Rumokai Experimental Station of the Lithuanian Center for Agriculture and Forest Sciences (54°43′15.7044″ N, 22°58′36.667″ E). The soil was Hapli-Epihypogleyic Luvisol (LVg-p-w-ha) [53] with a moderately heavy loam texture. The soil chemical properties at 0–20 cm, except for nitrogen form concentrations and available sulfur at the soil surface layer (0–30) cm, are shown in Table 1.

Table 1. Soil chemical characteristics before using fertilizers in 2018 and 2019.

Soil Properties	pH _{KCL}	SOC *	P ₂ O ₅	K ₂ O	S-SO ₄ **	Nitrogen (mg kg ⁻¹)		
	-	%	mg kg ⁻¹			Min. N	NO ₃ -N	NH ₄ -N
Depth (cm)		0–20				0–30		
2018	6.5	1.31	165	182	4.6	11.92	10.11	1.81
2019	7.4	1.41	249	198	5.9	13.68	11.82	1.86

* Soil organic carbon; ** Soil available sulfur.

2.2. Research Schema and Experimental Design

The field trials for 2 years (2018–2019) were laid out in a randomized complete block design (RCBD) with 20 experimental plots. Five treatments were arranged in four replicates with a total plot area of 4 m² (2 m × 2 m). The treatments used, consisted of:

1. Control (N0P80K160 kg ha⁻¹).
2. Urea (N150P80K160 kg ha⁻¹).
3. Urea + ammonium sulfate (N150P80K160S42.5 kg ha⁻¹).
4. Urea + calcium sulfate (N150P80K160S42.5Ca53 kg ha⁻¹).
5. Urea Cocrystal as CaSO₄.4urea (N150 P80K160S42.5Ca53 kg ha⁻¹).

2.3. Field Preparation and Maize Cultivation

The field preparation and maize cultivation dates during 2018 and 2019 are shown in Table 2. Maize (Ramirez, characterized as FAO 160) seeds were sown manually one day after fertilization. Row spacing was 50 cm, plant spacing was 20 cm and maize density was

10 plants per square meter (100,000 plants ha⁻¹). Pesticides were not used. Weeds were controlled manually as needed and plants were grown under arable farming conditions.

Table 2. Field preparation and maize cultivation dates in 2018 and 2019.

Process	2018	2019
Plowing (20–22 cm)	25 October 2017	27 October 2018
Surface tillage	25 April 2018	29 April 2019
Fertilization	2 May 2018	6 May 2019
Maize sowing	3 May 2018	7 May 2019
Harvest*	23 August 2018	20 September 2019

* The harvest was at the physiological maturity stage.

2.4. Soil Sampling and Analytical Procedures

The soil samples were taken at 0–30 cm depth from the non-treated and treated plots. A stainless-steel push probe was used to take the samples with three subsamples per plot composited to make one sample. The samples were air-dried and ground to pass through a 2 mm sieve. All the soil properties, mineral nitrogen and sulfur analyzes were performed in the Agrochemical Research Laboratory at Lithuanian Research Center for Agriculture and Forestry. Soil pH was determined using a 1:5 (v/v) soil suspension in the 1 M KCl (ISO 10390:2005) [54]. Soil-available phosphorus as P₂O₅ and potassium as K₂O were extracted using 1:20 (wt./v) soil suspension of ammonium lactate-acetic acid extractant (pH 3.7) [54]. Soil available P₂O₅ was determined using ammonium molybdate via the spectrometric method with a Shimadzu UV 1800 spectrophotometer (LVP D-07:2016). Mobile K₂O was determined using flame emission spectroscopy with a flame emission spectroscopy JENWAY PFP7 flame photometer (LVP D-07:2016).

Soil available sulfur was determined by laboratory-prepared the LVP D-12–2011 turbidimetric method. Mineral nitrogen was determined by using a spectrometric flow injection analysis (FIA) method developed by the laboratory; nitrate content (Sum of N-NO₃ and N-NO₂; LVP D-05:2016) and ammonium content (N-NH₄; LVP D-05:2016) were determined. The mineral nitrogen is calculated by adding the sum of nitrate and nitrite nitrogen to ammonium nitrogen. The organic soil carbon content was determined using dry combustion according to ISO 10694:1995, where the sample was heated to 900 °C in a stream of air and the carbon dioxide formed was measured using infrared spectroscopy. To evaluate plant biometric parameters, only the inner portion of the plots (2 × 2 m) was harvested at the physiological maturity stage. Twenty plants were randomly selected for grain yield and grain biomass quality determination. Samples were taken from all the replicates and oven-dried at 65 ± 5 °C until constant weight to obtain dry biomass and yield weight.

2.5. Nitrogen Uptake and Its Efficiency

The fertilizer N uptake and apparent nutrient recovery efficiency (ANR) were calculated by the following formulas [15,55]:

$$\text{N Uptake} = \%N \text{ in grains} \times \text{dry matter of grains (kg ha}^{-1}\text{)} \quad (1)$$

Apparent nitrogen recovery efficiency (ANR) has been used to reflect a plant's ability to acquire applied nutrients from soil [56]:

$$\% \text{ ANR} = \frac{\text{Uptake F, kg} - \text{Uptake C, Kg}}{\text{Quantity of fertilizer applied, kg}} \times 100 \quad (2)$$

2.6. Climatic Conditions

Considerable variations were observed in seasonal climatic conditions between 2018 and 2019, as shown in Figure 1. In 2018, the air temperature was warmer than average in

2019, except in June. As a result, harvesting occurred 1 month earlier that year (2018). On the other hand, the 2019 season was less rainy compared to 2018, especially in April and June, which affected delayed corn cultivation and early crop development.

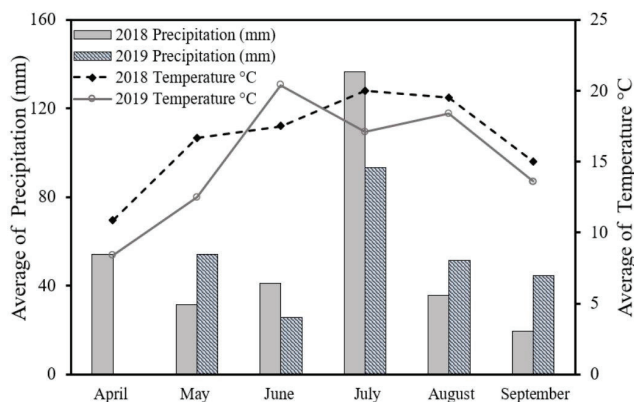


Figure 1. Mean monthly temperatures °C and precipitation (mm) during the growing maize season for the 2 years study (2018–2019).

2.7. Statistical Analysis

Analysis of variance (ANOVA) was performed using a general linear model on plants' density, total green matter, dry matter yield and grain yields. Grain characteristics (developed corn cobs, fresh cobs yields and dry cobs yields), N uptake and ANR. Person's correlation analysis was performed to determine the relationship between time and soil mineral N and its forms (nitrate and ammonium) and soil available sulfur content and grains total N content and N uptake. The statistical analysis software was IBM SPSS 25.0. and Duncan's test at the 5% level was performed to separate means according to ANOVA results.

3. Results

3.1. Nitrogen Release in Soil-Grown Maize from Urea-Sulfur Fertilizers

To investigate the influence of urea fertilizer on maize productivity and nitrogen accumulation and its uptake with sulfur fertilizers use, soil-grown maize plants were supplied with U (urea), UAS (urea + ammonium sulfate), UCS (urea + calcium sulfate) and UCSC (urea cocrystals–CaSO₄·4urea). The mineral nitrogen in the soil formed into nitrate (N-NO₃) and ammonium (N-NH₄) as shown in Figure 2. The results indicate that the concentration of nitrate N-NO₃ and ammonium N-NH₄ in the soil was higher in 2019 than in 2018.

The concentration of nitrate N-NO₃ in the soil in both years (2018 and 2019) correlated significantly ($p < 0.000$ and $p < 0.001$) with the time during the maize growth period ($r = -0.66$ and $r = -0.46$) in 2018 and 2019, respectively. The nitrate started with a low concentration before fertilization with means of 10.11 and 11.82 mg kg⁻¹ in 2018 and 2019, respectively (Figure 2A,B).

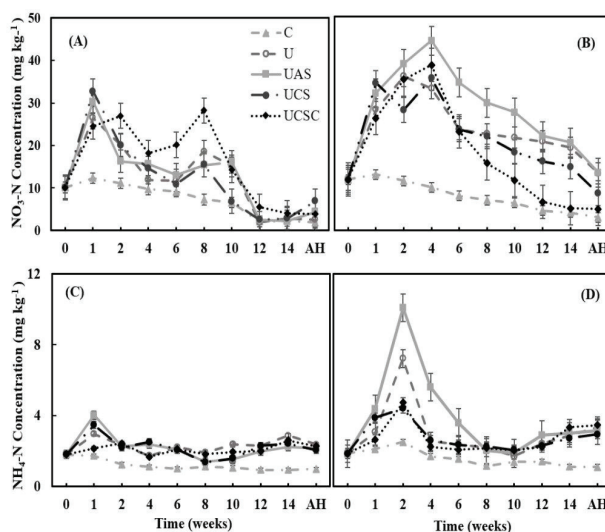


Figure 2. The release of nitrate $\text{NO}_3\text{-N}$ (A,B) and ammonium $\text{NH}_4\text{-N}$ (C,D) with time from the fertilizer treatments in soil surface layer 0–30 cm during the maize growth period and after harvest (AH) in 2018 (A,C) and 2019 (B,D). C = Control U = Urea, UAS = Urea + ammonium sulfate, UCS = Urea + CaSO_4 , and UCSC = Urea cocrystal ($\text{CaSO}_4\cdot 4\text{urea}$). (A) C $r = -0.956^{**}$; U $r = -0.715^*$; UAS $r = -0.705^*$; UCS $r = -0.714^*$ and UCSC $r = -0.654^*$; (B) C $r = -0.986^{**}$; U $r = -0.455$; UAS $r = -0.433$; UCS $r = -0.616$ and UCSC $r = -0.713^*$; (C) C $r = -0.802^{**}$; U $r = 0.267$; UAS $r = -0.359$; UCS $r = -0.259$ and UCSC $r = 0.350$; (D) C $r = -0.834^{**}$; U $r = -0.212$; UAS $r = -0.398$; UCS $r = -0.273$ and UCSC $r = 0.103$. * Significant differences at $p < 0.05$; ** Significant differences at $p < 0.01$.

After one week, in both years (2018–2019), the fertilizer treatment of UCS recorded the highest values of nitrate concentration in the soil with a mean of 32.75 and 34.46 mg kg^{-1} , respectively (Figure 2A,B), whereas, UCSC showed the lowest value of nitrate in both years, with a mean of 24.48 and 26.19 mg kg^{-1} , respectively, after the control. In 2018, nitrate concentrations correlated significantly with treatments. During the period from 2–10 weeks, concentration flow fluctuated from increase to decrease for all the treatments (Figure 2A).

By the end of the tenth week in 2018, the treatments of $\text{UAS} > \text{U} > \text{UCSC}$ showed high values of nitrate with means of $16.13 > 15.16 > 14.30$ mg kg^{-1} , respectively (Figure 2A). After 10 weeks, the nitrate concentration tended to decrease till the harvest. After the harvest (AH), the treatments of $\text{UCS} > \text{UAS} > \text{UCSC}$ recorded high nitrate concentration in the soil with means of $6.93 > 4.39 > 3.88$ mg kg^{-1} , respectively. In 2019, the nitrate concentration tended to increase for all the treatments after fertilization till 4 weeks.

After 4 weeks, the curve showed a decrease for all the treatments until the end of the maize growing period (Figure 2B). In addition, the treatment of UAS recorded the highest values of nitrate concentration in the soil during the whole period of maize growth (Figure 2B), then followed by the treatment of UCSC. The mean of UAS and UCSC nitrate concentration ranged from 11.82 mg kg^{-1} before fertilization to 44.29 and 38.67 mg kg^{-1} , respectively, after 4 weeks. Moreover, UAS recorded the highest nitrate concentration at 13.48 mg kg^{-1} after harvest (AH), as shown in Figure 2B. However, in the 2019 season the

concentration of nitrate was not correlated significantly with the time for all the fertilization treatments except for the treatment of UCSC ($r = -0.71^*$).

Furthermore, the results showed the concentration of ammonium in the soil was low in 2018 and 2019 compared to nitrate, as shown in Figure 2C,D. It represents approximately 9 and 17% of the total mineral nitrogen in the soil in 2018 and 2019, respectively. The ammonium concentration was not correlated significantly with the time or with the fertilization treatments in both years (2018–2019). The ammonium concentration started with means of 1.81 and 1.86 mg kg^{-1} in 2018 and 2019, respectively. In 2018, urea showed the highest value of ammonium with an average of 2.29 mg kg^{-1} , while in 2019 the treatment of UAS recorded the highest value of ammonium concentration (Figure 2D) followed by urea with averages of 3.85 and 2.97 mg kg^{-1} , respectively. After the harvest, the U and UCSC recorded high ammonium concentrations with means of 2.37 and 2.28 mg kg^{-1} in 2018 and 3.34 and 3.47 mg kg^{-1} in 2019, respectively (Figure 2C,D).

Figure 3A,B show the mineral nitrogen concentration in the soil during the maize growth period in 2018–2019. The soil mineral N concentration in both years (2018–2019) correlated significantly ($p > 0.000$ and $p > 0.001$) with time. The soil mineral N showed a negative linear relationship ($r = -0.65$ and $r = -0.45$) with time which means the concentration decreased over time. Before fertilization, soil mineral nitrogen was low with a mean of 11.92 and 13.68 mg kg^{-1} in 2018 and 2019, respectively.

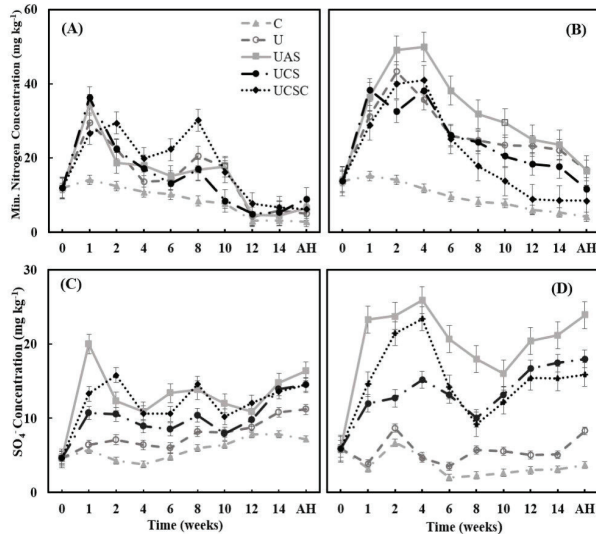


Figure 3. The release of mineral nitrogen (A,B) and soil available sulfur (C,D) with time from the fertilizer treatments in soil surface layer 0–30 cm during the maize growth period and after harvest (AH) in 2018 (A,C) and 2019 (B,D). C = Control U = Urea, UAS = Urea + ammonium sulfate, UCS = Urea + CaSO₄ and UCSC = Urea cocrystal (CaSO₄.4urea). (A) C $r = -0.964^{**}$; U $r = -0.698^*$; UAS $r = -0.699^*$; UCS $r = -0.704^*$ and UCSC $r = -0.648^*$; (B) C $r = -0.981^{**}$; U $r = -0.441$; UAS $r = -0.453$; UCS $r = -0.611$ and UCSC $r = -0.694^*$; (C) C $r = 0.843^{**}$; U $r = 0.927^{**}$; UAS $r = 0.279$; UCS $r = 0.670^*$ and UCSC $r = 0.380$; (D) C $r = -0.528$; U $r = 0.182$; UAS $r = 0.253$; UCS $r = 0.759^*$ and UCSC $r = 0.034$; * Significant differences at $p < 0.05$; ** Significant differences at $p < 0.01$.

In addition, the mineral nitrogen for the fertilizers' treatments correlated significantly with time in 2018, while in 2019 the concentration was not correlated significantly for all fertilization treatments except UCSC ($r = -0.69^*$). In 2018, during the first 2 weeks, the treatments of UCS and UAS had the highest mineral N concentration values, followed by U and UCSC (Figure 3A). After 2 weeks, UCSC showed the highest mineral N concentration till the maize harvest (Figure 3A).

In 2019, the UAS had the highest mineral N concentration during the whole of the maize growing season (Figure 3B). The highest residual values of the mineral nitrogen after the maize harvest were observed in the treatment of UAS with 6.54 and 16.63 mg kg⁻¹ in 2018 and 2019, respectively. The concentration of soil mineral N and its forms N-NO₃ and N-NH₄ correlated significantly ($p < 0.000$) with soil sulfur in 2019, but no significant correlation between the sulfur concentration in soil and the mineral N and nitrate was reported in 2018. However, ammonium correlated significantly ($p < 0.000$) with the sulfur in the soil ($r = 0.52$). UAS recorded the highest sulfur concentration during both years (2018–2019), followed by UCSC and UCS (Figure 3C,D).

3.2. Plants' Density, Green Matter and Dry Matter Yield

Table 3 shows the mean of the plants' density and green and dry matter yields after using conventional urea compared to urea-sulfur fertilizers. As was expected, in both years (2018–2019) the treatments were significantly higher than those obtained in the control. In 2018, the treatments significantly affected the plants' density and green matter yields compared to the control and urea + ammonium sulfate (UAS) recorded a high plant density and green matter yield (Table 3), while no significant effect was observed on plants' density and green matter yields in 2019. However, urea cocrystals (UCSC) recorded a significant density and green matter yield compared to urea, as shown in Table 3. For both years (2018–2019), the treatments had no significant effects on dry matter yields, but UCSC recorded the highest dry matter yields with 8.43 and 11.41 t ha⁻¹ for both seasons 2018–2019, respectively, as shown in Table 3.

Table 3. Means of plants' density, total fresh and dry matter yields after using urea-sulfur fertilizers for the 2-year study (2018–2019).

Treatments	Plants' Density	Green Matter	Dry Matter	% Moisture
	1000 Plant ha ⁻¹	t ha ⁻¹		
2018				
Control	92.50 a	17.90 a	6.29	64.86
Urea	97.50 b	20.00 b	7.52	62.40
Urea + (NH ₄) ₂ SO ₄	100.00 b	22.33 c	7.59	66.00
Urea + CaSO ₄	98.75 b	21.88 c	7.84	64.16
CaSO ₄ .4urea	97.50 b	22.05 c	8.43	61.77
SE±	1.21	0.38	0.53	-
<i>p</i> -value	0.009	0.000	ns *	-
2019				
Control	92.83 a	17.47 a	8.92	48.94
Urea	93.98 a	18.93 a	9.83	48.07
Urea + (NH ₄) ₂ SO ₄	97.60 ab	18.79 a	9.85	47.58
Urea + CaSO ₄	95.55 ab	18.22 a	9.66	46.98
CaSO ₄ .4urea	100.00 b	22.12 b	11.41	48.42
SE±	1.59	0.85	0.92	-
<i>p</i> -value	0.049	0.020	ns *	-

Note. values in the same column followed by the same letter are not different ($p < 0.05$) according to Duncan's multiple range test at the 5% level. * ns = not significant.

3.3. Grain Yields and Grain Quality

ANOVA showed significant treatment effects on developed corn cobs, fresh and dry cob yields and grain yields, and 1000 grains. The extent of treatments' impact on corn productivity differed across the two study years (2018–2019) as shown in Table 4, with better results in 2019 than in 2018.

Table 4. Means of developed corn cobs' number, fresh and dry cob yields, grain yields, and 1000 grains after using urea-sulfur fertilizers for the 2 years study (2018–2019).

Treatments	Developed Corn Cobs	Fresh Cobs Yields	Dry Cobs Yields	Grain Yields	1000 Grain
	1000 ha ⁻¹	t ha ⁻¹			g.
2018					
Control	80.00 a	12.14 a	7.82 a	6.86 a	222.52
Urea	93.75 b	17.39 b	11.34 b	9.17 b	247.02
Urea + (NH ₄) ₂ SO ₄	96.25 b	19.58 b	12.44 b	10.14 b	249.56
Urea + CaSO ₄	100.94 b	18.80 b	12.20 b	8.97 b	226.43
CaSO ₄ ·4urea	102.19 b	18.70 b	12.38 b	9.86 b	245.75
SE±	2.99	1.27	0.77	0.59	9.11
p-value	0.002	0.009	0.005	0.016	ns*
2019					
Control	83.25 a	16.63 a	10.07 a	8.50 a	265.00 a
Urea	88.00 a	17.35 ab	11.85 a	9.75 b	285.97 b
Urea + (NH ₄) ₂ SO ₄	89.25 a	19.23 bc	11.82 a	10.50 bc	287.17 b
Urea + CaSO ₄	85.00 a	18.44 abc	11.87 a	10.77 c	285.76 b
CaSO ₄ ·4urea	97.00 b	20.17 c	14.53 b	12.00 d	286.02 b
SE±	2.13	0.77	0.59	0.31	4.66
p-value	0.006	0.044	0.003	0.000	0.024

Note. values in the same column followed by the same letter are not different ($p < 0.05$) according to Duncan's multiple range test at the 5% level. * ns = not significant.

Generally, the maize with UAS and UCSC always had a significantly higher effect for all productivity parameters during both years. (2018–2019). In 2018, the maize with UAS recorded the significantly highest fresh and dry cob and grains yields and 1000 grains, while in 2019, UCSC was significantly the highest for all productivity parameters, as shown in Table 4. UCSC also recorded the highest values for the developed corn cobs' yield in both years (2018–2019).

The grain yields were affected significantly for both years (2018 and 2019), as shown in Figure 4, but there were no significant differences observed when the yield was compared in both seasons (2018–2019). In 2018, UAS and UCSC provided a significant increase in grain yields by 47.8% and 43.73%, respectively, higher than the control and 10.5% and 7.50%, respectively, higher than urea; whereas, in 2019, UCSC supplied the grain yields with a significant increase, 41.17% and 23.07% higher than the control and urea, respectively, followed by UCS, which provided a 26.70% and 10.46% increase higher than the control and urea, as shown in Table 4. The treatment of UAS was in the third rank by 23.52 and provided a 7.60% increase, higher than the control and urea, respectively. The 1000 grains weight was not affected by the treatments in 2018, but there was a significant effect in 2019 and UCSC recorded the highest weight with 286.02 g for 1000 grains as shown in Table 4.

Grain quality characteristics including the total nitrogen and crude protein and starch contents are listed in Table 5. The fertilization treatments significantly affected the grain's quality characteristics including the total nitrogen and crude protein contents, except that starch was affected significantly in 2019 only (Table 5).

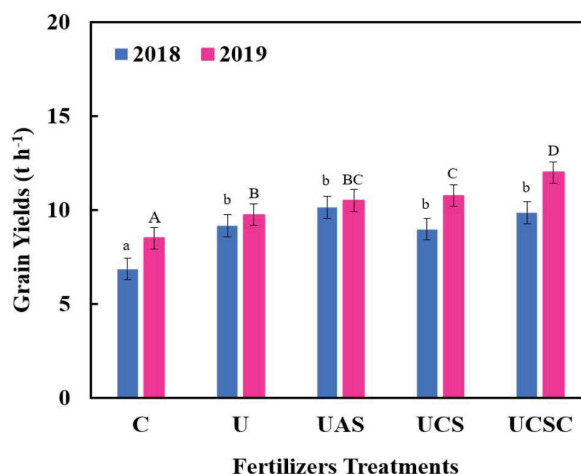


Figure 4. The effect of the urea-sulfur fertilizers on grain yields for 2 years. (2018–2019). Control U = Urea, UAS = Urea + ammonium sulfate, UCS = Urea + CaSO₄ and UCSC = Urea cocrystal (CaSO₄.4urea). Note 1. Columns followed by the same letter with the same size are not different ($p < 0.05$) according to Duncan's multiple range test at the 5% level. Note 2. No significant differences between both seasons.

In both years (2018 and 2019), UCSC recorded the highest total nitrogen content in grains by 1.42 and 1.47%, respectively. Additionally, UCSC showed the highest crude protein in grains by 8.87 and 9.22% in 2018 and 2019, respectively as shown in Table 5. The starch content had no significant effect by fertilizer treatments in 2018 but was affected significantly ($p < 0.000$) in 2019, and urea treatment showed the highest starch content at 74.99% followed by the control with 74.64%. In addition, the grain's sulfur content was affected significantly ($p < 0.000$) and the treatment of UAS recorded the highest mean average for both years. (2018–2019) by 975 mg kg⁻¹.

In 2018, soil mineral nitrogen and sulfur correlated significantly ($p < 0.000$) with the total nitrogen and the crude protein in the grains (Table 5). The correlation coefficients ($r = 0.94$ and $r = 0.93$) showed a strong positive linear relationship between soil mineral nitrogen and total nitrogen and the crude protein content in the grains, respectively. Moreover, sulfur ($r = 0.79$) showed a positive linear relationship between total nitrogen and the crude protein content in the grains (Table 5). Soil mineral nitrogen and sulfur also correlated significantly $p < 0.05$ and $p < 0.000$ with the grain's total nitrogen and the crude protein in 2019. A medium positive linear relationship between soil nitrogen and grain's total nitrogen and the crude protein content is shown by the correlation coefficient $r = 0.41$ and $r = 0.47$, respectively.

In addition, sulfur ($r = 0.61$ and $r = 0.58$) showed a positive linear relationship between total nitrogen and the crude protein content in the grains, respectively. The soil mineral N and sulfur had no significant correlation with the grain's starch content in both years. (2018–2019). Additionally, the grain's total nitrogen correlated significantly ($p < 0.000$) with the crude protein and starch content in the grain (Table 5) in both years (2018–2019).

The correlation coefficients ($r = 0.99$ and 0.98) showed a positive strong linear relationship between the total nitrogen and crude protein content in the grains in both years. (2018–2019), as shown in Figure 5A,B, while the starch content showed a significant correla-

tion ($p < 0.000$) with the grain's total N but with a negative linear relationship ($r = -0.77$ and $r = -0.39$) in both years (2018–2019), as shown in Figure 5A,B.

Table 5. Analysis of variance for the quality of the grain listed in total N, crude protein (%), starch (%) contents, and grain yields, including a summary of correlation relationships between these variables and soil mineral N and sulfur content for the 2-year study (2018–2019).

Treatments	Grain N %		Crude Protein %		Starch %		Grain Yields	
2018								
Control	1.24 a		7.77 a		69.71		6.86 a	
Urea	1.34 b		8.39 b		68.73		9.17 b	
Urea + (NH ₄) ₂ SO ₄	1.40 b		8.78 b		68.86		10.14 b	
Urea + CaSO ₄	1.38 b		8.62 b		67.60		8.97 b	
CaSO ₄ ·4urea	1.42 b		8.87 b		68.79		9.86 b	
<i>p</i> -value =	0.007		0.007		ns *		0.016	
2019								
Control	1.38 a		8.60 a		74.64 b		8.50 a	
Urea	1.40 a		8.77 a		74.99 b		9.75 b	
Urea + (NH ₄) ₂ SO ₄	1.43 ab		8.94 ab		73.41 b		10.50 bc	
Urea + CaSO ₄	1.43 ab		8.93 ab		71.67 a		10.77 c	
CaSO ₄ ·4urea	1.47 b		9.22 b		70.16 a		12.00 d	
<i>p</i> -value =	0.049		0.056		0.000		0.000	
Correlation coefficient	<i>P</i> < <i>F</i>	<i>R</i>	<i>P</i> < <i>F</i>	<i>R</i>	<i>P</i> < <i>F</i>	<i>R</i>	<i>P</i> < <i>F</i>	<i>R</i>
2018								
Soil mineral N	<0.000	0.94	<0.000	0.93	ns *	-0.03	<0.000	0.74
Soil available sulfur	<0.000	0.79	<0.000	0.79	ns *	-0.07	<0.000	0.55
Total N in grains	-	-	<0.000	0.99	<0.000	-0.77	<0.000	0.81
2019								
Soil mineral N	<0.05	0.46	<0.05	0.47	ns *	-0.02	<0.000	0.62
Soil available sulfur	<0.000	0.61	<0.000	0.58	ns *	-0.07	<0.000	0.71
Total N in grains	-	-	<0.000	0.98	<0.000	-0.39	<0.000	0.76

Note. values in the same column followed by the same letter are not different ($p < 0.05$) according to Duncan's multiple range test at the 5% level. * ns = not significant.

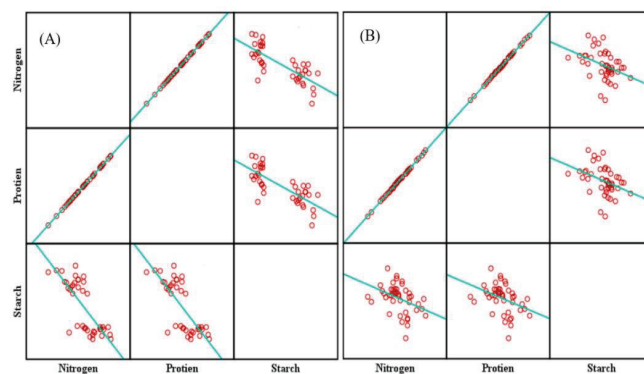


Figure 5. The matrix correlation between the total nitrogen (%) and the crude protein (%) and starch content (%) in the maize grains during 2018 (A) and 2019 (B).

3.4. Nitrogen Uptake and Apparent Nitrogen Recovery Efficiency in Grains

Analysis of variance for grain N uptake and apparent nitrogen recovery (ANR) values are listed in Table 6. The N uptake and ANR were affected significantly ($p < 0.000$) by the fertilizer treatments compared to the control in the 2 years (2018–2019). In 2018, there were no significant differences in N uptake and ANR between the fertilizers' treatments but the treatment of UAS recorded the highest N uptake by 142.45 kg ha⁻¹ and the highest nitrogen recovery value in the grains with 43.44%, respectively.

Table 6. Analysis of variance for grain N uptake and ANR including a summary of relationships between these variables in 2 years (2018–2019).

Treatments	N Uptake in Grain (kg ha ⁻¹)		ANR (%) in Grain	
	2018	2019	2018	2019
Control	77.24 a	117.30 a	0.00 a	0.00 a
Urea	123.13 b	136.76 b	30.66 b	12.98 b
Urea + (NH ₄) ₂ SO ₄	142.45 b	168.47 cd	43.44 b	34.12 cd
Urea + CaSO ₄	123.68 b	153.86 bc	30.94 b	24.38 bc
CaSO ₄ -4urea	139.90 b	173.31 d	41.79 b	37.34 d
<i>p</i> -value	<0.000	<0.000	<0.000	<0.000
Correlation coefficient	<i>P</i> < <i>F</i>	<i>R</i>	<i>P</i> < <i>F</i>	<i>R</i>
Soil mineral N	<0.000	0.79	<0.001	0.69
Soil available sulfur	<0.003	0.62	<0.000	0.73
Total N in grains	<0.000	0.87	<0.000	0.86
Grains yield	<0.000	0.99	<0.000	0.96

Note. values in the same column followed by the same letter are not different ($p < 0.05$) according to Duncan's multiple range test at the 5% level.

In 2019, the statistics showed significant differences between the fertilizers' treatments in N uptake and ANR as shown in Table 6. The treatment of UCSC recorded the highest N uptake and ANR with 173.31 kg ha⁻¹ and 37.34%, respectively. The soil mineral N correlated significantly ($p < 0.000$ and $p < 0.001$) in 2018–2019 with grain N uptake (Table 6). As a result of increasing the grain's N uptake, the grain's total N ($p < 0.007$ and $p < 0.49$) and grain yields increased significantly ($p < 0.016$ and $p < 0.000$) in 2018 and 2019, respectively. In 2018, the correlation coefficient provided a strong linear relationship (Figure 6) between the soil mineral N and the N uptake in the grains ($r = 0.79^{**}$).

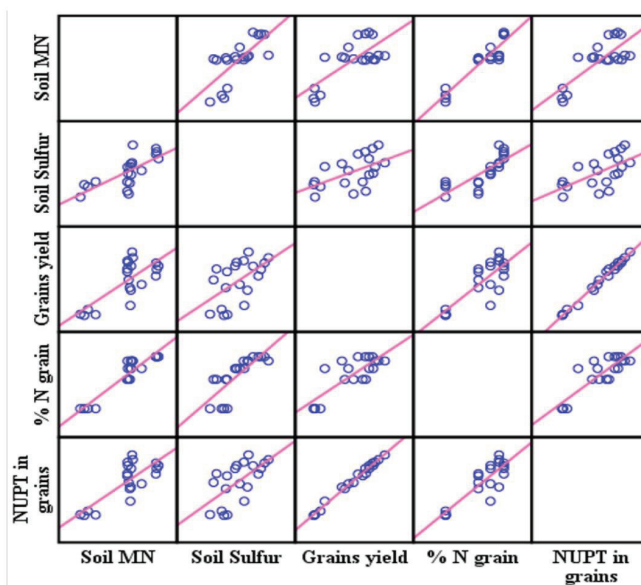


Figure 6. The correlation matrix relations effect of soil mineral N and sulfur on the N uptake in the grains, the grain's total N, and the grain's yield in 2018.

In 2019 the correlation coefficient also provided a medium linear relationship between the soil mineral N and the N uptake in the grains ($r = 0.62^{**}$) as shown in Figure 7, moreover providing a strong linear relationship between the N uptake and the grains yield ($r = 0.99^{**}$ and $r = 0.96^{**}$) in 2018 and 2019, respectively. In addition, soil available sulfur correlated highly significantly in both years. (2018 and 2019) with grains N uptake ($p < 0.003$ and $p < 0.000$), with a medium linear relationship as shown in Figures 6 and 7.

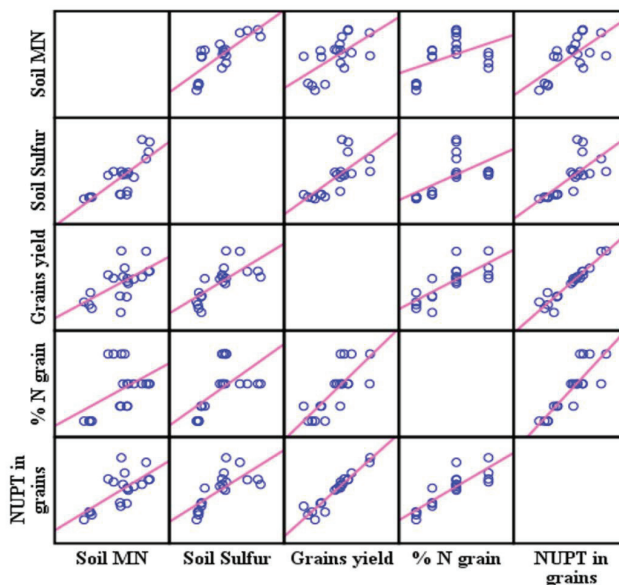


Figure 7. The correlation matrix relations effect of soil mineral N and sulfur on the N uptake in the grains, the grain's total N, and the grain yield in 2019.

4. Discussion

The extent to which treatments impacted corn productivity differed between the two study years (2018–2019), with 2019 showing better results than 2018. Generally, maize with UAS and UCSC had a significant effect on all productivity parameters during both years (2018–2019).

4.1. Effect of Sulfur Fertilizers on Mineral N Release and Nitrogen Uptake

Current results revealed a significant effect of participatory application of urea-sulfur fertilizers on the concentration of soil mineral N compared to conventional urea only. As was expected, the increase of sulfur in the soil enhanced significantly the release of soil mineral N from the urea granules [16,17,57].

The mineral nitrogen in the soil formed into nitrate (N-NO_3) and ammonium (N-NH_4) as shown in Figure 2. The results indicate that the concentration of nitrate N-NO_3 and ammonium N-NH_4 in the soil was significantly higher in 2019 than in 2018. Many factors affect the release process of nitrogen from the urea granules [58–60]. The meteorological conditions during the maize cultivation period played a vital role in the release of soil mineral N. The environmental variables, especially rainfall and temperature over the study period, had a high effect on the release of N and N uptake [58,59,61,62], which showed that the 2019 season was less rainy compared to 2018, and colder (Figure 1). This resulted in a slower release rate for the fertilizer treatments, less ammonia loss, and a lower nitrate leaching, which means a higher accumulation of nitrate and ammonium in the soil [59,63,64].

By detecting the role of sulfur fertilizers in enhancing the release of soil mineral N, the concentration of mineral N and its forms N-NO₃ and N-NH₄ correlated significantly in 2019 but with no significant correlation between the sulfur concentration in soil and the mineral N and nitrate in 2018. However, ammonium correlated significantly with sulfur in the soil. It is important to note that, while equivalent in performance in urea-sulfur fertilizers, S sources are different in their solubility. Therefore, the treatments were different in sulfur release [34,65]. UAS recorded the highest sulfur concentration during both years. (2018–2018), followed by UCSC and UCS (Figure 3C,D). The exact solubility of S in CaSO₄·4urea is not known but can be suggested to follow that of CaSO₄ or CaSO₄·2H₂O, while (NH₄)₂SO₄ is highly soluble and thus prone to nutrient loss. Hence, not only is it available to the crops but can potentially be available for the plants for a longer time in the environment [38,66–69]. This result is supported by several previous studies that reported that suitable S source application promotes the absorption of N in the soil [18–20,70].

As a result, increasing the concentration of soil mineral N enhanced the N uptake of the grains [18–20,57]. Maize N uptake of grain was significantly greater in 2019 than in 2018. The fertilizer treatments had significant effects on grain N uptake and ANR compared to the control in both years. (2018–2019). There were no significant differences in N uptake and ANR between the fertilizer treatments in 2018, but the treatment of UAS recorded the highest N uptake by 142.45 kg ha⁻¹ and the highest nitrogen recovery value in the grains with 43.44%, respectively. The statistics showed significant differences between fertilizer treatments in N uptake and ANR (Table 6) in 2019. The treatment of UCSC recorded the highest N uptake and ANR with 173.31 kg ha⁻¹ and 37.34%, respectively. The soil mineral N correlated significantly ($p < 0.000$ and $p < 0.001$) in 2018–2019 with grain N uptake (Table 6).

4.2. Effect of Combining Urea and Sulfur on Grain Yields and Grain Quality

The present study on maize crops demonstrated the positive effect of urea-N with S fertilization on grain yield. Nutrient management was an important strategy to increase maize yield and grain protein concentration [9,37,71–73]. In this study, the combination of urea and sulfur fertilizers could sustainably support the increase of accumulation of soil mineral N over time and increase the N uptake in grains, which means an increase in the grain's protein concentration [15,18–20]. Conventional nitrogen fertilization alone such as with urea could increase grain yield, but the urea-N losses were higher compared to urea with ammonium sulfate or calcium sulfate [15,31,42,67,74–77].

This resulted in less grain yield and less quality and characteristics of grains for both years. (2018–2019), as shown in Table 5. Nitrogen assimilation is linked to S-metabolism, so as S metabolism slows, so does N assimilation if the S supply is insufficient [59]. Sulfur is reported to improve the photosynthetic assimilation of N in proteins at the expense of nonproteins in crops [57,78], which increases dry matter yield, as 90% of plant dry weight is thought to be derived from photosynthesis products [19,78]. In this study, the significant increase in grain yield and ANR as a result of fertilization of urea with sulfur further showed a link of N with S. The increase in grain N concentration and content of protein was significant for both years. (2018 and 2019).

Response to N and S fertilization was mainly observed in maximizing grain yield, especially in 2019. The fertilization of urea + ammonium sulfate and urea cocrystal and urea + calcium sulfate provided a significant increase in grain yields, higher than the control and urea, in 2018 and 2019 as shown in Table 4, because of the high content of these treatments of sulfur compared to the treatments of urea and control [20,79,80].

In addition, the urea-sulfur treatments significantly affected the grain's quality characteristics including the total nitrogen and crude protein and sulfur contents. In both years. (2018 and 2019), urea cocrystals recorded the highest total nitrogen content in grains by 1.42 and 1.47%, respectively. In addition, urea cocrystals showed the highest crude protein in the grains by 8.87 and 9.22% in 2018 and 2019, respectively, as shown in Table 5. Sulfur fertilization significantly increased the S concentration in grains [57]. The highest sulfur

concentration was observed in the treatment of urea + ammonium sulfate due to its high solubility compared to urea+ calcium sulfate and urea cocrystal. Our results showed the same strong interaction between N and S as reported in many previous studies [18–20,70].

5. Conclusions

The use of N and S as urea-sulfur fertilizers had a significant impact on maize yield, characteristics and grain quality. The participatory regulation of N and S considerably enhanced maize N uptake and nutritional quality, meeting the requirements for sustainable development in maize production and providing a new theoretical basis and method for high-yield and high-quality maize production. This study reported that a positive trend of mineral sulfur-nitrogen (MSN) accumulation in soil over time increased N uptake, especially with the synthesized urea N source. This could reduce the potential for environmental pollution by nitrate leaching and ammonia volatilization. Appropriate sources of N such as urea mixed with sulfur additives could optimize crop nitrogen use efficiency.

Author Contributions: Conceptualization, R.M. and D.A.; Data curation, S.S. and D.A.; Formal analysis, R.M.; Investigation, D.A. and Z.B.; Methodology, D.A. and Z.B.; Supervision, R.M.; Validation, R.M.; Visualization, S.S.; Writing—original draft, S.S. All authors commented on previous versions of the manuscript. All authors have read and agreed to the published version of the manuscript.

Funding: This research received no external funding.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: All data has been included in the main text.

Acknowledgments: The authors acknowledge the Rumokai experimental station of the Lithuanian Research Center for Agriculture and Forestry team for providing help during the trials, including field preparation, irrigation and sampling.

Conflicts of Interest: The authors declare no conflict of interest.

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Article

Influence of Modified Urea Compounds to Improve Nitrogen Use Efficiency under Corn Growth System

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Abstract: Adopting new practices is an imperative need to increase the efficiency of nitrogen use (NUE), especially in selecting appropriate N-fertilizer sources and application doses. Regrettably, conventional urea's ability to supply nitrogen to soils is quickly lost as a result of volatilization, leaching, and denitrification. Thus, this study's main aim was to use various modified urea compounds with different doses and investigate their effect on mineral nitrogen release in the soil to improve nitrogen uptake and its use efficiency under the corn growth system. The field trial was conducted in a randomized complete block design (RCBD) by 28 experimental plots. Seven treatments including a control (C), urea (U100 and U200), urea + potassium humate (UPH100 and UPH200), and urea cocrystal (UC100 and UC200) with four replicates were used. The results reported that the treatments significantly ($p < 0.05$) affected grain yields. The urea treatments (U100 = 100 kg N ha⁻¹, U200 = 200 kg N ha⁻¹) increased the grain yields by 7.16% and 30.53%, respectively, compared to the control (C), while the urea + potassium humate treatments (UPH100 = 100 kg N ha⁻¹, UPH200 = 200 kg N ha⁻¹) and urea cocrystal treatments (UC100 = 100 kg N ha⁻¹, UC200 = 200 kg N ha⁻¹) provided a 30.51, 50.47, 39.23, and 56.63% increase in grain yields, respectively, compared to the control. The treatments had significant ($p \leq 0.05$) effects on the fresh leaves and stems yield and the dry matter, fresh cob, and dry cob yields. Moreover, the use of modified urea as urea + potassium humate and urea cocrystal at high rates of 200 kg N ha⁻¹ showed highly significant ($p < 0.01$) effects on the uptake in grain, stems, and total nitrogen uptake by corn compared to the control and urea alone. This study highlighted that modified urea fertilizers such as urea + potassium humate and urea cocrystal were better than conventional urea to improve corn yield productivity and N use efficiency.

Keywords: modified urea; nitrogen losses; cocrystal; nitrogen use efficiency; potassium humate



Citation: Swify, S.; Avizienyte, D.; Mazeika, R.; Braziene, Z. Influence of Modified Urea Compounds to Improve Nitrogen Use Efficiency under Corn Growth System. *Sustainability* **2022**, *14*, 14166. <https://doi.org/10.3390/su142114166>

Academic Editor: Georgios Koubouris

Received: 12 September 2022

Accepted: 26 October 2022

Published: 30 October 2022

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1. Introduction

Nitrogen (N) is an essential nutrient of utmost importance in plant nutrition and improving yield. Due to it being more responsible for plant biomass than other mineral nutrients, it is an indispensable component; additionally, it is the driver of plant growth and constitutes 1 to 4% of the dry matter of plants [1,2]. However, nutrition specialists face many problems in adjusting plant requirements and the soil stock of nitrogen. Thus, N fertilizers using have been suggested to enhance crop productivity [3,4]. One of the most significant determinants of crop productivity are nitrogenous fertilizers such as urea (46% N), which is extensively used in the agricultural production sector [5,6]. Furthermore, urea is a common fertilizer that is used due to its relative inexpensiveness, simple handling, and lower production costs compared to other N fertilizers [7]. Urea fertilizers have high solubility when applied to the soil; because of its high solubility, urea-nitrogen may be lost easily from the soil-plant system or become unavailable to plants. Urea loses nitrogen through many processes such as leaching, denitrification, immobilization, and fixation in soil solids as the NH₄-N form [8,9]. Nitrogen loss is a vital problem, mainly when used in high-pH soils or low-CEC [10–12]. Nitrogen loss causes urea to be less effective than

other N fertilizers such as ammonium nitrate (AN). A high potential environmental cost is associated with N losses via NH₃ volatilization, NO₃⁻ leaching, and N₂O emission to the atmosphere [13,14]. Moreover, plant nitrogen recovery from soluble fertilizers such as urea is reduced to approximately 30–40% [15]. As a result, immediate action is required in order to understand the factors influencing nitrogen availability and to select management practices that minimize nitrogen losses. An adopted suitable strategy will increase the amount of applied N recovered by the crop, improve production efficiency, and reduce the potential environmental impacts of N use [14,16]. A controlled or slow release is one of the most common attempts to reduce nitrogen fertilizer losses by making it in a controlled form, and it is among the most effective N management practices to improve nitrogen use efficiency (NUE) [16,17]. Many studies have been reported that apply to various plant species under different environmental conditions to improve nitrogen use efficiency [10,13,18–29]. The products can be coated, chemically and biochemically modified, or granularly modified [30–35]. Their combination can form stable chemical bonds, reduce the nitrogen release rate, and increase the crop fertilizer use efficiency [36–40]. The application of HA-N significantly raises crop yield, promotes nitrogen absorption and accumulation by crops, and increases nitrogen use efficiency (NUE) [21,36,39,40]. The purpose of this study was to test the hypothesis that modified urea fertilizers containing calcium sulfate and potassium humate could improve mineral nitrogen release and hence its uptake and efficiency as well as maize yield. Therefore, the main objectives of this study were: (i) to investigate the effects of using different modified urea compounds as a new fertilizer on soil mineral nitrogen kinetics, (ii) to enhance the potential to reduce urea nitrogen losses by using different modified urea compounds, (iii) to increase nitrogen uptake and improve nitrogen use efficiency, and (iv) to improve corn grain yield and quality.

2. Materials and Methods

2.1. Site Description and Experiment Design

This study was carried out in May 2020 in west south Lithuania at Rumokai experimental station of Lithuanian Research Centre for Agriculture and Forestry 54°43′15.7044″ N, 22°58′36.6672″ E to investigate different modified urea products on mineral nitrogen release and its use efficiency under the corn growth system as the test crop. The field soil type was Hapli-Epihyopogleyic Luvisol (LVg-p-w-ha) [41] with a moderately silty texture and frequent leaching. The soil chemical properties at 0–20 cm and nitrogen forms concentrations at the soil surface (0–30 cm) and subsurface (0–60 cm) layers are shown in Table 1.

Table 1. The chemical characteristics of field soil before using different urea compound fertilizers.

Soil Properties	Unit	Value	Depth (cm)
pH _{KCL}	-	6.8	0–20
P ₂ O ₅	mg kg ⁻¹	342	0–20
K ₂ O	mg kg ⁻¹	219	0–20
SOC	%	1.48	0–20
Nitrogen Mineral	mg kg ⁻¹	27.14	0–30
		15.68	30–60
NO ₃ -N	mg kg ⁻¹	25.64	0–30
		14.80	30–60
NH ₄ -N	mg kg ⁻¹	1.50	0–30
		0.88	30–60

SOC = soil organic carbon.

The trial plots were planted with a maize variety, ‘Ramirez FAO 160’, with a seed ratio of 100,000 pcs. ha⁻¹ with 50 cm row spacing and 20 cm seed spacing. The maize was grown without pesticides in a completely randomized block (RCBD) with an area of 4 m² (2 m × 2 m). The experiment was performed in seven treatments with four replicates and 28 experimental plots. Treatments consisted of control (C) = non-treated,

U100 = 100 kg N ha⁻¹ urea, U200 = 200 kg N ha⁻¹ urea, UPH100 = 100 kg N ha⁻¹ urea + potassium humate (UPH), UPH200 = 200 kg N ha⁻¹ urea + potassium humate (UPH), UC100 = 100 kg N ha⁻¹ urea cocrystal (UC) and UC200 = 200 kg N ha⁻¹ urea cocrystal (UC). The fertilizers were manually applied in accordance with the experimental scheme. The corn productivity and biometrics were measured manually during the corn physiological maturity phase in September 2020 (BBCH 88–89). After harvesting, the remainder of the plant remains were plowed at a depth of 22 cm. Next, 28 plants were randomly selected for grain yield and grain quality determination. For dry biomass and yield weight determinations, samples were taken from all the replicates and oven-dried at 65 ± 5 °C until constant weight.

2.2. Soil Sampling and Analytical Procedures

Three replicates of soil samples were collected at 0–30 and 30–60 cm deep in untreated and treated plots. The samples were taken using a stainless-steel push tube with three sub-samples per composite plot to form a sample. All soil samples were air-dried and crushed into a sieve with 2 mm openings. The Agrochemical Research Laboratory analyzed the soil and mineral nitrogen properties at the Lithuanian Agricultural and Forest Research Centre [42]. Soil mobile potassium as K₂O and phosphorus as P₂O₅ were extracted using 1:20 (wt./vol) soil suspension of ammonium lactate–acetic acid extractant (pH 3.7). The suspension was shaken for 4 h. Mobile P₂O₅ was extracted using ammonium molybdate via the spectrometric method with Shimadzu UV 1800 spectrophotometer, while mobile K₂O was determined using flame emission spectroscopy with flame emission spectroscopy JENWAY PFP7 flame photometer. The soil pH was determined with a 1:5 (vol/vol) soil suspension in 1M KCl. The mix was shaken for 60 min and allowed to sit for 1 h. The pH of the suspension was measured at 20 ± 2 °C while stirring with a pH meter. Mineral nitrogen was extracted in 1:5 (wt./vol) soil suspension of 1 M KCl solution. The suspension was shaken for 60 min at 20 ± 2 °C. After shaking, the suspension was filtrated and analyzed using a flow injection analysis (FIA) system by FIASTAR 5000 analyzer. After the addition of an acidic sulfanilamide solution, the nitrates in the soil extract were converted to nitrites in the cadmium column. They then reacted with N-(1-naphthyl) ethylenediamine dihydrochloride to form a purple azo dye whose absorbance can be measured at 540 nm and 720 nm. The sum of nitrate and nitrite nitrogen was determined in the soil extract. The soil extract was injected into a flowing carrier solution, where ammonium was mixed with sodium hydroxide to form gaseous ammonia, which passed through a gas-permeable membrane into the indicator stream. Acidic indicators change color in this stream when they react with ammonium gas. Photometric measurements were then performed at 540 nm and 720 nm. Calculating the mineral nitrogen involves adding the combined amounts of nitrate and nitrite nitrogen to the ammonia nitrogen. The organic carbon content was determined using dry combustion, where the sample was heated to 900 °C in a stream of air, and the carbon dioxide formed was measured using infrared spectroscopy.

2.3. Fertilizer Materials

The study was conducted by comparing urea as a mineral nitrogen fertilizer with other modified urea compound fertilizers such as urea + potassium humate (UPH) and urea cocrystal (UC):

1. Urea (Total N 46.2%).
2. Urea + potassium humate (UPH) contains 40% N and 1% potassium humate; produced by specialists of AB Achema scientific experimental laboratory by coating urea granules with potassium humate.
3. Urea cocrystal (4urea.CaSO₄) contains 29.8% N, 8.5% S, and 10.6% Ca. The fertilizer was mechanochemically produced by chemists from Kaunas Technology University (KTU), Faculty of Chemical Technology, Lithuania.

2.4. Metrological Conditions

The annual average precipitation during the period of 1982–2010 ranged from 32 to 81 mm, with a high average in August, and an annual average temperature of 15.38 °C. The area has a medium temperate climate with an average temperature of 16.23 °C during the maize-growing season in 2020, with the high-temperature values recorded in June and August being an average of 18.63 and 18.87 °C, respectively. The annual precipitation was 23.62 mm in 2020, which is less than the long-term average (Figure 1).

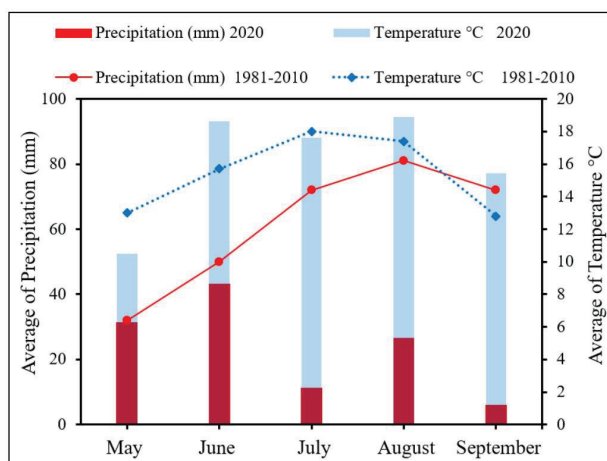


Figure 1. The distribution of monthly rainfall (mm) and temperature at the experimental site during 2020 and average rainfall and temperature for the past 30 years at the site.

2.5. Nitrogen Uptake and Use Efficiency Estimation

The term refers to nitrogen uptake and agronomic nitrogen use efficiency (ANUE) expressions as follows [28]:

$$N \text{ uptake} = N\% \text{ in grain or stems} \times \text{dry matter of grain or stems in } \left(\text{kg ha}^{-1} \right) \quad (1)$$

$$ANUE \left(\text{kg grain increased kg N}^{-1} \text{ applied} \right) = \frac{YN - Y0}{NR} \quad (2)$$

In the above expressions, YN and $Y0$ are the yields (kg ha^{-1}) in the fertilized and control (no fertilizer) plots, respectively, and NR refers to the rate of fertilizer applied (kg ha^{-1}).

2.6. Statistical Analysis

Analysis of variance (ANOVA) was performed using a general linear model on plant density, fresh leaves and stems yield, as well as dry matter, fresh and dry ear yields and grain yields, grain characteristics, N uptake, and ANUE. Pearson's correlation shows the relationship between time and mineral N with respect to its forms (nitrate and ammonium). The statistical analysis software was IBM SPSS 25.0, and Duncan's test at the 5% level was performed to separate means according to the ANOVA results.

3. Results

3.1. Plants' Density, Fresh Leaves and Stems, and Dry Matter Yields

There was a significant treatment effect on the observed corn plants' density. The plants' density ranged from 89,450 plants ha^{-1} in the control to 97,800 plants ha^{-1} in UC200. The treatments showed highly significant effects on the fresh leaves and stems yield and dry matter, as shown in Figure 2. The treatments of UPH200 > UC200 recorded the highest fresh leaves and stems yield with means of 48.05 and 50.27 t/ha^{-1} , respectively, followed by the treatment of UC200 > UPH100 with means of 43.61 and 44.72 t/ha^{-1} , respectively.

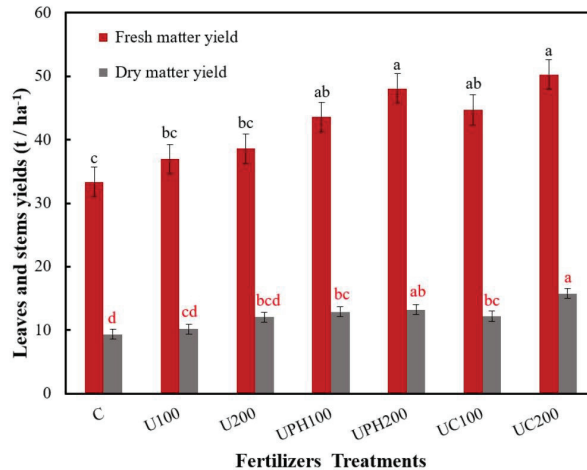


Figure 2. Fresh leaves and stems and dry matter yields followed by Duncan's multiple range test letters at 5% level. The letters with the same color have the same significance level test. Note. Control (C) = non-treated, U100 = 100 kg N ha^{-1} urea, U200 = 200 kg N ha^{-1} urea, UPH100 = 100 kg N ha^{-1} urea + potassium humate (UPH), UPH200 = 200 kg N ha^{-1} urea + potassium humate (UPH), UC100 = 100 kg N ha^{-1} urea cocrystal (4urea.CaSO₄), and UC200 = 200 kg N ha^{-1} , urea cocrystal (4urea.CaSO₄).

There were no significant differences recorded for the urea treatments U100 and U200 compared to the control, which recorded the lowest fresh leaves and stems weight among the fertilizer treatments with means of 36.94 and 38.61 t/ha^{-1} , respectively. The dry matter yields ranged from 9.34 t/ha^{-1} in the control to 15.75 t/ha^{-1} in UC200 (Table 2). The treatment had significant effects on fresh and dry matter yields compared to the control except for the urea treatments (U100 and U200), which exhibited nonsignificant effects on the control. The urea cocrystal treatments UC100 and UC200 recorded the highest fresh silage yields and dry matter with means of 44.72, 50.27 t/ha^{-1} , 12.19, and 15.75 t/ha^{-1} , respectively.

Table 2. Means (\pm standard deviation) of plants' density, silage dry matter, and fresh silage yields after using different urea compound fertilizers followed by Duncan's multiple range test letters at the 5% level.

Treatments	Plant Density	Fresh Leaves and Stems Yield	Dry Matter	% Moisture
	1000 plants ha ⁻¹	t/ha ⁻¹		
C	89.450 \pm 2.6 c	33.33 \pm 6.3 c	9.34 \pm 1.3 d	71.97
U100	90.825 \pm 4.7 c	36.94 \pm 6.7 bc	10.15 \pm 1.6 cd	72.52
U200	92.325 \pm 2.3 bc	38.61 \pm 7.4 bc	12.03 \pm 2.3 bcd	68.84
UPH100	93.350 \pm 5.1 abc	43.61 \pm 4.7 ab	12.88 \pm 1.6 bc	70.46
UPH200	96.675 \pm 2.3 ab	48.05 \pm 6.4 a	13.23 \pm 2.0 ab	80.88
UC100	96.675 \pm 2.3 ab	44.72 \pm 3.8 ab	12.19 \pm 1.2 bc	72.74
UC200	97.800 \pm 0.0 a	50.27 \pm 5.1 a	15.75 \pm 1.7 a	68.66
<i>p</i> -value	<i>p</i> < 0.011	<i>p</i> < 0.006	<i>p</i> < 0.002	-

Note 1. Control (C) = non-treated, U100 = 100 kg N ha⁻¹ urea, U200 = 200 kg N ha⁻¹ urea, UPH100 = 100 kg N ha⁻¹ urea + potassium humate (UPH), UPH200 = 200 kg N ha⁻¹ urea + potassium humate (UPH), UC100 = 100 kg N ha⁻¹ urea cocystal (4urea.CaSO₄), and UC200 = 200 kg N ha⁻¹ urea cocystal (4urea.CaSO₄). Note 2. Values in the same column followed by the same letter are not different (*p* < 0.05) according to Duncan's multiple range test at the 5% level.

3.2. Grain Yields and Grain Quality

The mean grain yields followed by Duncan's test letters are shown in Figure 3. There were highly significant differences between the effects of the treatments on grain yields. The mean grain yields ranged from 12.84 t/ha⁻¹ in the control to 20.11 t/ha⁻¹ in UC200, as shown in Table 3. The urea treatments (U100, U200) increased grain yields by 7.16% and 30.53%, respectively, compared to the control (C), while the urea + potassium humate (UPH100, UPH200) and urea cocystal treatments (UC100, UC200) provided a 30.51, 50.47, 39.23, and 56.63% increase in grain yields, respectively, compared to the control. Additionally, the treatments had significant effects on both the fresh and dry cob yields. The mean fresh cob yields ranged from 26.11 t/ha⁻¹ in the control to 36.95 t/ha⁻¹ in UC200, and the mean dry cob yields ranged from 18.69 t/ha⁻¹ in the control to 25.88 t/ha⁻¹ in UC200 (Table 3). Compared to the control, the modified urea treatments recorded the highest grain and cob yields, as well as fresh and dry matter yields (UC200 > UPH200 > UC100).

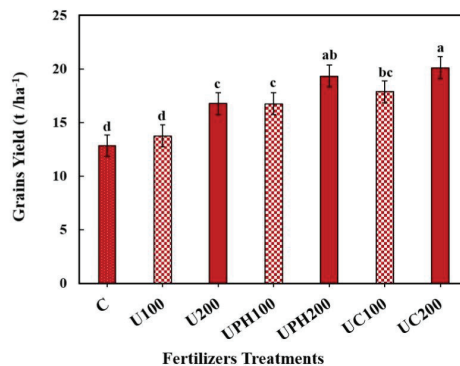


Figure 3. The corn grain yield means (t/ha⁻¹) of the field experiment after using different urea compounds fertilizers followed by Duncan's multiple range test letters at 5% level. Note. Control (C)

= non-treated, U100 = 100 kg N ha⁻¹ urea, U200 = 200 kg N ha⁻¹ urea, UPH100 = 100 kg N ha⁻¹ urea + potassium humate (UPH), UPH200 = 200 kg N ha⁻¹ urea + potassium humate (UPH), UC100 = 100 kg N ha⁻¹ urea cocrystal (4urea.CaSO₄), and UC200 = 200 kg N ha⁻¹, urea cocrystal (4urea.CaSO₄).

Table 3. Means (\pm standard deviation) of grain yields and fresh and dry cob yields after using different urea compound fertilizers followed by Duncan's test letters.

Treatments	Grain Yields	Fresh Ears Yield	Dry Ears Yield	% Moisture of Ears Yields
t/ha ⁻¹				
C	12.84 \pm 1.3 d	26.11 \pm 4.7 c	18.69 \pm 3.1 c	28.42
U100	13.75 \pm 1.7 d	28.89 \pm 6.3 bc	20.21 \pm 4.5 bc	30.04
U200	16.76 \pm 1.0 c	29.45 \pm 3.2 bc	21.16 \pm 1.4 bc	28.14
UPH100	16.76 \pm 0.7 c	32.22 \pm 2.2 abc	22.31 \pm 1.4 bc	30.75
UPH200	19.32 \pm 0.5 ab	33.62 \pm 4.7 ab	23.55 \pm 2.5 ab	29.95
UC100	17.88 \pm 2.5 bc	33.33 \pm 4.8 ab	22.18 \pm 4.6 abc	33.45
UC200	20.11 \pm 1.1 a	36.95 \pm 2.5 a	25.88 \pm 1.7 a	29.95
<i>p</i> -value	<i>p</i> < 0.001	<i>p</i> < 0.025	<i>p</i> < 0.043	-

Note 1. Control (C) = non-treated, U100 = 100 kg N ha⁻¹ urea, U200 = 200 kg N ha⁻¹ urea, UPH100 = 100 kg N ha⁻¹ urea + potassium humate (UPH), UPH200 = 200 kg N ha⁻¹ urea + potassium humate (UPH), UC100 = 100 kg N ha⁻¹ urea cocrystal (4urea.CaSO₄), and UC200 = 200 kg N ha⁻¹, urea cocrystal (4urea.CaSO₄). Note 2. Values in the same column followed by the same letter are not different (*p* < 0.05) according to Duncan's multiple range test at the 5% level.

Table 4 shows that the treatments had significant effects on the characteristics of the grains, including grain protein, total N, and grain carbohydrate content, but did not affect the grain dry matter. The grain protein means ranged from 6.21% in the control to 7.67% in UC200. The treatments of U100 and UPH100 recorded the lowest total N in the grains by 1.14% after the control. In contrast, UC200 had the highest total N concentration at 1.23%. The grain dry matter ranged from 93.68% to 95.13% in UPH200 and UPH100, respectively. The treatments had highly significant effects on the grain carbohydrate content. It ranged from 70.51% in the control to 76.69% in UC200.

Table 4. Means (\pm standard deviation) of grain characteristics (protein, total N, dry matter, and carbohydrates) after using different Urea compounds fertilizers.

Treatments	% Protein	% Total N	% Dry Matter	% Carbohydrates
C	6.21 \pm 0.2 b	0.99 \pm 0.0 b	94.02 \pm 1.2	70.51 \pm 0.8 d
U100	7.16 \pm 0.4 a	1.14 \pm 0.1 a	94.35 \pm 1.4	70.77 \pm 0.2 d
U200	7.19 \pm 0.7 a	1.18 \pm 0.0 a	94.56 \pm 0.9	72.39 \pm 0.2 c
UPH100	7.11 \pm 0.4 a	1.14 \pm 0.1 a	95.13 \pm 1.0	72.85 \pm 0.1 bc
UPH200	7.39 \pm 0.7 a	1.18 \pm 0.1 a	93.68 \pm 0.8	72.22 \pm 0.8 c
UC100	7.29 \pm 0.5 a	1.17 \pm 0.1 a	93.82 \pm 1.3	73.43 \pm 0.8 b
UC200	7.67 \pm 0.2 a	1.23 \pm 0.0 a	94.51 \pm 1.3	76.69 \pm 0.8 a
<i>p</i> -value	<i>p</i> < 0.007	<i>p</i> < 0.001	ns	<i>p</i> < 0.001

Note 1. Control (C) = non-treated, U100 = 100 kg N h⁻¹ urea, U200 = 200 kg N h⁻¹ urea, UPH100 = 100 kg N h⁻¹ urea + potassium humate (UPH), UPH200 = 200 kg N h⁻¹ urea + potassium humate (UPH), UC100 = 100 kg N h⁻¹ urea cocrystal (4urea.CaSO₄), and UC200 = 200 kg N h⁻¹, urea cocrystal (4urea.CaSO₄). Note 2. Values in the same column followed by the same letter are not different (*p* < 0.05) according to Duncan's multiple range test at the 5% level.

3.3. Mineral Nitrogen Release

Some pre-studies examined the release process of mineral nitrogen and its forms (NO₃⁻ and NH₄⁺) from urea compound granules in the soil without plants (Figure 4). The process was divided into three stages including (1) low concentration, (2) increased concentration and (3) stability of concentration. Additionally, the results showed that the concentration of ammonium, nitrate, and mineral nitrogen increased with time due to the decomposition of urea compound granules. The relation between the transformation of

soil mineral nitrogen forms depended on soil water content and urea compound type. The mineral nitrogen concentration started with a low concentration in the beginning until three days, then increased to a maximum over two weeks. After that, the nitrogen concentration remained somewhat stable or decreased depending on the microbial activity or ammonia volatilization.

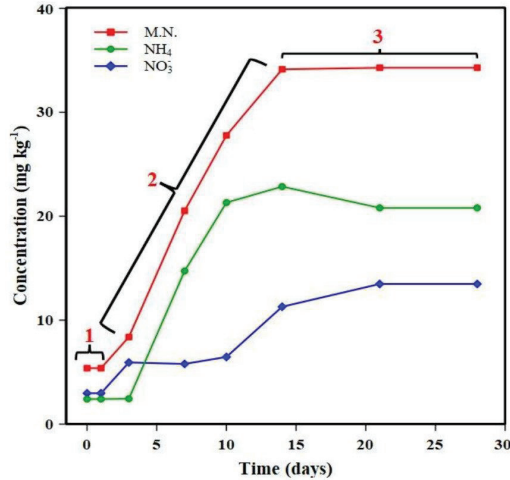


Figure 4. The release process of mineral nitrogen from urea compound granules as a relation between the concentration of mineral nitrogen forms (NO_3^- and NH_4^+) and time.

As shown in Table 5, the mineral N in the soil surface layer (0–30 cm) during the corn's growth was significantly correlated with time for all the treatments except U200 and UPH100. Additionally, the soil surface layer (0–30 cm) had a higher mineral nitrogen concentration than the soil subsurface layer (30–60 cm) as shown in Table 5.

However, the concentration correlated highly significantly with all the treatments in the soil subsurface layer (30–60 cm). Approximately 30% of the mineral nitrogen was found in the subsurface layer (30–60 cm) (Figure 5). The control recorded the lowest mineral nitrogen concentration values in the soil surface (0–30 cm) and subsurface (30–60 cm) layers with a mean of 16.05 and 10.72 mg kg⁻¹, respectively. The treatment of UC200 recorded the highest means of 29.34 and 13.74 mg kg⁻¹ in soil surface (0–30 cm) and subsurface (30–60 cm) layers, respectively. The treatments of U200 and UPH200 showed high means of mineral nitrogen after UC200 in the soil surface (0–30 cm) with values of 27.59 and 26.13 mg kg⁻¹, respectively, but in the soil subsurface (30–60 cm) layer, U100 and U200 recorded high concentrations with means of 13.59 and 13.50 mg kg⁻¹, respectively, after UC200.

Table 5. The relation between the time and mineral nitrogen concentration (mg kg^{-1}) in soil surface (0–30 cm) and subsurface (30–60 cm) layers during the corn's growth.

Treatments	Mean	Pearson Correlation	Sig (2-Tailed)
depth (0–30 cm)			
C	16.05	−0.820 **	0.007
U100	23.80	−0.733 *	0.025
U200	27.59	−0.666	0.050
UPH100	25.25	−0.587	0.097
UPH200	26.13	−0.727 *	0.026
UC100	21.72	−0.711 *	0.032
UC200	29.34	−0.703 *	0.035
depth (30–60 cm)			
C	10.72	−0.808 **	0.008
U100	13.59	−0.834 **	0.005
U200	13.50	−0.814 **	0.008
UPH100	12.11	−0.868 **	0.002
UPH200	12.52	−0.887 **	0.001
UC100	11.81	−0.867 **	0.002
UC200	13.74	−0.721 *	0.028

** Correlation is significant at the 0.01 level (two-tailed). * Correlation is significant at the 0.05 level (two-tailed).

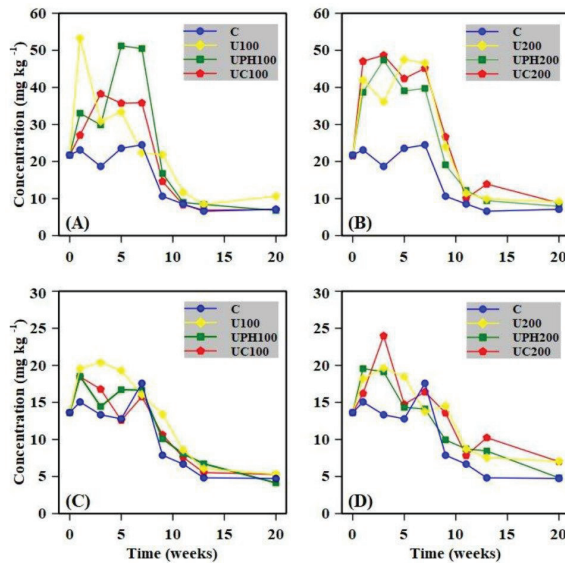


Figure 5. The relation between the mineral nitrogen concentration and time during the maize growth period in soil surface 0–30 cm (A,B) and subsurface 30–60 cm (C,D). Note. Control (C)= non-treated, U100 = 100 kg N ha^{-1} urea, U200 = 200 kg N ha^{-1} urea, UPH100 = 100 kg N ha^{-1} urea + potassium humate (UPH), UPH200 = 200 kg N ha^{-1} urea + potassium humate (UPH), UC100 = 100 kg N ha^{-1} urea cocrystal (4urea.CaSO₄), and UC200 = 200 kg N ha^{-1} urea cocrystal (4urea.CaSO₄).

The soil mineral nitrogen formed into ammonium ($N-NH_4^+$) and nitrate ($N-NO_3^-$) in all the different urea compound granules during the release process. The ammonium ($N-NH_4^+$) concentration was lower than the nitrate concentration for all the treatments. The soil surface (0–30 cm) layer recorded a higher ammonium concentration than the soil subsurface (30–60 cm) layer. Before fertilization and corn growth, the ammonium concentration means were 1.54 and 1.17 $mg\ kg^{-1}$ in the soil surface (0–30 cm) and subsurface (30–60 cm) layers, respectively. The ammonium concentration fluctuated slightly and decreased during the corn growth until harvest (Figure 6). Therefore, the concentration did not correlate with time during the corn growth, as shown in Table 6.

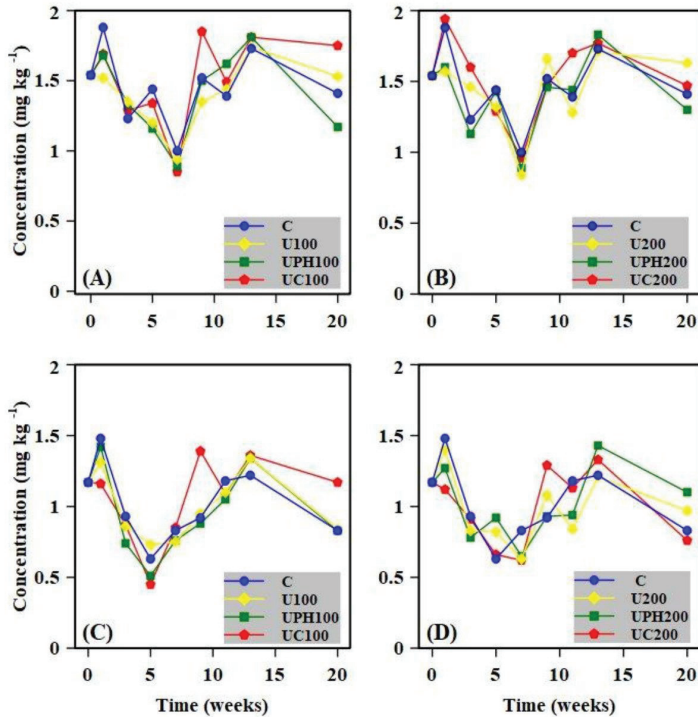


Figure 6. The relation between the ammonium concentration and time during the maize growth period in soil surface 0–30 cm (A,B) and subsurface 30–60 cm (C,D). Note. Control (C) = non-treated, U100 = 100 $kg\ N\ ha^{-1}$ urea, U200 = 200 $kg\ N\ ha^{-1}$ urea, UPH100 = 100 $kg\ N\ ha^{-1}$ urea + potassium humate (UPH), UPH200 = 200 $kg\ N\ ha^{-1}$ urea + potassium humate (UPH), UC100 = 100 $kg\ N\ ha^{-1}$ urea cocrystal (4urea.CaSO₄), and UC200 = 200 $kg\ N\ ha^{-1}$ urea cocrystal (4urea.CaSO₄).

Table 6. The relation between time and ammonium concentration (mg kg^{-1}) in soil surface (0–30 cm) and subsurface (30–60 cm) layers during the corn's growth.

Treatments	Means	Pearson Correlation	Sig (2-Tailed)
depth (0–30 cm)			
C	1.46	−0.100	0.799
U100	1.40	0.228	0.555
U200	1.45	0.184	0.636
UPH100	1.41	−0.094	0.810
UPH200	1.40	0.028	0.943
UC100	1.51	0.335	0.379
UC200	1.53	−0.075	0.848
depth (30–60 cm)			
C	1.02	−0.264	0.493
U100	1.01	−0.145	0.710
U200	0.99	−0.173	0.656
UPH100	0.97	−0.111	0.777
UPH200	1.02	0.128	0.742
UC100	1.06	0.310	0.417
UC200	1.00	−0.066	0.867

The treatments had no effect on the ammonium concentration in the soil surface layer (0–30 cm), but in the soil subsurface layer (30–60 cm), there were significant differences ($p < 0.003$) between the treatments after one, three, five, and nine weeks, and after the harvest as well. After the harvest, the ammonium recorded a slight decrease with a mean of 1.46 mg kg^{-1} in the soil surface layer (0–30 cm), and the soil subsurface (30–60 cm) layer recorded 0.93 mg kg^{-1} as shown in Figure 6.

The nitrate (N-NO_3^-) had the same trend as the mineral nitrogen, starting with a low concentration before the fertilization, and during corn growth recorded a mean of 20.19 and 12.45 mg kg^{-1} in the soil surface (0–30 cm) and subsurface (30–60 cm) layers, respectively (Figure 7). In the soil surface 0–30 cm layer, the nitrate concentration correlated significantly with time for all the treatments except U200 and UPH100, as shown in Table 7.

Table 7. The relation between time and nitrate concentration (mg kg^{-1}) in soil surface (0–30 cm) and subsurface (30–60 cm) layers during the corn's growth.

Treatments	Means	Pearson Correlation	Sig (2-Tailed)
depth (0–30 cm)			
C	14.59	−0.811 **	0.008
U100	22.39	−0.734 *	0.024
U200	26.14	−0.662	0.052
UPH100	23.84	−0.579	0.102
UPH200	24.73	−0.721 *	0.028
UC100	20.21	−0.707 *	0.033
UC200	28.36	−0.694 *	0.038
depth (30–60 cm)			
C	9.70	−0.791 *	0.011
U100	12.58	−0.819 **	0.007
U200	12.50	−0.803 **	0.009
UPH100	11.14	−0.855 **	0.003
UPH200	11.50	−0.882 **	0.002
UC100	10.75	−0.864 **	0.003
UC200	12.74	−0.709 *	0.033

** Correlation is significant at the 0.01 level (two-tailed). * Correlation is significant at the 0.05 level (two-tailed).

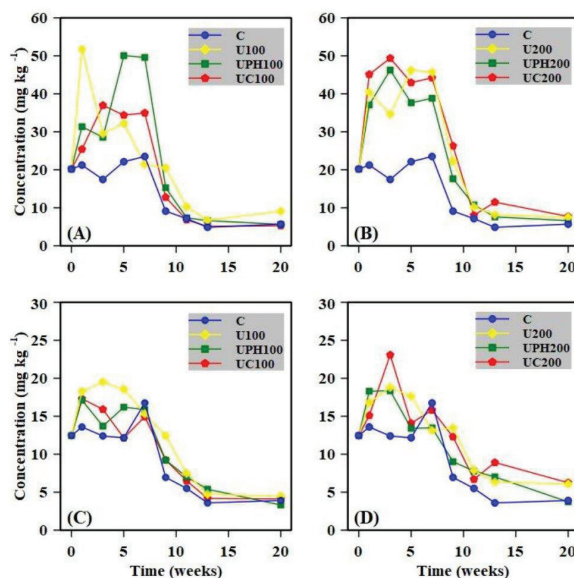


Figure 7. The relation between the nitrate concentration during the maize growth period in soil surface 0–30 cm (A,B) and subsurface 30–60 cm (C,D). Note. Control (C) = non-treated, U100 = 100 kg N ha⁻¹ urea, U200 = 200 kg N ha⁻¹ urea, UPH100 = 100 kg N ha⁻¹ urea + potassium humate (UPH), UPH200 = 200 kg N ha⁻¹ urea + potassium humate (UPH), UC100 = 100 kg N ha⁻¹ urea cocystal (4urea.CaSO₄), and UC200 = 200 kg N ha⁻¹, urea cocystal (4urea.CaSO₄).

The highest concentration was recorded after 5 weeks with a mean of 37.93 mg kg⁻¹. The treatments had significant effects on the soil nitrate concentration during all the corn growth periods and after the harvest ($p < 0.007$), except after eleven weeks it was not significant. The treatments of UC200 and U200 recorded the highest means of 28.36 and 26.14 mg kg⁻¹, respectively. The soil subsurface (30–60 cm) layer had approximately 25% nitrate concentration during corn growth. Thus, the nitrate concentration was significantly correlated with time for all the treatments in the soil subsurface layer (30–60 cm) (Table 7). The treatments significantly affected the nitrate concentration until the fifth week and after thirteen weeks with $p < 0.004$. The concentration after seven weeks started to decrease until the harvest for all treatments in the soil surface 0–30 cm and soil subsurface layers (30–60 cm). After the harvest, the concentration was 6.78 and 4.55 mg kg⁻¹ in the soil surface (0–30 cm) and soil subsurface (30–60 cm) layers, respectively (Figure 7).

3.4. Nitrogen Uptake and Use Efficiency

The statistics results in Table 8 showed that the use of modified urea as urea + potassium humate and urea cocystal with high rates of 200 kg N ha⁻¹ had highly significant effects on the N uptake in grain and stems and the total nitrogen uptake by the corn crop compared to the control and urea alone (Figure 8). In addition, the treatments of UPH200 and UC200 provided an increase of 79.15 and 93.677%, respectively, in grain N uptake compared to the control, and it recorded the highest N uptake in the stems with means of

133.58 and 168.49 kg ha⁻¹, respectively. The treatments significantly affected the agronomic nitrogen use efficiency (ANUE). Urea + potassium humate and urea cocystal improved the nitrogen use efficiency, recording means of 50.40, 39.20, 36.38, and 32.41 kg kg⁻¹ at UC100 > UPH100 > UC200 > UHP200, while urea alone recorded the lowest means of 9.20 and 19.61 kg kg⁻¹ at U200 > U100 for agronomic nitrogen use efficiency (ANUE) as shown in Figure 8.

Table 8. Effect of modified urea fertilizers on grain and stem N uptake, and agronomic N use efficiency (ANUE) in the corn crops.

Treatments	N Uptake in Grains	N Uptake in Stems	N Uptake [Grain + Stems]	ANUE
		kg ha ⁻¹		kg kg ⁻¹
C	127.62 e	73.79 d	201.41 e	-
U100	156.87 d	104.58 c	261.45 d	9.20 d
U200	199.16 bc	120.27 bc	319.43 bc	19.61 cd
UPH100	190.90 c	101.74 c	292.63 cd	39.20 ab
UPH200	228.64 ab	133.58 b	362.23 b	32.41 bc
UC100	209.09 bc	96.35 cd	305.44 dc	50.40 a
UC200	247.17 a	168.49 a	415.66 a	36.38 ab
SE±	8.09	6.09	13.42	3.53
p-value	p < 0.001	p < 0.001	p < 0.001	p < 0.001

Note 1. Control (C) = non-treated, U100 = 100 kg N h⁻¹ urea, U200 = 200 kg N h⁻¹ urea, UPH100 = 100 kg N h⁻¹ urea + potassium humate (UPH), UPH200 = 200 kg N h⁻¹ urea + potassium humate (UPH), UC100 = 100 kg N h⁻¹ urea cocystal (4urea.CaSO₄), and UC200 = 200 kg N h⁻¹ urea cocystal (4urea.CaSO₄). Note 2. Values in the same column followed by the same letter are not different (p < 0.05) according to Duncan's multiple range test at the 5% level.

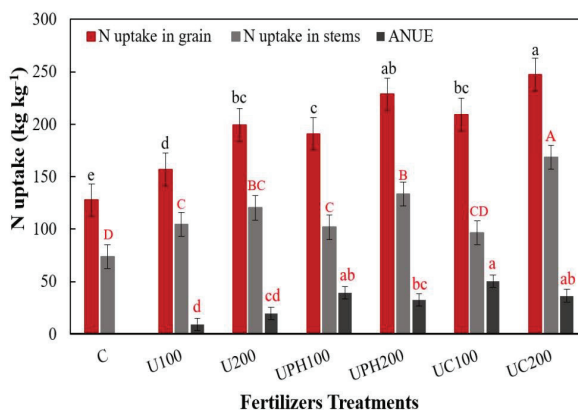


Figure 8. The effect of urea compound treatments on N uptake (kg kg⁻¹) in maize grains and stems, and ANUE (kg kg⁻¹) followed by Duncan's multiple range test letters at 5% level. The letters with the same color have the same significance level test. Note. Control (C) = non-treated, U100 = 100 kg N ha⁻¹ urea, U200 = 200 kg N ha⁻¹ urea, UPH100 = 100 kg N ha⁻¹ urea + potassium humate (UPH), UPH200 = 200 kg N ha⁻¹ urea + potassium humate (UPH), UC100 = 100 kg N ha⁻¹ urea cocystal (4urea.CaSO₄), and UC200 = 200 kg N ha⁻¹ urea cocystal (4urea.CaSO₄).

4. Discussion

4.1. Effect of Treatments on Fresh and Dry Silage Yields, Grain Yields, and Grain Characteristics

In the present study, the application of modified urea compounds provided a consistent improvement in grain yields and grain quality compared with conventional urea treatments. Moreover, the results were mostly supported by many previous studies that reported that the use of urea alone could increase nitrogen losses by more than 15% under the current climate change [16,17,43]. Furthermore, the N recovery by crops from soluble N fertilizers such as urea is often as low as 30–40%, with a potentially high environmental cost associated with N losses via NH_3 volatilization [32,44]. Therefore, it was necessary to use some compounds that help reduce urea N losses and improve the efficiency of using urea as an essential fertilizer, which will increase crop yields [45,46]. This study showed that the use of modified urea as urea + potassium humate and urea cocrystal, especially with high rates of 200 kg N ha^{-1} , had highly significant effects on all growth characteristics and yield attributes. These results are in accord with a previous study in 2018 [47]. It suggests that the mechanochemical synthesis of urea cocrystal (4urea.CaSO₄) provides it with unique reactive properties towards the water as relative humidity and different reactive behavior from urea in pure water. Therefore, the release of nitrogen is balanced for the plant's requirements [47]. So, the use of modified urea fertilizers will be more effective in reducing nitrogen loss, increasing N availability to the plants, and enhancing it at the beginning of the experiment in soil [48]. Additionally, the humic compounds have a positive effect on plant growth that is commonly associated not only with the direct interaction of these molecules with the plant root and the activation of physiological processes in the plant but also through exhibiting multiple indirect effects [39,49]. In addition, humic compounds buffer pH, increase water retention, and mobilize nutrient availability. On the other hand, humic compounds may be promising remediation agents for degraded lands due to their ability to improve the soil's physical, chemical, and biological properties [49].

In this study, the use of modified urea fertilizers such as urea cocrystal and urea + potassium humate significantly affected silage yields compared to urea alone [17,50,51]. The urea cocrystal and urea + potassium humate treatments resulted in higher silage yields than urea treatments, especially with high N rates of 200 kg ha^{-1} . The fresh and dry silage yields increased with the modified urea treatments due to the higher N uptake [52] (Table 8). Additionally, in response to using urea + potassium humate and urea cocrystal, there were increases in the corn grain yields by 16.88, 34.75, 24.69, and 40.28%, respectively, compared to the control. Urea treatments increased grain yields by 4.67% and 16.89%, respectively, compared to the control (Table 3). The N release rate can explain these findings from urea granules, which were higher than the urea cocrystal and urea + potassium humate in the beginning (until 3 weeks) of the corn growth [47], and that enhanced the nitrogen loss by leaching, indicated by the high concentration of mineral Nitrogen in the soil subsurface (30–60 cm) layer (Figure 5). While the release of nitrogen from urea cocrystal and urea + potassium humate increased after three weeks in most production systems, the grain development stage (starting at pollination) began about 75 to 95 days after planting [24].

In addition, the use of urea cocrystal had highly significant effects on the grain characteristics, including total N content, protein, and carbohydrates compared to the control, due to maintaining the balance of nitrogen release according to the plant requirements. Nitrogen levels also affect plant growth, leaf area production strength, and plant photosynthetic capacity. For example, the rate of photosynthesis in corn leaves decreases by reducing nitrogen levels [53]. Thus, grain yields, grain weight, and other components are significantly affected by nitrogen treatments [53]. A similar finding reported that the mixing of urea with gypsum increases its efficiency and is helpful for high-yielding aromatic rice varieties [26].

4.2. Mineral Nitrogen Transformations, Uptake, and Use Efficiency

The mineral nitrogen followed the same trend as the pre-studies without plants. Therefore, the release process was divided into three stages, starting with low concentration,

then an increase in concentration, then decreasing, and ending with concentration stability (Figure 4). The results showed that the concentration of ammonium, nitrate, and mineral nitrogen increased with time due to the decomposition of urea compound granules, which was enhanced by soil microbial activity [15]. The mineral nitrogen formed nitrate NO_3^- and ammonium NH_4^+ from urea compound granules in the soil surface 0–30 cm and subsurface (30–60 cm) layers during the corn growth. The mineral nitrogen was specifically characterized as the nitrate form more often than ammonium, leading to increased nitrate leaching [54]. The pathways of N transformation are altered by the concentrations of N microbial species and the microbial population size [55]. The lower ammonium concentration was due to the low microbial biomass [55]. It also indicates a slight rate of nitrification where there is no population of nitrifying organisms [55]. Therefore, the ammonium released in the soil might be either captured by the microbial biomass, oxidized to nitrate, or volatilized. The mineral fertilizer concentration in the soil surface layer (0–30 cm) was significantly correlated with time for all the treatments except U200 and UPH100 because they did not change at a similar rate. These treatments (U200, and UPH100) approximately released an equivalent amount of nitrogen and had similar N uptake and grain yields during the experiment (Table 8). The mineral nitrogen concentration in the soil subsurface (30–60 cm) represented approximately 38–70% of the mineral nitrogen concentration in the surface soil (0–30 cm) layer during the corn growth period. This indicated a high level of nitrogen leaching from the surface layers, especially for the urea treatments with rapid nitrogen release at the beginning of the corn growth. The use of modified urea as urea + potassium humate and urea cocrystal with high rates of 200 kg N ha⁻¹ showed highly significant effects on the N uptake in grain and stems and total nitrogen uptake by the corn crop compared to the control and urea alone (Figure 8). In addition, the treatments significantly affected the agronomic nitrogen use efficiency (ANUE) (Table 8). Urea + potassium humate and urea cocrystal improved the nitrogen use efficiency, especially at lower N rates (UC100 > UPH100 > UC200 > UHP200), while urea alone was not efficient, mainly when used in large quantities. Therefore, the optimal fertilizer application rate reduced the N rate, significantly increased N uptake in grains and dry matter, and improved ANUE as shown in Figure 8.

5. Conclusions

In this study, we show the unique effect of modified urea coated with potassium humate and synthesized with calcium sulfate on the soil mineral nitrogen release to increase its uptake and improve the use efficiency. The rapid release rates of conventional urea treatments at the beginning of the fertilization process compared to modified urea encourage increases in the chances of nitrogen loss through leaching to the subsurface layers, which is evident in the high content of the subsurface layer of mineral nitrogen. Therefore, the release rate of nitrogen is one of the most influential factors to reduce nitrogen loss and improve the nitrogen use efficiency of fertilizer. The release of nitrogen from any fertilizer depends on the reaction with water as relative humidity. Therefore, the coating of urea + potassium humate and the mechanochemical synthesis of urea cocrystal (4urea.CaSO₄) provides them with unique reactive properties towards the water as relative humidity and different reactive behavior from urea in pure water. This maintains the balance between the N soil content and the plant's basic needs. This study showed that the findings for fresh and dry matter yields and grain yields, grain characteristics and N uptake in grain and stems, and total nitrogen uptake and nitrogen use efficiency indicated that modified urea fertilizers such as urea + potassium humate and urea cocrystal were better than the conventional urea to improve corn yield productivity and N use efficiency.

Author Contributions: Conceptualization, S.S. and R.M.; Data curation, S.S. and D.A.; Formal analysis, R.M.; Investigation, D.A. and Z.B.; Methodology, D.A. and Z.B.; Supervision, R.M.; Validation, R.M.; Visualization, S.S.; Writing—original draft, S.S. All the authors commented on previous versions of the manuscript. All authors have read and agreed to the published version of the manuscript.

Funding: This research received no external funding.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Acknowledgments: The authors would like to thank everyone from the Rumokai experimental station of the Lithuanian Research Centre for Agriculture and Forestry for providing help during the trial, including field preparation, irrigation, and sampling. We also express our gratitude to AB Achema scientific experimental laboratory and Tadas Dambrauskas, Department of Silicate Technology, Faculty of Chemical Technology, Kaunas Technology University (KTU), Lithuania, for providing the fertilizers materials.

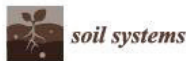
Conflicts of Interest: The authors declare no conflict of interest.

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Article

Mineral Nitrogen Release Patterns in Various Soil and Texture Types and the Impact of Urea and Coated Urea Potassium Humate on Barley Biomass

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Abstract: Controlled-release urea fertilization is an innovative approach and effective means to reduce the loss of nitrogen and enhance fertilizer use efficiency to optimize crop yield while minimizing the environmental impact. The objective of this study was to investigate the dynamic process of mineral nitrogen (N_{min}) release in Luvisols, Cambisols, Retisols, and Arenosols to understand the interaction between soil characteristics and mineral nitrogen release and evaluate the impact of conventional urea compared to coated urea potassium humate on barley biomass production. A pot experiment was conducted under glasshouse conditions (20 ± 2 °C and 60% Humidity). Five treatments including no fertilization as a control (C), 100 kg·N·ha⁻¹ of urea (U100), 200 kg·N·ha⁻¹ of urea (U200), 100 kg·N·ha⁻¹ of coated urea potassium humate (UPH100), and 200 kg·N·ha⁻¹ of coated urea potassium humate (UPH200) were applied to four soil and texture types. Our findings indicate that there are different patterns of mineral nitrogen release across the different soil and texture types. Ammonium levels reached their peak point in all soils within 2–7 days after application. On the other hand, the concentration of nitrate NO₃⁻-N showed a linear increase over 45 days during the experiment. The Retisol, which had a sandy clay texture, obtained the highest concentration of mineral nitrogen in both forms (NH₄ and NO₃), while the sandy texture of Arenosol showed the lowest accumulation of mineral nitrogen and its forms. The application of potassium humate caused a delay of 1–4 days in the peak of soil ammonium, which at peak accounted for approximately 25–44% of the mineral nitrogen in the soil. Furthermore, the application of urea and coated urea potassium humate exhibited significant effects on barley biomass with an increase of approximately 14–91% compared to the unfertilized treatment (control). This research contributes to our understanding of nutrient dynamics in diverse soil environments and provides insights into optimizing sustainable fertilization strategies such as controlled-release fertilizer application. The implications of these findings highlight the significance of tailored nutrient management practices based on soil texture type, which can lead to improved agricultural productivity and environmental impact.

Keywords: mineral nitrogen release; urea; soil texture type; potassium humate; coated; barley biomass; nutrient management



Citation: Swify, S.; Mažeika, R.; Volungevičius, J. Mineral Nitrogen Release Patterns in Various Soil and Texture Types and the Impact of Urea and Coated Urea Potassium Humate on Barley Biomass. *Soil Syst.* **2023**, *7*, 102. <https://doi.org/10.3390/soilsystems7040102>

Academic Editors: Yongchao Liang, Douglas Gueli, Heitor Cantarella and Flávio Henrique Silveira Rabelo

Received: 29 August 2023

Revised: 6 November 2023

Accepted: 9 November 2023

Published: 11 November 2023



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1. Introduction

Nitrogen is a crucial element for barley growth and serves as a fundamental component in various metabolic activities, encompassing the synthesis of proteins and the production of chlorophyll [1,2]. Urea is one of the most prevalent nitrogenous fertilizers and accounts for approximately 43% of global nitrogen fertilizer sales [3,4]. Urea is extensively utilized in the agricultural sector owing to its high nitrogen concentration and cost-effectiveness [5].

However, the efficiency of urea as a main nitrogen source can be influenced by several factors, including soil characteristics, microbial activity, and environmental conditions [6–9]. In commonly applied fertilizers such as urea, the predicted efficiency is around 30–70% of nitrogen application, but usually, the efficiency of urea is lower than 50% [10–13]. The nitrogen loss could cause ecological contamination via tainting groundwater by means of nitrate leaching and by adding to the emission of greenhouse gases into the atmosphere, with reports of up to $160 \text{ kg} \cdot \text{N} \cdot \text{ha}^{-1} \cdot \text{yr}^{-1}$ lost to leaching and up to $143 \text{ kg} \cdot \text{N} \cdot \text{ha}^{-1} \cdot \text{yr}^{-1}$ lost as greenhouse gases, which is a matter of great concern [13–15]. Therefore, it is essential to improve the use efficiency of urea fertilizer to reduce nitrogen loss [13,16,17].

The efficiency of urea-N fertilizer application can be enhanced by ensuring a balance between N supply and crop N demand, in conjunction with the minimization of N losses [13,18]. The utilization of controlled-release urea fertilizers (CRUF) is one strategy to minimize nitrogen losses and improve the uptake efficiency of the fertilizer [19–22]. Controlled-release urea fertilizers such as coated urea, which are intended to coordinate their N release pattern with crop N consumption rates, could potentially be a significant advance in resolving the synchrony issue [18,21,23–25] and reduce the rate of nitrogen loss to the environment [24,26–28].

Moreover, the application of CRUF is also a secure option for minimizing the damage to crop germination and increasing plant biomass [19,20,29–31]. The combination of inorganic fertilizers and organic materials by coating or granulation is progressively gaining popularity owing to its potential advantages on crop yields and soil health when compared to the use of organic material or inorganic fertilizer as the only source of nutrients [13,32–34]. Potassium humate, derived from organic matter, is known to enhance soil fertility and nutrient availability [35,36].

Humic substances are a type of macromolecular natural organic matter that comprises a polyelectrolyte with a negative charge [36–38] that comprises a polyelectrolyte with a negative charge [36–38]. This polyelectrolyte is characterized by the presence of a hydrophobic core and a diverse array of functional groups such as quinone, aldehyde, carboxyl, phenolic, and alcoholic hydroxyls, as well as ether [35,36,39–41]. Moreover, humic acid contains unbound carboxylic and amide groups, which demonstrate chelating capability, dispersibility, and adsorption when humic acid is used as a polymer [37,38]. This makes it suitable for use as a control-release agent and absorption enhancer in fertilizers [37,42]. Coating urea with humic acid can effectively slow down the release of urea by inhibiting the processes of ammonification and nitrification [32,37]. Therefore, the conversion rate of urea-N slowed due to the chemical reactions that occur between humic substances and urea, respectively. This is due to the bonding of urea-N with amino, carboxyl, and hydroxyl groups in humic molecules [37].

According to previous studies, it has been reported that combining urea with potassium humate can improve nitrogen use efficiency and mitigate losses through volatilization or leaching [35,39,40,43,44]. The application of a combination of urea with humic compounds enhances nitrogen transformation to the ammonium form $\text{NH}_4^+ \text{-N}$ rather than the ammonia form NH_3 , which would be expected to reduce environmental damage [22,34,39,40]. The higher bond strength with higher concentrations of humate can slow the release of urea into the ammonium form, which then also slows its conversion into the nitrate form, leading to lower N losses [34,37,39,41].

Moreover, the presence of humic acid can effectively impede the action of urease and thus decrease the rate of urea hydrolysis [45–47]. This phenomenon ultimately results in a diminished concentration of ammonium ($\text{NH}_4^+ \text{-N}$) in the soil, which consequently mitigates the hazards of ammonia (NH_3) volatilization and potential nitrification, leading to a significant reduction in N losses [22,45]. Humic acid has also exhibited advantageous properties in regulating soil acidification [10,48,49].

Furthermore, the application of urea potassium humate has been observed to stimulate the growth and development of roots, thereby resulting in a significant increase in root

biomass [50–52]. The humic-acid application also can increase soil water retention and reduce the inorganic fertilizer's solubility [53].

Coating urea with humate leads to a stable product [39] with controlled nitrogen release [39–41]. However, the effectiveness of this combination may vary depending on the soil type [19,54]. Different soils possess distinct physicochemical properties and microbial populations, which can influence nutrient availability and plant response [8,19,54,55].

Hence, the present investigation endeavors to (1) evaluate the patterns of mineral nitrogen release in diverse soil types, and (2) appraise the impact of urea and coated urea potassium humate on the production of barley biomass. By quantifying these aspects, we can further our understanding of the nitrogen dynamics in different soil types following application with uncoated and coated urea in different soil types and supply valuable information concerning nutrient management.

2. Materials and Methods

2.1. Nitrogen Sources

This research was conducted to compare urea as the main nitrogen fertilizer with coated urea potassium humate (UPH) as a modified urea compound fertilizer (coated form) in a pot experiment under glasshouse conditions (20 ± 2 °C and 60% Humidity). The nitrogen sources that were used (Figure 1) included Urea, which contains 46.2% as a total N, and coated urea potassium humate (UPH), which contains 40% N and 1% Potassium Humate; these were produced by ABAchema Company, Kaunas, Lithuania.

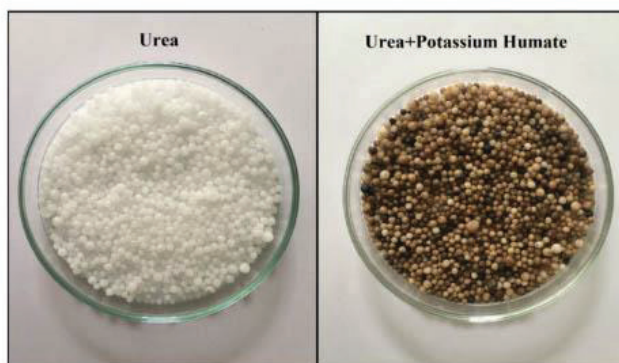


Figure 1. Nitrogen sources included urea granules and coated urea potassium humate granules.

2.2. Study Areas and Soil Characteristics

The study areas as shown in Figure 2 (in the Republic of Lithuania territory) are located in the mid-latitude, transitional climate zone. The soils are formed and developed under wet (600–820 mm) and cold (6.0–7.5 °C) climate conditions [56,57]. Four soil types used in our study were collected from Lithuania's agricultural soils. Soil profiles were classified and named according to the WRB 2022 classification [58]. The first soil was collected from the Rumokai (Vilkaviškis distr. mun.) research station field ($54^{\circ}41'41.3''$ N, $22^{\circ}59'35.0''$ E) of the Lithuanian Research Center of Agriculture and Forestry. The field soil type is Endogleyic Haplic Luvisol (Loamic, Aric) [58], which was chosen to represent the loam texture.

The second type was collected from the Dotnuva (Kėdainiai distr. Mun.) field ($55^{\circ}23'23.8''$ N, $23^{\circ}52'12.9''$ E) at the Lithuanian Research Center of Agriculture and Forestry. The soil type was Endogleyic Epistagnic Endocalcaric Cambisol (Loamic, Aric, Drainic) [58]

to represent the sandy loam texture. The third type was collected from Kazlu Ruda municipality ($54^{\circ}45'16.7''$ N, $23^{\circ}29'26.0''$ E). The soil is formed in limnoglacial sands and is therefore named Dystric Arenosol (Aric) [58]. The fourth type was collected from Vezaiciai (Klaipėda distr. Mun.) ($55^{\circ}42'41.6''$ N, $21^{\circ}26'25.5''$ E), which is the research station field of the Lithuanian Research Center of Agriculture and Forestry. The soil was Glosic Epigleyic Dystric Retisol (Clayic, Aric, Cutanic, Drainic) [58] and it is represented in sandy clay texture. Soil types and their physicochemical characteristics are shown in Table 1.

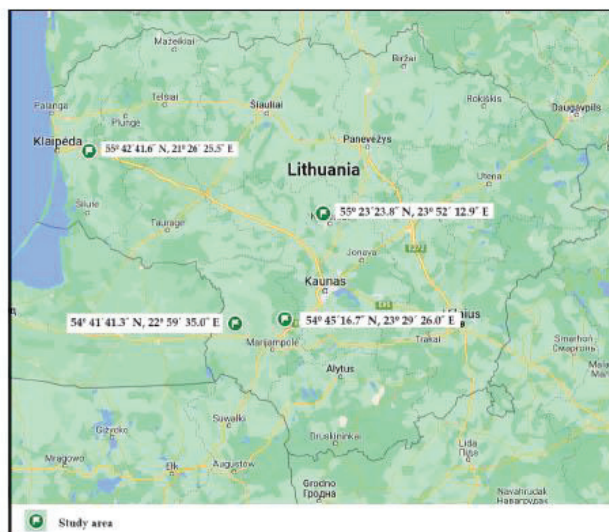


Figure 2. The study areas' locations (Source: Google Maps).

Table 1. Physicochemical characteristics of different soil types.

Soil Characteristics	Rumokai	Dotnuva	Kazlu Ruda	Vezaiciai
Soil Type	Endogleyic Haplic Luvisol (Loamic, Aric)	Endogleyic Epistagnic Endocalcaric Cambisol (Loamic, Aric, Drainic)	Dystric Arenosol (Aric)	Glosic Epigleyic Dystric Retisol (Clayic, Aric, Cutanic, Drainic)
Texture	Loam (L)	Sandy Loam (SL)	Sand (S)	Sandy Clay (SC)
pH _{KCl} mol/L	7.4	6.9	5.3	4.5
P ₂ O ₅ mg·kg ⁻¹	244	266	102	139
K ₂ O mg·kg ⁻¹	201	308	40	240
SOM* (%)	1.04	1.26	0.79	1.25
SOC** (%)	0.60	0.73	0.46	0.72
E _c mS/m	14.4	12.7	2.31	6.10
Total N (%)	0.148	0.151	0.013	0.120
N _{min} mg·kg ⁻¹	23.99	37.32	1.74	41.60
NH ₄ ⁺ -N mg·kg ⁻¹	2.06	1.33	0.98	3.68
NO ₃ ⁻ -N mg·kg ⁻¹	21.93	35.99	0.76	37.92

* SOM = Soil organic matter; ** SOC = Soil organic carbon.

2.3. Experimental Design and Treatments

A pot experiment was conducted at the glasshouse of the Lithuanian Research Center for Agriculture and Forestry, Agrobiological Laboratory in 2021 to investigate the effect of different soil and texture types on mineral nitrogen (N_{min}) release patterns by using conventional urea and coated urea potassium humate. The experiment was conducted for 45 days by growing spring barley (*Hordeum vulgare* L.) cultivar "Ema DS". The experimental design included 60 pots set in 4 groups (A, B, C, and D), one for each soil type, and each group consisted of 15 pots as shown in Figure 3. The pot size was 25 cm in diameter and 25 cm in height and was filled with 10 kg of soil packed to a bulk density of approximately 1.3–1.8 Mg m⁻³.

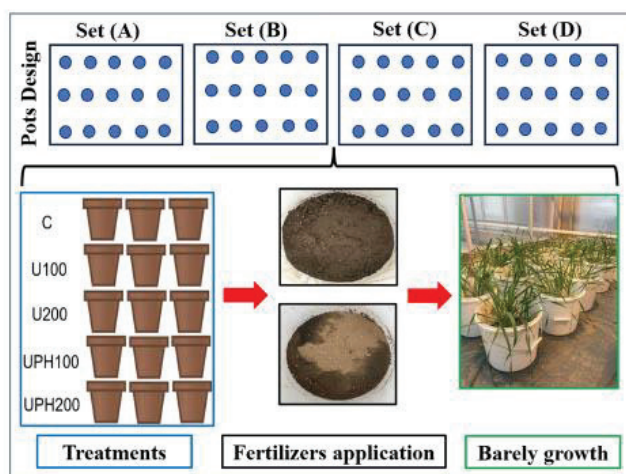


Figure 3. The general schema of the pot experiment included four sets of pots: loamy (A), sandy loam (B), sandy (C), and sandy clay (D) texture.

The pots were filled with 4 soil texture types (L, SL, S, and SC), and each group was filled with one soil texture type and divided into five treatments with three replicates. Treatments including control (C), urea 100 kg·N·ha⁻¹ (U100), urea 200 kg·N·ha⁻¹ (U200), coated urea potassium humate 100 kg·N·ha⁻¹ (UPH100), and coated urea potassium humate 200 kg·N·ha⁻¹ (UPH200) as shown in Figure 3.

The treatments were applied to the surface of the pots and then covered with a thin layer of soil and watered. The pots were maintained in the glasshouse climatic conditions (20 ± 2 °C and 60% Humidity) and irrigated manually according to their requirements. Soil samples were collected to a depth of 10 cm from each pot with a sample size of 100 g, commencing from day 1 of the experiment and subsequently on days 4, 7, 14, 21, 28, and 45, and this sequence of the dates was chosen based on a pre-study to study the release of these materials in incubation tests without plants. Spring barley (*Hordeum vulgare* L.) cultivar "Ema DS" was sown at a depth of 1 cm into the soil at equal intervals of distance. There are no additional mineral fertilizers applied.

2.4. Soil Sampling and Laboratory Analysis

Soil for the experiment was collected from the topsoil layer of four profiles at depths of 0–30 cm in order to represent the four various soil types (Table 1). The soil was air-dried and then ground to a size that could pass through a 2 mm sieve. Detailed analysis of the soil properties and mineral nitrogen content was performed by the Agrochemical Research Laboratory at the Lithuanian Research Center for Agriculture and Forestry. Soil pH was determined according to ISO 10390:2005 [59]. Soil-available K_2O and P_2O_5 were extracted by using soil suspension 1:20 (wt./vol) of ammonium lactate-acetic acid extraction (pH 3.7) and determined [60]. Soil electrical conductivity (Ece) determination was according to ISO 11265:1994 [61]. Total nitrogen was measured according to ISO 11261:1995 [62,63]. Mineral nitrogen in the top 10 cm of the pots was determined by using a spectrometric flow injection analysis (FIA) method developed by the laboratory, including both nitrate concentration (Sum of NO_3^- -N and NO_2^- -N) and ammonium concentration (NH_4^+ -N) [43]. The mineral nitrogen (Nmin) was calculated by adding the sum of nitrate and nitrite nitrogen to ammonium nitrogen. The organic soil carbon content was determined using dry combustion according to ISO 10694:1995 [64]. Barley vegetative material was cut 45 days after sowing and dried at +105 °C.

2.5. Statistics Analysis

The statistical analysis software IBM SPSS 25.0 (Armonk, NY, USA) was used for data on mineral N, ammonium NH_4^+ -N, nitrate NO_3^- -N, barley fresh weight, and dry matter. All the data were subjected to analysis of variance (ANOVA), and separate statistical significance by Duncan's multiple range test at the 5% level. Pearson's correlation was performed on the relationship between the time and mineral N release and its forms nitrate NO_3^- -N and ammonium NH_4^+ -N.

3. Results

3.1. Mineral Nitrogen Patterns in Different Soil and Texture Types

The concentration of mineral nitrogen and its main forms (NH_4^+ -N and NO_3^- -N) exhibited distinct variations and different patterns of release according to the soil and texture type as shown in Figure 4. The concentration of ammonium-N in the top 10 cm of soil in the pots increased rapidly after urea application, reaching a peak after 2–7 days, followed by a gradual decline to near-zero levels in all soils except the Retisol (sandy clay) as in Figure 4. The peak of ammonium concentration varied with soil type, urea source, and rate, and it was highest in the Retisol (sandy clay), followed in sequential order by the Cambisol (sandy loam), Luvisol (loam), and Arenosol (sand). The highest peak concentrations were in the U200 and UPH200 treatments. However, there was no significant linear relationship between ammonium-N concentration and time.

Conversely, the release patterns of NO_3^- -N exhibited a degree of variation after a fortnight (the fifth point in the graphs of NO_3^-) as shown in Figure 4. The concentration of nitrate NO_3^- -N exhibited a highly significant correlation with time across all treatments and soil types (Table 2). The highest peak was found in the Retisol (sandy clay), followed by the Luvisol (loam), Cambisol (sandy loam), and Arenosol (sand). Notably, U200 treatment achieved the highest significant mean of NO_3^- -N concentration in Cambisol followed by the treatment of UPH200 in Luvisol. The nitrate-N concentration increased at a linear rate over the 45 days of measurements, without further change until the end of the experiment (Figure 4, Table 2). The total mineral N also increased with time but only achieved significance at the 5% level in 11 of the 16 soil-fertilizer combinations tested (Figure 4, Table 2). At the conclusion of the experiment on day 45, soil in the pots to a depth of 30 cm was analyzed for mineral N. Among the soils (Table 3), the highest mineral N concentrations were in the Retisol (sandy clay), followed by the Cambisol (loam) and Luvisol (sandy loam), while the lowest concentrations were in the Renosol (sand). Among the fertilizer treatments, the highest concentration was in U200 followed by UPH200, UPH100, and U100.

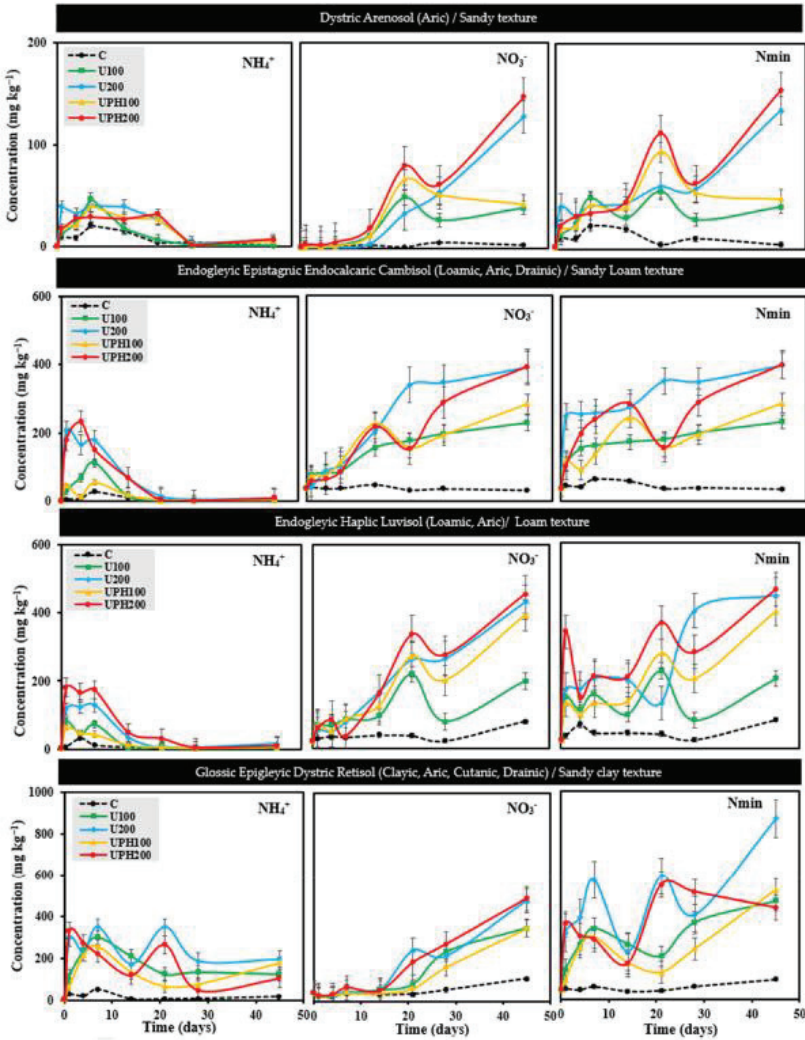


Figure 4. The release patterns of mineral nitrogen (Nmin) and its forms ammonium (NH_4^+-N) and nitrate (NO_3^--N) as a relation between concentration ($\text{mg}\cdot\text{kg}^{-1}$) and time (days) in different soil and texture types.

Table 2. Pearson's correlation between the time, nitrate (NO_3^- -N), and mineral nitrogen (Nmin) release concentration ($\text{mg}\cdot\text{kg}^{-1}$) in different soil types.

Treatments	Mean		Correlation Coefficient		p-Value	
	NO_3^- -N	Nmin	NO_3^- -N	Nmin	NO_3^- -N	Nmin
Dystric Arenosol (Aric)/Sandy Texture						
Control (C)	2.22	10.36	0.612	-0.249	0.107	0.552
U100	16.70	30.52	0.827 *	0.519	0.011	0.188
U200	27.98	51.68	0.953 **	0.918 **	0.000	0.001
UPH100	22.29	40.32	0.770 *	0.593	0.025	0.121
UPH200	40.24	58.23	0.961 **	0.920 **	0.000	0.001
Endogleyic Epistagnic Endocalcaric Cambisol (Loamic, Aric, Drainic)/Sandy loam texture						
Control (C)	36.88	43.57	-0.432	-0.422	0.285	0.298
U100	130.46	155.84	0.948 **	0.826 *	0.000	0.012
U200	194.21	271.25	0.942 **	0.785 *	0.000	0.021
UPH100	144.50	158.10	0.898 **	0.844 **	0.002	0.008
UPH200	161.42	212.78	0.964 **	0.819 *	0.000	0.013
Endogleyic Haplic Luvisol (Loamic, Aric)/Loamy texture						
Control (C)	37.80	45.95	0.740 *	0.455	0.036	0.258
U100	104.26	131.79	0.742 *	0.478	0.035	0.231
U200	165.83	219.56	0.989 **	0.846 **	0.000	0.008
UPH100	152.56	175.51	0.957 **	0.924 **	0.000	0.001
UPH200	178.23	255.47	0.956 **	0.737 *	0.000	0.037
Glossic Epigleyic Dystric Retisol (Clayic, Aric, Cutanic, Drainic)/Sandy clay texture						
Control (C)	42.99	53.15	0.879 **	0.753 *	0.004	0.031
U100	105.72	260.86	0.946 **	0.793 *	0.000	0.019
U200	139.95	425.08	0.958 **	0.750 *	0.000	0.032
UPH100	92.28	216.81	0.922 **	0.754 *	0.001	0.031
UPH200	144.67	331.69	0.969 **	0.621	0.000	0.100

**Correlation is significant at the 0.01 level (two-tailed). *Correlation is significant at the 0.05 level (two-tailed).

Table 3. The effect of the soil texture type and urea fertilizers application on accumulative mineral nitrogen and its forms (NH_4^+ -N and NO_3^- -N) in the surface layer 0-30 cm depth after 45 days.

Soil Texture Type	NH_4^+ -N	NO_3^- -N	Nmin
	$\text{mg}\cdot\text{kg}^{-1}$		
Sand	16.33 ^a	21.89 ^a	38.22 ^a
Sandy loam	43.03 ^a	133.49 ^c	168.31 ^b
Loam	37.92 ^a	127.74 ^{bc}	165.66 ^b
Sandy clay	137.55 ^b	105.12 ^{bc}	257.52 ^c
p-value	$p < 0.003$	$p < 0.002$	$p < 0.001$
Treatments			
Control (C)	9.87 ^a	29.97 ^a	38.26 ^a
U100	56.60 ^{abc}	89.29 ^b	144.75 ^b
U200	94.84 ^c	132.00 ^d	241.89 ^d
UPH100	45.71 ^{abc}	102.91 ^{bcd}	147.69 ^b
UPH200	86.51 ^{bc}	131.14 ^{cd}	214.54 ^{bcd}
p-value	$p < 0.021$	$p < 0.003$	$p < 0.001$

Numbers followed by the same letter in the same column are not significantly different at the 5% level of Duncan's test.

3.2. Impact of Soil and Texture Types on Mineral Nitrogen Accumulation

The accumulative mineral nitrogen (N_{min}) released during 45 days of the pot experiment and its forms (NH₄⁺-N and NO₃⁻-N) were significantly ($p \leq 0.01$) influenced by the soil texture type (Table 3). The Arenosol with a sandy texture exhibited the lowest accumulative mineral nitrogen, ammonium, and nitrate concentration at means of 38.22, 16.33, and 21.89 mg·kg⁻¹, respectively. Otherwise, the highest significant concentration of mineral nitrogen and ammonium was observed in the Retisol with sandy clay texture at 257.52 and 137.55 mg·kg⁻¹, respectively. By contrast, the highest significant concentration of nitrate was observed in Cambisols with sandy loam texture at 133.49 mg·kg⁻¹.

Furthermore, the urea and coated urea treatments significantly ($p \leq 0.01$) affected the mineral nitrogen, ammonium, and nitrate (Table 3). The U200 treatment recorded the highest significant concentration of the mineral nitrogen at 241.89 mg·kg⁻¹ followed by UPH 200 at 214.54 mg·kg⁻¹ and UPH100 at 147.69 mg·kg⁻¹. Moreover, the application of U200 significantly increased the accumulation of ammonium and nitrate at 94.84 mg·kg⁻¹ and 132 mg·kg⁻¹, respectively. Treatments of UPH200 and UPH100 showed significantly higher concentrations of nitrate NO₃⁻-N than U100 as shown in Table 3. By contrast, UPH100 exhibited significantly lower levels of ammonium NH₄⁺-N concentration than U100.

One of the important factors that could affect the release and accumulation of mineral nitrogen is the soil pH. These soil types, Arenosol, Cambisol, Luvisol, and Retisol, had varied in their pH values as presented in Table 1. Based on the USDA classification of pH [65], the Retisol is a very strongly acidic soil at pH 4.5 followed by Arenosol, which is strongly acidic soil at pH 5.3 [65]. Otherwise, Cambisol and Luvisol are classified as neutral and slightly alkaline soil at 6.9 and 7.4 [65].

The application of urea and coated urea increased the pH of the treated soils after 45 days, but there were no significant differences observed as shown in Table 4. The application of urea and coated urea increased the values of the pH of the Arenosol compared to the control. Otherwise, the application of the urea and coated urea did not affect the pH in Cambisols. Moreover, treating Luvisols with urea and coated urea slightly decreased the pH. However, the application of U200 increased the pH in the Retisol compared to the other treatments. The pH can affect the release of nitrogen by delaying the hydrolysis of urea and inhibiting urease activity as well as quickening the nitrification process [66,67]. The pH of the soil played a vital role in delaying the peak of the ammonium in the Arenosols and Retisols to 7 days compared to the other soil types, which reached the peak in 2–4 days.

Table 4. The changes in pH values of the 0–10 cm layer of the pots after the application of urea and coated urea in different soil types.

The Application	Arenosol (S)	Cambisol (SL)	Luvisol (L)	Retisol (SC)
Before	5.3	6.9	7.4	4.5
Control	6.00 ^a	6.90 ^a	7.03 ^b	4.27 ^{abc}
U100	6.20 ^{abc}	6.93 ^a	7.03 ^b	4.03 ^a
U200	6.63 ^c	6.83 ^a	6.93 ^{ab}	4.67 ^c
UPH100	6.37 ^{abc}	6.83 ^a	7.00 ^{ab}	4.10 ^a
UPH200	6.47 ^{abc}	6.87 ^a	6.93 ^{ab}	4.33 ^{abc}
p-value	0.16	0.29	0.68	0.11

Numbers followed by the same letter in the same column are not significantly different at the 5% level of Duncan's test.

3.3. Availability Assessment of Mineral Nitrogen in the Soil

The results of the descriptive statistics exhibit significant fluctuations in the soil contents of mineral nitrogen, which are presented in Table 5. The data reveal that N_{min} soil content varied between 10.36 and 8.23 mg·kg⁻¹ in Arenosol (sandy), while in Cambisol (sandy loam), it ranged from 43.57 to 271.25 mg·kg⁻¹, from 45.95 to 255.47 mg·kg⁻¹ in Luvisol (loamy), and in Retisol (sandy clay), it ranged from 53.15 to 425.08 mg·kg⁻¹.

Table 5. Descriptive statistics of soil mineral nitrogen (Nmin), ammonium, and nitrate of the study soil texture types

	Soil Texture Type	Min.	Max.	Mean	SD	CV (%)
Nmin (mg·kg ⁻¹)	Sand	10.36	58.23	38.22	18.85	23.41
	Sandy loam	43.57	271.25	168.31	84.25	104.61
	Loam	45.95	255.47	165.66	81.46	101.15
	Sandy clay	53.15	425.08	257.52	138.76	172.29
NH ₄ ⁺ -N (mg·kg ⁻¹)	Sand	8.14	23.70	16.33	5.77	7.17
	Sandy loam	6.69	80.96	43.03	35.26	43.78
	Loam	8.15	77.24	37.92	27.45	34.08
	Sandy clay	16.53	221.70	137.55	76.24	94.66
NO ₃ ⁻ -N (mg·kg ⁻¹)	Sand	2.22	40.24	21.89	14.03	17.43
	Sandy loam	36.88	194.21	133.49	59.01	73.28
	Loam	37.80	178.23	127.74	57.57	71.48
	Sandy clay	42.99	144.67	105.12	41.24	51.21

The coefficient of variation (CV) is a valuable statistic to compare the degree of variation between different datasets, even if the means differ significantly. A coefficient of variation (CV) of less than 10% indicates low variability, 10–100% suggests moderate variability, and a CV greater than 100% indicates high variability [68]. In this research, the coefficient of variation (CV) of the soil Nmin was determined. The CV of the soil Nmin was found to be 23.41 in the Arenosol with a sandy texture, which indicated that the sandy texture samples had moderate variability of the soil Nmin. Conversely, the Cambisol (sandy loam), Luvisol (loamy), and Retisol (sandy clay) soils had a CV greater than 100%, signifying high variability of mineral nitrogen in these soil samples.

The availability of Nmin in soils can be categorized as Low < 40, Moderate 40–80, and High > 80 mg·kg⁻¹ [69]. Based on this classification, the Arenosol (sandy) soil had a low availability of mineral nitrogen at 38.85 mg·kg⁻¹. In contrast, the Cambisol (sandy loam), Luvisol (loamy), and Retisol (sandy clay) soils had a high availability of mineral nitrogen at 168.31, 165.66, and 257.52 mg·kg⁻¹, respectively.

3.4. Effect of Urea Compounds on Germination and Barley Biomass

Germination of the barley seed in the pots commenced on the fourth day following the application of the fertilizers with a rate of 70–90%. The utilization of urea fertilizers impacted the germination of barley significantly ($p \leq 0.01$).

In all the soil texture types, UPH200 and U200 exhibited noticeably lower significant germination rates compared to the control. Conversely, no significant differences were observed between UPH100 and U100 in comparison to the control. The outcome in terms of barley green biomass yield at the conclusion of the 45 days in the pots experiment under the glasshouse conditions is presented in Figure 5.

Furthermore, the utilization of urea and coated urea potassium humate treatments had a significant effect ($p \leq 0.05$) on the barley's green biomass. Among these treatments, UPH200 recorded the highest significant mean of 31.44 g followed by U200 with a similar mean of 31.25 g. Conversely, there was no significant disparity recorded between U100 with a mean of 25.91 g, and UPH100 with a mean of 25.05 g in comparison to the control at 20.47 g. Within the soil type groups, the treatments displayed significant differences from one another as shown in Figure 6.

Notably, within the Arenosol (sandy), the application of these treatments significantly impacted the green biomass of barley ($p \leq 0.01$). The highest significant biomass was obtained under treatment of UPH200 at 16.57 g followed by U200 at 14.71 g. U200 and UPH100 had no differences observed between each other. Similarly, U100 showed no significant difference when contrasted with the control (Figure 6).



Figure 5. Barley's green biomass after the application of urea and coated urea potassium humate in different soil types with different textures: loamy (A), sandy loam (B), sandy (C), and sandy clay (D).

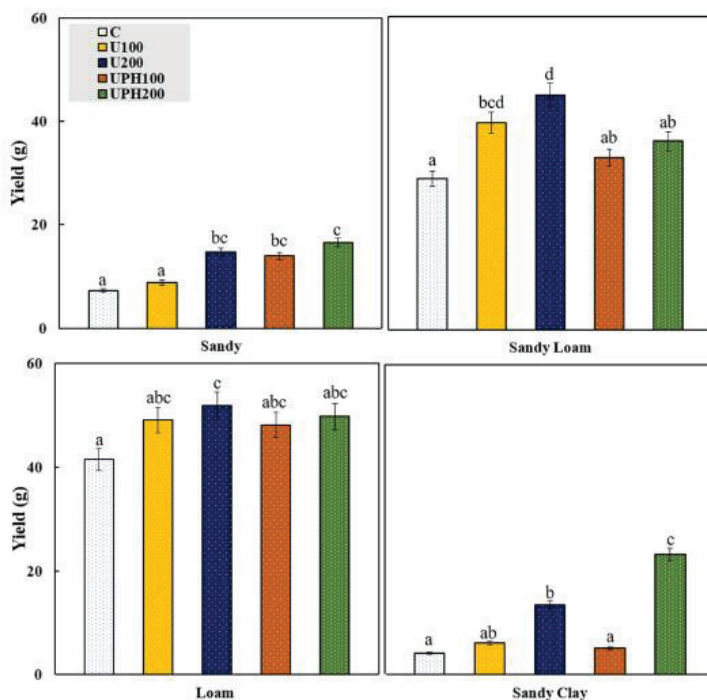


Figure 6. The effect of urea (U100 and U200) and coated urea potassium humate (UPH100 and UPH200) on the green barley biomasses in four soil types with different soil textures, Arenosol (sandy), Cambisol (sandy loam), Luvisol (loam), and Retisol (sandy clay). The columns with the same letter are not significantly different at the 5% level of Duncan's test.

In the Retisol with sandy clay texture, there were no differences between the biomass under the treatments of U100 and UPH100 in comparison to the control. However, UPH200 recorded the highest significant biomass with an average of 23.32 g followed by U200 with approximately 42% less biomass at 13.45 g.

Moreover, the green biomass was increased significantly ($p \leq 0.05$) by N application in the Cambisol (sandy loam). The U200 and U100 treatments had the highest significant effect on biomass with averages of 45.04 g and 39.66 g, respectively. UPH200 and UPH100 did not affect the biomass compared to one another and control (Figure 6).

The fourth soil texture type is loamy, which represented the Luvisol even though its treatments recorded the highest values of green biomass of barley compared to the other soil texture types. However, the treatment had no statistically significant effect on the barley biomass. U200 recorded the highest significant average of 51.8 g followed by UPH200 at 49.7 g as shown in Figure 6. Furthermore, the soil and texture types had a significant ($p \leq 0.05$) impact on the dry matter of barley. The sequence of average dry matter values for each respective soil texture type was, as such, sandy loam (Cambisol) with the highest dry matter at 75.27 g followed by sandy clay (Retisol) at 71.55 g. The loamy (Luvisol) and sandy (Arenosol) soil recorded lower dry matter at 71.03 g and 70.15 g, respectively. On the other hand, the treatments showed no significant effects on the dry matter. The average dry matter values for each treatment, in sequential order, are as follows: U200: 74.96 g followed by UPH200: 73.1 g, UPH100: 71.42 g, U100: 70.84 g, and the control: 69.68 g.

4. Discussion

Observing the impact of both conventional urea and coated urea potassium humate on the dynamics of soil mineral nitrogen release in various soil with different texture types, we reported that the fertilization treatments significantly ($p \leq 0.01$) generated different release patterns of mineral nitrogen and its forms (NH_4^+ -N and NO_3^- -N) as shown in Figure 4.

Regarding the fertilization treatments, the control recorded the lowest concentration of mineral nitrogen and its forms among all the treatments. Urea treatments obtained a significantly higher concentration of ammonium than coated urea potassium humate treatments in all soil and texture types in the following sequences U200 > UPH200 and U100 > UPH100. The explanation for the above is due to urea's rapid hydrolysis into ammonia (NH_3) and ammonium (NH_4^+) forms once applied in the soil [70,71] and an intensive nitrification process started so early [70,72]. The other reason is that coating urea with potassium humate caused a delay of 1–4 days in the peak of ammonium in various soils [12,22,37]. Potassium humate could absorb the ammonium due to the extensive porous surface area and the high cation exchange capacity [73]. Moreover, the reduced NH_4^+ -N concentration observed as a result of the utilization of coated urea potassium humate treatments could potentially be attributed to the existence of a substantial quantity of acidic functional groups provided by the potassium humate [13,34,74].

This rapid release and the high concentration of ammonium and nitrate caused by urea treatments can be the main reasons for nitrogen loss via volatilization and leaching [75,76]. Therefore, coated urea potassium humate can provide a more enduring process of nitrogen release as it flattens the peak NH_4^+ -N concentration, which would be expected to slow the nitrification and denitrification processes, allows more mineral N uptake by the plant, and leads to reduced N losses [22,37,47,77].

Among the four soil texture types, the mineral nitrogen and its forms (NH_4^+ -N and NO_3^- -N) showed different patterns of release based on the variation in soil characteristics [8,70,78–80]. That implies that the chemical–physical traits of the soil that receives the fertilizer can significantly impact the fertilizers' efficacy and release rate [6,81]. It has been observed that Arenosol (sandy) exhibits the lowest concentration of mineral nitrogen right from the outset and this trend persists even after the application of fertilizers with low availability and low variability based on %CV [68]. Probably, the low content of nitrogen in Arenosol is because it is a light soil (i.e., low cation exchange capacity) [70,78,81]. The

peak of ammonium was recorded in the Arenosol, which is represented by a sandy texture after 7 days. Relative to the other soil types such as Cambisol and Luvisol, the peak of ammonium was delayed in Arenosol. The explanation for the delayed peak of ammonium in sandy soil (Arenosol) may be that the remainder of ammonium was consumed through processes of nitrification and leaching [78,79], or owing to the absence of microbial activity in this soil texture type [73,78,80]. The concentration of ammonium represented approximately 25% of the mineral nitrogen content in Arenosols.

Furthermore, Arenosol recorded the lowest content of nitrate, possibly due to low microbial activity in this soil type. The limited microbial activity in this soil type is due to its low organic matter content as presented in Table 1 [78]. This phenomenon can be attributed to the high potential for leaching losses of nitrate [78,81]. Notably, nitrate (NO_3^-), which is a negatively charged ion, is not retained by soil particles and is prone to leaching through the soil. As sandy soils have a relatively lower water-holding capacity, nitrates tend to leach at a faster rate as compared to soils with finer textures [78].

In Retisols (sandy clay), the low pH (Table 4) played an essential role in delaying urea hydrolysis due to inhibiting the urease enzyme activity [10,13,70]. However, the sandy clay (Retisol) soil obtained a higher significant concentration of mineral nitrogen and both forms of ammonium and nitrate compared to the other soil types. Due to the low pH, the peak of ammonium was delayed and recorded after 7 days, and at the time of the ammonium peak it comprised 44.4% of the mineral nitrogen content. Moreover, the highest significant concentration of nitrate was observed in Retisols with sandy loam texture.

There were no significant differences in mineral nitrogen concentration and its forms between the Cambisol (sandy loam) and Luvisol (loamy) (Table 5). The release was very rapid in Cambisol as a sandy loam textured soil. Therefore, the peak of NH_4^+-N derived from the fertilizer treatments and present in the soil was obtained at the beginning of the second day of the experiment. By contrast, the Luvisol present in a loamy texture obtained the peak after 4 days. The ammonium concentration represented approximately 30.7% and 33.3% of the mineral nitrogen content in the Luvisol and the Cambisol, respectively.

These soil types with a higher mineral nitrogen content are located in central and western parts of Lithuania, which are more fertile than the soils of the eastern part [81,82]. These findings were similar to a previous study on the mineral nitrogen content in the Lithuanian agricultural lands in 2014 [81]. The study revealed that sandy soils had the lowest levels of Nmin, while loamy sand and sandy loam soils had average levels. On the other hand, medium loam, clay loam, and clay soils had high levels of Nmin [81]. The explanation is that heavier textured soils contain larger amounts of mineral nitrogen with high availability [81,83].

The dynamics accumulation of mineral nitrogen and nitrate (NO_3^-) increased approximately linearly starting 1–2 weeks after application in all fertilizers treatments (Table 2). By contrast, ammonium concentrations increased rapidly to a peak 2–7 days after application followed by a decrease as the ammonium-N nitrified to nitrate, which means the nitrification process started at a very rapid rate [6]. The explanation is that, as time progresses, the levels of mineral nitrogen and its forms (NH_4^+-N and NO_3^--N) can increase due to the disintegration of fertilizer compounds [1,43,73]. However, the release rate possibly does not correlate in a linear relation with the time because that process goes according to the needs of the plants for nutrients and their uptake [73,84]. The crucial role of microbial activity in the soil cannot be overlooked in this process [1,73].

The ammonium demonstrated a peak net accumulation after 28 days of the experiment, and nitrate exhibited persistent net accumulation until the conclusion of the experiment, owing to the continued presence of exchangeable NH_4^+-N in the soil as illustrated in Figure 4 [6]. What is more, the observed increase in the accumulation of NO_3^--N toward the end of the experiment suggests a higher possibility for nitrification and, generally, for nitrogen mineralization and transformation [6].

Additionally, the barley's green biomass was influenced significantly ($p \leq 0.05$) by the application of urea and coated urea potassium humate treatments. The treatment of

UPH200 recorded the highest green biomass followed by U200 > U100 > UPH100, respectively. As illustrated in Figure 6, there were significant differences among the treatments within the soil type groups. Luvisol (loamy) under the treatments of urea and coated urea potassium humate obtained the highest biomass compared to the other soil types even though its accumulative mineral nitrogen during the investigation was less than the Cambisol (sandy loam) and Retisol (sandy clay) soils. There were no significant differences among the fertilization treatments for the barley biomass observed in Luvisol (Figure 6). The increase in the green biomass in Luvisol can be attributed to the nitrate concentration exhibiting a greater magnitude in comparison to the ammonium concentration within the loamy soil. Consequently, this led to a decreased loss of nitrogen and an increase in plant uptake, ultimately resulting in a higher yield of green biomass [85].

The Cambisol (sandy loam) exhibited the second highest values of the green biomass under the application of urea and coated urea potassium humate with notable ($p \leq 0.05$) variations among its fertilization treatments as depicted in Figure 6. The application of urea in Cambisol resulted in higher green biomass in comparison to the treatments of coated urea potassium humate. U200 showed a significantly higher biomass in comparison to UPH200 and UPH100, although no significant differences were observed between U100 and the other treatments. Cambisol is an agricultural land with good levels of nitrogen and neutral pH soil [81]. Therefore, the application of urea and coated urea took the normal path of release which leads to good productivity [86].

The Arenosol (sandy soil) impacted the green biomass of the barley significantly ($p \leq 0.01$). However, it is notable that the sandy soil displayed the lowest accumulative mineral nitrogen levels across all treatments. The treatments of coated urea potassium humate exhibited a significantly higher biomass of barley, especially with a high nitrogen application rate at 200 kg-N-ha^{-1} followed by U200 > UPH100 with the same mean. Interestingly, the application of coated urea potassium humate proved to be more efficacious in promoting the highest significant biomass yield, as compared to both the urea and control treatments in Arenosol. This finding indicates that the implementation of coated urea potassium humate has the potential to enhance fertilizer use efficiency while concurrently alleviating N loss [46]. This is primarily due to the reduction in the rate of urea hydrolysis and N fertilizer conversion in the soil [45,46,87].

On the other hand, the sandy clay soil (Retisol) recorded the lowest values for the barley biomass. The coated urea potassium humate recorded the highest significant biomass followed by urea with the same application rate at 200 kg-N-ha^{-1} . The unimpressive barley biomass yielded in the sandy clay soil, despite it exhibiting the highest significant concentration of mineral nitrogen. The explanation is found in the sensitivity to aluminium toxicity, which is caused by very high levels of aluminium dissolved in the soil water [88]. It is one of the factors that lead to a decrease in barley yields in acid soils [88,89]. This mineral is particularly detrimental to barley due to its high sensitivity toward it [88].

5. Conclusions

Controlled-release fertilizers such as urea coated with potassium humate have the capacity to enhance the levels of soil mineral nitrogen. This includes the fundamental forms (ammonium $\text{NH}_4^+\text{-N}$ and nitrate $\text{NO}_3^-\text{-N}$) content, thereby fulfilling the nitrogen necessities for the growth of barley. The potassium humate as a coating cover can be a beneficial instrument to mitigate the risk of N loss by delaying the release of nitrogen in ammonium form for 1–4 days to mitigate nitrogen losses by leaching or volatilization which is caused by the rapid release of urea. However, the efficacy of such fertilizers is significantly reliant on their chemical properties and application rate, as well as the chemical–physical properties of the soil in which they are applied. The addition of different fertilizer materials elicited varied responses from the soils. The coated urea potassium humate granules proved to be more efficient in soils such as Arenosol (sandy) and Retisol (sandy clay) than the Cambisol (sandy loam) and Luvisol (loam) in terms of maintaining optimal nitrogen levels and reducing the risk of nitrogen losses.

Author Contributions: Conceptualization, R.M. and S.S.; methodology, R.M., J.V. and S.S.; formal analysis, R.M.; investigation, S.S.; data curation, S.S.; writing—original draft preparation, S.S.; writing—review and editing, R.M. and J.V.; visualization, S.S.; supervision, R.M. All authors have read and agreed to the published version of the manuscript.

Funding: This research received no external funding.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: The datasets generated and analyzed during the current study are available from the corresponding author upon reasonable request.

Acknowledgments: The authors would like to thank everyone from the Rumokai, Dotnuva, and Vezaicai experimental stations of the Lithuanian Research Centre for Agriculture and Forestry for providing help during the experiment, including sampling collection. We also express our gratitude to AB Achema Scientific Experimental Laboratory, Lithuania, for providing us with the fertilizer materials.

Conflicts of Interest: The authors declare that they have no known competing financial interest or personal relationships that could have appeared to influence the work reported in this paper.

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Review

Review: Modified Urea Fertilizers and Their Effects on Improving Nitrogen Use Efficiency (NUE)

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Abstract: Urea has served as the primary nitrogenous fertilizer globally since the early 1950s. It is widely recognized as the most concentrated nitrogen source, containing approximately 46% nitrogen. Presently, around 220 million t/year of urea compounds are manufactured globally to fit the requirements of the agricultural sector. However, a significant drawback of this is that approximately 30–35% of the urea used in soil can be lost to the environment because of its limited effectiveness. Enhancing the efficiency of urea utilization can be achieved by regulating the release of urea-nitrogen in the soil. Numerous researchers have reported that the use of slow or controlled fertilizers can regulate the release and accumulation of nitrogen in the soil. Moreover, the augmentation of soil nitrogen levels can be accomplished by using the slow or controlled release of urea fertilizers. The regulation of the release process can play a vital role in the peril of N loss. This can be effectively alleviated by delaying the release of nitrogen in ammonium form configuration for several days. This delay functions to diminish nitrogen losses, which are caused by the rapid hydrolysis of urea, and loss by leaching or volatilization. Therefore, this review aims to comprehensively explore the use of conventional urea and various materials employed for modifying urea. It will explain the distinctions among modification processes and their respective mechanisms. This review will also discuss the pros and cons of applying slow- and controlled-release nitrogen, the impact of modified urea compounds on crop productivity, and nitrogen use efficiency (NUE).

Keywords: modified urea; nitrogen loss; slow release; coating; uncoating; nitrogen use efficiency



Citation: Swify, S.; Mažeika, R.; Baltrusaitis, J.; Drapanauskaitė, D.; Barčauskaitė, K. Review: Modified Urea Fertilizers and Their Effects on Improving Nitrogen Use Efficiency (NUE). *Sustainability* **2024**, *16*, 188. <https://doi.org/10.3390/su16010188>

Academic Editor: Roberto Mancinelli

Received: 14 November 2023

Revised: 16 December 2023

Accepted: 19 December 2023

Published: 25 December 2023



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1. Introduction

Presently, several challenges have emerged with the growing world population. The most important challenge is food security. Crop production requires nitrogenous fertilizers in relatively large amounts, it's making the nutrient most often deficient, especially with the loss of soil fertility.

Urea, as one of the most important nitrogenous fertilizers, is a major player in plant nutrition and soil fertility. Urea is the cheapest and richest fertilizer in nitrogen (46%). Despite urea being the root of nitrogenous fertilization, it has less effectiveness in comparison with other nitrogen fertilizers. The urea's inadequate efficiency arises from its rapid release in the soil, leading to nitrogen loss. Upon application of urea fertilizer to the soil, it can move away from the plant's root or soil system and become unattainable for the plants due to many processes such as denitrification, leaching, immobilization, and fixation [1–4]. Moreover, crops often recover only a small portion of nitrogen from soluble N fertilizers like urea, typically ranging between 30% and 40%. This inefficiency comes with a significant environmental cost [3,5–8].

Therefore, nitrogen loss through NH_3 volatilization, caused by surface-applicable urea, is a critical environmental issue since it is influenced by soil properties and meteorological conditions. All of the aforementioned factors resulted in reduced urea use efficiency and an increased demand for nitrogen fertilizers. The agricultural sector will need to use even greater quantities of fertilizer to live up to the rising food demand [9]. The use of conventional urea impairs agronomic nitrogen use efficiency (ANUE), limiting yields [4,10].

Accordingly, many technological interventions, especially those geared towards the use of different compounds based on ecological raw materials, improve urea use efficiency as a main fertilizer of nitrogen and reduce the emissions to the environment [10]. Making nitrogen fertilizer in a controlled- or slow-release form is one of the most prevalent strategies to decrease nitrogen losses, and several methods and materials have been described [10,11]. Thus, the release of nitrogen is controlled so that the amount of excess nitrogen in the soil is reduced in the form of ammonium, which is lost via ammonia to the air, as well as nitrates entering the water, thereby reducing water and air pollution [10–12].

To this end, it is important to understand the difference between modified urea nitrogen fertilizer types and the benefits of using them. Therefore, this review aims to focus on conventional urea usage and the technologies that are used to modify urea, the different materials used for urea modification, the differences between the modification processes, and the differences in their mechanisms. This review also outlines the advantages and disadvantages of each process.

2. The Methodology for Preparing This Review

This review extensively covers the establishment of modified urea (slow- and controlled-release) fertilizers. To gather relevant research articles, a literature review was conducted in two steps, as follows:

- i. Initially, a search was conducted on Web of Science and Google Scholar using specific keywords like “slow and controlled release fertilizer”, “coated materials”, “coated urea”, “advantages of controlled-release fertilizers”, “disadvantages of slow-release fertilizers”, and “nitrogen use efficiency”. Further inclusion of relevant articles was based on their pertinence to the review’s topic. Figure 1 provides a depiction of the article count from 1970 to 2022.
- ii. Subsequently, the gathered articles were carefully reviewed and classified into distinct sections for the purpose of this review paper. Some articles were cited multiple times to showcase their relevance to different aspects. Overall, 120 articles published between 1970 and 2022 were chosen, and additional references were included to bolster their relevance to specific research topics.

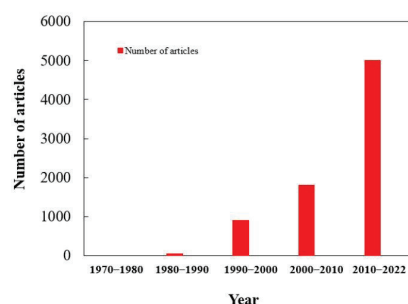


Figure 1. Number of articles published during the period from 1970–2022.

3. Conventional Urea Application

Manufacturing urea fertilizer commercially involves the combination of gaseous CO_2 and liquid ammonia under conditions of high compression and temperature. After dehydration, ammonium carbamate is added, and the mixture is passed through a granulator or prilling tower to produce either prills or pellets.

Periodically, farmers require nitrogen fertilizer to supply the precise nutrients necessary for optimal plant growth in their farms and gardens. Urea stands out as the predominant form of solid nitrogen fertilizer, especially in developing regions of the world [13]. Around 80–85% of the production is used as a fertilizer [13,14]. Notably, over 40% of global food production relies on urea fertilization [14]. Around 57% of the world's agricultural nitrogen usage is currently met by urea addition, and the demand for urea is expected to rise by 1.5% annually shortly [13,15,16].

Furthermore, urea is the most extensively used solid nitrogenous fertilizer in the world, and it has excellent water solubility. In comparison to other nitrogenous fertilizers, urea offers more nitrogen quantity to plants and soil because of its high nitrogen concentration (46%). One of the advantages of using conventional urea is that it holds flexibility in application methods. It can be broadcast over large areas, applied in a band near the plant roots, or incorporated into the soil through tillage. This makes it an excellent choice for both small- and large-scale farming operations. However, there are also some potential drawbacks to using conventional urea.

The transformation processes of N as urea fertilizer to the plant in the soil system are shown in Figure 2. Once urea is applied to soil, urea is hydrolyzed by the urease enzyme, which must be converted to ammonium before it can be used by plants [3,16]. Ammonia (NH_3) possesses the highest content of N, nearly 82%, and plants can use it directly [3]. However, before plants can utilize ammonia (NH_3) it undergoes conversion from ammonia to ammonium (NH_4) and nitrates. As a result, urea, which has an NUE (nitrogen use efficiency) of only 50%, faced hurdles in gaining widespread acceptance as a primary nitrogen fertilizer due to the significant nitrogen loss pathways through the volatilization, fixation, denitrification, and leaching as shown in Figure 2 [17].

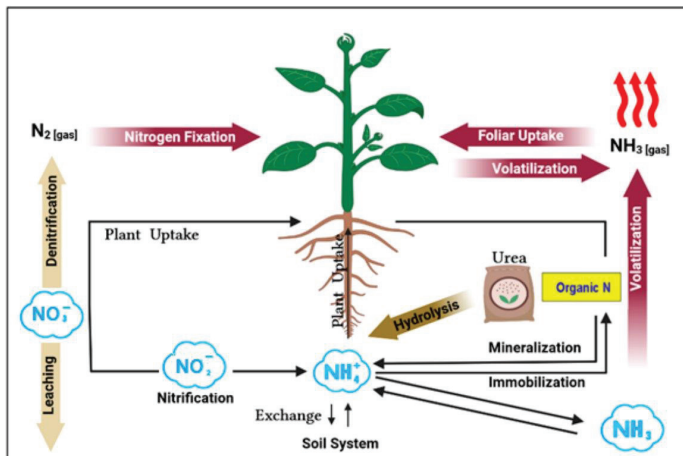


Figure 2. Urea transformation in the soil system.

This is primarily attributed to urea's higher susceptibility to N loss through NH_3 volatilization, ranging from 2–20% [3,18], reaction in the soil with organic components, which leads to a loss of 15–25%, and leaching into water systems, causing a loss of 2–10% [17]. The hydrolysis process raises the soil pH surrounding the granules, leading to ammonia losses averaging 16% of the applied nitrogen on a global scale, and it can reach 40% or more under warm and humid conditions [3,16]. Although urea and fluids containing urea have the highest potential for volatilization, all surface-applied ammonia and ammonium-based N fertilizers have the capacity to do so. Volatilization alone results in a loss of 20–50% of the nitrogen given to the soil [3]. These losses are contributing to significant environmental concerns [19,20].

4. Urea Modification Approach

Following World War II, the introduction of inorganic nitrogen (N) fertilizers in the 1950s aimed to boost crop productivity and address the growing global population's food demands. This development paved the way for the "Green Revolution", which emerged in the 1960s with the introduction of high-yielding crop varieties responsive to fertilizers. Remarkably, over the past five decades, the doubling of crop yields has been closely linked to a seven-fold increase in global N fertilizer usage [21]. From 10.8 million metric tons in 1960, N fertilizer usage surged to 82 million metric tons by the year 2000, with further projections anticipating a rise to 249 million metric tons by 2050. Notably, approximately half of the global food production is estimated to benefit from N fertilizer applications, facilitating rapid crop growth and increased yields [22].

Furthermore, the desire to enhance food security has had a significant impact on global fertilizer consumption during the last few decades. Future demands will most likely be driven by a larger range of issues, such as the desire to limit the environmental implications of nutrient losses. Additionally, the area of accessible arable farmland is shrinking as a result of excessive economic expansion, the conversion of arable land to residential areas, land degradation, and climate change globally [23].

To overcome these issues, careful planning and action are necessary to assess global food shortfalls and future needs. Specific actions, including adjustments in the agriculture sector, are already in place to address these concerns. Some of these issues may be solved by covering urea fertilizer and controlling its release rate. At this stage, using slow- and controlled-release fertilizers would not only increase agricultural output but also minimize environmental damage [24,25]. The growth of slow- and controlled-release fertilizers, as well as stabilized fertilizers, largely fulfills the criteria of an optimal fertilizer. However, it is important to remember that controlled- and slow-release and stabilized fertilizers cannot make up for mistakes in field and crop management. Nonetheless, they can help improve NUE and reduce some environmental impacts. Thus, it is necessary for these unique types of fertilizers to constantly be incorporated into a strong agricultural strategy or best management practices approach [13,26].

5. Modified Urea Fertilizers

Urea modification is a process used to improve the properties of materials by reacting them with urea. Urea is a compound containing nitrogen, carbon, and oxygen that is often used to increase the tolerance of materials to hot and humid climates. This process can also be used to make materials more resistant to corrosion, UV radiation, and other environmental factors. Urea modification is an efficient way to improve the durability and performance of a wide range of materials. Chissoasahi was the first creator of Polyolefin-coated urea (POCU), which is designed to have a sigmoidal release and permits a single, basal application and the simultaneous placement of the fertilizer [26].

The two most common types of modified urea fertilizers are described as "slow-release nitrogen" (SRN) and "controlled-release nitrogen" (CRN) [11,12,27]. Although these terms are often used interchangeably, they have different meanings. Slow-release nitrogen (SRN) and controlled-release nitrogen (CRN) are essentially synonymous and can be collectively

referred to as “Enhanced Efficiency Nitrogen.” However, Trenkel (1997) provided a good clarification on the distinction between both [26]. Synthetic-modified urea compounds can be classified into two main categories. The first category is produced by chemical reactions such as urea-formaldehyde to achieve slow release as a by-product.

The second category accomplishes controlled release by employing a coating made of sulfur, wax, or resin around the fertilizer prills [28]. Different factors can affect the release-rate mechanism of nutrients from slow-release fertilizer, such as the soil type and its properties and metrological conditions [26,29]. The mechanism of slow-release fertilizer is completely random. Otherwise, the mechanism of controlled-release nitrogen fertilizer, amount, and rate of release are comprehensively predictable [25,26,29,30].

Even though slow or controlled fertilizers release nitrogen at a rate more gradual than typical urea, their mechanisms are radically different. Furthermore, SRN and CRN sources are separated at the most fundamental level by a single distinguishing feature: whether they are uncoated or coated [17]. SRN doesn’t depend on coatings to deliver extended-release nitrogen, whereas CRN relies entirely on coatings to delay nitrogen release (Figure 3).

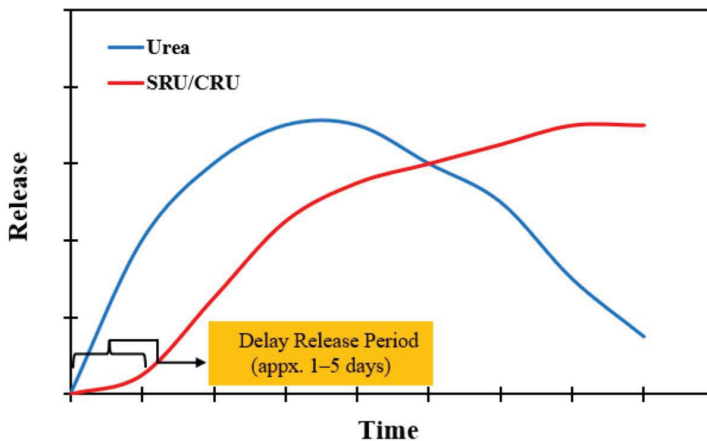


Figure 3. Differences between the release rate of conventional urea and slow-release (SRU) and controlled-release (CRU) urea.

The major difference between these two forms of nitrogen is based on these coatings. Numerous studies have demonstrated that slow-release or controlled-release fertilizer can enhance nutrient use efficiency, improve crop yields, and reduce environmental harm because it is Eco-friendly and pollutes the environment minimally [19,20,31–35].

5.1. Slow-Release Nitrogen (SRN) Fertilizers and Their Methods

There are many terms identified for slow-release fertilizer (SRF). The Association of American Plant Food Control Officials (AAPFCO) defined slow-release fertilizer as a fertilizer that contains a specific plant nutrient in a form that delays its availability for uptake and utilization by plants after it is applied. This delay in availability can be performed either by retarding the release of the nutrient or by prolonging its availability to the plant for a more extended period compared to a reference fertilizer that provides nutrients rapidly and readily [26,36].

Moreover, SRF has been identified as “a result of interactions with mineral or organic materials” [17,27]. Therefore, according to that definition of (AAPFCO), two major categories of slow-release nitrogen fertilizers may be distinguished [36]. The initial category is composed of natural organic fertilizers such as compost. The term “natural” implies that the nitrogen in these fertilizers comes from animal waste and agricultural processing or any biodegradable sources, rather than being artificially synthesized through industrial processes like urea nitrogen [36]. Synthesized fertilizers are the second type of slow-release N source and include three subsets of chemically reacted slow-release products, physically granulated (crystallization), and mechanosynthesis products [28], as shown in Figure 4.

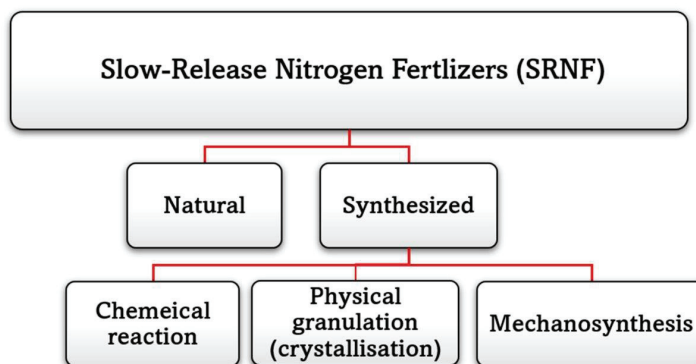


Figure 4. Slow-release Nitrogen Fertilizers Categories.

The effectiveness of urea over a specific period is influenced by the quantity of nitrogen absorbed by the plants. Slow release of nutrients through fertilizers can be used to counter the swift depletion and wastage seen with conventional urea fertilizers. This gradual release of nutrients is seen as the best way to provide plants with a continuous source of nitrogen to accomplish their requirements [30,37,38]. This has been seen to significantly raise the effectiveness of urea while maintaining adequate crop growth. The slow-release nitrogen fertilizers are produced from urea that has undergone chemical reactions, physical granulation (crystallization), or Mechanosynthesis to delay their release into the soil solution.

The products that have been formulated by the chemical reaction can be grouped into three general categories: urea-formaldehyde (UF) reaction products, isobutylidenediurea (IBDU), and triazone [28]. Urea and formaldehyde are combined to produce slow-release nitrogen fertilizers of the urea-formaldehyde category at various temperatures and reaction durations, resulting in the creation of urea chains and carbon-hydrogen groups. These products are also commonly referred to as “methylene urea” (MUs); however, MUs only represent one step in the UF reaction process. IBDU, on the other hand, is produced through a urea and isobutyraldehyde combination, which releases nitrogen occurring through the hydrolysis process when the reactive product degrades.

Nitrogen release is faster in smaller particles and warmer soil temperatures. Triazones are ammonia-containing cyclic substances that are frequently supplied as a slow-release liquid. While significant attention has been paid to their usage as foliar fertilizers. Triazones are also effective as slow-release nitrogen fertilizers [28]. The other type of slow-release urea is produced by Mechanosynthesis or physical granulated urea fertilizer. Mechanochemical

synthesis is a process of chemical synthesis that is accomplished by utilizing mechanical energy.

One of the applications of mechanochemical synthesis is the production of urea plus gypsum as a complex [37–39]. This process has become increasingly popular due to its ability to produce high-purity urea with a low environmental impact. Otherwise, physical granulation is a method of producing urea that involves the formation of small pellets or granules. This process involves spraying liquid urea onto a bed of seeds or recycled granules, which are then rotated and heated to form small, spherical particles. Physical granulation typically requires the use of solvents and binders to create the desired shape and size of the urea granules. The final product may contain impurities, such as dust or fines, which can affect the urea's quality. In terms of the differences between these two methods, the main distinction lies in the process used to produce urea.

Mechanochemical synthesis does not involve the use of solvents or binders, resulting in a high-purity product. Physical granulation, on the other hand, requires the use of solvents and binders, which can introduce impurities into the final product. Additionally, mechanochemical synthesis can be carried out using simple equipment, while physical granulation requires specialized machinery. Mechanochemical synthesis offers a more environmentally friendly and sustainable option for producing high-purity urea. Physical granulation is also a viable option.

5.1.1. Slow-Release Nitrogen (SRN) Materials

Several innovative materials have been used to enhance the effectiveness of urea [26,27]. Three major groups of materials can be employed to provide slow-release nitrogen as shown in Figure 5.

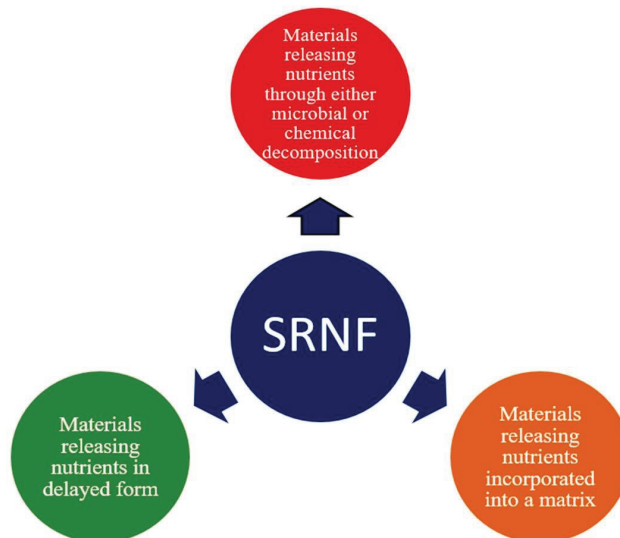


Figure 5. Classification of materials used to produce slow-release nitrogen fertilizers.

Modifying urea with formaldehyde was the first method to produce a urea blend that enabled nitrogen to be released slowly. Moreover, formaldehyde was used as a material that can release nitrogen through either microbial decomposition [26,28] or compounds that decompose chemically (e.g., isobutylene diurea—IBDU). This process begins with urea with formaldehyde combining in the catalyst presence, resulting in a white, odor-free solid that contains approximately 38% nitrogen [28,40]. These urea compounds were initially introduced as first-sold fertilizers in 1955. By varying the urea/formaldehyde ratio, temperature, pH, and time of the reaction, different types of UF reaction products can be produced, which can release nitrogen at varying rates [40].

The second type of slow-release fertilizers is renowned water-soluble fertilizers that are equipped with physical barriers produced by incorporating into the matrix using ecologically friendly materials, including cellulose, starch, and lignin, which emerged as substitute materials for SRF performing instead of synthetic polymers [41–43]. Starch has gained recognition as a sustainable, affordable, and completely biodegradable polymer that can be combined with synthetic polymers, such as polyvinyl alcohol (PVA), to create starch-based goods that conserve petrochemical resources and reduce the impact on the environment [27,42].

Additional chemical crosslinking techniques can be used to strengthen the blend's structural integrity [42]. The blend can serve as an effective polymer matrix for the slow release of chemical substances through derivatization and cross-linking. This matrix allows for effective control over fertilizers for extended periods [42]. The matrix component can adopt either a hydrophobic nature, such as polyolefin, rubber, and the like, or a gel-forming polymer that is often denoted as a hydrogel. The hydrogel is endowed with hydrophilic properties, thereby obstructing the dissolution of fertilizer that is dispersed within the hydrogel material due to its capacity to retain considerable volumes of water, leading to swelling [11].

The third category pertained to substances that emit nitrogen over a prolonged period owing to their limited surface area. One of the most prevalent uses of nitrogen-releasing materials with restricted surface areas is gypsum, a naturally occurring mineral that is frequently employed in construction materials. It contains calcium sulfate, which is the critical component utilized in the mechanochemical synthesis of urea [12,37].

The process of producing urea with gypsum involves grinding the gypsum into a fine powder and then adding it to a mixture of ammonia and carbon dioxide [12,44]. The grinding process is crucial in this synthesis method as it helps to break down the gypsum into smaller particles, increasing the surface area for reaction. The ammonia is added to carbon dioxide, they are mixed in a closed chamber, and the reaction is initiated by the mechanical energy provided by the grinding process [44].

The chemical reaction that ensues is the amalgamation of ammonia and carbon dioxide, resulting in the formation of ammonium carbamate. The ammonium carbamate then reacts with the calcium sulfate present in the gypsum to produce urea and calcium carbonate [12]. The urea product is of exceptional purity because the manufacturing procedure does not involve the utilization of any solvents or other substances that could contaminate the outcome. Additionally, the process has a low environmental impact, as it does not produce any harmful by-products.

The mechanochemical synthesis of urea from gypsum has several advantages over traditional methods of urea production. It is a more sustainable and environmentally friendly process that can be carried out using simple equipment. The process can also be easily scaled up to produce large quantities of urea. The mechanochemical synthesis of urea from gypsum is an innovative and sustainable method of urea production. It has significant advantages over traditional methods and offers a more environmentally friendly solution to the growing demand for urea in various industries.

Numerous studies have extensively documented the utilization of diverse substances to generate slow-release nitrogen fertilizers as listed in Table S1. These materials all work by releasing nitrogen slowly over an extended period, which can reduce the amount of

fertilizer needed and prevent environmental problems associated with excessive nitrogen runoff. Various techniques have been devised to enhance the dispensation qualities of these substances as shown in Figure 6, guaranteeing the timely and appropriate release of nitrogen for optimal cultivation. Overall, the application of slow-release nitrogen fertilizers is a highly encouraging tactic to advance harvest output whilst mitigating the ecological aftermath of farming.

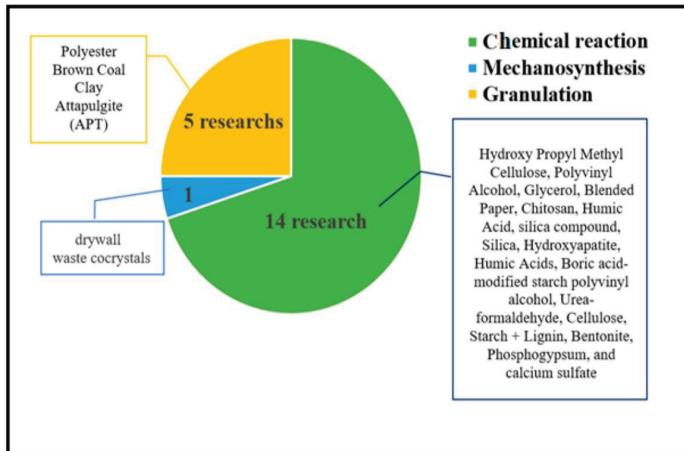


Figure 6. Various techniques and their substances are used to produce slow-release fertilizers.

5.1.2. Mechanism of Slow-Release Nitrogen (SRN) Fertilizers and the Release Rate

The slow-release nitrogen mechanism mainly depends on the delay of urea blend degradation to save the balance between the plant's requirements and the fertilizer stock. The postponement of the initial accessibility or the extension of the period of sustained availability can be attributed to diverse mechanisms [45]. These mechanisms may involve the regulated water solubility of the substance by altering the characteristics of the fertilizer in novel chemical configurations, gradually hydrolyzing low molecular weight water-soluble compounds over time, or using alternative, less commonly employed methods. Furthermore, it has been established that the liberation of nitrogen can be attributed to microbial processes and/or chemical hydrolysis [46]. In particular, it has been observed that the length of the reacted chain serves as a key determinant of the temporal profile of nitrogen release from UF products, with longer chains exhibiting a slower rate of nitrogen liberation [28]. The breakdown of these chains into shorter lengths by microorganisms ultimately leads to the release of urea. The necessary release rate of the nutrients for SRN relies on the metabolic needs of the specific crop over a designated period.

The European Standardization Committee (CEN) Task Force has established SRNF certain criteria, specifying that the nutrient release rate must be slower than that of traditional fertilizers, with no more than 15% of nutrients being released within 24 h, and no more than 75% of nutrients being released within 28 days. Moreover, at least 75% of the nutrients must be released within the stated release timeframe [23]. In addition, SRNF must meet certain requirements including cost-effectiveness, environmental friendliness, and sustainability [47,48].

5.2. Controlled Release Nitrogen (CRN) Fertilizers

Controlled-release nitrogen fertilizers (CRNF) are an entirely distinct breed of slow-release nitrogen fertilizers (SRNF), not only in terms of technological advancements but also in the way nitrogen is dispensed. Nevertheless, a few voices in the field have opined that CRF is simply a subset of SRF which belongs to a group of fertilizers that are obstructed by a physical barrier [11,17,49].

Moreover, controlled-release fertilizers (CRF) may be recognized as a type of product that contains a combination of nutrients coated with a polymer or other substance that undergoes gradual degradation in reaction to soil conditions such as moisture and temperature [17,36]. The particles of control-release nitrogen fertilizers are enveloped within either organic or inorganic materials or polymer coatings [11,17,49,50], thereby resulting in the delay of nitrogen release in a controlled-release form. The coatings serve as the key to achieving this effect. Furthermore, controlled urea use (CRU) is an approach that improves nitrogen use efficiency (NUE) and reduces environmental pollution.

Several methods and their materials have been reported in a large number of previous studies [10,11,20,49–54]. The physical incorporation of urea pellets into a coating material is one of the most prevalent methods utilized in the manufacture of controlled-release coated urea (CRCU) [11]. This technique involves coating urea granules with appropriate materials that can impede its release into the soil by reducing its solubility in water. This type of fertilizer typically releases nitrogen over several weeks to several months [55].

Polymer-coated urea is like coated urea, but the coating material is a polymer that gradually breaks down over time, releasing nitrogen in a controlled manner. This type of fertilizer can release nitrogen over several months to several years. Sulfur-coated urea is another material used for controlled-release nitrogen production. It is produced by coating urea granules with a sulfur crust that reacts with moisture in the soil to release nitrogen slowly [30,56].

Sulfur-coated urea typically releases nitrogen over 8–10 weeks. The controlled-release coated urea development is an ecological technology that has emerged as a responsible alternative for curtailing nitrogen losses resulting from volatilization and leaching. Additionally, it serves to enhance nitrogen release kinetics and maintain a balance between plants' needs and nutrient stocks, thus aligning with their metabolic requirements [11,12,32].

5.2.1. Categorization of Coating Materials

The utilization of environmentally friendly natural or semi-natural macromolecule materials for coating has been reported in numerous previous studies [20,57,58]. These materials possess properties that fall between hydrophobicity and hydrophilicity [11,50]. This unique feature allows water to penetrate the coated surface, resulting in the release of nitrogen from the fertilizer. At the same time, the nature of the coating material, which is water-repellent and water-resistant, can reduce the rapid release of nutrients, thus fulfilling the essential nutrient needs for ideal crop growth [11].

The classification of controlled-release fertilizers (CRFs) has been accomplished in a variety of ways in previous research studies, concerning the mechanism and type of coating material employed. By analyzing the previous work of Shaviv [59], Liu [24], Trenkel [26], Azeem [11], Beig [49], Lawrencía [17], and Gutierrez [60], the coating materials could be widely classified into two major categories as illustrated and explained below in Figure 7. The first category is comprised of organic polymer materials, which can be either synthetic polymers (such as polyurethane, polyethylene, and alkyd resin) or natural polymers (such as starch, chitosan, cellulose, and others) [17,26]. The second category comprises inorganic materials such as sulfur and zeolite and other minerals such as clay, bentonite and phosphogypsum [11,38,49].

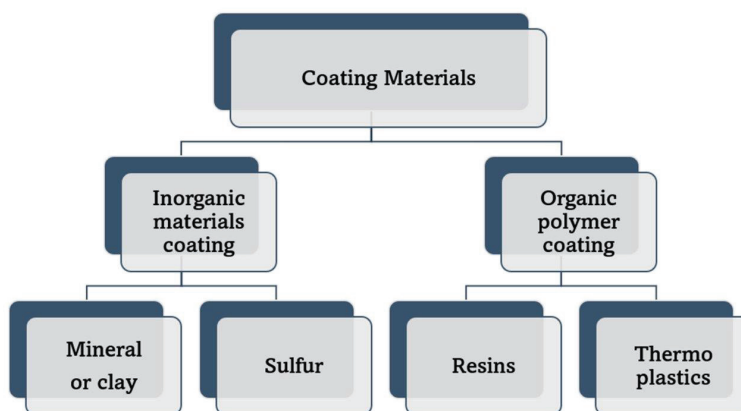


Figure 7. The classification of coating materials that are used to produce controlled-release nitrogen fertilizers (CRNF).

Furthermore, recent investigations reveal that organic substances like biochar, rosin, and polyphenol are currently in use [20,58,61,62]. Scientists have investigated various mixtures of these materials to assess their impact on the release rate of urea and discover their potential as coatings for controlled-release fertilizers (CRFs). As a result, the scientific community has been very interested in the technology of coating urea fertilizer granules to control the release of nutrients. At first, the most popular urea-coating material was sulfur. Due to their apparent advantages over natural polymers, such as set-to-set consistency, predictable physicochemical properties, and ability to be customized, various synthetic polymers, such as polyethylene, polystyrene, and polyesters, have recently been used.

5.2.2. Constant Diffusion Mechanism

To clarify, the previous studies classified controlled-release fertilizers based on the way they release nutrients (the mechanism), either through the “failure mechanism” and/or the “diffusion mechanism” [11,24,26,49,63]. Figure 8 below shows how water can permeate the protective coating layer of the fertilizer, resulting in the controllable release of nitrogen pellets to the surrounding soil.

The CRF’s effectiveness highly depends on its release mechanism, which is challenging to determine due to several variables such as the properties of coating materials, control release fertilizer type, and the agricultural environment. The scientific literature outlines several different release mechanisms, which are continuously evolving. Among these mechanisms, the multi-stage diffusion model is a commonly suggested approach for coated fertilizers’ release [64].

The nutrients’ release from controlled-release fertilizer occurs through three distinct stages according to the multi-stage diffusion model: the lag stage, the constant release stage, and the decay stage [17,65]. During the lag stage, which is the first stage, the irrigation water breaks through the coating layer and condenses on the core of the solid fertilizer. At this point, one might observe a minuscule fraction of the urea fertilizer dissolving, as depicted in Figure 8. The lag period in this process could be ascribed to two potential variables: the temporal necessity to engorge the internal cavities with an indispensable quantity of water or to establish equilibrium between the influx of water and the outflow of solute [17,64]. During the second stage, as water continues to penetrate the coating, the

osmotic pressure inside the granules increases, causing more solid fertilizers to dissolve (Figure 8).

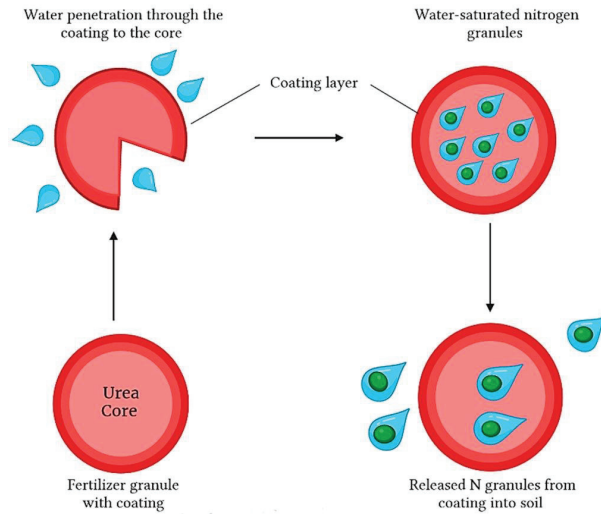


Figure 8. Constant diffusion mechanism of coated release fertilizers.

The gradual release of fertilizer from a polymer coating occurs upon the accumulation of a critical volume of the saturated solution. At this point, there are two ways in which the nutrients can be released [11]. The first scenario is observed when osmotic pressure exceeds the resistance of the membrane, resulting in the rupture of the coating, and the entire core is spontaneously released. This mechanism is known as the “failure mechanism” or “catastrophic release”.

The second scenario is in case the membrane withstands the increasing pressure, the fertilizer core is released slowly through diffusion. This release may be driven by a concentration or pressure gradient or a combination of both. This mechanism is defined as the “diffusion mechanism” and is commonly observed in polymer coatings, such as polyolefin. On the other hand, weaker coatings like sulfur or modified sulfur typically exhibit a failure mechanism. Most of the fertilizer has already been dissolved and released during the decay stage, which lowers the concentration gradient and driving force and slows the release rate [17].

6. The Pros and Cons of SRN and CRN Application

The slow-release nitrogen fertilizers usage provides nitrogen to plants over a longer period, while controlled-release nitrogen fertilizers provide nitrogen at a controlled rate. Here, we will discuss the pros and cons of using slow- and controlled-release nitrogen fertilizers. One of the main advantages of slow- or controlled-release nitrogen fertilizers is the long-lasting effect on the soil. The nitrogen is released slowly, and the rate of release can be controlled, which means that the plants receive the nitrogen they need when they need it and can absorb it over a more extended period. This reduces the need for frequent fertilization, costs, time, and energy in terms of economic advantage [66–68].

Furthermore, the utilization of slow- or controlled-release nitrogen fertilizers has been shown to improve nitrogen use efficiency (NUE) and diminish nitrogen loss [53,69], mainly by mitigating nitrate leaching, volatilization, and nitrous oxide emissions, resulting in a diminished environmental footprint when compared to conventional nitrogen fertilizers [1]. Additionally, slow- and controlled-release nitrogen fertilizers can increase crop yields by providing a steady supply of nitrogen to the plants. This can help farmers maximize their profits [70–73].

The controlled- or slow-release nitrogen fertilizers have another advantage; they promote healthy root growth [74,75]. As the nitrogen is released slowly, it allows the roots to grow deeper into the soil in search of nutrients. This helps improve the overall health of the plants and makes them more resilient to environmental stressors such as drought. Furthermore, releasing nutrients in a gradual and regulated manner at an optimal rate can contribute to agronomic safety by mitigating the toxicity levels that plants experience, particularly throughout the initial stages of growth.

This approach is unlike the conventional approach of applying chemical fertilizers which often results in a high local build-up of ions, creating a high concentration that leads to osmotic stress and ultimately harms plants [17,65]. On the other hand, there are disadvantages of controlled- or slow-release nitrogen fertilizers, such that they can be less flexible than traditional nitrogen fertilizers. Once they have been applied, it can be difficult to adjust the release rate if environmental conditions change, such as heavy rainfall [26]. This can lead to a loss of nitrogen from the soil or over-fertilization.

Controlled- or slow-release nitrogen fertilizers are more expensive than conventional nitrogen fertilizers. This can be a significant disadvantage for farmers who are on a tight budget. Controlled- or slow-release nitrogen fertilizers take longer to have an effect on plant growth than traditional nitrogen fertilizers. This means that farmers may have to wait longer to see the results of their fertilization efforts. Controlled-release nitrogen fertilizers can lead to over-fertilization if not used correctly [76]. Therefore, it is important to note that the choice between controlled-release and slow-release nitrogen fertilizers depends on various variables, such as crop type, soil type, and environmental conditions.

For example, slow-release nitrogen fertilizers are more suitable for crops that require a regular supply of nitrogen during the season of growth, while controlled-release nitrogen fertilizers are more suitable for crops that have specific nitrogen requirements during different growth stages. In addition to these advantages and disadvantages, it is worth considering the overall sustainability of using nitrogen fertilizers in the agriculture sector depending on the specific needs of the crop and the farming system. Overuse of nitrogenous fertilizers can have a negative environmental impact, including eutrophication of waterways, greenhouse gas emissions, and soil degradation. Consequently, it is critical to use nitrogen fertilizers judiciously and in combination with other sustainable agriculture practices such as crop rotation, cover cropping, and conservation tillage.

7. Impact of Modified Urea Fertilizers on Crop Yield and NUE

Numerous studies have reported that controlled- or slow-release fertilizers can positively impact nitrogen use efficiency based on several factors including crop type and soil conditions. The increase in crop yield is the main motivation for producers to use controlled- or slow-release fertilizers. Various studies investigated controlled- or slow-release fertilizers to improve crop yield and nitrogen use efficiency as listed in Table 1.

The fertilizer's use efficiency is crucial in crop production to enhance yields and crop management and decrease the loss of nitrogen. Urea is a common nitrogenous fertilizer that has been utilized in agriculture for over a century. However, the traditional application of urea fertilizer is known to have negative environmental impacts [19,20]. Many studies reported that urea is less effective and its NUE is only around 50%, with 2–20% lost due to ammonia volatilization, approximately 15–25% reacting with soil organic components, and around 2–10% leaching into water systems [17,19,77]. Therefore, there was a necessity to enhance urea nitrogen use efficiency (UNUE) to reduce its negative environmental impacts.

Table 1. Controlled- and slow-release nitrogen (CRN/SRN) fertilizers and their impact on crop yield and NUE.

Fertilizer Type	Crop Type	Research Findings	Year	Ref.
Controlled/slow release	Rice	The NUE increased from 35.7% (Control) to 44.9% (SCRf). The application rate exceeding 90% could have a significant impact on the rice yield.	2023	[78]
Controlled-release fertilizer	Winter wheat	The applied CRU treatments significantly increased the grain yields by 9.96–15.11% and NUE by 6.71–10.33%.	2021	[79]
Controlled-release fertilizer	Rice	The results showed that 24% significant increase in N levels in the leaves of plants with CRF.	2020	[54]
Controlled-release urea	Rice	The CRU treatment reduced the rate of the N application by 20% compared to conventional urea.	2020	[80]
Controlled-release urea for	Wheat, maize, and rice	The utilization of CRU increased the grain yield by 7.23%, and a substantial upsurge of NUE, NAE, NUR, and NPE by an average of 23.4%, 34.65%, 25.83%, and 15.8%, respectively.	2020	[81]
Controlled-release urea	Maize	The application of CRU in comparison to urea (the same N rates) increased maize yield by 5.3% and NUE by 24.1%.	2019	[82]
Controlled-release urea	Wheat-maize	The application of CRF affected the NUE by an increase of 35.7–37.6% for wheat and 13.2–14.3% for maize.	2017	[71]
Controlled-release urea	Spring Wheat	Grain yields significantly increased from 9.58 to 11.21% and the N level from 19.06 to 23.94%.	2016	[83]
Controlled-release fertilizer	Rapeseed	An increase in N accumulation and NUE of CRF was 13.66% and 9.74% respectively.	2016	[84]
Combined application of urea and CRU		The combined application of urea and CRU increased the yield by 11.4% to 12.9% compared to 100% CRU.	2013	[85]
Controlled-release fertilizer	Summer maize	The four yield-enhanced CRF treatments exhibited higher N uptake and physiological NUE compared to CCF.	2013	[86]
Slow-Release	Corn	There were noticeable augmentations in the absorption of nitrogen by plants and nitrogen recovery efficiency with slow-release fertilizers.	2009	[87]

Recently, almost all fertilization research has tended to develop and modify urea compounds that aim to enhance nitrogen utilization and reduce nitrogen losses [66]. Here, we will try to explain the factors that affected the NUE and explore the influences of modified urea compounds on the yields and the agronomic nitrogen use efficiency (ANUE). Controlled- or slow-release nitrogen fertilizers possess the capacity to markedly enhance the efficiency of nitrogen use whilst concurrently preserving crop productivity [88].

Furthermore, controlled- or slow-release nitrogen (CRN/SRN) has the potential to serve as an exceedingly effective nitrogen source for grain crops, thereby augmenting yields. Controlled- or slow-release fertilizers can reduce the recommended rate of the application by 20–30% (or more) compared to conventional fertilizers [26]. Various factors influence nutrient use efficiency (NUE) with a particular emphasis on nitrogen losses. This involves enhancing nutrient uptake by plants, thereby decreasing the amount left in the soil that is vulnerable to environmental loss [26].

The decision to use controlled- or slow-release fertilizers may be influenced by several direct economic factors, including potential nutrient losses and the cost of fertilizer applications [59]. These factors play a vital role in affecting the agronomic use efficiency of controlled- or slow-release fertilizers (CRFs or SRFs). Nutrient loss potentiality is the most important factor, which can occur through various physical, biological, and chemical processes such as surface runoff, leaching, volatilization, denitrification, immobilization,

or fixation [89]. The use of SRFs/CRFs and bio-amended ammonium fertilizers has been shown to reduce such losses, leading to better nutrient recovery and crop yield [58,59,90,91].

Another key economic factor is the cost of fertilizer applications [66,69]. Using SRFs or CRFs can result in significant cost savings, as simply one application can provide nutrients for the whole season of growth, reducing the need for multiple applications and spreading costs [66,92]. SRFs or CRFs with a lag in the release can also be applied during less restricted trafficability periods, including fall for spring or winter-planted crops, or before the annual spring rush [51,93].

In addition, SRFs/CRFs may decrease the insistence on short-season and hand labor for top-dressing, which is critical during peak periods such as in rice paddies [20]. Furthermore, applying controlled- or slow-release fertilizers could provide notable benefits in terms of enhancing plant nutrition and physiological functions [26,92]. Conventional soluble fertilizers can lead to an excessive nutrient supply, increasing the concentration of soluble salts in the root area [94,95]. Consequently, this results in several issues, including osmotic stress, particular injuries to plants at different stages of development, and unfavorable developments like lodging; these are just a few issues that can occur [96,97].

In contrast, the application of SRFs or CRFs is accompanied by reduced stress and specific toxicity, as they release nutrients slowly over an extended period, thus reducing the risk of over-fertilization [46,98]. This slow-release mechanism allows plants to absorb the nutrients as needed, avoiding the accumulation of toxic concentrations of nutrients in the soil [24,46]. Research has also shown that the use of SRFs and CRFs is associated with heightened rates of germination and crop productivity and the decreased burning of leaves, stalk breakage, and infestation of disease [71,95,99,100].

In summary, the use of SRFs can improve plant growth, increase yield, and improve crop quality. Additionally, providing the preferred chemical forms of nutrients for plants was one of the factors that affected fertilizer use efficiency [92]. The focus on providing plant nutrients in their preferred chemical forms has received considerable attention over the past two decades, especially in terms of supplying mixed ammonium-nitrate nutrition [34]. Multiple research endeavors have divulged noteworthy advancements in grain production and protein density by employing mixed-N nourishment, by comparison to exclusively nitrate or ammonium consumption alone [66,92,101–104].

However, it was only in experiments where a proper regulation of the ammonium/nitrate ratio in soil was upheld, that these results were observed. To attain a boost in ammonium nourishment, diverse methods can be employed including the utilization of nitrification inhibitors, controlled or slow fertigation, or heightened local concentrations of ammonium or ammonia [105,106]. Finally, there is assembling evidence to show that different nutrients can work together especially when they are supplied at the same time or placed close to the root surface's absorption sites or near the root.

For instance, NH_4 or K can significantly increase the availability of Fe in calcareous soils, likely as a result of the rhizosphere's physiological acidification [107]. The utilization of K_2SO_4 co-granulated with FeSO_4 has been demonstrated by researchers as an effective method for correcting Fe deficiency in highly calcareous soils. Conversely, the application of Fe and K sulfates alone resulted in inadequate outcomes. Another example of the efficacy of soil amendments is the ability of NH_4 to increase P bioavailability when its nitrification rate is reduced, presumably through rhizosphere acidification. Additionally, the provision of mixed ammonium-nitrate nutrition to plants requires an adequate K supply to achieve increases in yield and protein content. Proper management of the pattern and chemical form of nutrient release from SRFs or CRFs can facilitate the beneficial physiological effects offered by these treatments [108]. However, the effects mentioned above require intensified attention, particularly on the field level, to assess their actual contribution, besides simply reducing nutrient losses [92].

8. Conclusions

In recent times, the utilization of urea-modified fertilizers has emerged as a crucial factor in improving the availability of mineral nitrogen in the soil. These fertilizers not only enhance nitrogen levels but also can decrease the nitrogen release rate, resulting in higher efficiency of fertilizers in crop cultivation. Moreover, numerous studies have highlighted the beneficial impact of urea-controlled or slow-release compounds on crop productivity. However, despite these advancements, there is still a requirement for more extensive investigations to better understand the effects of these compounds. By conducting further research, scientists aim to refine the formulations of urea-modified fertilizers and integrate them with effective agronomic practices, ultimately leading to reduced nitrogen losses and improved nitrogen use efficiency in agriculture.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/su16010188/s1>. References [27,37,38,40,42,52,57,108–120] are cited in the Supplementary Materials.

Author Contributions: R.M. and J.B. conceived the study. S.S. collected and analyzed the works of literature, visualized the data, and wrote the original draft of the manuscript. K.B. and D.D. revised the manuscript. All the authors commented on previous versions of the manuscript. All authors have read and agreed to the published version of the manuscript.

Funding: This work is supported by the Engineering for Agricultural Production Systems program grant no. 2020-67022-31144 from the USDA National Institute of Food and Agriculture.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: The datasets used in the current study are available from the corresponding author upon reasonable request.

Conflicts of Interest: The authors declare no conflict of interest.

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ACKNOWLEDGEMENTS

First and foremost, I offer my deepest gratitude to "Allah," the most Gracious and Merciful, for His blessings, Who gave me patience, and strength that enabled me to complete successfully this endeavor.

I am thankful to the Lithuania Research Centre for Agriculture and Forestry (LAMMC) for providing a conducive environment that supported my accomplishments during my doctoral studies. I extend my appreciation to my supervisor, Dr. Romas Mažeika, and the other members of my committee, including my consultant supervisors, Dr. Jonas Volungevičius and Dr. Dalia Feizienė, for their invaluable assistance in furthering my career and scientific goals. Their guidance, mentorship, and encouragement have truly enriched the past four years of my journey.

I am indebted to the Agrobiolology laboratory, particularly to Dr. Karolina Barčauskaitė, the lab's head, for her unwavering support and dedication throughout my research. My heartfelt thanks also go to my lab mates, Donata Drapanauskaitė, Kristina Bunevičienė, Urtė Stulpinaitė, and Dovilė Motiejauskaitė, whose assistance was invaluable during my research endeavors. I am grateful to my other friends in the Agrobiolology laboratory, whose companionship added joy to my academic pursuits.

I extend my gratitude to the staff of Rumokai and Vėžaičiai Experimental Stations for their assistance in facilitating my experimental fieldwork.

Lastly, I express profound thanks and appreciation to the soul of my dear father, my beloved mother, my siblings, and my friends for their unwavering encouragement and belief in my abilities to accomplish this work.

SANTRAUKA

IVADAS

Karbamidas yra viena iš vyraujančių azoto trąšų, sudarančių maždaug 43 % pasaulinių pardavimų [1–2]. Dėl didelės azoto koncentracijos ir ekonomiškumo jis plačiai naudojamas žemės ūkyje [3–4]. Nepaisant to, karbamido, kaip pirminio azoto šaltinio, veiksmingumą gali paveikti įvairūs veiksniai, įskaitant dirvožemio savybės, mikrobu aktyvumas ir aplinka [5–8]. Karbamido trąšos gerai tirpsta dirvožemyje. Dėl didelio tirpumo karbamide esantis azotas gali lengvai pasišalinti iš dirvožemio-augalo sistemos arba tapti augalams nepasiekiamu. Karbamidas praranda azotą dėl daugelio procesų, tokių kaip išplovimas, denitrifikacija, imobilizacija ir fiksavimas dirvožemyje, kai susidaro NH_4 [9]. Paprastai naudojant karbamido trąšas, jame esančio azoto panaudojimo efektyvumas svyruoja nuo 30 % iki 70 %, tačiau vidutiniškai siekia apie 50 % [10–12]. Pasėliai iš karbamido dažnai pasisavina tik apie 30–40 % azoto. Karbamido trąšų naudojimo efektyvumą galima padidinti išlaikant pusiausvyrą tarp azoto patekimo ir pasėlių poreikio jam, tuo pačiu sumažinant azoto nuostolius [11],[19]. Tinkamai pritaikytos agronomijos strategijos gali padidinti pasėliuose panaudoto azoto pasisavinimą, gamybos efektyvumą ir sumažinti galimas ekologines pasekmes, susijusias su azoto naudojimu [20–21]. Be agronominių priemonių, didinti azoto panaudojimo efektyvumą, dar yra cheminės technologinės priemonės, kurios skirtos naudoti įvairius junginius, gautus iš aplinkai nekenksmingų šaltinių [22], šios priemonės gali padidinti karbamido, kaip pirminės azoto trąšos, veiksmingumą, kartu mažinant emisijas į aplinką [23]. Įprasta strategija apima azoto trąšų kūrimą kontroliuojamoje arba lėto atpalaidavimo formoje [23–24], chemiškai ir biochemiškai modifikuojant arba granuliuojant [25]. Kontroliuojamas arba lėtas azoto išsiskyrimas riboja perteklinio azoto transformavimą į amoniaką ir tuo pačiu jo emisiją į atmosferą; ir nitratus, kurie galėtų patekti į vandens ekosistemas. Dėl to, šis metodas sumažina oro ir vandens taršą [23], [24], [26]. Pagrindinis šio tyrimo tikslas yra panaudojus tiriamus karbamido junginius, skirtingose dirvožemio tipologinėse grupėse ištirti dirvožemio savybių ir mineralinio azoto dinamikos sąveiką, bei įvertinti įprastinio karbamido efektyvumą lyginant su modifikuotais karbamido junginiais.

Tyrimo objektas

Skirtingų karbamido junginių, tokių kaip karbamidas, karbamido kalio humatas ir karbamido gipso kokristalas, poveikis mineralinio azoto išsiskyrimui skirtinguose dirvožemio tipoose, siekiant suprasti dirvožemio savybių ir mineralinio azoto dinamikos sąveiką. Tyrimas

buvo atliktas siekiant ištirti šių junginių poveikį kukurūzų augimui ir produktyvumui lauko sąlygomis bei šiltnamio eksperimente, bei ištirti poveikį miežių biomasei.

Tyrimo hipotezė

Tikėtina, kad įvairių karbamido junginių sąveika su skirtingos granulometrinės sudėties dirvožemiais turės skirtingą mineralinio azoto koncentraciją ir jo kaitą laike. Modifikuoti karbamido junginiai - tai naujos, stabilesnės trąšos, kurios gali padidinti karbamido panaudojimo efektyvumą ir azoto įsisavinimą augaluose.

Tyrimo tikslas

Šio tyrimo tikslas yra panaudojus skirtingus karbamido junginius, skirtingos granulometrinės sudėties dirvožemiuose ištirti dirvožemio savybių ir mineralinio azoto dinamikos sąveiką, bei įvertinti ir palyginti įprastinio karbamido efektyvumą su modifikuotais karbamido junginiais, tuo pačiu pagerinant azoto pasisavinimą ir kukurūzų derliaus didinimą bei grūdų kokybę.

Tyrimo uždaviniai

1. Ištirti karbamido ir modifikuotų karbamido junginių panaudojimo įtaką mineralinio azoto transformacijai ir jo išsiskyrimo skirtinguose dirvožemio tipuose dėsningumus.
2. Įvertinti modifikuotų karbamido junginių įtaką kukurūzų augimo ir grūdų derlingumo gerinimui lauko sąlygomis.
3. Įvertinti karbamido ir karbamido kalio humato poveikį miežių žaliajai biomasei skirtinguose dirvožemio tipuose šiltnamio sąlygomis.

Ginamieji teiginiai

1. Mineralinio azoto koncentracijos dinamika dirvožemyje reikšmingai priklauso nuo dirvožemio granulometrinės sudėties.
2. Modifikuotos karbamido trąšos, tokios kaip karbamido ir amonio sulfato mišiniai, karbamido – gipso kokristalai ir karbamidas padengtas kalio humatu, gali pagerinti kukurūzų derliaus produktyvumą ir grūdų kokybę.
3. Modifikuoto karbamido naudojimas turėjo reikšmingą poveikį azoto pasisavinimui, palyginti su įprastiniu karbamidu, ir reikšmingai paveikė agronominį azoto naudojimo efektyvumą ir azoto atkūrimo efektyvumą.
4. Karbamidas padengtas kalio humatu gali sumažinti azoto nuostolius ir taip patenkinti azoto poreikį miežių augimui.

Tyrimo naujumas

Nustatyta, kad modifikuotų karbamido junginių naudojimas ženkliai pagerina mineralinio azoto pasisavinimą dirvožemyje lyginant su karbamidu. Modifikuotų karbamido junginių naudojimas turi teigiamą poveikį tiek augalų augimui, tiek pasėlių produktyvumui. Lėtai atsipalaiduojančios karbamido trąšos, tokios kaip karbamido kokristalai, palaiko optimalią pusiausvyrą tarp augalo azoto poreikio ir mineralinio azoto esančio dirvožemyje, tai leidžia sumažinti azoto nuostolius į aplinką. Karbamido derinimas su kalio humatu turi teigiamą poveikį, nes sumažina karbamido azoto praradimą ir padidina azoto pasisavinimą augaluose. Tyrimo metodikoje taikyta mineralinio azoto koncentracijos kaitos - kinetikos priklausomybės nuo cheminių junginių formos ir dirvožemio tyrimai, kurie susieti su agronominiais lauko augalų tyrimais. Cheminių ir agronominių tyrimų metodų dėmė leido atlikti eksperimentinių trąšų palyginamą bei efektyvumo įvertinimą naujoms karbamido pagrindu sukurtoms trąšoms.

Praktinė tyrimo reikšmė

Šio tyrimo išvados atskleidė, kad modifikuotų karbamido trąšų naudojimas gali būti naudingas optimizuojant azoto prieinamumą augalams ir didinant trąšų efektyvumą, siekiant išsaugoti pusiausvyrą tarp azoto atsargų dirvožemyje ir augalų poreikio, didinant derlių ir sumažinant azoto praradimo riziką.

TYRIMŲ METODIKA

2.1. Tyrimo teritorijos aprašymas ir dirvožemio charakteristikos

Eksperimentinis darbas buvo atliktas lauko ir šiltnamio sąlygomis. Lietuvos agrarinių ir miškų mokslų centro Rumokų bandymų stotyje (54°43'15.7044" N, 22°58'736"E), buvo atlikti du eksperimentai 2018–2019 m. ir vienas 2020 m. Dirvožemio tipas buvo Hapli-Epihypogleyic Luvisol, o granulimetrinė sudėtis – vidutinio sunkumo priemolis [86]. Pirmasis eksperimentas buvo atliktas tręšiant kukurūzus ir siekiant įvertinti įprasto karbamido santykinį pranašumą, lyginant jį su karbamidu + amonio sulfatu, karbamidu + kalcio sulfatu ir karbamido gipso kokristalais. Dirvožemio cheminės savybės (0–20 cm. gylyje) ir azoto bei sieros kiekiai (0–30 cm. gylyje), pateikiami 1 lentelėje (publikacija 1). Antrasis eksperimentas atliktas siekiant iširti skirtingai modifikuoto karbamido (karbamido kalio humatą ir karbamido kokristalus) naudojimo efektyvumą kukurūzų augimo sistemoje. Dirvožemio cheminės savybės (0–20 cm) ir azoto formų koncentracijos dirvožemio paviršiniame (0–30 cm.) ir podirvio (30–60 cm.) sluoksniuose pateiktos 1 lentelėje (publikacija 2). Eksperimentas šiltnamyje atliktas naudojant keturis skirtingos granulimetrinės sudėties dirvožemius. Dirvožemio mėginiai paimti iš žemės ūkio paskirties vietos 4 profilių paviršinio sluoksnio 0–30 cm. gylio. Jais buvo užpildyti vegetacinio eksperimento indai. Dirvožemis vegetaciniams eksperimentams buvo atrinktas prieš tai atrinkus atskiriems regionams būdingus tipingus dirvožemius. Dirvožemio profilių identifikavimas buvo atliktas pagal WRB 2022 klasifikaciją [89]. *Endogleyic Haplic Luvisol (Loamic, Aric)* [89] (priemolio dirvožemis); *Endogleyic Epistagnic Endocalcaric Cambisol (priemolio, Aric, Drainic)* [89] (priesmėlio dirvožemis); *Dystric Arenosol (Aric)* [89] (limnoglacialinio smėlio dirvožemis) ir *Glossic Epigleyic Dystric Retisol (Molio, Aric, Cutanic, Drainic)* [89] (smėlingo molio dirvožemis). Dirvožemio tipai ir jų fizinės bei cheminės savybės pateiktos 1 lentelėje (publikacija 3). Tyrimų vietose dirvožemio profilių aprašymai nebuvo daromi. Atliktame tyrime remtasi ankstesniais tyrimais ir kt. literatūros šaltiniais [28], [90], [91].

2.2. Tyrimo schemos

Šis tyrimas apėmė vieną vegetacinį ir du lauko eksperimentus. Pirmasis, 2 metų lauko eksperimentas (2018–2019 m.) buvo atliktas atsitiktinių imčių pilno bloko principu (RCBD) su 20 eksperimentinių sklypų. Eksperimentą sudarė penki variantai su keturiais pakartojimais: kontrolė, karbamidas, karbamidas + amonio sulfatas, karbamidas + kalcio sulfatas ir karbamido – gipso kokristalai $[\text{CaSO}_4 \cdot 4\text{CO}(\text{NH}_2)_2]$. Lauko paruošimo ir kukurūzų auginimo informacija (2018 ir 2019 m.) pateikti 2 lentelėje (publikacija 1). Antrasis eksperimentas (2020 m.) buvo atliktas pagal tą patį principą, bet su septyniais variantais bei keturiais pakartojimais. Jį sudarė 28 eksperimentiniai sklypai. Eksperimentą sudarė: kontrolė, 100 ir 200 kg N ha⁻¹ karbamido, 100

ir 200 kg N ha⁻¹ karbamido kalio humato ir 100 ir 200 kg N ha⁻¹ karbamido – gipso kokristalo [CaSO₄·4CO(NH₂)₂] variantai. Kukurūzų (Ramirez, apibūdinamas kaip FAO 160) sėklos buvo sėjamos rankiniu būdu vieną dieną po tręšimo abiejuose lauko eksperimentuose 2018–2019 m. ir 2020 m. Atstumas tarp eilučių buvo 50 cm., atstumas tarp augalų – 20 cm, o kukurūzų tankis – 10 augalų kvadratiniam metre. (100 000 augalų ha⁻¹). Pesticidai nebuvo naudojami. Kukurūzų produktyvumas ir biometriniai duomenys buvo matuojami rankiniu būdu kukurūzų fiziologinės brandos fazės metu (BBCH 88-89). Nuėmus derlių, likusios augalų liekanos buvo suartos 22 cm gylyje. Vegetacinis eksperimentas atliktas Lietuvos agrarinių ir miškų mokslų centro Agrobiologijos laboratorijos šiltnamyje 2021 m. Buvo siekiama ištirti skirtingos granulimetrinės sudėties dirvožemio įtaką azoto mineralų išsiskyrimui naudojant įprastą karbamidą ir karbamidą padengtą kalio humatu. Eksperimentas truko 45 dienas, pasirenkant vasarinių miežių (*Hordeum vulgare* L.) veislę „*Ema DS*“. Eksperimentą sudarė penki vairantai su trimis pakartojimais: kontrolė, U100, U200, UPH100 ir UPH200 (2 pav., 3 publikacija). Buvo 60 vegetacinių eksperimento indų, sudėtų į 4 grupes (A, B, C ir D), kaip parodyta 1 paveiksle (publikacija 3). Vazonai (25 cm aukštis × 25 cm skersmuo) buvo užpildyti 10 kg viršutinio humusingo sluoksnio dirvožemiu (0–30 cm.).

2.3. Dirvožemio mėginių ėmimas ir analizės procedūros

Lauko eksperimentai buvo atliekami 2018–2019 metais. Dirvožemio mėginiai (Rumokų bandymo stotis) paimti 0–30 cm gylyje iš neapdorotų ir apdorotų sklypų. 2020 metais mėginiai buvo paimti tris kartus 0–30 ir 30–60 cm gylyje. Mėginiai paimti naudojant nerūdijančio plieno kalamą zondą ir formuojami iš trijų dalinių ėminių kiekviename sklype. Vegetacinio eksperimento dirvožemio mėginiai buvo imami 10 cm gylyje, pradedant nuo pirmosios eksperimento dienos, o vėliau 4, 7, 14, 21, 28 ir 45 eksperimento dienomis. Išsami dirvožemio savybių ir mineralinio azoto analizė buvo atlikta Lietuvos agrarinių ir miškų mokslų centro, Agrocheminių tyrimų laboratorijoje (1, 2 ir 3 straipsniai). Dirvožemio pH nustatytas pagal ISO 10390:2005 [92], [93]. Dirvožemyje esantis K₂O ir P₂O₅ pagal LVP D-07:2019 [94]. Grunto elektrinis laidumas nustatytas pagal ISO 11265:1994 [95]. Bendras azoto kiekis buvo matuojamas pagal ISO 11261-1995 [96], [97]. Mineralinis azotas nustatytas laboratorijoje sukurtu spektrometriniu srauto įpurškimo analizės (FIA) metodu [18], [98]. Organinės anglies kiekis dirvožemyje nustatytas naudojant sausą deginimą pagal ISO 10694:1995 [18]. Dirvožemio granulimetrinė sudėtis įvertinta naudojant ISO 11277-2020 [99].

2.4. Augalų biometriniai parametrai, derlius ir grūdų kokybė

Norint įvertinti kukurūzų biometrinius parametrus, derlius buvo imamas fiziologinėje brandoje ir tik vidinėje sklypų dalyje (2×2 m.). Grūdų derliui ir grūdų biomasės kokybei nustatyti atsitiktine tvarka buvo atrinkta 20 augalų. Mėginiai paimti iš visų pakartojimų ir džiovinami džiovyklėje 65 ± 5 °C temperatūroje iki pastovios masės siekiant gauti sausą biomasę ir derliaus. Grūdų kokybės charakteristikas, tokias kaip bendras azotas, angliavandeniai ir krakmolai nustatė Lietuvos agrarinių ir miškų mokslų centro Agrocheminių tyrimų laboratorija.

2.5. Meteorologinės sąlygos

2018 m., 2019 m. ir 2020 m. laikotarpyje pastebėti dideli sezoninių klimato sąlygų svyravimai. 2018 m. oro temperatūra buvo šiltesnė nei vidutinė 2019 m., išskyrus birželio mėnesį. Dėl to derlius 2018 m. buvo nuimtas 1 mėnesiu anksčiau. Kita vertus, 2019 m. sezonas buvo sausesnis, lyginant su 2018 m., ypač balandžio ir birželio mėnesiais, o tai pavėlino kukurūzų auginimą ir ankstyvą pasėlių vystymąsi. 2020 m. kukurūzų auginimo sezono metų vidutinė temperatūra siekė 16,23 °C, o birželio ir rugpjūčio mėnesiais užfiksuotos aukščiausios temperatūros vertės.

2.6. Statistinė analizė

Dispersijos analizė (ANOVA) ir Duncan Multiple testas buvo taikomas norint nustatyti reikšmingus skirtumus tarp vidurkių su $p < 0,05$ reikšmę. Koreliacijos analizė buvo naudojama siekiant nustatyti ryšį tarp laiko (dienomis arba savaitėmis) ir mineralinio azoto koncentracijos dirvožemyje, įskaitant jo formas (nitrato ir amonio). Buvo naudojama statistinės analizės programinė įranga IBM SPSS 25.0.

TYRIMŲ REZULTATAI

3.1. Mineralinio azoto koncentracijos kaita dirvožemyje

3.1.1. Mineralinio azoto išsiskyrimas iš karbamido-sieros trąšų auginant kukurūzus

Rumokų bandymų stotyje buvo atlikti lauko bandymai 2018–2019 m. Kukurūzai tręšti karbamido-sieros trąšomis ir tirtas jų poveikis kukurūzų produktyvumui ir azoto kaupimuisi bei jo pasisavinimui dirvožemyje (Publikacija 1). Tyrimo rezultatai parodė reikšmingą karbamido ir sieros trąšų naudojimo poveikį mineralinio azoto išsiskyrimui dirvožemyje, lyginant su įprasto karbamido naudojimu. Kaip buvo numatyta, sieros padidėjimas dirvožemyje žymiai padidino mineralinio azoto išsiskyrimą iš karbamido granuliu [101–103]. Rezultatai parodė, kad nitratų NO_3 ir amonio NH_4 suformuoto mineralinio azoto koncentracija dirvožemyje 2019 m. buvo didesnė nei 2018 m. dėl kaupiamojo efekto [104]. Nitratų NO_3 koncentracija dirvožemyje reikšmingai ($p \leq 0,01$) koreliavo su kukurūzų augimo laiku abiem metais (2018 ir 2019 m.). Be to, rezultatai parodė, kad 2018 ir 2019 m. amonio koncentracija dirvožemyje buvo mažesnė lyginant su nitratų kiekiu. Amonio NH_4 koncentracija sudarė atitinkamai apie 9 ir 17 % viso mineralinio azoto kiekio dirvožemyje 2018 ir 2019 m. Amonio koncentracija reikšmingai nekoreliavo nei su laiku, nei su tręšimo normomis abiem metais (2018–2019). Mineralinio azoto koncentracija dirvožemyje 2018–2019 m. kukurūzų augimo laikotarpiu reikšmingai koreliavo ($p \leq 0,01$) su laiku. Dirvožemio mineralinis azotas neigiamai tiesiškai koreliavo su laiku, o tai reiškia, kad laikui bėgant koncentracija sumažėjo. Išsamūs rezultatai aptariamai 1 publikacijoje.

3.1.2. Mineralinio azoto išsiskyrimas iš įvairių modifikuoto karbamido trąšų

Vieno sezono (2020 m.) lauko eksperimentas buvo atliktas siekiant ištirti įvairių modifikuotų karbamido trąšų, tokių kaip sintezuotas karbamido kokristalas ir karbamido kalio humatas (skirtingomis dozėmis), poveikį mineralinio azoto išsiskyrimui paviršiniame (0–30 cm) ir podirvio (30–60 cm) sluoksniuose, siekiant sumažinti azoto praradimą, pagerinti pasisavinimą ir padidinti jo panaudojimo efektyvumą auginant kukurūzus (2 publikacija). Rezultatai parodė, kad mineralinio azoto išsiskyrimas dirvožemyje 0–30 cm ir 30–60 cm gylyje kukurūzų augimo metu neigiamai reikšmingai koreliavo su laiku (savaitėmis) visuose variantuose, išskyrus U200 ir UPH100 0–30 cm paviršiniame sluoksnyje. Dirvožemio paviršiniame sluoksnyje (0–30 cm) mineralinio azoto koncentracija buvo didesnė nei podirvyje (30–60 cm). Daugiau rezultatų pateikta 2 publikacijoje.

3.1.3. Mineralinio azoto modeliai skirtingos granulometrinės sudėties dirvožemiuose

Šiltnamio sąlygomis buvo atliktas vegetacinis eksperimentas (20 ± 2 °C ir 60 % drėgmės). Šio tyrimo pagrindiniai tikslai buvo ištirti mineralinio azoto išsiskyrimo dinamiką skirtingos granulometrinės sudėties dirvožemiuose, siekiant suprasti sąveiką tarp dirvožemio rodiklių ir mineralinio azoto išsiskyrimo, bei įvertinti tradicinio karbamido poveikį miežių biomasei, lyginant su karbamido padentgas kalio humatu (3 publikacija). Mineralinio azoto išsiskyrimo dinamika ir jo pagrindinės formos (NH_4 ir NO_3) demonstravo ryškius skirtumus priklausomai nuo dirvožemio granulometrinės sudėties (5 pav.). Rezultatai parodė, kad dirvožemio mineralinis azotas ir jo pagrindinės formos (NH_4 ir NO_3) buvo reikšmingai paveiktos ($p \leq 0,01$) karbamido ir karbamido su kalio humatu. Trąšų poveikis skirtingiems granulometrinės sudėties dirvožemiams sukūrė skirtingas mineralinio azoto ir jo formų NH_4 ir NO_3 dinamikas. Mineralinio azoto ir nitrato NO_3 dinamika itin negatyviai koreliavo su laiku visose trąšų grupėse vidutiniu ($p \leq 0,05$) stiprumu. Mažiausios mineralinio azoto vertės gautos apdorojant smėlingos dirvožemį (5 pav.). Dengtuose karbamido kalio humato preparatuose (UPH200 ir UPH100) užfiksuotos didesnės mineralinio azoto vertės nei karbamido preparatuose (U200 ir U100).

UPH200 užfiksuotos didžiausios mineralinio azoto vertės – atitinkamai $47,87 \text{ mg kg}^{-1}$, $27,71 \text{ mg kg}^{-1}$ ir $6,55 \text{ mg kg}^{-1}$ daugiau nei kontroliniame, U100 ir U200 variantuose (2 lentelė, 3 publikacija). Taikant dengto karbamido kalio humato variantus (UPH200 ir UPH100), gautas didesnis mineralinio azoto kiekis, lyginant su kitais karbamido variantais (U200 ir U100) priemolio dirvožemyje (2 lentelė, 3 publikacija). Smėlingo priemolio dirvožemyje su U200 užfiksuotas didžiausias kiekis – $271,25 \text{ mg kg}^{-1}$, kuris buvo $58,47 \text{ mg kg}^{-1}$ didesnis už UPH200 variantą. Kitais atvejais skirtumo tarp U100 ir UPH100 nepastebėta. Karbamido trąšomis (U200 ir U100) tręštuose smėlingo priemolio dirvožemiuose užfiksuoti didesni mineralinio azoto kiekiai, palyginti su dengtomis karbamido kalio humato trąšomis (UPH200 ir UPH100), naudojant U200 gautas didžiausias mineralinio azoto kiekis – $425,08 \text{ mg kg}^{-1}$, $93,39 \text{ mg kg}^{-1}$ didesnis nei UPH200, o U100 $44,05 \text{ mg kg}^{-1}$ didesnis nei UPH100 (2 lentelė, 3 publikacija).

3.2. Modifikuoto karbamido įtaka derliaus produktyvumui, derliui ir biomasei

3.2.1. Karbamido-sieros trąšų įtaka augalų tankiui, žaliosios masės ir sausosios masės kiekiui, grūdų derliui bei grūdų kokybei (1 publikacija)

Augalų tankio, žaliosios ir sausosios masės derlius rezultatų palyginimas po tradicinio karbamido ir karbamido-sieros trąšų panaudojimo pateikiamas 3 lentelėje (1 publikacija). 2018 metais buvo pastebėta, kad tręšimo būdai turėjo reikšmingą ($p \leq 0,01$) poveikį augalų tankiui ir žaliųjų medžiagų derliui, lyginant su kontrole. Karbamidas + amonio sulfatas sąlygojo didelį augalų tankį ir žaliosios medžiagų derlių. 2019 metais tarp tręšimo būdų ir augalų tankio bei

žaliųjų medžiagų masės reikšmingų skirtumų. Tuo tarpu gipso karbamido kokristalai palyginti su tradiciniu karbamidu ir kontrolė parodė reikšmingą augalų tankio ir žaliųjų medžiagų masės derliaus skirtumą (3 lentelė, 1 publikacija). Taigi, 2018 ir 2019 metais nustatyta, kad tręšimo metodai neturėjo reikšmingo poveikio sausosios medžiagos masei. Tačiau UCSC sąlygojo didžiausią sausųjų medžiagų masę abiem tyrimo metais (2018 ir 2019) (3 lentelė, 1 publikacija).

Tręšimas turėjo reikšmingą poveikį kukurūzų biometriniais matavimams. Buvo matuotos kukurūzų šviežios ir sausos burbuolės, jų derlius ir 1000 grūdų masė 2018 ir 2019 m., (4 lentelė, 1 publikacija). 2019 metų rodikliai buvo geresni nei 2018 metų. Kitais atžvilgiais reikšmingų skirtumų tarp tirtų trąšų 2018 m. nepastebėta, o apdorojimas karbamidu ir amonio sulfatu (UAS) turėjo didesnę poveikį visiems produktyvumo rodikliams, išskyrus išsivysčiusių kukurūzų burbuolių derlių. Apdorojimas trąšomis reikšmingai paveikė kukurūzų biometrinius matavimus, įskaitant išsivysčiusias kukurūzų burbuoles, šviežių ir sausų burbuolių derlių ir grūdų derlių, palyginti su kontroliniu. Dviejų metų tyrimo (2018–2019 m.) rezultatai pateikti 4 lentelėje (1 publikacija). 2019 m. rezultatai buvo geresni palyginti su 2018 m. Reikšmingų skirtumų tarp tirtų trąšų 2018 m. nebuvo pastebėta, o naudojant karbamidą + amonio sulfatą (UAS), buvo gautas didesnis efektas visiems produktyvumo parametrams, išskyrus išvystytą kukurūzų burbuolių derlių. 2019 m. karbamido gipso kokristalai pasižymėjo reikšmingai ($p < 0,01$) didesniais produktyvumo rodikliais, po išsivysčiusių kukurūzų burbuolių, sausų burbuolių derliaus ir grūdų derliaus rodikliais, palyginti su kitais lyginamaisiais variantais.

Tai galima matyti 2018 ir 2019 m. sezonų grūdų derliaus rezultatuose, jie pateikiami 6 paveiksle. Tačiau lyginant derlių tarp dviejų sezonų (2018–2019 m.) reikšmingų skirtumų nepastebėta. Trąšų, tokių kaip karbamidas+amonio sulfatas, karbamidas+kalcio sulfatas ir karbamido gipso kokristalo panaudojimas lėmė pastebimą grūdų derliaus pagerėjimą tiek 2018, tiek 2019 metais. Pagerėjimas buvo susijęs su didesniu sieros kiekiu naudojant šias trąšas, palyginti su karbamidu be priedų ir kontroline medžiaga [110], [111], [112]. 2018 m. naudojant karbamidą+amonio sulfatą ir karbamido kokristalų trąšas grūdų derlius padidėjo atitinkamai 47,8 % ir 43,73 %, daugiau nei kontrolė, taip pat 10,5% ir 7,50% nei karbamidą. 2019 m., karbamido kokristalų naudojimas žymiai padidino grūdų derlių, kuris buvo atitinkamai 41,17 % ir 23,07 % didesnis nei kontrolinio ir karbamido be priedų variantuose. Stebint UCS, nustatytas 26,70% ir 10,46% didesnis grūdų derlius lyginant su kontrole ir karbamidu, kaip pateikta 4 lentelėje (1 publikacija).

UAS užėmė trečią vietą ir padidino derlių 23,52 %, atitinkamai 7,60 % daugiau nei kontrolinis ir karbamidas. Kombinuotas karbamido ir sieros trąšų naudojimas parodė tvarų poveikį laipsniškai didinant mineralinio azoto kaupimąsi dirvožemyje ir skatinant padidėjusį azoto pasisavinimą grūduose, dėl ko ir padidėjo grūdų derlius [110], [113], [114], [115]. Svarbu

tai, kad teigiamas atsakas į tręšimą azotu ir siera buvo ypač akivaizdus didinant grūdų derlių, ypač 2019 m. Trąšų panaudojimas turėjo didelės įtakos įvairioms grūdų kokybės savybėms, įskaitant bendrą azoto ir žalių baltymų kiekį, tiek 2018 m., tiek 2019 m., palyginti su kontrole, be reikšmingų skirtumų, kaip nurodyta 5 lentelėje (1 publikacija). Taigi, trąšų įterpimas neturėjo reikšmingos įtakos krakmolo kiekiui nei vienais metais (2018 ir 2019 m.). Naudojant karbamido kokristalų trąšas rastas didžiausias bendrasis azoto kiekis grūduose, 2018 m. – 1,42 % didesnis už kitus variantus, o 2019 m. – 1,47 %. Taip pat gautas didžiausias žalių baltymų kiekis grūduose abiem metais.

3.2.2. Karbamido kokristalo ir karbamido kalio humato poveikis augalų tankiui, šviežių lapų ir stiebų, bei sausųjų medžiagų masės derliui (2 publikacija)

Modifikuoto karbamido naudojimas, nesvarbu, ar tai būtų kokristalas, ar padengtas kalio humatu, turėjo didelę įtaką kukurūzų auglų tankumui, šviežiems lapams ir stiebams bei sausosioms medžiagoms. Augalų tankis, švieži lapai ir stiebai bei sausųjų medžiagų derlius pateikti 2 lentelėje (2 publikacija). 7 paveiksle parodyta, kad UC200>UPH200 variantas užfiksavo žymiai ($p < 0,01$) didesnę šviežių lapų ir stiebų derlių, palyginti su kontrolė ir karbamido variantu, o po to buvo apdorotas UC100>UPH100. Be to, tos pačios trąšos reikšmingai ($p < 0,01$) paveikė sausųjų medžiagų kiekį, palyginti su kontrole. Tuo tarpu karbamido naudojimas (U100 ir U200) parodė nereikšmingą poveikį lyginant su kontrole analizuojant šviežių lapų ir stiebų masę bei sausųjų medžiagų kiekį. Karbamido kokristalo ir padengto karbamido kalio humato panaudojimas reikšmingai paveikė grūdų derlių ($p \leq 0,01$), kaip parodyta 8 paveiksle. Apdorojimas U100 neženkliai skyrėsi nuo kontrolės, bet padidino grūdų derlių 7,1 %. U200 reikšmingai ($p < 0,01$) davė didesnę grūdų derlių nei kontrolė ir U100, atitinkamai 30,53 % ir 21,89 %. Priešingai, karbamido + kalio humato (UPH100, UPH200) ir karbamido kokristalų (UC100, UC200) naudojimas parodė reikšmingą ($p < 0,01$) grūdų derliaus padidėjimą, atitinkamai 30,53 %, 50,47 %, 39,25 % ir 56,62 %. Panaudojus UC200>UPH200 buvo užfiksuotas didesnis reikšmingas grūdų derlius nei U200, taip pat UC100>UPH100 grūdų derlius buvo ženkliai didesnis nei U100, kaip parodyta 3 lentelėje (2 publikacija).

Palyginti su kontrole, kukurūzų burbulės, įskaitant šviežių ir sausų burbulės medžiagų derlių, buvo reikšmingai paveiktos modifikuoto karbamido trąšų naudojimo. 3 lentelėje (2 publikacija) pateiktos šviežių ir sausų burbulių derliaus priemonės. Modifikuotas karbamido variantas reikšmingai paveikė grūdų charakteristikas, įskaitant grūdų baltymų, bendro azoto ir angliavandenių kiekį, kaip nurodyta 4 lentelėje (2 publikacija). Grūdų sausajai medžiagai reikšmingo poveikio neturėjo. Kontroliniame variante nustatytas mažiausias reikšmingas ($p < 0,01$) bendrojo azoto grūduose ir grūdų baltymuose kiekis, palyginti su kitais tirtais

variantais, tačiau reikšmingų skirtumų tarp kitų trąšų nepastebėta. Priešingai, naudojant UC200 nustatyta didžiausia bendro azoto koncentracija – 1,23 %, o bendras grūdų baltymas – 7,67 %. Grūdų sausosios medžiagos UPH200 ir UPH100 svyravo atitinkamai nuo 93,68 % iki 95,13 %, be reikšmingų skirtumų tarp lyginamųjų variantų. Trąšų naudojimas labai reikšmingai paveikė grūdų angliavandenių kiekį. Naudojant karbamido kokristalų trąšas (UC200 ir UC100) gautas didesnis reikšmingas ($p < 0,01$) angliavandenių kiekis – 76,69 ir 73,43 %, palyginti su kitais, ir tai gali būti paaiškinta šiose trąšose esančiu didesniu sieros kiekiu, kuri atlieka svarbų vaidmenį didinant angliavandenių kaupimąsi [115].

3.2.3. Karbamido junginių poveikis daigumui ir miežių biomasei (3 publikacija)

Sėklos sudygo praėjus 4-ioms dienoms nuo tręšimo, daigumas siekė 70–90 %. Modifikuotą karbamido trąšų naudojimas reikšmingai įtakojo miežių daigumą ($p \leq 0,01$). Nepaisant skirtingos dirvožemio granulometrinės sudėties UPH200 ir U200 demonstravo slopinantį poveikį sėklų daigumui lyginant su kontrole. Ir atvirkščiai, reikšmingų skirtumų tarp UPH100 ir U100, palyginti su kontrole, kaip parodyta 5 lentelėje, nepastebėta. Apdorojimas karbamidu ir karbamido kalio humatu turėjo reikšmingą poveikį ($p < 0,05$) miežių žaliajai biomasei skirtinguose granulometrinės sudėties dirvožemiuose, palyginti su kontrole. Išbandžius skirtingus trąšų variantus reikšmingų skirtumų neužfiksuota, tačiau UPH200 ir U200 turėjo didžiausią poveikį, biomasės kiekis atitinkamai siekė 31,44 g ir 31,25 g. Nebuvo skirtumo tarp U100 ir UPH100, lyginant su kontrole, kurios biomasė buvo mažiausia – vidutiniškai 20,47 g. Analizuojant variantų poveikį tarp skirtingos granulometrinės sudėties dirvožemių išryškėjo aiškūs skirtumai, kaip pavaizduota 9 paveiksle. Ypač smėlingame dirvožemyje skirtingų trąšų naudojimas turėjo pastebimą poveikį miežių žaliajai biomasei ($p \leq 0,01$). UPH200 ir UPH100 naudojimas davė reikšmingai didesnę biomasę lyginant su U100 ir kontrole, o naudojant U200 reikšmingo skirtumo nepastebėta (9 pav.). Smėlingame molingame dirvožemyje karbamido junginių įtaka žaliajai biomasei buvo statistiškai reikšminga ($p \leq 0,05$). Apdorojant UPH200 biomasė buvo didžiausia, palyginti su kitais variantais.

Po U200 naudojimo biomasė buvo ženkliai mažesnė, apie 42 %. Reikšmingų biomasės skirtumų tarp U100 ir UPH100 apdorojimų, palyginti su kontrole, nenustatyta. Poveikis pastebėtas ir priemolio dirvožemyje, kur U200 ir U100 variantai rodė reikšmingai didesnę poveikį biomasei ($p < 0,05$), palyginti su kontrole. Ir atvirkščiai, UPH200 ir UPH100 neturėjo pastebimo poveikio biomasei, palyginti vienas su kitu arba su kontrole (9 pav.). Nors trąšų naudojimas lėmė didžiausią miežių biomasę priemolio dirvožemyje, palyginti su kitų tipų dirvožemiais, šie rezultatai neturėjo statistinio reikšmingumo. Didžiausia reikšminga biomasė buvo U200 – 51,8 g, po to sekė UPH200 – 49,7 g, kaip parodyta 9 paveiksle. Sausosioms medžiagoms reikšmingą įtaką ($p \leq 0,05$)

turėjo dirvožemio granulimetrinė sudėtis. Kiekvienam dirvožemio granulimetrinės sudėties vidutinės sausųjų medžiagų vertės buvo tokios: daugiausia sausųjų medžiagų buvo priesmėlyje, po to – priesmėlio molyje. Mažesnės sausųjų medžiagų vertės buvo smėlingame ir priemolio dirvožemyje, atitinkamai 70,15 g ir 71,03 g. Tačiau naudotos skirtingos trąšos sausai medžiagai pastebimo poveikio neturėjo. Toliau pateikiamos vidutinės kiekvieno apdorojimo sausųjų medžiagų vertės, išvardytos chronologine tvarka: U200 svėrė 74,96 g, UPH200 – 73,11 g, UPH100 – 71,42 g, U100 – 70,84 g, kontrolinė svėrė 69,68 g.

3.3. Azoto įsisavinimas, azoto atgavimo ir azoto naudojimo efektyvumas

3.3.1. Azoto įsisavinimas, tiesioginis azoto atgavimo efektyvumas grūduose (1 publikacija)

2018–2019 m. dirvožemio mineralinis azotas turėjo reikšmingą koreliaciją ($p < 0,01$) su grūdų azoto pasisavinimu, kaip parodyta 10 paveiksle. Grūdų azoto pasisavinimo padidėjimas reikšmingai ($p < 0,01$) prisidėjo prie bendro N kiekio padidėjimo grūduose. Derliuje abiem tyrimo metais (2018 ir 2019). 2018 m. pastebėtas stiprus teigiamas tiesinis ryšys tarp dirvožemio mineralinio azoto ir azoto pasisavinimo grūduose. Panašiai 2019 m. koreliacijos koeficientas (r) rodė teigiamą tiesinį ryšį tarp mineralinio azoto dirvožemyje ir azoto pasisavinimo grūduose. Taigi grūdų derlius abiem tyrimo metais reikšmingai koreliavo su mineralinio azoto kiekiu dirvožemyje, kaip parodyta 10 paveiksle. Koreliacija suteikė stiprų teigiamą tiesinį ryšį tarp azoto pasisavinimo ir grūdų derliaus (5 lentelė, 1 publikacija). Sieros kiekis dirvožemyje reikšmingai koreliavo ($p < 0,01$) tiek su mineralinio azoto kiekiu dirvožemyje, tiek su grūdų azoto pasisavinimu, teigiama tiesine priklausomybe, kaip parodyta 11 paveiksle. Tuo tarpu grūdų derlius reikšmingai ($p < 0,05$) koreliavo su dirvožemio siera vidutiniu teigiamu tiesiniu ryšiu 2018 m. ir reikšmingu ($p < 0,01$) stipriu teigiamu tiesiniu ryšiu 2019 m., kaip parodyta 11 paveiksle. Šie ryšiai gali būti įrodymas, kad karbamido naudojimas kartu su siera gali padidinti mineralų išsiskyrimą dirvožemyje ir pagerinti azoto pasisavinimą, kad būtų gautas geras grūdų derlius [101], [110].

3.3.2. Azoto įsisavinimas ir agronominis azoto naudojimo efektyvumas (2 publikacija)

8 lentelėje, 2 straipsnyje pateikta statistika, parodė, kad padengto karbamido kalio humato ir karbamido kokristalų naudojimas dideliu kiekiu (200 kg N ha^{-1}) turėjo itin reikšmingą poveikį azoto pasisavinimui tiek grūduose, tiek stiebuose, taip pat bendram azoto kiekiui, kukurūzų pasėlių pasisavinimą, palyginti su kontroliniu ir vien tik įprastu karbamidu (12 pav.). Naudojant UPH200 ir UC200, grūdų azoto pasisavinimas padidėjo atitinkamai 79,15 % ir 93,677 %, palyginti su kontrole, o didžiausias N pasisavinimas stiebuose buvo atitinkamai 133,58 ir $168,49 \text{ kg ha}^{-1}$. Šios trąšos reikšmingai paveikė agronominį azoto naudojimo efektyvumą, kaip parodyta 12 paveiksle. Karbamido kokristalai ir padengtas karbamido kalio humatas padidino

azoto naudojimo efektyvumą, ypač esant 100 kg N ha⁻¹ normai. UC100 parodė didžiausią azoto naudojimo efektyvumą, po to sekė UPH100. Tai rodo, kad didesnėmis nei 100 kg N ha⁻¹ trąšų normomis galima gauti didesnę derlių, tačiau jos yra mažiau efektyvios, palyginti su ekonomine 100 kg N ha⁻¹ doze [116].

3.4. Mineralinio azoto prieinamumo dirvožemyje vertinimas (3 publikacija)

Aprašomųjų statistikos rezultatų išvados atskleidžia pastebimus mineralinio azoto kiekio svyravimus dirvožemyje. Šie svyravimai pateikiami 4 lentelėje. Dirvožemyje esamo azoto kiekį galima suskirstyti taip: žemas (<40 mg kg⁻¹), vidutinis (40–80 mg kg⁻¹) ir aukštas (>80 mg kg⁻¹) [108]. Remiantis šia klasifikacija, smėlio dirvožemis pasižymėjo mažu mineralinio azoto kiekiu, kuris sudarė 38,85 mg kg⁻¹. Priešingai, smėlingo priemolio, priemolio ir smėlingo molio dirvožemiai parodė aukštą mineralinio azoto prieinamumo lygį, siekiantį atitinkamai 168,31 mg kg⁻¹, 165,66 mg kg⁻¹ ir 257,52 mg kg⁻¹. Šiuos skirtumus galima paaiškinti įvairiomis dirvožemio fizikinėmis ir cheminėmis savybėmis, įskaitant dirvožemio granulimetrinę sudėtį, organinės medžiagos kiekį, mainų katijonų gebą, pH ir kt. Šios dirvožemio savybės yra svarbios maistinių medžiagų gausumui ir prieinamumui dirvožemyje [109], [110]. Pavyzdžiui, smėlio dirvožemis yra lengvas ir neproduktyvus dirvožemis, todėl jo maistinių medžiagų kiekis yra mažas [99], [108].

Priešingai, smėlingas priemolis pasižymi didesniu derlingumu ir jo agronominės savybės yra geresnės, todėl maistinės medžiagos yra prieinamesnės [100], [111]. Variacijos koeficientas (VK) yra vertingas statistinis matas, skirtas įvertinti variacijos lygį tarp skirtingų duomenų rinkinių, net jei vidurkiai rodo reikšmingus skirtumus [108], [112]. VK mažesnis nei 10 %, rodo riboto kintamumo būklę, o nuo 10 % iki 100 % diapazonas rodo vidutinį kintamumą [112]. Priešingai, VK, viršijantis 100 %, rodo aukštą variacijos laipsnį [112]. Šio tyrimo metu nustatytas mineralinio azoto N_{min} koeficientas. Smėlio dirvožemio mėginiai rodo mineralinio azoto 23,41 VK, tai reiškia vidutinį kintamumą (4 lentelė). Priešingai, smėlingo priemolio, priemolio ir smėlingo molio dirvožemiuose fiksuotas VK yra didesnis nei 100 %, tai reiškia aukštą kintamumą mineralinio azoto atžvilgiu šių dirvožemių mėginiuose. Todėl pastebimas didelis kintamumas rodo, kad augalai gali potencialiai pasisavinti azotą iš trąšų per ilgą laiką.

IŠVADOS

1. Išsamūs šio tyrimo rezultatai, apimančios šviežių ir sausųjų medžiagų derlių, grūdų derlių, grūdų charakteristikas, azoto pasisavinimą grūduose ir stiebuose, taip pat bendrą azoto pasisavinimą ir azoto panaudojimo efektyvumą, bendrai parodo modifikuotų karbamido trąšų (karbamido kalio humatas ir karbamido kokristalas) pranašumą, lyginant su įprastu karbamidu, kukurūzų derliaus produktyvumo ir azoto naudojimo efektyvumo didinimo kontekste.

2. Karbamido-sieros trąšų naudojimas parodė teigiamą koreliaciją tarp mineralinio sieros-azoto (MSN) kaupimosi dirvožemyje laikui bėgant ir ženkliai padidinto azoto pasisavinimą, ypač kai azoto šaltiniu naudojamas sintezuotas karbamidas. Todėl ši metodika pristato novatorišką sistemą ir metodą, leidžiantį gauti didesnę derlių ir aukščiausią kukurūzų kokybę. Ši strategija gali leisti optimaliai panaudoti azotą pasėliuose ir potencialiai sumažinti aplinkos problemų, tokių kaip nitratų išplovimas ir amoniako išgaravimas, riziką.

3. Azoto išsiskyrimo greitis yra vienas iš labiausiai įtakančių veiksnių mažinant azoto nuostolius ir gerinant trąšų azoto panaudojimo efektyvumą. Įprastinio karbamido greitas išsiskyrimas tręšimo pradžioje padidina azoto nuostolių riziką. Todėl karbamido kokristalų, kaip lėto atpalaidavimo trąšų, naudojimas atlieka pagrindinį vaidmenį išlaikant pusiausvyrą tarp augalų azoto poreikio ir mineralinio azoto atsargų dirvožemyje. Karbamido padengimas kalio humatu, kaip kontroliuojamo karbamido trąša, pasižymi teigiamu poveikiu, nes sumažina karbamido azoto nuostolius ir padidina azoto pasisavinimą augaluose.

4. Modifikuotų karbamido trąšų efektyvumas labai priklauso nuo jų cheminių savybių, įpurškimo normų ir būdingų cheminių-fizinių dirvožemio, į kurį jos yra įterpiamos, savybių. Įvairių trąšų įterpimas demonstruoja skirtingus dirvožemio atsakus. Svarbu atkreipti dėmesį, kad dengto karbamido kalio humato efektyvumas pranoko įprastinio karbamido efektyvumą smėlio ir priemolio dirvožemyje. Tuo tarpu įprastinis karbamidas ypač paveikė smėlingą priemolį, priesmėlingą molį, padidėjus azoto kiekiui.

PRAKTINĖ SVARBA / REKOMENDACIJA

Šiame tyrime buvo aptartas modifikuotų karbamido trąšų vaidmuo pasėlių produktyvumui ir manoma, kad šio tyrimo rezultatai bus naudingi mokslininkams, kurie tiria ryšį tarp trąšų pramonės ir žemės ūkio sektoriaus, siekiant padidinti pasėlių produktyvumą. Todėl, pateikiame keletą rekomendacijų karbamido junginių, kaip įvairių tipų dirvožemio trąšų, naudojimui: pirmiausia, karbamido trąšų išbėrimo normą patariama koreguoti pagal dirvožemio tipą ir granulimetrinę klasę.

Karbamido trąšų normą patartina koreguoti atsižvelgiant į dirvožemio granulimetrinę sudėtį. Pavyzdžiui, stambios ir smėlingos granulimetrinės sudėties dirvožemiams, paprastai reikia didesnių trąšų normų, o smulkios granulimetrinės sudėties dirvožemiams gali prireikti mažesnių normų dėl didesnio maistinių medžiagų sulaikymo pajėgumo.

Be to, kaip rodo šis tyrimas, mažesnės arba ekonomiškos karbamido dozės yra veiksmingesnės, palyginti su didelėmis azoto normomis. Nustatyta, kad dirvožemiuose, kuriuose yra mažesnis organinės medžiagos kiekis arba aukštas pH lygis, naudingiau karbamidą įterpti į dirvožemį, o ne paskleisti ant paviršiaus. Toks metodas gali padėti sumažinti azoto nuostolius dėl garavimo.

Galiausiai, siekiant sumažinti nuostolius, šiame tyrime rekomenduojama naudoti modifikuojančias karbamido trąšas dengiant arba sintezuojant, kad sulėtintų karbamido virsmą amoniaku ir taip sumažėtų azoto praradimas. Todėl šiame tyrime modifikuoti karbamido junginiai buvo rekomenduojami kaip naudingos ir veiksmingos trąšos, palyginti su įprastu karbamidu.

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EFFECT OF UREA COMPOUNDS AS FERTILIZER ON DIFFERENT SOIL TYPES

Doctoral Dissertation

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Užsakymo Nr. 24-037. Tiražas 15 egz. 2024 04 08.
Nemokamai