

Article

Release of Nitrogen from Granulate Mineral and Organic Fertilizers and Its Effect on Selected Chemical Parameters of Soil

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Abstract: The objective of this work was the evaluation of the release patterns of nitrogen from various types of fertilizers and their impact on selected chemical parameters of calcareous soil. Three mineral fertilizers and two organic fertilizers were tested in the laboratory for 35 days. This study showed the rapid release of nitrogen from mineral types. More than 70% of the nitrogen was released from the ammonium granules and 98% from the urea granules. The rate of nitrogen release from pellets of organic origin was much slower than from mineral pellets, the released N was 15–28% of the original amount. Soil pH was altered by incubation. The content of soil N changed significantly due to the incubation of N mineral fertilizers; no changes were observed for organic fertilizers. The EC value of the soil solution was significantly modified under the influence of mineral granules, it reached a maximum of 1147 $\mu\text{S cm}^{-1}$ on the 10th day, and for organic fertilizers of 944 $\mu\text{S cm}^{-1}$ on the 35th day. The results of this study characterize each N release pattern, providing data to support a more efficient nutrient management strategy in calcareous soils and the effect of incubated fertilizers on soil chemical parameters.

Keywords: mineral fertilizers; organic fertilizers; soil nitrogen; nitrogen release rate



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1. Introduction

In the contemporary fertilization system, solutions are sought that are characterized by high precision in the application of nutrients enabling more effective management of nutrients, one of them may be application directly to the root development zone. N-urea fertilizers in calcareous soil are characterized by a low fertilization efficiency index of 30–40% [1]. Factors affected by N losses in calcareous soils are ammonia volatilization, nitrate leaching, and denitrification processes [2]. The gaseous losses of ammonium are related to soil moisture [3,4], soil pH [5], granular size and shape [6], the salinity of the soil environment [7], and fertilizer placement [8]. NO_3^- is highly susceptible to nitrate leaching as it moves through the soil with diffusion [9] and mass flow of water [10]. The increase in soil pH to the value of 7–8 has an impact on nitrogen transformation, stimulating the formation of nitrates, which form nitrous oxide [11,12], this process is strongly inhibited at pH 8.5 [13]. The conversion rate of organic compounds into mineral compounds underlies processes responding to N efficiency and losses. Calcareous soil (pH 8.2 or higher) has been proven to increase urea hydrolysis, which reaches completion within two days of application [5]. Intensive agricultural systems that are quite fertilizer based demand high inputs with increased chances of N losses resulting in huge economic loss [14]. Some practices, such as deep-band placement application [15], high doses of ammonium nitrogen localized in special depots, time of application [16], and slow-release fertilizers [17,18],

work to minimize nutrient risk pollution and maximize economic aspects [19]. The toxic effect of ammonium ion on the root system when the fertilizer is placed deeply is mitigated by the minimal contact between the source of N in the deposit and the surface of the root system [20,21], the use of SRF (slow-release fertilizer) is also a safe solution, causing minimal damage to germination [22]. Furthermore, new local conditions created within the nitrogen source zone slow down nitrobacteria activity [23], and less NO_3^- loss occurs [21,24]. If the release rate is more compatible with the metabolic needs of plants, high productivity of fertilization can be achieved [25]. Plant nutrient availability is controlled by soil properties and microbe interactions [26,27]. High soil pH accelerates nitrification, with an optimum pH of 8.3 to 9.3 for *Nitrobacter* and 8.5 to 8.8 for *Nitrosomonas* [28]. Beyond that, the availability of nutrients differs substantially in the root zone and as a medium of plant growth in bulk soil [29]. Inorganic nitrogen forms N-NH_4^+ and N-NO_3^- , and can trigger pH changes in soil of up to 1.2 pH units under field conditions [30,31]. A surface application of urea increases the pH until the nitrification process accelerates [8]. If the relative concentration of NH_3 in soil increases from 0.1 to 1%, 10%, or 50%, the soil pH value increases from 6 to 7, 8, or 9, respectively [32,33]. Organic biomass i.e., manure, increases total organic carbon and total nitrogen in soil [34]. This improvement can be accomplished faster with higher soil temperature and soil humidity [35,36]. The individual physical and chemical properties of granules influence the soil characteristics, changing the soil parameters until a new balance is reached. Analyzing release rate patterns enables a better understanding of how each N fertilizer works in calcareous soils. Optimal nutrient management can then be achieved by supplying crops according to the nutrient uptake requirements of each stage.

To achieve the objective of this study, a laboratory experiment was carried out using a soil incubation method which is common practice for slow-release rate pattern measurement [37,38]. The 35-day incubation of fertilizers in calcareous soil allows the nitrogen release pattern to be analyzed throughout the incubation period and at different soil moisture levels. Additionally, the soil chemical parameters, soil N, soil pH, and EC (electric conductivity) were monitored in parallel.

2. Materials and Methods

2.1. Study Fertilizers

This research was carried out in laboratory conditions in Centro de Investigaciones Energéticas, Medioambientales y Tecnológicas (CIEMAT), Madrid.

Two mineral fertilizers called UreaPhoS (U-PS_c and U-PS_f) were used in this study, containing the same quantity and types of chemical components, but with different size granules with a diameter of 10 mm and 3–5 mm, respectively.

Urea as a nitrogen source in this study was in the form of an adduct with calcium, being chemically bonded to N–Ca hydrogen and classified as a slow-release fertilizer (SRF). The granulate contained nitrogen (N), sulfur (S) in $\text{CaSO}_4 \cdot 4\text{CO}(\text{NH}_2)_2$, and phosphorus (P) in $\text{Ca}(\text{H}_2\text{PO}_4)_2$ chemical form. Granules were formulated using a plate granulator [39,40], and the compressive strength of the granules was 36 and 222 N, respectively [39].

The third mineral fertilizer, DAP—diammonium phosphate, contained 18% nitrogen in ammonium form, and 46% P— P_2O_5 in the form of $(\text{NH}_4\text{H}_2\text{PO}_4)$ and $(\text{NH}_4)_2(\text{HPO}_4)$. This fertilizer consisted of granules 3–5 mm in diameter. The compressive strength of the granules was 71.1 N.

Two organic fertilizers were prepared in an experimental station in a pilot installation of pellet production in Skierniewice, Poland. One was made from turkey manure (T_M) and the other was from post-mushroom substrate (M_S). Nitrogen in these pellets occurs as ammonium (mineral) and as organic compounds.

The determination of ammonium N and Kjeldahl nitrogen [41] was carried out in an automated way using KjelFlex K-360 equipment (distillation and titration units, Buchi, Basel, Switzerland) coupled to a digestion module (Digestion K-435 and a Scrubber B-414, Buchi). The modular setup allowed the adaptation of the KjelFlex K-360 to the other

mentioned modules for ease of operation. With this set of modules, it was possible to carry out a distillation and a titration of samples, allowing the ammonia N to be directly measured, or for N Kjeldahl to be measured following the digestion process.

The total, organic, and ammonium nitrogen was determined in the dry mass of 0.3 g randomly chosen samples (Table 1). The ammonium N was determined with equipment without a mineralization section, only carrying out the distillation process. The organic N was calculated as the difference between the total and ammonium N.

Table 1. Fertilizer characteristics—nitrogen content in dry mass (%).

Fertilizer	Mass Percentage—N (%)		
	NH ₄ -N	N _{org} -N	N _{tot} -N
U-PS _c	-	20.81	20.81
U-PS _f	-	20.89	20.89
DAP	18.67	-	18.67
M _T	1.09	2.77	3.86
M _s	0.55	1.97	2.52

2.2. Study Soil

The soil was taken from the top 0–20 cm layer of cultivated soil, from a plot located in Buendia (Castilla-La Mancha region), in the central part of Spain which is under the influence of a Continental Mediterranean climate. The soil was extremely calcareous according to the classification for these types of soil [42] based on carbonate content [43], which limits crop production due to the low nutrient availability, available moisture, or organic matter [27,44]. Oxidizable organic carbon (OC) in soil was determined by wet acid oxidation [45,46]. The soil pH was determined by the potentiometric method in water with a proportion of soil to water (*m/m*) equal 1 to 2.5. The soil chemical characteristics were measured in dry soil sieved through 2.0 mm mesh (Table 2).

Table 2. The chemical properties of calcareous soil.

pH _(H₂O)	CaCO ₃ (%)	μS·cm ⁻¹	N _{tot} (%)	NH ₄ ⁺ -N (%)	C _{org} (%)	C _{tot} (%)
8.39	52.0	113.85	0.17	0.01	0.66	1.14

The water content capacity was measured using the cylinder method by placing an absorbent membrane until the excess water is drawn away by gravity. Once equilibrium is reached, the water holding capacity is calculated based on the weight of the water held in the sample vs. the sample dry weight at 105 °C.

2.3. Experimental Design

Every fertilizer granule or pellet was covered by the soil. A proportion of 1 to 50 (10 g of fertilizer and 500 g of soil) were arranged in rectangular boxes with dimensions: 25 cm × 15 cm × 4 cm (Figure 1).

The experiment was designed as follows: 4 times × 2 soil moisture levels × 5 fertilizers × 3 replication = 120 treatments. The granules/pellets in all boxes were covered by the soil so that no granules were visible above the soil surface. For each incubation time, the boxes were then dried at room temperature, before the fertilizer granules/pellets were separated from the soil by hand. The crumbled and ground samples of separated granules/pellets and soil were taken into the chemical analysis. This sampling was done at a termination time of 5, 10, 20, and 35 days. Throughout the incubation, two levels of humidity, 30% and 60% of maximum water holding capacity, were maintained. Appropriate soil humidity was maintained day-to-day by weighing samples, and water was added to soil where water declined. Determination of ammonium, organic and total nitrogen in granules, and total nitrogen in soil were detected according to the Kjeldahl procedure [41]. Additionally, pH and EC in water for each soil sample were measured using the potentiometric method.

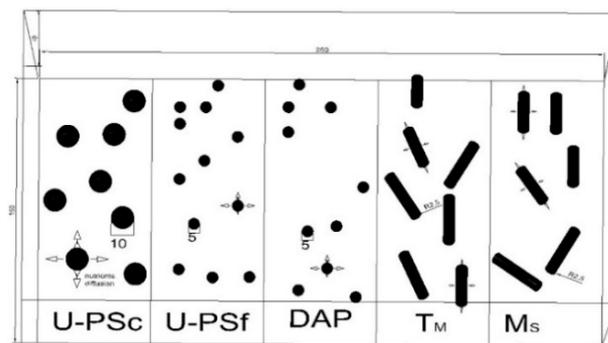


Figure 1. The scheme of incubation boxes with fertilizers (without soil).

The experiment was set up in a random system with three replications for each treatment. Statistical differences were evaluated by an analysis of variance (ANOVA), using the Tukey procedure for homogeneous groups. The statistical elaboration was conducted using the software STATISTICA 13.1. The significance level of analysis was $\alpha = 0.05$.

3. Results

3.1. Total Nitrogen

The release rate of total nitrogen was characterized specifically for mineral and organic forms of nitrogen N. The two mineral fertilizers called UreaPhoS (U-PS_c and U-PS_f) released a similar amount of nitrogen by the end of the experiment (Table 3). The most rapid changes were observed during the first five days, and over 98% of the N was released throughout the 35 days.

Table 3. Effect of incubation time and soil moisture on the release rate of total nitrogen from mineral fertilizers (%N in dry mass).

Time (Days)	U-PS _c				U-PS _f				DAP			
	30% MWHC	% Relative Content	60% MWHC	% Relative Content	30% MWHC	% Relative Content	60% MWHC	% Relative Content	30% MWHC	% Relative Content	60% MWHC	% Relative Content
0	20.8a *	100	20.8a	100	20.9a	100	20.9a	100	18.7a	100	18.7a	100
5	3.4b	16.1	1.9c	9.3	1.7b	8.0	1.9b	9.0	6.5b	34.8	5.2de	27.7
10	1.7c	7.9	0.5d	2.2	0.7c	3.4	0.3cd	1.4	5.8c	31.2	4.8ef	25.6
20	0.5d	2.4	0.3d	1.5	0.4cd	2.1	0.3cd	1.3	5.6cd	30.0	4.5f	24.2
35	0.4d	2.0	0.3d	1.4	0.3cd	1.2	0.2d	1.1	5.3d	28.2	4.0g	21.3
Average	5.3A **	25.7	4.8B	22.9	4.8A	22.9	4.7A	22.5	8.4A	44.8	7.5B	40.0

* small letters (incubation time), ** capital letters (soil moisture) indicate significant difference from one another based on Tukey's test at $p < 0.05$.

The ammonium N, the only N form in DAP, was characterized with high dynamic changes, with the most rapid occurring in the first five days. In the subsequent periods, in addition to the significant influence of incubation time, the release slowed. In the final incubation period, more than 70% of the ammonium was released. The urea and ammonium granules reacted with a more dynamic release when the soil was kept at a higher moisture level, with the exception of U-PS_f. In the case of small U-PS_f granules (3–5 mm), the higher soil moisture level had no significant influence on the N release rate.

The release rate of total N from organic pellets turned out to be slow in dynamics. The total percentage of N released by T_M and M_S was only 20–32% and 15–20%, respectively for 35 days. As there was a significant decrease in N over time with T_M, higher soil moisture corresponded to much higher N release. However, a different pattern of N release from M_S showed no statistical difference between the 5 to 35 day incubation periods, and there was no effect from higher soil moisture (Table 4).

Table 4. Effect of incubation time and soil moisture on a release rate of total nitrogen from organic fertilizers (%N in dry mass).

Time	T_M				M_S			
	30% MWHC	% Relative Content	60% MWHC	% Relative Content	30% MWHC	% Relative Content	60% MWHC	% Relative Content
0	3.9a *	100	3.9a	100	2.5a	100	2.5a	100
5	3.5b.0	91.2	3.0de	77.5	2.4ab	94.0	2.3abc	90.9
10	3.4bc	88.1	2.9def	75.9	2.3abc	89.3	2.2bc	86.5
20	3.2cd	83.4	2.8ef	73.1	2.2bc	86.1	2.0bc	81.0
35	3.1de	79.8	2.6f	68.1	2.2bc	85.7	2.0c	80.2
Average	3.4A **	88.3	3.0B	79.0	2.3A	90.9	2.2A	88.5

* small letters (incubation time), ** capital letters (soil moisture) indicate significant differences from one another based on Tukey's test at $p < 0.05$.

3.2. Ammonium Nitrogen in Organic Pellets

The incubation time and soil moisture levels significantly affected the release of N from T_M and M_S (Table 5). A significant steady decrease in N ammonium in the pellets occurred up to 20 days of incubation. A large amount of ammonium was released from the pellets in the first 20 days, accounting for about 40 to 60% of the total initial amount in T_M and M_S , respectively. Higher soil moisture resulted in greater ammonium release. It must be noted that ammonium DAP and T_M , M_S are the same chemical forms. However, the results show an approximately 25–30% faster release from DAP (Table 3) compared to ammonium from organic pellets. The final release varied from 45 to 70% and 65 to 70% ammonium for the T_M and M_S pellets, respectively.

Table 5. Effect of incubation time and soil moisture on the release rate of ammonium from organic fertilizers (%N in dry mass).

Time (Days)	T_M				M_S			
	30% MWHC	% Relative Content	60% MWHC	% Relative Content	30% MWHC	% Relative Content	60% MWHC	% Relative Content
0	1.09a *	100	1.09a	100	0.55a	100	0.55a	100
5	0.89b	81.7	0.65c	59.6	0.41b	74.5	0.33c	60.0
10	0.86b	78.9	0.60c	55.0	0.29c	52.7	0.23d	41.8
20	0.66c	60.6	0.48d	44.0	0.22de	40.0	0.22de	40.0
35	0.59c	54.1	0.33e	30.3	0.20de	36.4	0.17e	30.9
Average	0.82A **	75.2	0.63B	57.8	0.33A	60.0	0.30B	54.5

* small letters (incubation time), ** capital letters (soil moisture) indicate significant differences from one another based on Tukey's test at $p < 0.05$.

3.3. Organic Nitrogen

Data obtained from organic N incubation showed slow-release characteristics. Regarding the incubation time, only a small amount of organic N was released. During 35 days of soil incubation, 12–16% and 3–8% of N were decomposed by T_M and M_S , respectively (Table 6, Figure 2).

Table 6. Effect of incubation time and soil moisture on the release rate of organic nitrogen from organic fertilizers.

Time (Days)	T_M				M_S			
	30% MWHC	% Relative Content	60% MWHC	% Relative Content	30% MWHC	% Relative Content	60% MWHC	% Relative Content
0	2.75a *	100	2.74a	100	1.97a	100	1.97a	100
5	2.61abc	94.9	2.39de	87.2	1.96a	99.5	1.95a	99.0
10	2.65bcd	96.4	2.34e	85.4	1.96a	99.5	1.93ab	98.0
20	2.55cd	92.7	2.32e	84.7	1.94ab	98.5	1.90b	96.4
35	2.44cde	88.7	2.29e	83.6	1.92ab	97.5	1.82c	92.4
Average	2.58A **	93.8	2.41B	88.0	1.95A	99.0	1.91B	97.0

* small letters (incubation time), ** capital letters (soil moisture) indicate significant difference from one another based on Tukey's test at $p < 0.05$.

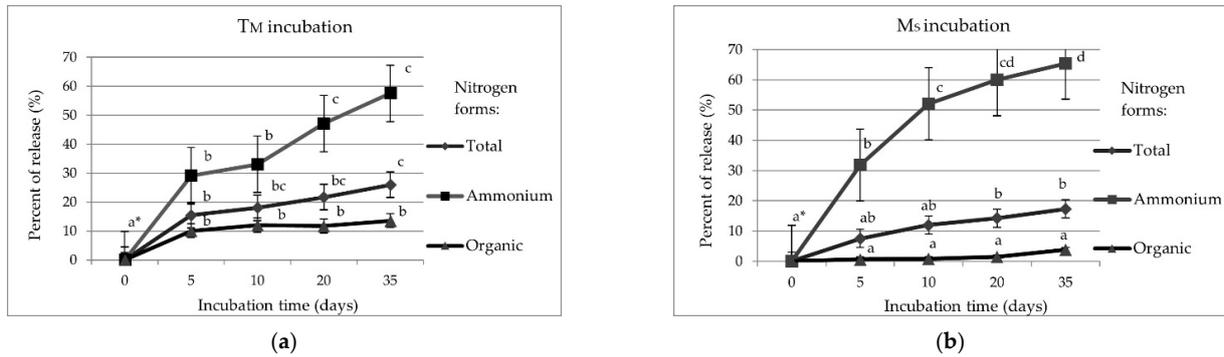


Figure 2. Effect of incubation time on cumulative released nitrogen under incubation of two organic pellets TM (a) and MS (b); values are mean ± standard error; * small letters indicate a significant difference (separate analyses were made for each form of nitrogen) from one another based on Tukey’s test at $p < 0.05$.

Organic nitrogen release indicates the need to extend the range of incubation time, and long-term studies should be carried out to comprehensively evaluate the organic N release pattern. Statistically, it has been demonstrated that higher amounts of N are released with higher soil moisture content for T_M fertilizer. The curve of ammoniacal, organic, and total nitrogen release as a function of time for T_M and M_S pellets is presented below (Figure 2).

3.4. Soil Nitrogen

The study of soil nitrogen content showed that there were significant changes in its concentration. After the second (10 days) and third (20 days) sampling dates, there was a significant increase in % N in the soil with incubation of the mineral granules. In the initial period (10 days), the maximum concentration of Kjeldahl nitrogen ranged from 0.32 to 0.35% and then decreased until the end of incubation (Figure 3). Moreover, a significant influence of soil moisture on the measured amount of N in the soil was found. Higher N concentration after 20 days of U-PSc and DAP incubation was maintained at higher soil moisture levels. In the final sampling (35 days), different soil moisture levels had no effect on the N status of the soil. In contrast to organic pellets, incubation had no significant effect on the growth of Kjeldahl N in soil, both as a function of time and of soil moisture.

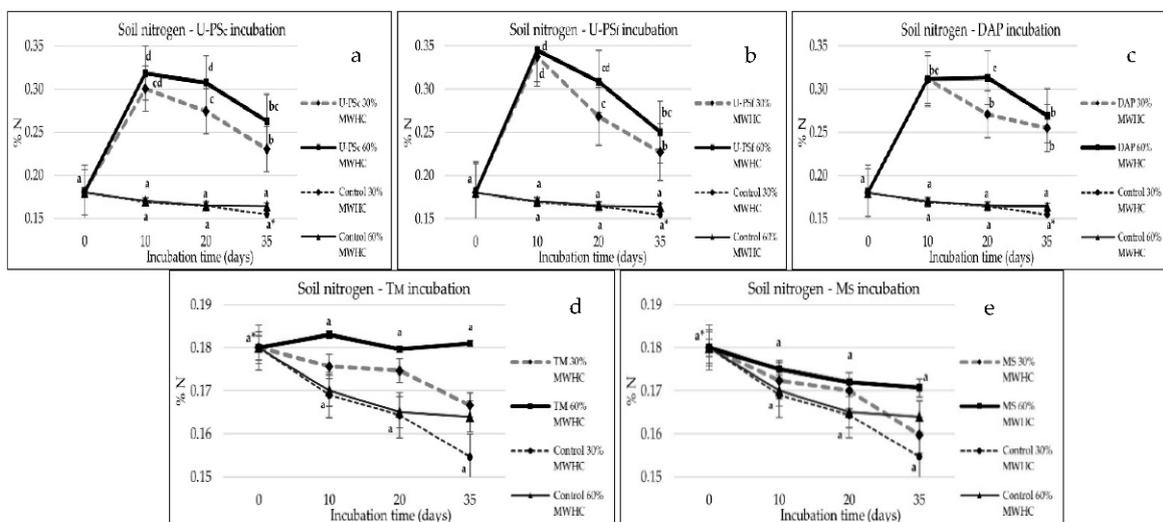


Figure 3. Effect of incubation time and soil moisture on soil nitrogen content under incubation of mineral (a–c; b, c) and organic fertilizers (d,e); values are mean ± standard error; * small letters indicate significant difference from one another based on Tukey’s test at $p < 0.05$.

Detailed analysis of nitrogen distribution in the soil–fertilizer system shows significant differences, characterizing each N source separately from the beginning to the end of the incubation period, as depicted below (Figure 4).

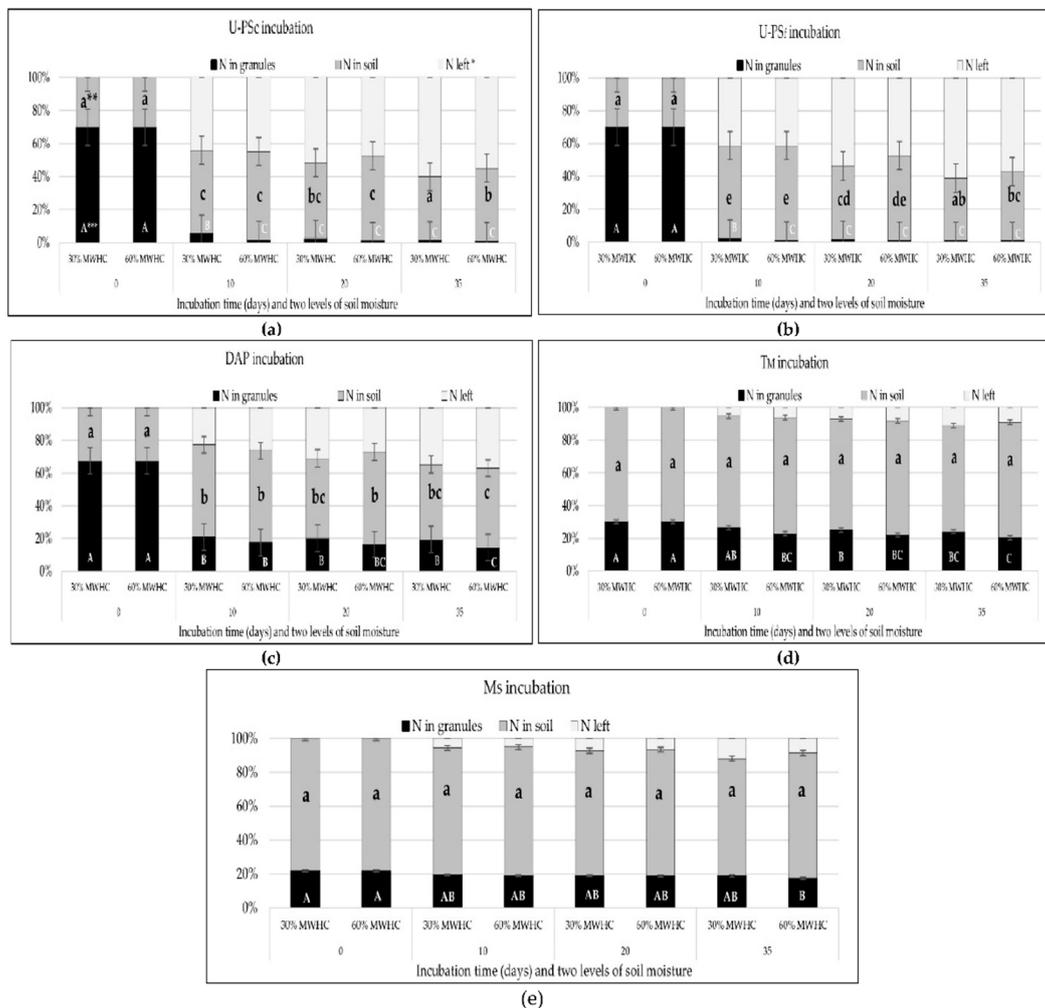
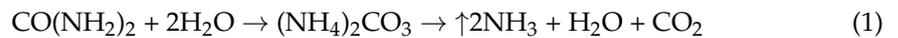


Figure 4. Nitrogen distribution in soil–fertilizer system throughout incubation time and soil moisture under incubation of mineral (a–c; a; b; c; a; b; c;) and organic fertilizers (d,e); * N left—the nitrogen participation was not detected by Kjeldahl procedure; values are mean \pm standard error; ** small (N in soil) and *** capital (N in granules) letters indicate significant difference from one another based on Tukey's test at $p < 0.05$.

The total (soil, fertilizer) amount of N expressed as 100% was represented as the sum of the N of the soil and fertilizer before incubation (zero days). Incubation periods after zero days showed differences in the distribution of N and the share of nitrogen between the fertilizer and the soil. Kjeldahl nitrogen was the sum of ammoniacal and organic nitrogen from both sources, soil and fertilizer, which decreased over time in all facilities, and some nitrogen was not measured by the Kjeldahl procedure. Throughout the experiment, the most intense processes were assigned to urea, the medium ones to DAP, and the slowest to organic sources. Statistically significant differences in the distribution of N occurred in all analyzed mineral fertilizers. In the case of organic pellets incubation, there were no statistical differences in nitrogen distribution between the pellets and the soil. Throughout the incubation period, the share of measured nitrogen in pellets and soil was not statistically different. As in the case of mineral granules, part of the nitrogen in the soil fertilizer system was not detected by the Kjeldahl procedure. This phenomenon may be the result of the high pH of the soil and, as a consequence, the influence of the alkaline reaction on the loss of some nitrogen. The portion of nitrogen that was not measured by the Kjeldahl procedure

is described in Figure 4 as N left. Nitrogen that has not been measured against the starting amount of zero days as a reference amount could possibly be converted to other forms of nitrogen, such as ammonia and nitrates. Calcareous soil conditions with alkaline pH may generate ammonia losses if the soil pH exceeds 7.0, the course of losses is described by the following reaction:



3.5. Soil pH

Data presented in Figure 5 clearly show the influence of each treatment on soil pH. Incubated mineral granules were characterized by an increase in soil pH at initial sampling, with a peak between 5 and 10 days. It is likely that the hydrolysis products, as evidenced by Equation (1), triggered an alkaline reaction. Moreover, this growth was significantly stimulated by higher soil moisture only for U-PSc and U-PSf, but only after 10 days of incubation. In contrast to the mineral granulates, the changes in T_M and M_S showed a significant decrease at 20 days of incubation below the soil pH before the start of incubation. Moreover, a significant effect of higher soil moisture on the decrease in pH was shown, resulting in a greater decrease under the influence of higher humidity.

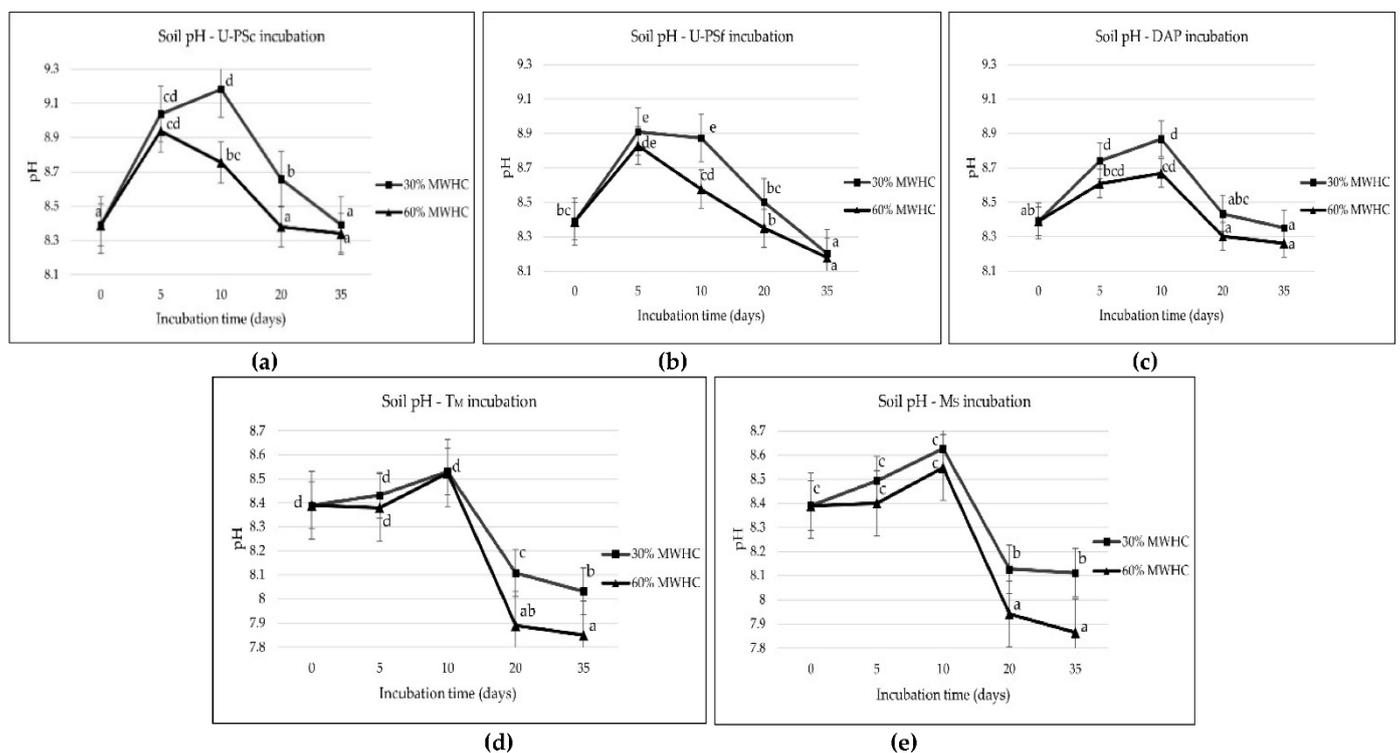


Figure 5. Effect of incubation time and soil moisture on soil pH under incubation of mineral (a–c; a; b; c; a; b; c;) and organic (d,e) fertilizers; values are mean \pm standard error; small letters indicate significant difference from one another based on Tukey's test at $p < 0.05$ (the pH value was converted into the concentration of hydrogen ions, then statistical analysis was performed).

3.6. Electric Conductivity (EC) of Soil Solution

The data presented in Table 7 revealed the effect of the test conditions on the EC value ($\mu\text{S cm}^{-1}$). The obtained results showed a significant influence of time on the EC value. The first incubation periods between 10 and 20 days resulted in a significant increase in EC due to the incubation of mineral fertilizers, followed by a significant decrease in the value by the end of the experiment. Table 7 shows that treatments with higher soil moisture significantly increased the EC for all incubated mineral fertilizers.

Table 7. Effect of incubation time and soil moisture on EC value ($\mu\text{S cm}^{-1}$) of soil solution under incubation of mineral fertilizers.

Time (Days)	U-PS _c				U-PS _f				DAP			
	30% MWHC	% Relative Content	60% MWHC	% Relative Content	30% MWHC	% Relative Content	60% MWHC	% Relative Content	30% MWHC	% Relative Content	60% MWHC	% Relative Content
0	129a *	100	120a	100	129a	100	120a	100	129a	100	120a	100
5	772b	598	798b	665	905b	702	1042e	868	833e	646	929fg	774
10	940e	729	1107g	923	996de	772	1376g	1147	872ef	676	946g	788
20	893d	692	1037f	864	967cd	750	1323fg	1103	679c	526	849e	708
35	816b	633	1001f	834	931bc	722	1312f	1093	610b	473	766d	638
Average	710A **	550	813B	678	786A	609	1034B	862	625A	484	722B	602

* small letters (incubation time), ** capital letters (soil moisture) indicate significant differences from one another based on Tukey's test at $p < 0.05$.

The study of the influence of incubation time and soil moisture shows the opposite trend than for mineral fertilizers. During incubation, there was a steady increase in EC values, reaching a maximum on day 35, and ranging from 698 to 944 and from 424 and 797 $\mu\text{S cm}^{-1}$ for T_M and M_S, respectively (Table 8). These data also indicate that higher soil moisture had a significant effect on the EC value.

Table 8. Effect of incubation time and soil moisture on EC value ($\mu\text{S cm}^{-1}$) of soil solution under incubation of organic fertilizers.

Time (Days)	T _M				M _S			
	30% MWHC	% Relative Content	60% MWHC	% Relative Content	30% MWHC	% Relative Content	60% MWHC	% Relative Content
0	129a *	100	120a	100	129a	100	120a	100
5	371b	288	576c	480	293b	227	357c	298
10	403b	312	697d	581	325bc	252	511e	426
20	523c	405	764d	637	337c	261	540e	450
35	698d	541	944e	787	424d	329	797f	664
Average	425A **	329	618B	515	301A	233	465B	388

* small letters (incubation time), ** capital letters (soil moisture) indicate significant differences from one another based on Tukey's test at $p < 0.05$.

4. Discussion

The results of this research demonstrate the effect of different N forms, granulation or pellet preparation properties, incubation time, and different humidity on the N release model from incubated fertilizers in calcareous soil. The second aim was to evaluate their influence on the chemical properties of the soil as a function of time and humidity.

The urea nitrogen and ammonium reactions have revealed themselves as very fast sources of nitrogen, which were quickly released from the granules into the soil within a few days. N released at the end of the experiment by U-PS_c and U-PS_f accounted for more than 98%, and by DAP about 70–80% of the initial amount. After the first 5 days, the percentage of N released was still high, with 85–90% N released from urea and 65–75% N released from DAP. Following Trenkel 2010 [47], U-PS_c granules can be classified as a slow-release fertilizer. The 10 mm size classifies them as super granules, with retarded nutrient release materials due to their low surface area to volume ratio. The analysis of data for the U-PS_c fertilizer showed that this fertilizer, granulated to a large granule diameter, did not meet the criteria for slow-release fertilizers. Taking into account the calcareous soils and the very high risk of nitrogen loss in gaseous form, this fertilizer should be applied to soil and covered before sowing. Placing the granulate in calcareous soils causes a greater or lesser loss of nitrogen, due to the conditions in which the fertilizer is located. Various studies show that losses from ammonia volatilization vary from 11 to 60% depending on the applied method of fertilization, with the greatest losses occurring during surface application to soil with a high pH of around 9.0 [48].

The study reveals the effects of the granulation process on the release patterns. Two mineral fertilizers, U-PS_c and U-PS_f, granulated from chemically identical components, were tested for the effect of different granulation diameters on the release rate. Based on the research, a significantly higher rate of N released during incubation in soil with higher

humidity was found for super-granules (U-PS_c). Incubation of small diameter granules of 3–5 mm (U-PS_f) showed no reaction in the rate of nitrogen release from the granule to the higher level of soil moisture. An equal amount of N was released at both soil moisture levels. U-PS_f fertilizer with small granule diameters should be recommended for initial fertilization, as this fertilizer more dynamically modulates the environment in which it dissolves, quickly creating new conditions for plant growth [49]. This fertilizer can be used for crops grown in wide inter-row spaces, such as maize, beetroot, potatoes, vegetables.

Analysis of the DAP data indicated that nitrogen N was released systematically throughout the 35 days of incubation. The rate of nitrogen release was significantly affected by soil moisture, releasing more N in conditions of increased humidity. Conventional fertilizer can be used to pre-fertilize crops such as potato, corn, beet, as described above.

The implementation of practices such as split application and sowing fertilization can increase the efficiency of nitrogen use by up to 16–17% in calcareous soils [50]. A higher level of available nitrogen in calcareous soil results in a higher yield of plants, even in semi-dry soil conditions [51]. The small granules of U-PS_f can be recommended for these conditions with a high dissolving capacity. In calcareous conditions, it is recommended to apply fertilizers 5.0 to 7.5 cm below the soil surface [8], even at a fertilization depth of 3–5 cm below the soil surface, as this allows to minimize ammonia volatilization by 85–95% [52].

Incubation of the organic pellets showed that the release rate was very slow. This type of fertilizer can be used as an additive to mineral nitrogen sources, as a background for mineral fertilization. This type of nitrogen source should be recommended for crops with long growing periods, e.g., corn, potato, beetroot.

All mineral fertilizers tested in this study can be recommended for fertilizing plants with a fast growth rate, such as vegetables and crops, but due to the form of urea or ammonia, it is necessary to mix with the soil before sowing or during planting. Most of the N transformation in calcareous soil occurs during the first few days of fertilizer incubation in the soil [5]. The fate of the applied fertilization depends on the amount of available nitrogen in the soil, as in poor soils it can be immobilized, and in rich soils, it can undergo mineralization as a source of available nitrogen [53]. When urea is applied in concentrated amounts in narrow bands, the formation of NH₄⁺ ions leads to the consumption of protons and localized alkalization in the band [54]. This effect has been demonstrated in various studies, in which the local pH increased up to approximately 9.3 in response to the hydrolyzing urea band [55]. These conditions promote nitrogen losses via volatilization [56,57].

It was confirmed in the present study that the incubation of urea and ammonium brought the soil pH peak from 8.39 to 8.9–9.17. A higher concentration of ammonia in the soil is responsible for an increase in soil pH [32]. Moreover, high concentrations of NH₄⁺ and an increase in pH increase the potential formation of phytotoxic concentrations of NH₃, which may also have an inhibitory effect on nitrifying microorganisms [58].

The data clearly shows that all treatments significantly influenced the EC value. Incubation of mineral N resulted in a rapid increase in EC values, reaching a maximum of 1323 μS cm⁻¹ for U-PS_f. Incubation of organic pellets showed a steady gradual increase in soil EC from 194 to 394 μS cm⁻¹. The significance of the influence of higher soil moisture on a significantly higher EC value was confirmed [59]. The maximum value measured in our research could have an impact on microbiological processes such as the nitrification process (10–37%), due to exceeding the threshold value of 0.7 dS m⁻¹ [60,61]. A further increase in nitrification inhibition can reach up to 98%, with an increase in EC to 3–6 dS m⁻¹ [62]. EC values from all treatments do not exceed the safe threshold causing damage to seedlings of cultivated plants. The EC from the analyzed treatments was below the threshold tolerated by maize (7.0 dS·m⁻¹) or potato (1.7 dS·m⁻¹) [63].

The results of studies on the pattern of nitrogen release from granules to soil showed statistical differences in release rates from different fertilizers. Incubation of these fertilizers showed a clear effect of the influence of various forms of granules on the chemical properties of carbonate soil.

5. Conclusions

Calcareous soil makes up more than 30% of the world's soil, and their CaCO₃ content ranges from a few percent to 95% [9] which influences their physico-chemical characteristics. Management practices in calcareous soils differ from those in non-calcareous soils due to the effect of soil pH and CaCO₃ content on plant growth properties and due to chemical reactions that affect the loss or fixation of almost all nutrients [9,64]. Thus, the results of the experiments can be used to expand knowledge to improve fertilizer utilization in these soils, especially in highly calcareous soils.

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