agronomy

MDPI

Article

^{15}N-Fertilizer Recovery in Maize as an Additional Strategy for Understanding Nitrogen Fertilization Management with Blends of Controlled-Release and Conventional Urea

Pedro Lopes Garcia [1,*], Renata Alcarde Sermarini [2], Carlos Roberto de Sant Ana Filho [3], José Albertino Bendassolli [1], Beatriz Nastaro Boschiero [1] and Paulo Cesar Ocheuze Trivelin [1]

1 Stable Isotopes Laboratory, Center for Nuclear Energy in Agriculture (CENA), University of São Paulo (USP), Piracicaba 13416-000, SP, Brazil; jab@cena.usp.br (J.A.B.); bianastaro@gmail.com (B.N.B.); pcotrive@cena.usp.br (P.C.O.T.)

2 Exact Sciences Department, "Luiz de Queiroz" College of Agriculture (ESALQ), USP, Piracicaba 13418-900, SP, Brazil; ralcarde@usp.br

3 Innovation Center, Compass Minerals Plant Nutrition, Iracemápolis 13495-000, SP, Brazil; carlos.santana@compassminerals.com.br

* Correspondence: plgarcia@usp.br

Received: 10 October 2020; Accepted: 23 November 2020; Published: 9 December 2020

check for updates

Abstract: A single application of polymer-sulfur coated urea (PSCU) and conventional urea (U) is expected to ensure nitrogen (N) throughout the maize (*Zea mays* L.) growth cycle being U the likely main N-fertilizer supplier at the beginning and PSCU during the maize growth cycle. This research aimed to evaluate N fertilization management (split, incorporated, and broadcast application) and fertilizer blends (30%PSCU + 70%U and 70%PSCU + 30%U) on volatilization of ammonia (AV) and soil N mineral content (NM); plant N uptake (NU) and ^{15}N-fertilizer recovery (NR); and yield (GY). Field experiments were conducted for two growing seasons (2017–2018 and 2019–2020) in Rhodic Eutrustox soil. U was treated with NBPT (N-(n-butyl) thiophosphoric triamide). N rate was 180 kg ha^{-1}. AV reached 12% of the applied N (broadcast-applied 70%PSCU + 30%U, 2017–2018). The 30%PSCU + 70%U application resulted in higher NM at 40–60 cm depth in vegetative and reproductive stages in both seasons. The 70%PSCU + 30%U application resulted in the highest GY in 2017–2018, and the N treatments did not affect GY in 2019–2020. NR was 3% on average at vegetative leaf stage 4 (V4), and PSCU, the main N-fertilizer supplier applying 70%PSCU + 30%U. After V4, the main N-fertilizer supplier is PSCU for 70%PSCU + 30%U and U for 30%PSCU + 70%U application. These blends (incorporated, broadcast, and split application) can ensure N during the maize growth cycle, with NR of 72.5% at maturity (R6) being 47.9% in the grain.

Keywords: polymer-sulfur coated urea; NBPT-treated urea; mixture; nitrogen balance; *Zea mays* L.

1. Introduction

Conventional urea is the nitrogen source most used in maize (*Zea mays* L.) production in China [1] and Brazil, the second and third world's largest maize producer [2], respectively. Although its lower acquisition cost and higher N content than other N sources (i.e., ammonium nitrate and ammonium sulfate), U is more prone to ammonia volatilization losses when applied on the soil surface, reducing N use efficiency (NUE) in maize [3]. To increase NUE and yield is necessary to split U application [4], increasing costs with mechanized operations and the risks to lose the second U application [5].

India and China have a good acceptance for new technologies to improve NUE of U [6], and Brazil and Paraguay have a growing demand for that [7]. Among the available technologies, there are the coating of U with sulfur and polymers or just polymers, considered controlled-release U (CRU), and the use of urease inhibitors in the U treatment [8]. In the first case, the polymers and their micropores provide the U dissolution by diffusion with the soil humidity controlling the N release. It improves the synchronism of N release and maize needs [9], increasing NUE [10] by reducing ammonia losses [11] and N leaching [12], but it can provide low N release at the beginning of maize growth cycle and consequently yield reduction [13]. In the second case, the urease inhibitor most effective in the U treatment is the NBPT (N-(n-butyl) thiophosphoric triamide) compared to hydroquinone, copper, boric acid, and catechol [3,4]. The NBPT-treated U reduces N conversion rate from amidic (N-NH_2) to ammoniacal form (N-NH_4^+) for a period of 3 to 7 days in applications on the soil surface in Brazilian conditions [7]. After that, it can be incorporated by rain and better used by plants, but it is a soluble N source, and the split N application is also necessary to avoid salt effect in plants [14] and N leaching [15].

Blends of polymer-sulfur coated urea (PSCU), and U applied incorporated at maize sowing [16,17] is an alternative to supplying N throughout the maize growth cycle in Brazilian conditions and to avoid low N release at the beginning by single CRU application [13]. It probably occurred because U (soluble source) provided N at the beginning and PSCU (controlled-release source) during the maize growth cycle. To confirm that hypothesis, the use of nitrogen-15 (^{15}N) tracer is necessary for the U and PSCU sources. Although the N incorporated is available at the right time and place for optimal root uptake [18], the N broadcast application on the soil surface can reduce application costs.

In the current crop system management, the straw of the previous crop is left on the soil surface. In that situation, the N-fertilizer dynamic in the soil-plant system probably changes applying different ratios of CRU and U. The optimal ratio can vary based on the soil, climate conditions, and economic benefits, and is normally determined by the ammonia volatilization, N uptake, crop yield, and NUE [19,20]. 70%CRU + 30%U was recommended in North China [21] and in a Typic Haplustox soil in Brazil [16,22]. 30%CRU + 70%U was recommended in Northeast China [19]. N can also suffer immobilization depending on the straw C/N (carbon/N) ratio [23], and 30%CRU + 70%U would avoid a possible N lack at the beginning of the maize cycle provided by N immobilization.

In this context, we hypothesize that N fertilization management (incorporated, broadcast, and split application) with straw in the system is more efficient to supply nitrogen during the maize cycle applying 70%PSCU + 30%U than 30%PSCU + 70%U in Brazilian conditions. U is the likely main N-fertilizer supplier at V4 (vegetative leaf stage 4), and PSCU from V4 to maturity (R6) applying 70%PSCU + 30%U. This research aimed to evaluate the influence of N fertilization management and blends of U (treated with NBPT) and PSCU on ammonia volatilization, soil N mineral content, N uptake, ^{15}N-fertilizer recovery (NR) in plants, and maize yield in Brazilian tropical conditions.

2. Materials and Methods

2.1. Field Site Description

Two maize field experiments were conducted at Compass Minerals Innovation Center in Iracemápolis, state of São Paulo, Brazil (22°39′ S, 47°30′ W, 608 m elevation), during 2017–2018 (season 1) and 2019–2020 (season 2) spring-summer growing seasons. The experimental area has a soil classified as Rhodic Eutrustox (USDA classification; [24]) with a clayey texture: 41.9% sand, 11.9% silt, and 46.2% clay [25]. Common bean was the previous crop of season 1 and season 2, and 5.6 ± 0.4 Mg ha^{-1} of common bean straw with a 44:1 C/N ratio was left on the soil for season 1, and 5.7 ± 0.6 Mg ha^{-1} with a 43:1 C/N ratio was left on the soil for season 2. The straw was quantified using twelve samples of one meter square (three samples per block) before starting the experiments. Each sample was weighed. Subsamples were oven-dried at 65 °C to a constant weight, weighed, and ground with a Wiley mill to pass through a 0.5-mm sieve to analyze C and N contents [26]. Plowing, harrowing, and limestone application were performed before the previous crop of season 2. The mean annual temperature and annual precipitations were 21.8 °C and 1200 mm, respectively (3-year average).

The soil chemical characterization was performed in three depths before starting the experiments (Table 1).

Table 1. Soil chemical attributes on which maize is grown in Brazil.

Depth	pH	SOM [1]	TSN [2]	NH_4^+	NO_3^-	S	P	K	Ca	Mg	Al	CEC [3]	AlS [4]	BS [5]
cm		g dm^{-3}	mg kg^{-1}			mg dm^{-3}		mmol$_c$ dm^{-3}					%	
						Season 1: 2017–2018								
0–20	5.0	24	1100	3.7	15	125	10	2.5	28	12	1	68	2	63
20–40	4.3	18	800	1.7	4.8	269	<3	1.3	6	5	11	43	47	28
40–60	4.2	15	600	3.0	4.3	318	<3	1.0	2	3	11	34	65	18
						Season 2: 2019–2020								
0–20	5.5	25	1100	1.5	22	14	30	5.4	39	26	0	95	0	74
20–40	5.1	23	900	1.4	12	38	14	4.7	25	16	3	90	5	62
40–60	5.0	23	700	0.7	9	46	12	4.9	27	16	2	82	4	58

[1]SOM, soil organic matter; [2]TSN, total soil nitrogen; [3]CEC, cation exchange capacity at pH 7.0; [4]AIS, aluminum saturation; [5]BS, base saturation.

Fifteen soil samples per depth were mixed for analysis. The determination of the soil pH was performed using 0.01 mol L^{-1} $CaCl_2$ (1:2.5 soil/solution; [27]), soil organic matter using the Walkley-Black procedure [28], total N content using mass spectrometry [29], NH_4^+-N and NO_3^--N contents using 2 mol L^{-1} KCl (1:5 soil/solution ratio; [27]). The extraction of nutrient available was performed by ion-exchange (phosphorus (P), potassium (K), calcium (Ca), and magnesium (Mg)) and using a solution of $Ca(H_2PO_4)_2$ for SO_4^{2-}-S. Al was extracted by KCl solution. The quantification was performed by colorimetric (P), flame photometric (K), and atomic absorption (Ca and Mg) spectroscopy. Al was determined by titration, while SO_4^{2-}-S by turbidimetry (van Raij et al., 2001). Summing exchangeable cations (Ca, Mg and K) and potential acidity (H + Al) determined the cation exchange capacity (CEC) at pH 7.0. Dividing the total exchangeable cations by CEC and multiplying by 100 determined the base saturation. Multiplying Al by 100 and dividing by (exchangeable cations + Al) determined the Al saturation.

2.2. Experimental Setup and Treatment Description

The experiments were in a factorial (3 × 2) + 1 randomized block design with four replications. The treatments consisted of three N fertilization management practices (split application: 1/3 of N applied incorporated at sowing and 2/3 as a side-dressing at V4; broadcast application: a single topdressing N application at sowing; incorporated application: a single N application incorporated at sowing). Two blends: 70%PSCU + 30%U and 30%PSCU + 70%U. A control treatment (without N-urea) was also included. The N rate used was 180 kg ha^{-1}, which would be expected to produce maize grain yields higher than 10 Mg ha^{-1} in São Paulo state, Brazil [30]. All treatments were applied by hand. The fertilizer incorporation was performed at 15 cm depth and 10 cm to the side of the seed row to avoid salt effect in the maize plant [14]. The U was treated with 530 mg NBPT kg^{-1} and has 45%N. The PSCU (Patent n. EP 0574541) was manufactured by an industrial process in which a large quantity of U (prill) is sprayed by molten elemental sulfur (S^0) and then by polymers (biodegradable and insoluble in water). In the final process, the PSCU has 39% N and 12% S, and the manufacturer indicates that ~80% of the N is released within 60 days after application [31].

To evaluate the ^{15}N-fertilizer recovery by plants, the ^{15}N-enriched U ($CO(^{15}NH_2)_2$) with 1.6 and 1.15 atom % ^{15}N was manufactured in a small quantity at Stable Isotopes Laboratory from the Center for Nuclear Energy in Agriculture (CENA/USP). Firstly, the ^{15}N-U (powder) went through a granulation process [32]. Secondly, the particle size distribution of granules were classified using ABNT (Brazilian Association of Technical Standards) sieve n. 6 and 10 (2 and 3.35 mm), and the hardness of granules was 2 kgf. Finally, the ^{15}N-U with 1.6 atom % ^{15}N was treated with NBPT (530 mg NBPT kg^{-1}), and the ^{15}N-U with 1.15 atom % ^{15}N was coated (by the industrial manufacturer) with elemental sulfur and polymers using a similar industrial process method adapted to coat a small quantity of U and ensuring the same N release. In the final process, it has 38.6% N and 11.8% S. The microtomography (Micro-CT; [33]) shows the PSCU granules after both manufacture processes (Figure 1). The N cumulative release of the ^{15}N-PSCU (Figure 2) was tested in the water at 25 °C (1:5 fertilizer/deionized water ratio), the supernatant sampled and replaced at 1, 5, 10, 20, 30, 40, 50, and 60 days, and the N released were measured in a mass spectrometer.

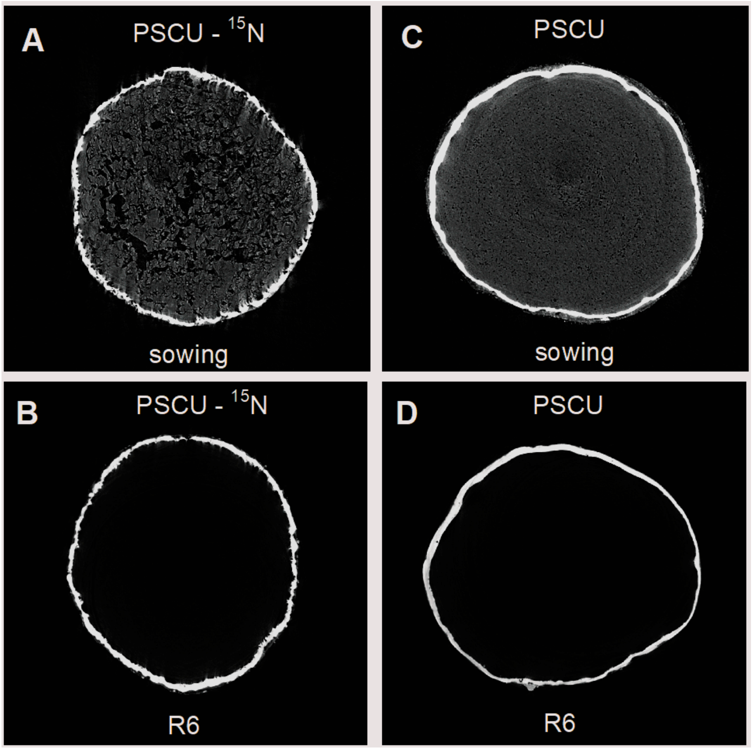

Figure 1. Microtomography images of granules of polymer-sulfur coated urea (PSCU-^{15}N and PSCU) applied at sowing (**A**,**C**) and its residual granules at R6 maize growth stage (**B**,**D**). The PSCU-^{15}N (**A**) was manufactured with a similar process to the industrial PSCU (**C**). The empty granules (**B**,**D**) represent the N-fertilizer applied incorporated, broadcast, and split.

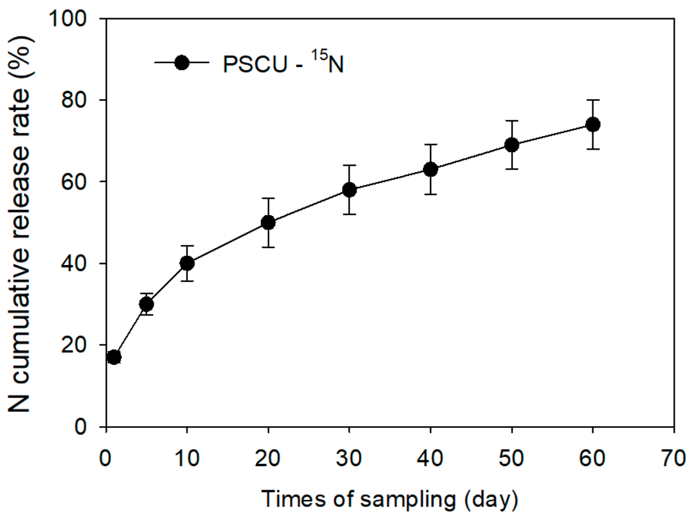

Figure 2. Cumulative nitrogen release of the polymer-sulfur coated urea with ^{15}N (PSCU-^{15}N) in the water at 25 °C. Vertical bars indicate the standard error of the mean (n = 3).

The maize experimental plot had 45 m^2 with 10 maize rows (10 m in length and 0.45-m spacing) and a density of 79,500 plants ha^{-1}. In season 2, two microplots were setup within plots to apply ^{15}N-fertilizer (^{15}N-PSCU + U and PSCU + ^{15}N-U). PSCU without ^{15}N was also manufactured by the adapted method to mix with ^{15}N-U to apply in microplots. Each microplot had 2.7 m^2: 2 m long and 1.35 m wide that includes three maize rows (Figure 3).

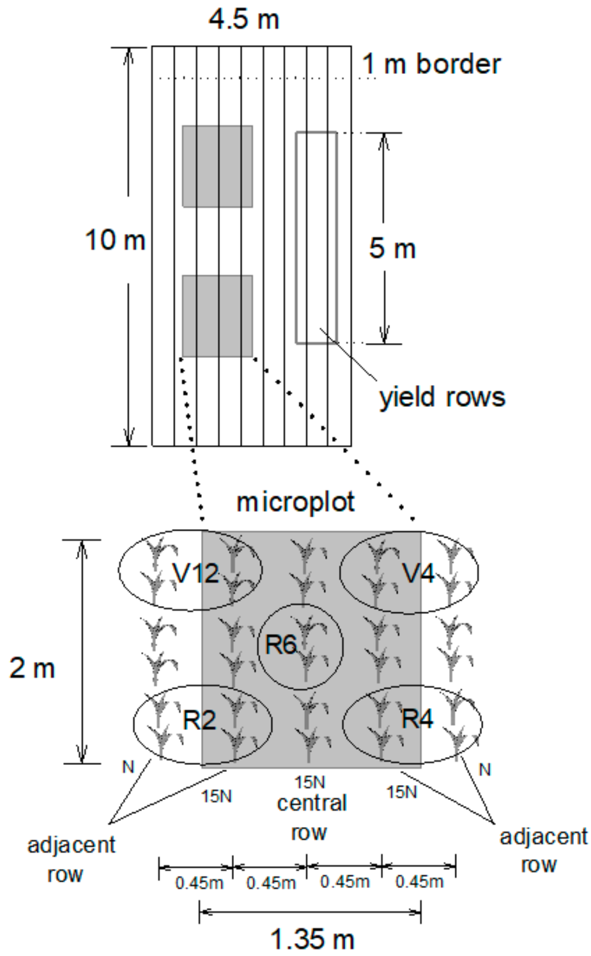

Figure 3. The plot and microplot representation. The microplots are inside the plot. The ^{15}N-fertilizers were applied, incorporated, broadcast, and split in the microplots. A sampling of plants were performed in adjacent rows at V4, V12, R2, and R4 maize growth stage. At R6, plants were sampled in the central row.

The maize hybrid (DKB 390) was sown on 1 December 2017 in season 1 and on 26 November 2019 in season 2. In season 1 and season 2, 120 kg P_2O_5 ha^{-1} as triple superphosphate was applied at sowing (beneath of seed row). Sixty and one-hundred and twenty kg K_2O ha^{-1} as potassium chloride (KCl) was applied broadcast on the soil surface at V4 (season 1) and before sowing (season 2), respectively. S^0 was applied at sowing in the control and in the treatments with 30%PSCU + 70%U to equalize the S^0 that had in the 70%PSCU + 30%U. 3 kg B ha^{-1} and 2 kg Zn ha^{-1} were applied at sowing mixed with N treatments and in the control with S^0 in both seasons. The control of weeds, insects, and diseases were performed in season 1 and season 2 when needed. The maize was harvested on 9 April 2018 in season 1 and 15 April 2020 in season 2. Two maize rows of 5 m long were selected to measure yield in season 1 and season 2 (Figure 3).

2.3. Quantification of Ammonia Volatilization

In season 1, ammonia (NH_3-N) volatilization was quantified during 34 days after N broadcast application (180 kg N ha^{-1}) and split application (side dressing at V4: 120 kg N ha^{-1}) on the soil surface. The ammonia capture was performed using open collectors (14 cm × 14 cm × 7cm) with a foam disc (15 cm in diameter, 6 cm in height and density of 0.02 g cm^{-3}) soaked in 25 mL of phosphoric acid (1.5 mol L^{-1} and 5% of glycerol) allocated on the open side of the collectors. It was positioned 1 cm above the soil surface in the N-fertilizer application region. The foams were sampled and replaced at 2, 3, 4, 5, 6, 7, 9, 12, 16, 21, 27, and 34 days after N application. To extract NH_4^+-N retained in the foams as ammonium phosphate, each foam was put in a beaker contained 300 mL of deionized water and squeezed. After that, beakers were weighted, and an aliquot of each solution was analyzed by flow injection analysis (FIA) to determine the NH_4^+-N [34]. The NH_3-N volatilization was determined by dividing the NH_4^+-N (mg per collector) by the N-fertilizer applied per collector (broadcast: 350 mg; split (side dressing at V4): 792 mg) and multiplying the result by the N rate (kg ha^{-1}). The capture efficiency of the collector (26%) was also considered [35]. The NH_3-N daily losses (kg ha^{-1} day^{-1}) were calculated by dividing the losses by the sample time (day), and the cumulative losses (kg ha^{-1}) were determined by summing the losses from each sample. The ammonia volatilization was not evaluated in season 2 because of the limited space in the plot, due to microplots (Figure 3), and the evaluations in season 2 were focused on soil and plant in the plot and microplots.

2.4. Analyses of Plant and Soil Samples

In season 1 and season 2, soil and plant sampling were performed during the maize cycle at the V4, V12 (vegetative leaf stage 12), R2 (blister stage), R4 (dough stage), and R6 (physiological maturity) [36] stages. Three soil samples per plot were taken at three depths (0–20, 20–40, and 40–60 cm) based on the N fertilizer row. The samples of each depth were mixed for analysis. NO_3^--N and NH_4^+-N content were extracted by 2 mol L^{-1} KCl and determined by FIA (1:5 soil/solution ratio; [27]). The soil results were expressed as mineral N content (NO_3^--N + NH_4^+-N). Four plants per plot were cut on the soil surface, separated (leaves, stalk, cobs, and grain), oven-dried to a constant weight (at 65 °C), weighed, and ground in a Wiley mill (0.5-mm sieve). The N concentration (g kg^{-1}) of each plant component was determined by titration after acid digestion (micro-Kjeldahl; [26]). The dry weight of each plant component was multiplied by its N concentration to determine N uptake (kg ha^{-1}). The N uptake of each plant component was summed to determine the total N uptake. Plant dry matter was expressed as Mg ha^{-1}. The maximum rates of dry matter and N accumulation were determined by subtracting the accumulation (dry matter and N) at the inflection point of a nonlinear sigmoid regression by the previous day's accumulation [16,37]. Two rows of 5 m were harvested by hand to determine the grain yield (13% moisture content) expressed as Mg ha^{-1}.

2.5. ^{15}N-Fertilizer Recovery Analyses

In season 2, the ^{15}N-PSCU + U was applied by hand in one microplot and PSCU + ^{15}N-U in the other one in the same manner as the N treatments in the plot. At V4, V12, R2, and R4, the aboveground of two plants were sampled in the internal and adjacent external row of the microplots (Figure 3) and were analyzed separately. The results of ^{15}N-fertilizer recovery in these plants were summed in each abovementioned growth stage: plants in the adjacent external row (N-fertilizer without ^{15}N) can recovery the ^{15}N-fertilizer applied to the plants in the adjacent internal row of microplots [38]. At R6, the aboveground of two plants were sampled in the central row of the microplot (Figure 3). Roots of a plant and soil were sampled in the center of the microplot (40 cm length × 40 cm width × 20 cm depth) at R6 to include in the N balance. Roots and the aboveground plant components separated (leaf, stalk, cob and grain) were oven-dried (at 65 °C), weighed, and ground (0.5-mm sieve). The total N concentration and ^{15}N abundance in the soil and each plant component were determined in an automatic N analyzer interfaced to an isotope ratio mass spectrometer (PDZ Europa ANCA-GLS, 20-20, Sercon Ltd., Crewe, UK). The control treatment was also analyzed. The ^{15}N recovery was determined according to the following equations [38,39]:

$$\text{Ndff } (\%) = \left(\frac{\text{a} - \text{c}}{\text{b} - \text{c}}\right) \times 100 \tag{1}$$

$$\text{Ndff } (\text{kg ha}^{-1}) = \left[\frac{\text{Ndff } (\%)}{100}\right] \times \text{Total N} \tag{2}$$

$$^{15}\text{N recovery } (\%) = \left[\frac{\text{Ndff } (\text{kg ha}^{-1})}{\text{N rate}}\right] \times 100 \tag{3}$$

where Ndff (% and kg ha^{-1}) is the N derived from the fertilizer in the plant components or in the soil; a is the ^{15}N abundance (atom % ^{15}N excess) in the plant components or in the soil; b is the ^{15}N abundance (atom % ^{15}N excess) in the fertilizer; c is the natural ^{15}N abundance (atom % ^{15}N) in the control treatment. Total N is the plant N content (kg N ha^{-1}). ^{15}N recovery is the N-fertilizer recovered by the maize plant (%). N rate is the N-fertilizer rate in kg N ha^{-1} that was 180 kg N ha^{-1}.

2.6. Statistical Analyses

A combined analysis of variance (ANOVA) was performed for the variables measured in season 1 and season 2. N fertilization management practices, fertilizer blend, and season, were considered fixed effects. A new factor was also included to compare the control treatment. The ANOVA ($p \leq 0.05$) was performed using the PROC MIXED procedure of SAS (version 9.0, SAS Institute Inc., Cary, NC, USA), and the means were tested using Fisher's least-test difference (LSD) at the 0.05 significance level. Mixed models were performed for variables from the ^{15}N-fertilizer analyses in season 2. N fertilization management, fertilizer blend, and ^{15}N-fertilizer were considered fixed effects and were tested by the Wald-F test. Multiple comparisons were performed by the LSD test. The software R [40] and its asreml and asremlPlus package were used. The level of significance was 0.05. The seasonal dry matter (biomass) and N partitioning (leaves, stalks, cobs, and grains) during the maize cycle were fitted to a Gaussian equation [16]. The total N uptake and ^{15}N recovery (leaves, stalks, and cobs) at R2 were subtracted by that at R6 to estimate the N remobilization based on the N accumulation models.

3. Results

3.1. Weather Conditions

The average daily air temperature was 25 °C during the maize growing seasons (Figure 4A,B). In season 1, the total precipitation was 643 mm, of which 421 mm occurred from maize sowing to V12, 204 mm occurred from V12 to R5 (dent stage), and 18 mm occurred from R5 to R6 (Figure 4A). In addition, three irrigations of 3 mm were performed three days after sowing and 8 mm at V4 (Figure 4A). In season 2, the total precipitation was 669 mm, of which 394 mm occurred from maize sowing to V12, 199 mm occurred from V12 to R5, and 76 mm occurred from R5 to R6 (Figure 4B). In addition, two irrigations of 8 mm were performed between V4 and V6 (vegetative leaf stage 6) (Figure 4B).

3.2. Ammonia Volatilization

In season 1, the 70%PSCU + 30%U broadcast application resulted in the maximum daily NH_3-N loss (2% of the applied N) on the sixth day after N application and a cumulative NH_3-N loss of 12% of the applied N on the 34th day after N application. It was higher than the 30%PSCU + 70%U broadcast application ($p \leq 0.05$) that resulted in the maximum daily and cumulative NH_3-N loss of 1.4% and 9% of the applied N, respectively (Figure 5A,B). The split N application at V4 resulted in the maximum daily NH_3-N loss (0.5% of the applied N) on the second day after the N application and a cumulative NH_3-N loss of 2.6% of the applied N on the 34th day after 70%PSCU + 30%U application. It was higher than the 30%PSCU + 70%U split application ($p \leq 0.05$) that resulted in the cumulative NH_3-N loss of 0.8% of the applied N (Figure 5C,D).

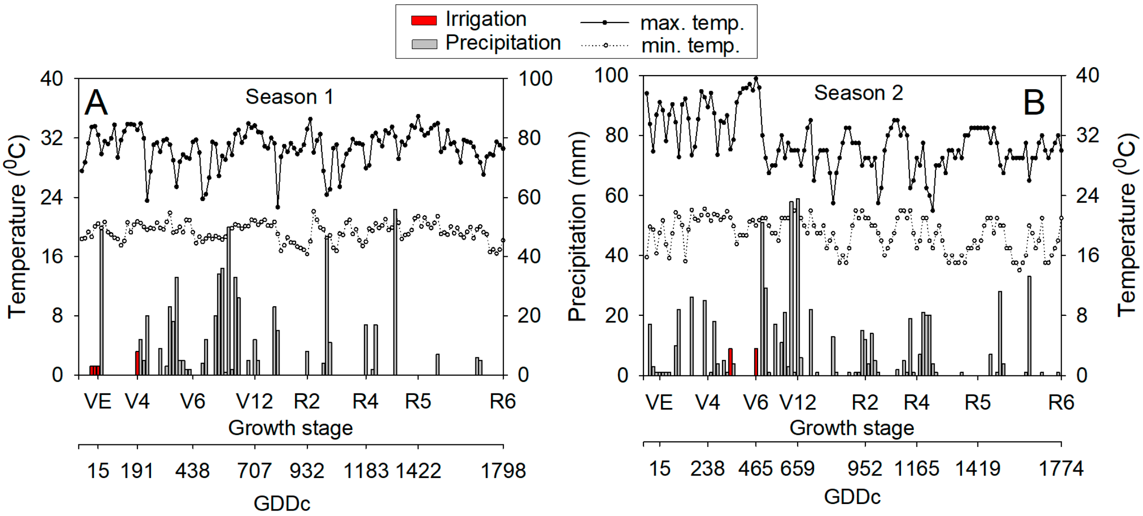

Figure 4. Daily minimum and maximum air temperature, daily rainfall, and irrigation for the maize growing seasons ((**A**): Season 1 (2017–2018); (**B**): Season 2 (2019–2020). GDDc: Growing degree days in Celsius calculated according to [41].

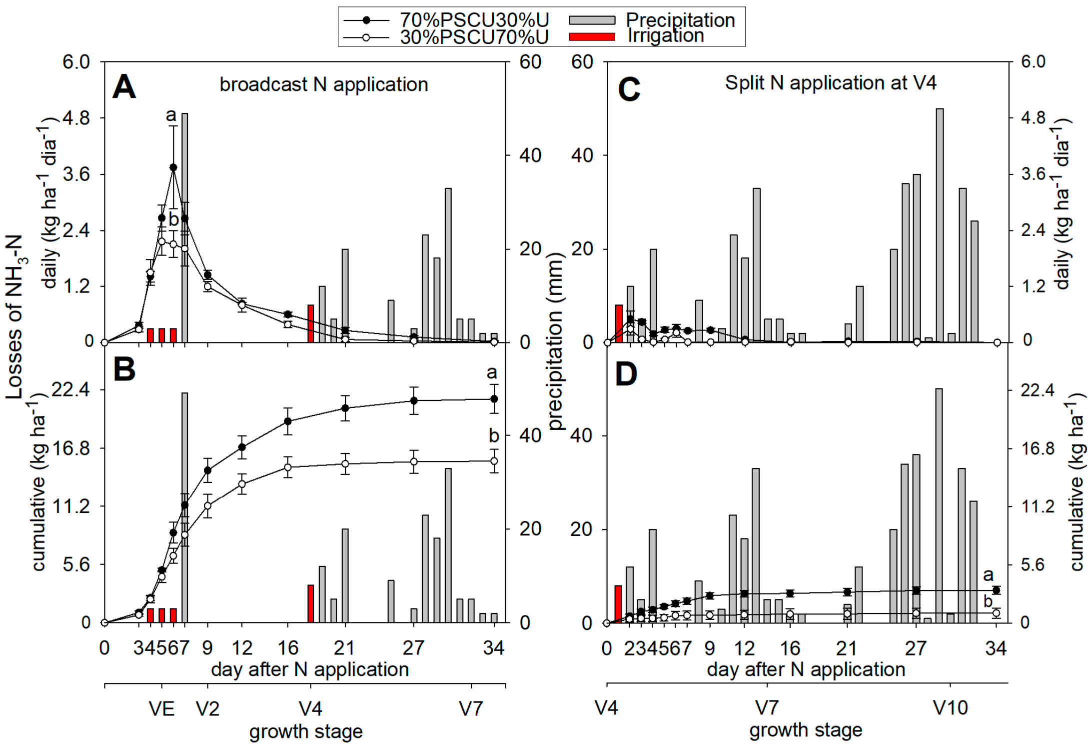

Figure 5. Daily and cumulative losses of NH_3-N in broadcast N application at sowing (180 kg N ha^{-1}) on the soil surface (**A**,**B**) and split N application side dressing at V4 (120 kg N ha^{-1}) maize growth stage (**C**,**D**). Vertical bars indicate the standard error of the mean. Means followed by different letters are significantly different ($p \leq 0.05$).

3.3. Mineral N Content in the Soil

In season 1 and season 2, the N fertilization management practice and fertilizer blend affected the mineral N content during the maize growth cycle (Figure 6). At V4, the incorporated N application resulted in higher mineral N content than the other N fertilization management practices at depths of 0–20 and 20–40 cm, and the experiment in season 1 resulted in higher mineral N content than in season 2 at 40–60 cm depth. At V12, the incorporated N application and split N application resulted in higher mineral N content than the broadcast N application at 0–20 cm depth. At V12, the experiment in season 2 resulted in higher mineral N content than in season 1 at 20–40 cm depth, and the 30%PSCU + 70%U application resulted in higher mineral N content than the 70%PSCU + 30%U application at 40–60 cm depth. At R2, the incorporated N application (in season 1) and the split N application (in season 2) resulted in higher mineral N content than the other N fertilization management treatments at 0–20 cm depth. At R2, the 30%PSCU + 70%U application resulted in higher mineral N content than the 70%PSCU + 30%U application at depths of 20–40 cm (in season 2) and 40–60 cm (both seasons). At R4, N treatments did not affect mineral N content ($p > 0.05$). At R6, the incorporated N application resulted in higher mineral N content than the broadcast application at 0–20 cm depth, and the N treatments did not affect mineral N content at 20–40 and 40–60 cm depth.

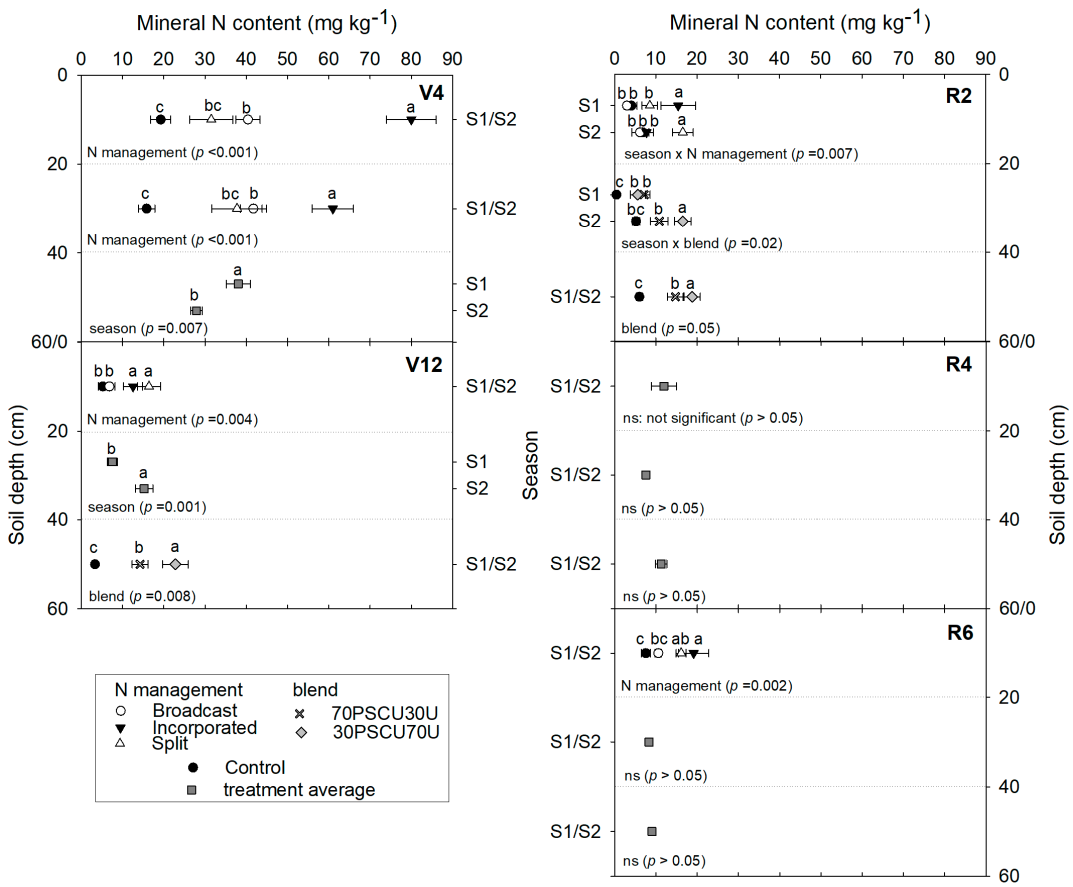

Figure 6. Effect of blends of polymer-sulfur coated urea (PSCU) and conventional urea (U) (70%PSCU + 30%U and 30%PSCU + 70%U) applied incorporated, broadcast, and split on soil N mineral content during the maize growing seasons (S1: season 1 (2017–2018); S2: season 2 (2019–2020)). Vertical bars indicate the standard error of the mean. Means followed by different letters are significantly different ($p \leq 0.05$) at each depth.

3.4. Biomass (Dry Matter) Accumulation in Plants and Maize Yield

The N fertilization management practice affected the total dry matter accumulation in vegetative and reproductive maize growth stages, and the fertilizer blend affected the maize yield (Figure 7). At V4, the incorporated N application provided higher dry matter accumulation (0.17 Mg ha^{-1}) than the other N management treatments (0.16 Mg ha^{-1}) in both seasons, and the experiment in season 2 resulted in higher dry matter accumulation (0.22 Mg ha^{-1}) than in season 1 (0.1 Mg ha^{-1}). At V12, the experiment in season 1 resulted in higher dry matter accumulation (6.8 Mg ha^{-1}) than in season 2 (5.7 Mg ha^{-1}). The N treatments did not affect the dry matter accumulation ($p > 0.05$) at R2 (12.7 Mg ha^{-1}) and R4 (16 Mg ha^{-1}). At R6, the N fertilization management practices resulted in higher dry matter accumulation (20 Mg ha^{-1}) than the control (16 Mg ha^{-1}) in season 1. At R6, N treatments did not affect dry matter accumulation (26 Mg ha^{-1}) in season 2, and the experiment in season 2 resulted in higher dry matter accumulation (26 Mg ha^{-1}) than in season 1 (19 Mg ha^{-1}). The 70%PSCU + 30%U application resulted in higher maize yield (8.3 Mg ha^{-1}) than 30%PSCU + 70%U application (7.6 Mg ha^{-1}) in season 1. The N treatments did not affect the maize yield in season 2 (12.1 Mg ha^{-1}), and the experiment in season 2 resulted in higher maize yield (12.1 Mg ha^{-1}) than in season 1 (7.5 Mg ha^{-1}). In season 1, the maximum rate of dry matter accumulation in the control (420 kg ha^{-1} day^{-1}) occurred on the 58th day after maize emergence (VE) and in the N treatments (361 kg ha^{-1} day^{-1}) on the 56th day after VE (Figure 8D,E). In season 2, the maximum rate of dry matter accumulation in the treatments (361 kg ha^{-1} day^{-1}) occurred on the 60th day after VE (Figures 8F and 9A).

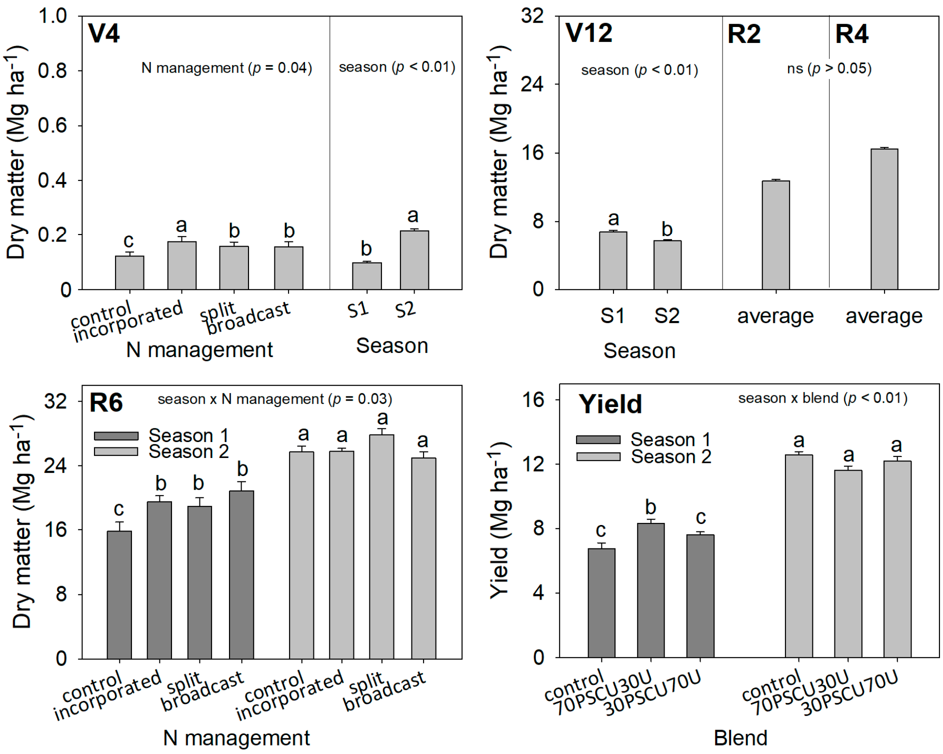

Figure 7. Effect of blends of polymer-sulfur coated urea (PSCU) and conventional urea (U) (70%PSCU + 30%U and 30%PSCU + 70%U) applied incorporated, broadcast, and split on maize yield and dry matter accumulation (aerial part) during the maize growing seasons (Season 1 (S1): 2017–2018; Season 2 (S2): 2019–2020). Vertical bars indicate the standard error of the mean. Means followed by different letters are significantly different ($p \leq 0.05$) in each maize growth stage.

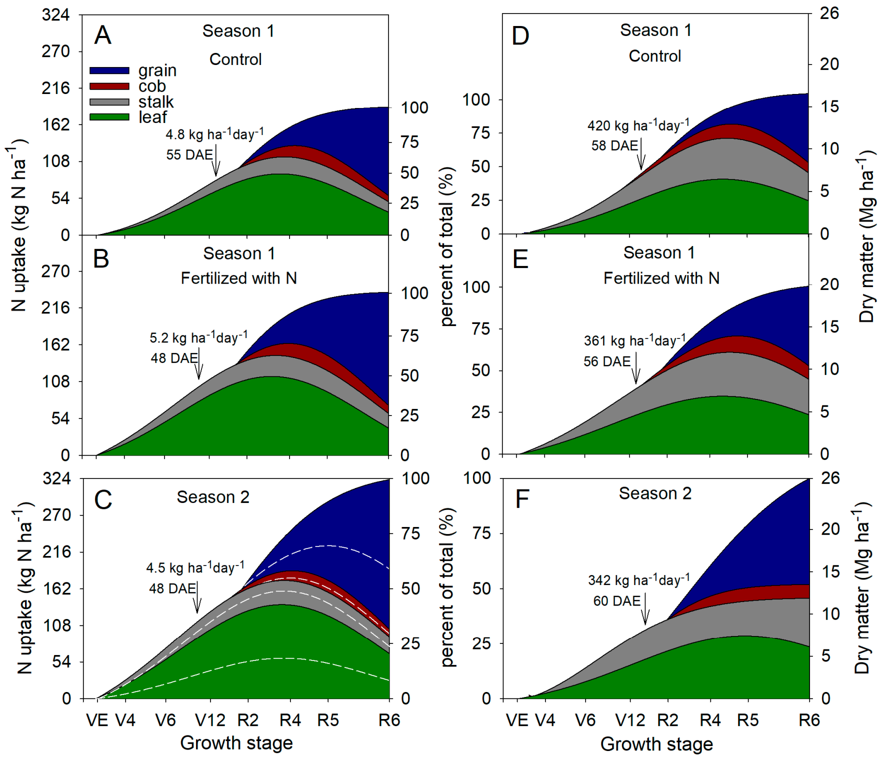

Figure 8. Seasonal dry matter and N accumulation and partitioning in the control (**A**,**D**) and in the N treatments (**B**,**E**) during the maize growing season 1 (2017–2018) and in the treatments (**C**,**F**) during the maize growing season 2 (2019–2020). The arrow indicates the maximum daily rate of dry matter and N accumulation. DAE is the day after maize emergence. The dashed line is the N derived from the fertilizer (Ndff) in each plant component during the maize growing season 2 (**C**).

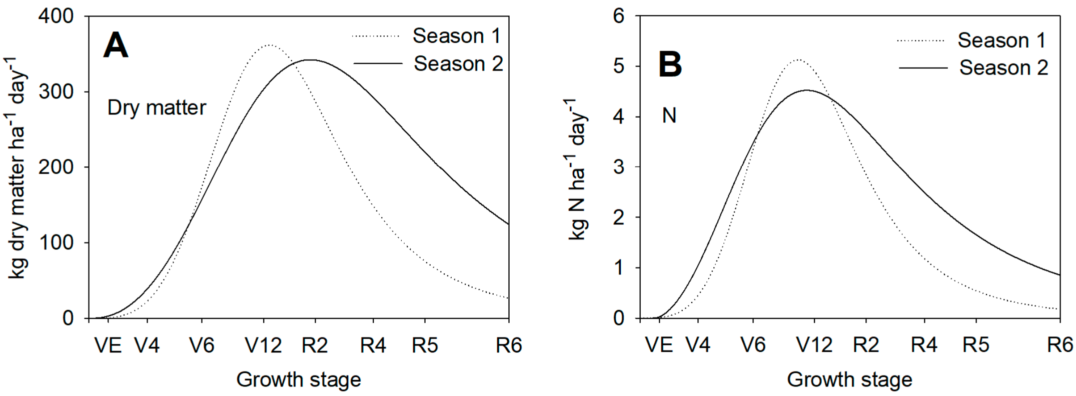

Figure 9. The daily rate of dry matter (**A**) and N accumulation (**B**) (kg ha^{-1} day^{-1}) in maize during two growing seasons (season 1: 2017–2018; season 2: 2019–2020). Average of treatments (two fertilizer blends, three N fertilization management practices, and a control treatment) in each growing season.

3.5. Nitrogen Uptake in Maize Plants

The N fertilization management practices affected the total N uptake in the vegetative and reproductive maize growth stages (Figure 10).

At V4, the incorporated N application resulted in higher N uptake (8 kg ha^{-1}) than the other N fertilization management treatments (7 kg ha^{-1}) in both seasons. At V4, the experiment in season 2 resulted in higher N uptake (9 kg ha^{-1}) than in season 1 (4 kg ha^{-1}), and the Ndff in season 2 was 3.8 kg ha^{-1} on average. At V12, the experiment in season 2 resulted in higher N uptake (138 kg ha^{-1}) than in season 1 (118 kg ha^{-1}), and the Ndff in season 2 was 55 kg ha^{-1} on average. At R2, the experiment in season 2 resulted in higher N uptake (205 kg ha^{-1}) than in season 1 (171 kg ha^{-1}), and the Ndff in season 2 was 95 kg ha^{-1} on average. At R4, the experiment in season 2 resulted in higher N uptake (253 kg ha^{-1}) than in season 1 (221 kg ha^{-1}), and the Ndff in season 2 was 102 kg ha^{-1} on average. At R6, the N broadcast application resulted in higher N uptake (261 kg ha^{-1}) than split N application (215 kg ha^{-1}) in season 1, the N treatments did not affect total N uptake (324 kg ha^{-1}) in season 2, and the Ndff in season 2 was 130 kg ha^{-1} on average. The experiment in season 2 resulted in higher total N uptake (324 kg ha^{-1}) than in season 1 (221 kg ha^{-1}). The N broadcast application resulted in higher N uptake in the grain (179 kg ha^{-1}) than the other N fertilization management treatments (144 kg ha^{-1}) in season 1. The N treatments did not affect the N uptake in the grain (216 kg ha^{-1}) in season 2, and the Ndff in the grain in season 2 was 86 kg ha^{-1} (Figures 8C and 9). The experiment in season 2 provided higher N uptake in the grain (216 kg ha^{-1}) than in season 1 (146 kg ha^{-1}). In season 1, the maximum rate of N uptake in the control (4.8 kg ha^{-1} day^{-1}) occurred on the 55th day after VE and in the N treatments (5.2 kg ha^{-1} day^{-1}) occurred on the 48th day after VE (Figure 8A,B). In season 2, the maximum rate of N uptake in the treatments (4.5 kg ha^{-1} day^{-1}) occurred on the 48th day after VE (Figures 8C and 9B). The N remobilization from R2 (leaf, stalk, and cob) to R6 (grain) was 57 kg N ha^{-1} in the control (Figure 8A) and 73 kg N ha^{-1} in the N treatments (Figure 8B) in season 1, and 77 kg N ha^{-1} (Figure 8C) in the treatments in season 2. The remobilization in terms of Ndff was 42 kg N ha^{-1} in the N treatments in season 2 (Figure 8C).

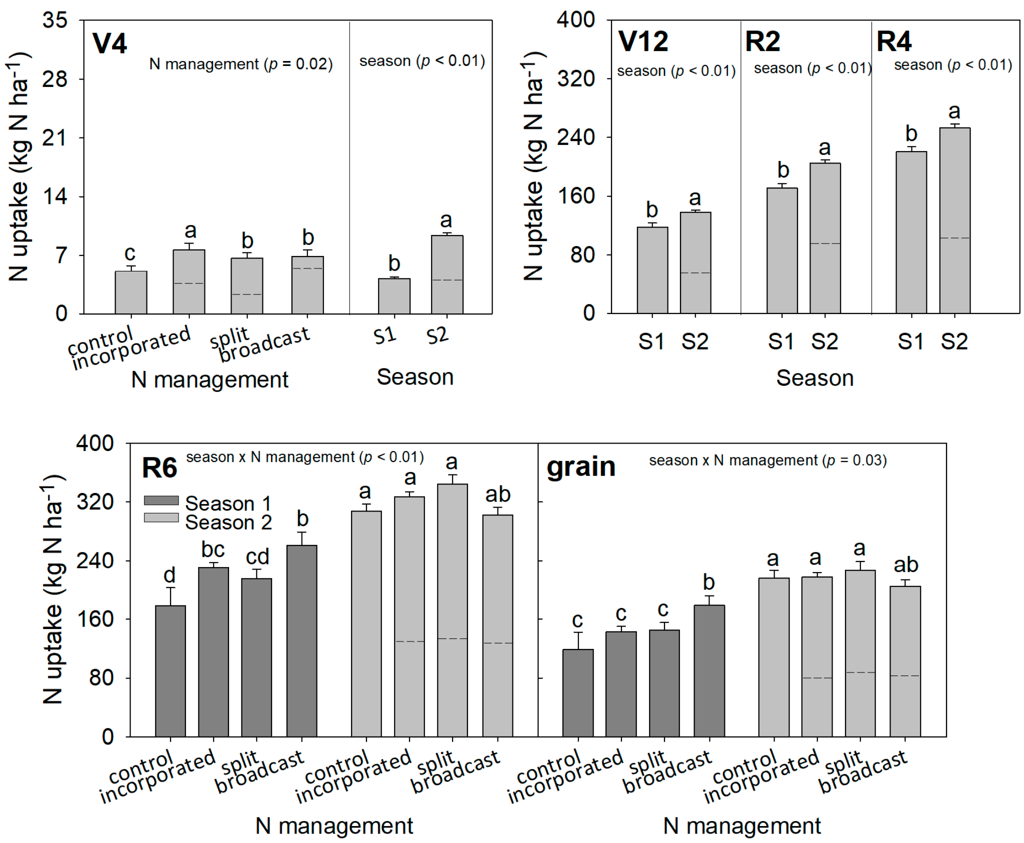

Figure 10. Effect of blends of polymer-sulfur coated urea (PSCU) and conventional urea (U) (70%PSCU + 30%U and 30%PSCU + 70%U) applied incorporated, broadcast, and split on N uptake (aerial part) during the maize growing seasons (Season 1 (S1): 2017–2018; Season 2 (S2): 2019–2020). The dashed line is the N derived from the fertilizer (Ndff) in the plant in season 2. Vertical bars indicate the standard error of the mean. Means followed by different letters are significantly different ($p \leq 0.05$) in each maize growth stage.

3.6. ^{15}N-Fertilizer Recovery in Maize Plants and Nitrogen Balance

In season 2, the N fertilization management practice and fertilizer blend affected the ^{15}N recovery (NR) from fertilizer N source by plants during the maize growth cycle (Figure 11). At V4, the split N application resulted in higher total NR (3.6%) than the broadcast (3.1%) and incorporated (2.1%) application, and the 70%PSCU + 30%U application resulted in higher total NR (3.4%) than 30%PSCU + 70%U application (2.5%). The PSCU resulted in higher NR (2.6%) than the U (0.8%) under 70%PSCU + 30%U application, and it was also observed under split N application. At V12, the N broadcast application resulted in higher total NR (37%) than the other N fertilization management treatments (27%), and the 30%PSCU + 70%U application resulted in higher total NR (33%) than the 70%PSCU + 30%U application (28%). The PSCU resulted in higher NR (20%) than U (8%) under 70%PSCU + 30%U application, and the U resulted in higher NR (21%) than the PSCU (12%) under 30%PSCU+70%U application. At R2, the incorporated N application and split N application resulted in higher total NR (60%) than the N broadcast application (39%), and the fertilizer blend did not affect the total NR (54%). The PSCU resulted in higher NR (38%) than the U (16%) under 70%PSCU + 30%U application, and the U resulted in higher NR (35%) than the PSCU (19%) under 30%PSCU + 70%U application. At R4, the split N application resulted in higher total NR (67%) than the N broadcast application (49%), and the 30%PSCU + 70%U application resulted in higher total NR (68%) than the 70%PSCU + 30%U application (50%). The PSCU resulted in higher NR (34%) than the U (16%) under 70%PSCU + 30%U application, and the U resulted in higher NR (49%) than the PSCU (19%) under 30%PSCU + 70%U application. At R6, the N fertilization management practice and fertilizer blend did not affect the total NR (72%). The PSCU resulted in higher NR (51%) than the U (23%) under 70%PSCU + 30%U application, and the U resulted in higher NR (50%) than the PSCU (22%) under 30%PSCU + 70%U application. From the total NR at R6 (plant aboveground), it was in grain (47.91%), leaf (15.4%), stalk (6.84%), and cob (2.34%). It was also found 1.37% of NR in root and 0.02% in the soil at 0–20 cm depth (Figure 12). The PSCU resulted in higher NR in the grain (34%) than the U (15%) under 70%PSCU + 30%U application, and the U resulted in higher NR in the grain (34%) than the PSCU (14%) under 30%PSCU + 70%U application. The incorporated N application and split N application resulted in higher N remobilization from R2 (leaf, stalk, and cob) to R6 (grain) in terms of NR (30%) than N broadcast application (13%) (Figure 11).

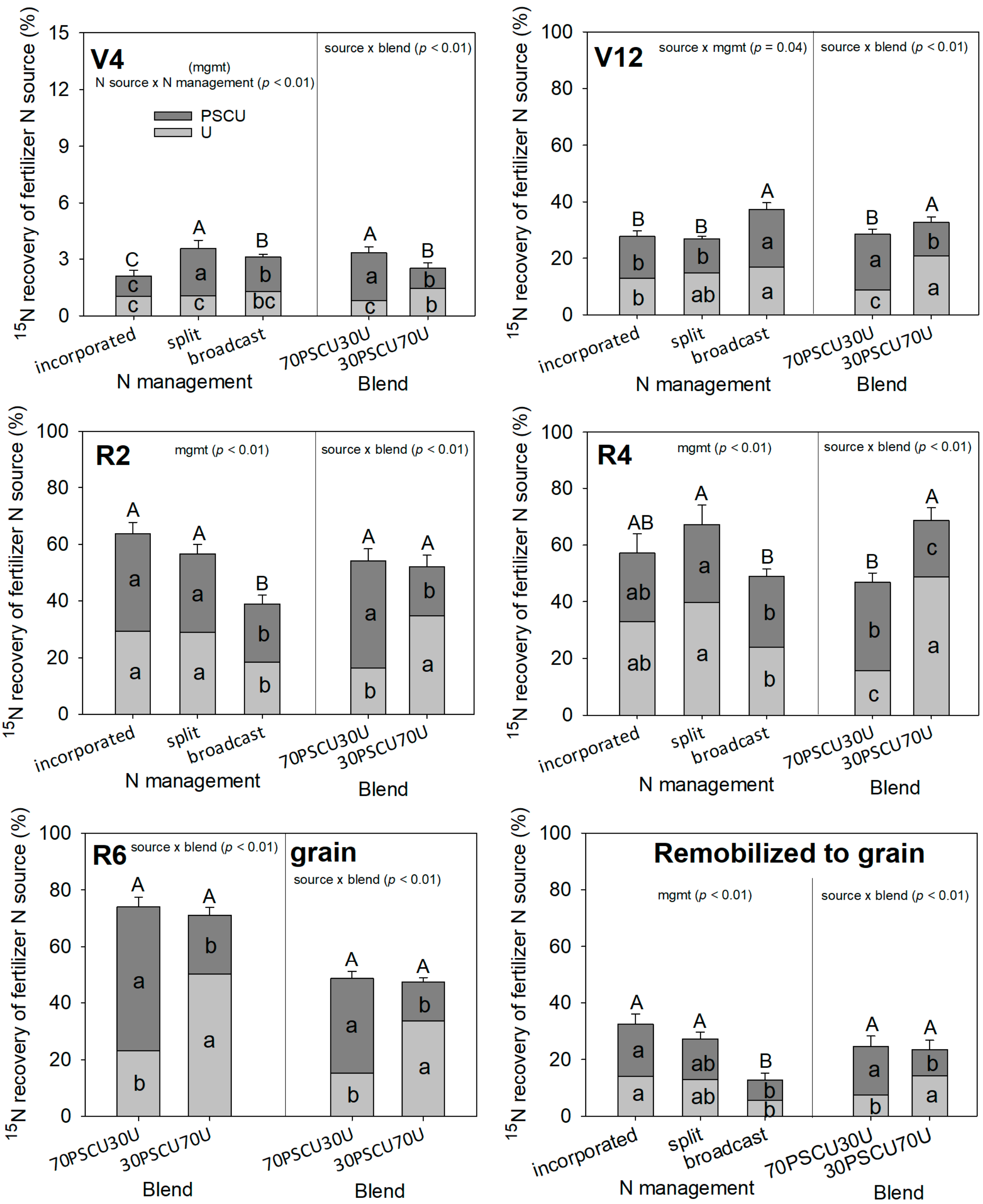

Figure 11. Effect of blends of polymer-sulfur coated urea (PSCU) and conventional urea (U) (70%PSCU + 30%U and 30%PSCU + 70%U) applied incorporated, broadcast, and split on ^{15}N-fertilizer recovery (aerial part) during the maize growing season (2019–2020). Vertical bars indicate the standard error of the mean. Means followed by different lowercase letters indicate difference ($p \leq 0.05$) between ^{15}N source (^{15}N-PSCU and ^{15}N-U) and among treatments, while different capital letters indicate difference ($p \leq 0.05$) of total ^{15}N-fertilizer recovery among treatments in each maize growth stage.

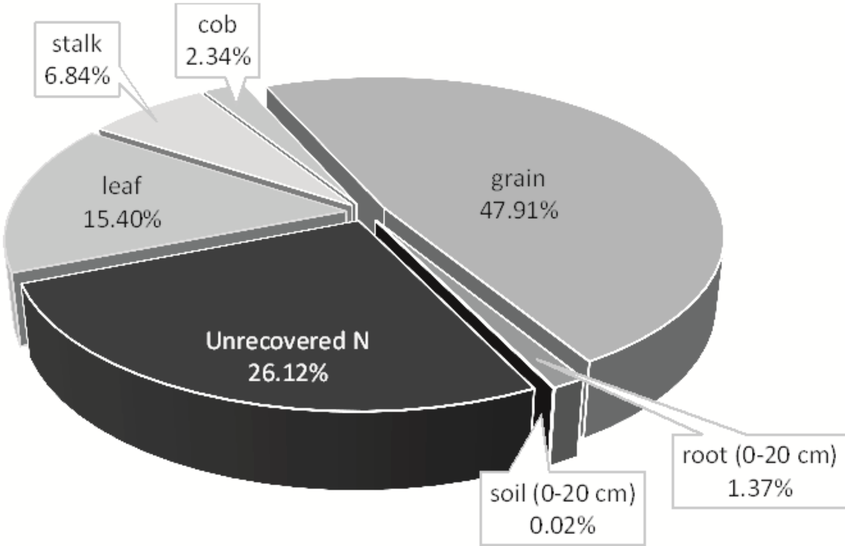

Figure 12. Balance of ^{15}N-fertilizer recovery (%) in the soil-plant system applying blends of polymer-sulfur coated urea (PSCU) and conventional urea (U), 70%PSCU + 30%U and 30%PSCU + 70%U, incorporated, broadcast, and split in maize in Brazilian tropical conditions. The graph represents all N treatments, and the rate of N was 180 kg ha^{-1}.

4. Discussion

In season 1, the 70%PSCU + 30%U application produced 1552 kg grain ha^{-1} more than the control treatment that had no difference compared to the 30%PSCU + 70%U application. In terms of agronomic efficiency, it is the same to say that each 1 kg N ha^{-1} applied with 70%PSCU + 30%U produced 8.6 kg grain ha^{-1} more than the control. However, the N rate (180 kg N ha^{-1}) adopted in our experiments was aiming yields higher than 10 Mg ha^{-1} [30] and the highest yield obtained in season 1 was 8.3 Mg ha^{-1}. Another study, in Brazilian condition evaluating blends of PSCU + U (180 kg N ha^{-1}), incorporated at maize sowing in a sandy loam soil found the agronomic efficiency of 16 kg grain ha^{-1} and a yield of 10.5 Mg ha^{-1} [16]. In Chinese conditions, blends of CRU + U applied as basal fertilizer in maize provided an agronomic efficiency of 21 kg grain ha^{-1} and a yield of 9.7 Mg ha^{-1} in sandy soil (185 kg N ha^{-1}), and 15.7 kg grain ha^{-1} and a yield of 12.2 Mg ha^{-1} in a clayey soil (171 kg N ha^{-1}) [19]. The maize yield can be affected by the genetic of hybrids, pests and diseases, weather conditions, and nutritional management (IPNI, 2003). The loss of NH_3-N by volatilization reached 22 kg N ha^{-1} under the broadcast-applied 70%PSCU + 30%U treatment that represented 6 kg N ha^{-1} more than the observed under the broadcast-applied 30%PSCU + 70%U treatment in season 1. Subtracting that loss by the N rate (180 kg N ha^{-1}), the result is close to the N rate of 150 kg N ha^{-1} that is recommended expecting maize grain yields between 8 and 10 Mg ha^{-1} [30] in São Paulo state, Brazil. The irrigations performed days after the N broadcast application favored the volatilization of ammonia. After the 50 mm precipitation in one day, the U probably incorporated and reduced the ammonia volatilization. The PSCU (the insoluble source) probably stayed on the soil surface, providing more ammonia volatilization in the blend with more PSCU. The U, treated with NBPT, probably inhibited the ammonia volatilization during the irrigated days. It also occurred on a lesser scale in the split N application (side dressing at V4) followed by the precipitations after N application. In a study evaluating blends of PSCU + U in coffee in Brazilian conditions were observed 20 kg ha^{-1} of NH_3-N volatilization applying 220 kg N ha^{-1} using another type of ammonia collector at 42 days after fertilizer application [42]. In that study was also found loss of 40 kg ha^{-1} of NH_3-N applying just U (150 kg N ha^{-1}). In our study, the precipitation also provided the soil N mineral percolation to 40–60 cm soil layer at the V12 and R2 growth stages in both seasons. It disfavors 30%PSCU + 70%U application that resulted in higher soil N mineral content at 40–60 cm depth than 70%PSCU + 30%U application, probably by the N from the U that is a soluble N source, and 30%PSCU + 70%U application consequently provided lower yield in season 1. In Chinese conditions, blends of CRU + U resulted in a similar soil N mineral content at 40–60 cm depth in a clayey soil, but at R6 maize growth stage [19]. In that study, the authors used a CRU with a different pattern of N release (80% of N was released within 120 days after application) [19] compared to our study. Other effects of blends of CRU and U and just CRU (with polymer without S^0) on ammonia volatilization, maize yield, and soil N mineral in Chinese conditions can be found in [1,20], and in Brazilian conditions in [43].

The experiment in season 2, in general, resulted in higher dry matter, N uptake, and maize yield than in season 1. It can be explained by the difference in the daily rate of dry matter and N accumulation during the maize growth cycle (Figure 9) that was probably affected by the agricultural history of the experiments. The better condition observed in season 2 for the maize growth, that was non-responsive to N-fertilizer application, can be associated with the recent application of limestone and the soil preparation (plowing and harrowing), that provided an optimal base saturation to maize production, and accelerated the mineralization of soil organic N [44]. In addition, the precipitation in season 2 was better distributed than in season 1, especially between R5 and R6, and hydric stress at R5 can anticipate the physiological maturity and reduce the weight of grains [45]. The roots growth of maize plants in season 1 probably was limited at 0–20 cm depth based on the aluminum saturation (>20%) at 20–40 and 40–60 cm depth, and in favorable conditions, 48% of maize roots can develop below of 30 cm depth depending on soil texture [46]. It probably limited the water and nutrient uptake at 0–20 cm depth, favoring the N broadcast application and the N-fertilizer with more PSCU that stayed on the soil surface, and limiting maize yield in season 1. The aluminum saturation higher than 20% is typically found in no-tillage systems, and it is normally recommended to apply gypsum to reduce the aluminum saturation, in-depth [47]. The nonresponse to N fertilization using blends of CRU and U and just U was also observed in maize in Rhodic Haplustox sites [16,48], which also has a clayey texture, and in another crop in a Typic Hapludox site [49] in Brazilian conditions.

The incorporated N-fertilizer application tended to result in higher soil N mineral content at 0–20 cm depth during the maize growth cycle than the other N fertilization management treatments once this application is concentrated in the fertilizer row and the soil samples were performed in this region. However, the incorporated N application resulted in higher N uptake and dry matter accumulation only at V4 (both seasons) and the incorporated N application was not sufficient to affect the maize yield potential [50]. Similar results of dry matter accumulation and N uptake in maize at the V4 growth stage applying blends of PSCU + U just incorporated at sowing were observed by [16] in a sandy loam soil and a clayey soil. Contrary to our hypothesis, the CRU was the main N-fertilizer supplier at the V4 growth stage based on the NR in the 70%PSCU + 30%U application, and the CRU resulted in the same NR compared to the U in the 30%PSCU + 70%U application at V4. It shows that the PSCU of our study applied in Brazilian conditions can provide N to maize plants in the early stages, different from what happened in North America using another CRU based on the low soil N availability [13]. It probably can be explained by the N released from our PSCU that reached ~20% of the applied N in the first day tested in water. Although the 30%PSCU + 70%U application resulted in lower total NR at V4 and higher soil N mineral content at 40–60 cm (V12 and R2 stages) than the 70%PSCU + 30%U application, 30%PSCU + 70%U resulted in the same and in some cases higher total NR than 70%PSCU + 30%U after V4 maize growth stage. It probably is associated with the development of roots below of 0–20 cm soil layer in season 2 (low in-depth aluminum saturation), resulting in the NR of the U (30%PSCU + 70%U application) similar to the NR of the CRU (70%PSCU + 30%U application). The split N application resulted in higher NR at V4 than the other N fertilization management treatments, but the split N application treatments just received 30% of N-fertilizer at sowing; lower N rates tend to provide higher NR [51,52]. The N broadcast application resulted in higher total NR at V12 and lower total NR at R2 and R4 growth stages than other N management treatments, but the total N uptake had no difference among treatments. In this situation, the priming effect [53] could be higher after V12 and until the R4 growth stage in the N broadcast application, although the control treatment resulted in similar N uptake. The broadcast application also resulted in lower remobilization of NR to the grain from R2 to R6 compared to the other N fertilization management treatments; it indicated that maize plants tended to absorb more N from the fertilizer after R2 in the broadcast application. At R6, the N treatments resulted in the same NR in season 2, and the unrecovered N-fertilizer (26.12%) can be associated with the ammonia volatilization and the N percolation. This is the first study that evaluated the ^{15}N-fertilizer recovery in maize using blends of PSCU and U with ^{15}N in both sources of the blends. Other studies just evaluated the ^{15}N-fertilizer recovery from the U source of a blend of PSCU + U, and just applied 70%PSCU + 30%U broadcast [54] or incorporated [17] in the same type of soil of our experiment. They found an average of 12% of NR from the U source by maize using N rate around 180 kg N ha^{-1}. The main challenge in a study like that is to manufacture the PSCU-^{15}N with the same characteristics as the industrial product, providing high costs to the research. It can restrict the studies on this topic. In our study, it was just possible to work in one-year experiment using ^{15}N-fertilizers. If we used ^{15}N in season 1, the results of NR could change because of the aluminum saturation at 20–40 and 40–60 cm depths (>20%) that can restrict the N uptake at 0–20 cm depth, and plants could likely recovery more N from the 70%PSCU + 30%U compared to the 30%PSCU + 70%U application. The average of NR in cereals worldwide is 33% [55]. In specific conditions in Brazil, the NR of maize applying different N sources ranged from 19% [56] to 89% [57]. In China, the NR ranged from 26% to 35% [58], in America can be found 52%, and in Europe, 62% on average [54] in most cereals. These variations of NR are normally attributed to the type of the soil, weather conditions [59,60], the N-fertilizer source [57,61], the N fertilization management practice, the N rate, and the soil management practice [56,61,62]. It would be of interest in future studies to evaluate the dynamics of blends of CRU + U and other enhanced efficiency fertilizers using ^{15}N in sandy loam soil that is normally more responsible for N fertilizer application in maize than clayey soil [16], and it would improve the recommendation for these fertilizers in Brazilian conditions. Our study can help future studies that will use ^{15}N in blends of CRU and U and help to improve CRU fertilizers aiming to increase the N-fertilizer recovery.

The broadcast, incorporated, and split application using 70%PSCU + 30%U and 30%PSCU + 70%U can ensure N throughout the maize cycle at Rhodic Eutrustox soil with common bean straw on the soil surface in Brazil. According to the agricultural history, the precipitation and the NR in season 2, in addition to the ammonia loss observed in season 1, the broadcast-applied 30%PSCU + 70%U treatment can be the most cost-effective alternative aiming to replace the N extracted by maize grain, considering that the experiment in season 2 was non-responsive to N-fertilizer application. The cost of the PSCU is higher than the U treated with NBPT, and broadcast application tends to be cheaper than incorporated application and split application. In this situation, reducing the N-fertilizer rate using 30%PSCU + 70%U would be another choice to reduce economic losses and environmental pollution in non-responsive sites.

5. Conclusions

In Rhodic Eutrustox soil, blends of PSCU and U treated with NBPT (70%PSCU + 30%U and 30%PSCU + 70%U), at a rate of 180 kg N ha^{-1}, applied incorporated at sowing, broadcast on the soil surface at sowing, and split (30% incorporated at sowing and 70% side-dressing at V4) can ensure N throughout the maize cycle in Brazilian condition. In season 2, the PSCU was the main N-fertilizer supplier at the V4 growth stage, applying 70%PSCU + 30%U, and both blends can ensure 73.8% of N-fertilizer recovery (maize aerial part + root) of which 47.9% in the grain. The unrecovered N can be attributed to the ammonia volatilization losses that reached 11% on average in season 1 and the N percolation that was prominent at 40–60 cm depth in important maize growth stages in applications with 30%PSCU + 70%U in both seasons. Recent application of limestone, plowing, and harrowing can provide a nonresponse to N fertilization in a Rhodic Eutrustox soil with common bean straw left on the soil surface, and to replace the N extracted by harvest, farmers can choose the most cost-effective option.

Author Contributions: P.L.G. conceived, designed and performed the experiments, field sampling, laboratory and data analyses, funding acquisition, writing, review and editing; R.A.S. review and data analyses; C.R.d.S.A.F. review, coated the ^{15}N-fertilizer and validated its release; J.A.B. review and funding acquisition; B.N.B. review; P.C.O.T. supervision, conceived and designed the experiments, funding acquisition, project administration and review. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by FUNDAÇÃO DE AMPARO À PESQUISA DO ESTADO DE SÃO PAULO (FAPESP; grant number 2017/25813-5 and grant number 2017/24516-7). This research was also funded by COMPASS MINERALS PLANT NUTRITION and by CENTER FOR NUCLEAR ENERGY IN AGRICULTURE (CENA/USP).

Acknowledgments: Pedro L. Garcia thank Fundação de Amparo à Pesquisa do Estado de São Paulo (FAPESP; grant number 2017/25813-5) for the granted scholarship. The authors thank Fundação de Amparo à Pesquisa do Estado de São Paulo (FAPESP; grant number 2017/24516-7). We are most grateful to Stable Isotopes Laboratory team for the strong laboratory and field assistance. Technicians: Hugo, Ana, Miguel, Pingin, Clélber and Bento. Interns: Cátia, Henrique, Matheus, Carla, Pablo, Leonardo, Monique, Maick, Bianca, Everton, Maria Roberta and Magrão (in memoriam). Graduate students: Nicole, Bruno, Gabriela and Saulo. The researcher: José Lavres Junior. We also thank Compass Minerals South America research team (Ithamar Prada, Michel Castellani, José Marcos Leite, Bruno Saito, Daniela Vitti, Robson Mauri, Gabriel Uehara, Douglas, Linker, interns and the previous research manager Fabio Scudeler) for the strong field assistance. Special thanks to the researcher Caue Ribeiro, Paulo Lasso, Embrapa Instrumentation and Rede Agronano for the X-ray microtomography analyses.

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

References

1. Ke, J.; Xing, X.; Li, G.; Ding, Y.; Dou, F.; Wang, S.; Liu, Z.; Tang, S.; Ding, C.; Chen, L. Effects of different controlled-release nitrogen fertilisers on ammonia volatilisation, nitrogen use efficiency and yield on blanket-seeding machine-transplanted rice. *Field Crop. Res.* **2017**, *205*, 147–156. [CrossRef]
2. [USDA] United States Department of Agriculture. World Corn Supply and Use. 2020. Available online: https://www.usda.gov/oce/commodity/wasde/wasde0720.pdf (accessed on 24 November 2020).
3. Rinaldi, L.F.; Garcia, P.L.; Sermarini, R.A.; Trivelin, P.C.O. ^{15}N-Urea efficiency in maize as influenced by humic substances and urease inhibitors treatments. *Commun. Soil Sci. Plant Anal.* **2019**, *50*, 198–208. [CrossRef]
4. Cantarella, H. Nitrogen. In *Soil Fertility*; Novais, R.F., Ed.; Brazilian Society of Soil Science: Viçosa, Brazil, 2007; pp. 271–276.
5. Graming, B.M.; Massey, R.; Yun, S.D. Nitrogen application decision-making under climate risk in the U.S. Corn Belt. *Clim. Risk Manag.* **2017**, *15*, 82–89. [CrossRef]
6. Apostolopoulou, E. *The Global Market for Slow-Release, Controlled-Release and Stabilized Fertilizers*; International Fertilizer Association—IFA: Beijing, China, 2016; 19p.
7. IPNI. Slow or Controlled Release and Stabilized Nitrogen Fertilizers 2017. Available online: http://www.ipni.net/PUBLICATION/IA-BRASIL.NSF/0/90DE38570A7216CB832580FB0066E3B4/$FILE/Jornal-157.pdf (accessed on 24 November 2020).
8. Trenkel, M.E. *Slow and Controlled Release and Stabilized Fertilizers: An Option for Enhancing Nutrient Use Efficiency in Agriculture*; International Fertilizer Industry Association: Paris, France, 2010; 160p.
9. Shapiro, C.; Attia, A.; Ulloa, S.; Mainz, M. Use of five nitrogen source and placement systems for improved nitrogen management of irrigated corn. *Soil Sci. Soc. Am. J.* **2016**, *80*, 1663–1674. [CrossRef]
10. Guo, L.; Ning, T.; Nie, L.; Li, Z.; Lal, R. Interaction of deep placed controlled-release urea and water retention agent on nitrogen and water use and maize yield. *Eur. J. Agron.* **2016**, *75*, 118–129. [CrossRef]
11. Cancellier, E.L.; Silva, G.R.D.; Faquin, V.; Gonçalvez, A.B.; Cancellier, L.L.; Spehar, R.C. Ammonia volatilization from enhanced-efficiency urea on no-till maize in Brazilian cerrado with improved soil fertility. *Ciência Agrotecnol.* **2016**, *40*, 133–144. [CrossRef]
12. Wilson, M.L.; Rosen, C.J.; Moncrief, J.F. Potato response to polymer coated-urea on an irrigated coarsed-texture soil. *Agron. J.* **2009**, *101*, 897–905. [CrossRef]
13. Grant, C.A.; Wu, R.; Selles, F.; Harker, K.N.; Clayton, G.W.; Bittman, S.; Zebarth, B.J.; Lupwayi, N.Z. Crop yield and nitrogen concentration with controlled release urea and split applications of nitrogen as compared to non-coated urea applied at seeding. *Field Crop. Res.* **2012**, *127*, 170–180. [CrossRef]
14. Garcia, P.L.; Sermarini, R.A.; Trivelin, P.C.O. Effects of nitrogen rates applying controlled-release and conventional urea blend in maize. *J. Plant Nutr.* **2019**, *42*, 2199–2208. [CrossRef]

15. Hong, N.; Scharf, P.C.; Davis, J.G.; Kitchen, N.R.; Sudduth, K.A. Economically optimal nitrogen rate reduces soil residual nitrate. *J. Environ. Qual.* **2007**, *36*, 354–362. [CrossRef]
16. Garcia, P.L.; González-Villalba, H.A.; Sermarini, R.A.; Trivelin, P.C.O. Nitrogen use efficiency and nutrient partitioning in maize as affected by blends of controlled-release and conventional urea. *Arch. Agron. Soil Sci.* **2018**, *64*, 1944–1962. [CrossRef]
17. Villalba, H.A.G. Blending Polymer-Sulfur Coated and NBPT-Treated Urea to Improve Nitrogen Use Efficiency and Grain Yield in Corn Production Systems. Ph.D. Dissertation, University of São Paulo, Piracicaba, Brazil, 2018. Available online: https://www.teses.usp.br/teses/disponiveis/11/11140/tde-14082018-100857/pt-br.php (accessed on 24 November 2020).
18. Nkebiwe, P.M.; Weinmann, M.; Bar-Tal, A.; Müller, T. Fertilizer placement to improve crop nutrient acquisition and yield: A review and meta-analysis. *Field Crop. Res.* **2016**, *196*, 389–401. [CrossRef]
19. Li, C.; Wang, Y.; Li, V.; Zhu, L.; Cao, Y.; Zhao, X.; Feng, G.; Gao, Q. Mixture of controlled-release and normal urea to improve nitrogen management for maize across contrasting soil types. *Agron. J.* **2020**, *112*, 3101–3313. [CrossRef]
20. Li, C.L.; Cao, Y.Q.; Wang, Y.; Li, X.Y.; Li, Y.X.; Zhu, L.; Zhao, X.H.; Gao, Q. Effects of mixed controlled release and normal urea on maize (*Zea mays* L.) growth, grain yield and nitrogen balance and use efficiency in northeast China. *Appl. Ecol. Environ. Res.* **2020**, *18*, 5367–5382. [CrossRef]
21. Guo, J.; Wang, Y.; Blaylock, A.D.; Chen, X. Mixture of controlled release and normal urea to optimize nitrogen management for high-yielding (>15 Mg ha^{-1}) maize. *Field Crop. Res.* **2017**, *204*, 23–30. [CrossRef]
22. Garcia, P.L.; Sermarini, R.A.; Trivelin, P.C.O. Placement effect of controlled-release and conventional urea blend in maize. *Commun. Soil Sci. Plant Anal.* **2019**, *50*, 2321–2329. [CrossRef]
23. Kong, L. Maize residues, soil quality, and wheat growth in China: A review. *Agron. Sustain. Dev.* **2014**, *34*, 405–416. [CrossRef]
24. Soil Survey Staff. *Keys to Soil Taxonomy*, 12th ed.; USDA-NRCS.: Whashington, DC, USA, 2014.
25. Gee, G.W.; Bauder, J.W. Particle-size analyzis. In *Methods of Soil Analysis: Physical and Mineralogical Methods*; Klaute, A., Ed.; ASA and SSSA: Madison, WI, USA, 1986; pp. 383–411.
26. Bataglia, O.C.; Furlani, A.M.C.; Teixeira, J.P.F.; Furlani, P.R.; Gallo, J.R. *Methods of Chemical Analysis of Plants*; Instituto Agronômico: Campinas, Brazil, 1983; pp. 1–48.
27. van Raij, B.; Andrade, J.C.; Cantarella, H.; Quaggio, J.A. *Chemical Analysis for Fertility Evaluation of Tropical Soils*; Instituto Agronômico: Campinas, Brazil, 2001.
28. Nelson, D.W.; Sommers, L.E. Total Carbon, organic carbon and organic matter. In *Methods of Soil Analysis: Chemical Methods*; Sparks, D.L., Ed.; ASA and SSSA: Madison, WI, USA, 1996; pp. 961–1010.
29. Barrie, A.; Prosser, S.J. Automated analyses of light-element stable isotopes by isotope ratio mass spectrometry. In *Mass Spectrometry of Soils*; Boutton, T.W., Yamasaki, S., Eds.; Marcel Dekker: New York, NY, USA, 1996; pp. 1–46.
30. van Raij, B.; Cantarella, H. Corn for grain and silage. In *Recommendation of Fertilization and Liming for the State of São Paulo*; Cantarella, H., Quaggio, J.A., Furlani, A.M.C., Eds.; Instituto Agronômico: Campinas, Brazil, 1997; pp. 56–59.
31. Mariano, E.; Filho, C.R.S.A.; Bortoletto-Santos, R.; Bendassoli, J.A.; Trivelin, P.C.O. Ammonia losses following surface application of enhanced-efficiency nitrogen fertilizers and urea. *Atmos. Environ.* **2019**, *203*, 242–251. [CrossRef]
32. Fritsche, L.S. Urea-^{15}N. Master's Thesis, University of São Paulo, Piracicaba, Brazil, 2019. Available online: https://www.teses.usp.br/teses/disponiveis/64/64135/tde-09102019-091454/publico/Leticia_Sbrana_Fritsche_Revisada.pdf (accessed on 24 November 2020).
33. Landis, E.N.; Keane, D.T. X-ray microtomography. *Mater. Charact.* **2010**, *61*, 1305–1316. [CrossRef]
34. Reis, B.F.; Vieira, J.A.; Krug, F.J.; Giné, M.F. Development of a flow injections system two analytical paths for ammonium determination in soil extracts by conductometry. *J. Braz. Chem. Soc.* **1997**, *8*, 524–528. [CrossRef]
35. Gonzaga, M.M.; Trivelin, P.C.O. Open Collector Efficiency to Capture NH3 Volatilized from the Soil. SIICUSP. 2018. Available online: https://uspdigital.usp.br/siicusp/siicPublicacao.jsp?codmnu=7210 (accessed on 24 November 2020).
36. Ritchie, S.W.; Hanway, J.J.; Benson, G.O. *How a Corn Plant Develops*; Special Report 48; Iowa State University Cooperative Extension Service: Ames, IA, USA, 1997.

37. Laviola, B.G.; Martinez, H.E.P.; Souza, R.B.; Salomão, L.C.C.; Cruz, C.D. Macronutrient accumulation in coffee fruits at Brazilian Zona da Mata conditions. *J. Plant Nutr.* **2009**, *32*, 980–995. [CrossRef]
38. Trivelin, P.C.O.; Lara Cabezas, W.A.R.; Victoria, R.L.; Reichardt, K. Evaluation of a ^{15}N plot design for estimating plant recovery of fertilizer nitrogen applied to sugar cane. *Sci. Agric.* **1994**, *51*, 226–234. [CrossRef]
39. Hauck, R.D.; Bremmer, J.M. Use of tracers for soil and fertilizer nitrogen research. *Adv. Agron.* **1976**, *28*, 219–260.
40. R development Core Team. R: A Language and Environment for Statistical Computing, R. Foundation for Statistical Computing 2015. Available online: http://www.R-project.org/ (accessed on 24 November 2020).
41. Karlen, D.L.; Flannery, R.L.; Sadler, E.J. 1988. Aerial accumulation and partitioning of nutrients by corn. *Agron. J.* **1988**, *80*, 232–242. [CrossRef]
42. Ghagas, W.F.T.; Guelfi, D.R.; Caputo, A.L.C.; Souza, T.L.; Andrade, A.B.; Faquim, V. Ammonia volatilization from blends with stabilized and controlled-release urea in the coffee system. *Ciênc. Agrotecnol.* **2016**, *40*, 497–509.
43. Miyazawa, M.; Gil, L.G.; Costa, A.; Anjos Reis Júnior, R.; Tiski, I. Volatilization of ammonia in tropical soil with different moisture after application of polymer-coated urea. *Aust. J. Crop Sci.* **2020**, *14*, 712–720. [CrossRef]
44. Loss, A.; Pereira, M.G.; Costa, E.M.; Beutler, S.J. Carbon, nitrogen and the natural abundance of ^{13}C and ^{15}N in macro and microaggregates. *Idesia* **2014**, *32*, 15–21.
45. Magalhães, P.C.; Durães, F.O.M. *Physiology of Maize Production*; Embrapa: Sete Lagoas, Brazil, 2006; Volume 76, pp. 1–10. Available online: https://www.embrapa.br/busca-de-publicacoes/-/publicacao/490408/fisiologia-da-producao-de-milho (accessed on 24 November 2020).
46. Feldman, L. The maize root. In *The Maize Handbook*; Freeling, M., Walbot, V., Eds.; Springer Lab Manuals: New York, NY, USA, 1994; pp. 29–37.
47. Vicensi, M.; Lopes, C.; Koszalka, V.; Umburanas, R.C.; Kawakami, J.; Pott, C.A.; Müller, M.M.L. Gypsum Rates and Splitting Under No-Till: Soil Fertility, Corn Performance, Accumulated Yield and Profits. *J. Soil Sci. Plant Nutr.* **2020**, *20*, 690–702. [CrossRef]
48. Schoninger, E.L.; Villalba, H.A.G.; Bendassolli, A.; Trivelin, P.C.O. Corn grain yield and ^{15}N-fertilizer recovery as a function of urea sidedress timing. *Ann. Braz. Acad. Sci.* **2018**, *90*, 3299–3312. [CrossRef] [PubMed]
49. Boschiero, B.N.; Mariano, E.; Torres-Dorante, L.O.; Sattolo, T.M.S.; Otto, R.; Garcia, P.L.; Dias, C.T.S.D.; Trivelin, P.C.O. Nitrogen fertilizer effects on sugarcane growth, nutritional status, and productivity in tropical acid soils. *Nutr. Cycl. Agroecosyst.* **2020**, *117*, 367–382. [CrossRef]
50. Sangoi, L. Understanding plant density effects on maize growth and development: An important issue to maximize grain yield. *Ciência Rural* **2001**, *31*, 159–168. [CrossRef]
51. Roberts, T.L.; Slaton, N.A.; Kelley, J.P.; Greub, C.E.; Fulford, A.M. Fertilizer nitrogen recovery efficiency of furrow-irrigated corn. *Agron. J.* **2016**, *108*, 2123–2128. [CrossRef]
52. Walsh, O.; Raun, W.; Klatt, A.; Solie, J. Effect of delayed nitrogen fertilization on maize (*Zea mays* L.) grain yields and nitrogen use efficiency. *J. Plant Nutr.* **2012**, *35*, 538–555. [CrossRef]
53. Chen, L.; Liu, L.; Qin, S.; Yang, G.; Frang, K.; Zhu, B.; Kuzyakov, Y.; Chen, P.; Xu, Y.; Yang, Y. Regulation of priming effect by soil organic matter stability over a broad geography scale. *Nat. Commun.* **2019**, *10*, 5112. [CrossRef]
54. Moschini, B.P. Management of Nitrogen Fertilization with Mixtures of NBPT-Treated Urea and Polymer Sulfur Coated Urea in Corn Production Systems. Ph.D. Dissertation, University of São Paulo, Piracicaba, Brazil, 2019. Available online: https://www.teses.usp.br/teses/disponiveis/11/11140/tde-07052019-180546/pt-br.php (accessed on 24 November 2020).
55. Ladha, J.K.; Pathak, H.; Krupinic, T.J.; Six, J.; van Kessel, C. Efficiency of fertilizer nitrogen in cereal production: Retrospects and prospects. *Adv. Agron.* **2005**, *87*, 85–156.
56. Gava, G.J.C.; Oliveira, M.W.; Silva, M.A.; Jerônimo, E.M.; Cruz, J.C.S.; Trivelin, P.C.O. Phytomass production and nitrogen accumulation in maize cultivated with different doses of ^{15}N-urea. *Semina* **2010**, *31*, 851–862.
57. Lara Cabezas, W.A.R.; Couto, P.A. Nitrogen immobilization of urea and ammonium sulphate applied to maize before planting and as top-dressing in a no-till system. *Rev. Bras. Cienc. Solo* **2005**, *29*, 215–226.
58. Wang, S.; Luo, S.; Yue, S.; Shen, Y.; Li, S. Fate of ^{15}N fertilizer under different nitrogen split applications to plastic mulched maize in semiarid farmland. *Nutr. Cycl. Agroecosyst.* **2016**, *105*, 129–140. [CrossRef]

59. Hauck, R.D. Nitrogen tracers in nitrogen cycle studies-past use and future needs. *J. Environ. Qual.* **1973**, *2*, 317–327. [CrossRef]
60. Torbert, H.A.; Mulvaney, R.M.; Heuvel, V.; Hoeft, R.G. Soil type and moisture regime effects on fertilizer efficiency calculation methods in a N-15 tracer study. *Agron. J.* **1992**, *84*, 66–70. [CrossRef]
61. Lange, A.; Lara Cabezas, W.A.R.; Trivelin, P.C.O. Timing and sources of sidedress nitrogen on no-tillage corn two years after soy crop. *Rev. Ceres* **2010**, *57*, 817–824. [CrossRef]
62. Gava, G.J.C.; Trivelin, P.C.O.; Oliveira, M.W.; Heinrichs, R.; Silva, M.A. Balance of nitrogen from urea (^{15}N) in the soil-plant system at the establishment of no-till in maize. *Bragantia* **2006**, *65*, 477–486. [CrossRef]

Publisher's Note: MDPI stays neutral with regard to jurisdictional claims in published maps and institutional affiliations.