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Article

Blending Controlled-Release and Urease-Inhibitor Technologies as Innovative Solutions to Reduce Ammonia Emissions in Coffee Environments

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Abstract: Enhanced efficiency fertilizers, such as urea treated with a urease inhibitor, controlled-release fertilizers (CRFs), and fertilizer blends, compose important strategies for improving efficiency in nitrogen (N) use by plants and mitigating ammonia (N-NH_3) emissions. The physical mixture of fertilizers in blends can favor synchronization of N-release from the fertilizers and N-uptake by coffee plants and also dilute the costs of acquiring a pure CRF, making fertilizer blends more accessible to growers. To investigate this, a field experiment was conducted over two consecutive crop years with *Coffea arabica* with the aim of evaluating nitrogen fertilizer technologies at application rates ranging from 0 to 450 kg N ha^{-1}. The fertilizers were characterized, and analyses were performed to quantify N-release from the fertilizers, ammonia volatilization, and nutritional and yield aspects of the coffee plant. The fertilizers used were urea (UCon), urea treated with N-(n-butyl) thiophosphoric-triamide (UNBPT), urea-coated with polymer of the E-Max technology (with 41%N (EMax41) or 43%N (EMax43)), and blends of UNBPT with E-Max (Blend41–Blend43). The cumulative N-release for EMax41 always remained below that for EMax43, just as occurred for Blend41 in relation to Blend43. Over the two crop years, the greatest volatilization of N-NH_3 occurred with UCon (~25%) and the least with EMax41 (9%). The results indicate that the technologies mitigated the N-NH_3 emissions in relation to UCon [EMax41 (63% mitigation) > Blend41 (43%) > EMax43 (32%) > UNBPT (28%) > Blend43 (19%)]. Crop management affects coffee yield. The yield increase went from 20% in the first crop year to 75% in the second, with better results from fertilizers containing CRF. We present information that can assist fertilizer producers and coffee growers, and, above all, we seek to contribute to environmental action for the reduction of agricultural NH_3, clarifying potential strategies for mitigation of these emissions and strategies that generate advances in research on technologies for coffee growing.

Keywords: agricultural ammonia mitigation strategies; N-fertilizer release test; N-(n-butyl) thiophosphoric triamide (NBPT); coated urea

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1. Introduction

It is now imperative to adopt technologies and innovations in fertilizers with the aim of reducing emissions of reactive forms of agricultural nitrogen (N) to the atmosphere, increasing efficiency in the use of N, and linking these technologies and innovations to agronomic, economic, social, and environmental gains. However, this is a difficult challenge, above all because of the complex dynamics of this nutrient in the direction of better use by crops. Studies on 15 N indicate the N-fertilizer recovery rate in the coffee crop is 39% [1,2]. Part of the N not taken up by the crop tends to be immobilized and composes the organic fraction of the soil, or it becomes susceptible to losses through volatilization, leaching, and denitrification.

Worldwide consumption of nitrogen N fertilizers exceeded 110 Mt of N in 2021, and 50% of this amount was applied through urea [3,4]. A great concern in regard to the use of this fertilizer is its susceptibility to volatilization (the main cause of N losses in agriculture).

Results indicate losses of ammonia (N-NH_3) from 20% to 40% of the N applied in crop production systems fertilized with urea [5,6]. Specifically in the coffee crop, numbers are around 30%; that is, on average, for every three fertilizer applications with urea, one is lost by volatilization [7–9].

According to estimates, Brazil's coffee-growing sector required 363,111 tons of N fertilizer for the 2021–2022 crop year. This amount would supply the total planted area of 1452.44 thousand hectares with an average application rate of 250 kg N ha^{-1} $year^{-1}$. Considering that urea contains 44–46% N and that it is the source used in around 50% of the coffee fields of Brazil, we would therefore have a theoretical potential emission of 4736 tons of N-NH_3 [7,10–12]. In the agronomic context, this N loss would not always result in immediate harm because the plant could be supplied by the consumption of organic N stocks in the soil. That would, however, diminish soil fertility and, in the medium to long term, reduce yield.

Environmental actions established by the European Union (EU) (Directive 2016/2284) [13] and applied to the countries of the group advocate that, on average, 19% of the ammonia emissions recorded in 2005 will be reduced by 2030. The directive, furthermore, defines that the use of urea in agricultural crops can only be conceded in the case of the use of methods that minimize these emissions by at least 30% in reference to their application on the soil surface [14,15]. In Germany, these actions were put in place as of 2020, with the use of urea only being allowed in association with urease inhibitors or through its incorporation in the soil at most four hours after its application [14].

Initiatives such as those in the EU are a tendency worldwide. A specific challenge is developing fertilizer technologies with reduced emissions of N-NH_3 that combine efficiency in supplying N to crops with a price accessible to farmers.

Among the strategies proposed worldwide for minimizing agri-N losses is the principle of fertilizer management by the 4R method (right source, right rate, right time, and right place). This method has been considered a key factor for the sustainable use of N sources and clean agricultural production [16]. Its practical application is correlated with the use of enhanced efficiency fertilizers, such as slow- or controlled-release fertilizers, stabilized fertilizers, and blends (physical mixtures) of different technologies [17].

Stabilized fertilizers have additives that are able to inhibit the transformation of N into some undesirable form. Fertilizers with urease- and nitrification-inhibiting additives are prominent in this group. The main urease inhibitors used globally are N-(n-butyl) thiophosphoric triamide (or NBPT), N-(n-propyl) thiophosphoric triamide (NPPT) in formulation with NBPT (75% NBPT: 25% NPPT ratio), N-(2-nitrophenyl) phosphoric triamide (2-NPT), and Duromide [18–20]. There are reports of mitigation of 43–80% of N-NH_3 losses in crops with the use of NBPT associated with urea [5,14,21,22]. However, this efficiency depends on edaphic and climatic conditions and on the effective concentration of the NBPT in the fertilizer [19,23,24].

Controlled-release fertilizers (CRFs) have granules with a coating that acts as a physical barrier, releasing the nutrient through a diffusion process [25–27]. This release is affected by the type, thickness, permeability, and integrity of the coating, as well as the response of the coating material to external conditions such as temperature and soil moisture [10,25,26,28–32]. The longevity of a CRF is indicated by the time necessary to reach a cumulative release of 75% of the nutrient at rest in water at 25 °C (or at the temperature specified by the manufacturer) [33]. This is the primary information used in formulating recommendations for the CRF application.

The advantages of controlling nutrient release are related to synchronization with the nutritional demand of the crops (which leads to enhanced efficiency in plant nutrient uptake) and minimization of losses to the environment [21,34,35]. Specifically, in relation to N in CRFs, benefits have been described in various environments and crops [26,29,30,34,35], with advantages over urea. For coffee, however, little is known regarding the application of this technology. In that perennial crop, in which parceled applications of N are necessary to meet plant needs and reduce losses, CRFs could facilitate operational logistics and even indirectly reduce machine traffic and the burning of fossil fuels, providing for cleaner coffee growing.

However, there is an increase in the cost per unit of N of the CRF in relation to the cost of conventional fertilizer. An alternative to dilute this value is the use of blends (physical mixtures) of fertilizer technologies [17,25]—a category of enhanced efficiency fertilizers that aims at aggregating the benefits of two or more types of technologies.

There are positives about the use of urea and CRF blends in grain production systems [36,37]. But this has not yet been well clarified in the coffee crop. Guidelines in this respect would allow a single application, avoiding the costs of parceled applications. The benefits could even be increased if blends composed of stabilized fertilizers with urease inhibitors and CRFs of different longevities are used. A soluble fraction containing NBPT, for example, would supply the most immediate needs of the coffee plant for N, while the portion with CRF would be released gradually over the cycle. That is, the components would act to combine their optimal characteristics to minimize N losses, adjusting the release of the nutrient according to the needs of the coffee plant. All this would be at a more accessible cost by reducing the cost of CRF in the final composition of the blend by reducing its proportion in the fertilizer.

This would be an advancement in the direction of more sustainable coffee growing, and with this justification, we have performed this scientific study with the following objectives: (i) monitor the release of N from CRFs of different longevities and from blends of these CRFs with urea stabilized with NBPT (UNBPT) and correlate field results with laboratory results; (ii) quantify the mitigation of losses of N-NH_3 from the blends in relation to urea; and (iii) determine the most efficient N fertilizer technologies and the most suitable N application rates (0, 150, 300, and 450 kg ha^{-1} crop year^{-1}, with the UNBPT and urea applied in three parceled applications and the others in a single application) for improvements in coffee yield.

2. Materials and Methods

Experiments were conducted with the following N fertilizers: common urea (conventional fertilizer, hereafter designated UCon); urea + N-(n-butyl) thiophosphoric triamide—NBPT (stabilized fertilizer, UNBPT); E-Max urea (EMax41 and EMax43; both are controlled-release fertilizers—CRFs); and the mixture of technologies (constituting the fertilizers here designated as Blend41 and Blend43).

The fertilizers UCon and UNBPT contained 45% N and 44% N, respectively, and the latter was treated with 530 mg NBPT kg^{-1}, as declared by the manufacturer. The CRFs EMax41 and EMax43 (with 41% and 43% N, respectively) were constituted of urea granules coated with polyurethane and were manufactured with an innovative technology for polymer coating (E-Max). The longevity, indicating the period necessary for the release of 75% of N content in the fertilizers of the Emax43 and Emax41 technologies, is respectively 3–4 months and 5–6 months [38]. The fertilizers Blend41 (with 40% UNBPT and 60% EMax41) and Blend43 (with 40% UNBPT and 60% EMax43) resulted from the physical mixtures of the technologies of stabilized action and controlled release, here called blends.

2.1. Characterization of the Controlled-Release Fertilizers—CRFs

The CRFs were examined by scanning electron microscopy and energy dispersive X-ray spectroscopy for the characterization and measurement of the thickness and uniformity of the coating. To do so, the samples were cut with a scalpel, placed on aluminum stubs, and then coated using a carbon evaporator. The samples of EMax41 and EMax43 were observed using a scanning electron microscope with a secondary electron detector, a 20 kV voltage, and a working distance of 7.5 to 9.5 mm.

2.2. Experimental Conditions

The experiments were performed from October 2017 to July 2019. The laboratory facilities were at the Department of Soil Science of the Universidade Federal de Lavras. In the field, the experiment was carried out over two consecutive crop years (2017–2018 and 2018–2019) in a *Coffea arabica* L. crop field in the municipality of Carmo da Cachoeira, Minas Gerais, Brazil (21°27′34″ S; 45°16′11″ W; altitude of 1050 m). The climate in the region is Cwa—mesothermal, with mild summers and a dry winter. The crop was established in December 2013 in a fertile Latossolo Vermelho Amarelo distrófico [39], as determined by the results of soil analyses (Table S1), equivalent to Haplustox [40].

2.3. Details of Field Experiments

The experimental design in the field was randomized blocks with three replications and a 6×4 factorial arrangement that involved the 6 fertilizer treatments described above under four rates of fertilizer application (0, 150, 300, and 450 kg N ha^{-1} year^{-1}). The blocks were laid out in rows (rows of coffee) (Figure 1). Parallel rows were considered border rows. The experimental plot (32.73 m^2) contained ten coffee plants at a spacing of 3.85 × 0.85 m, and the area used for data collection was the eight central plants.

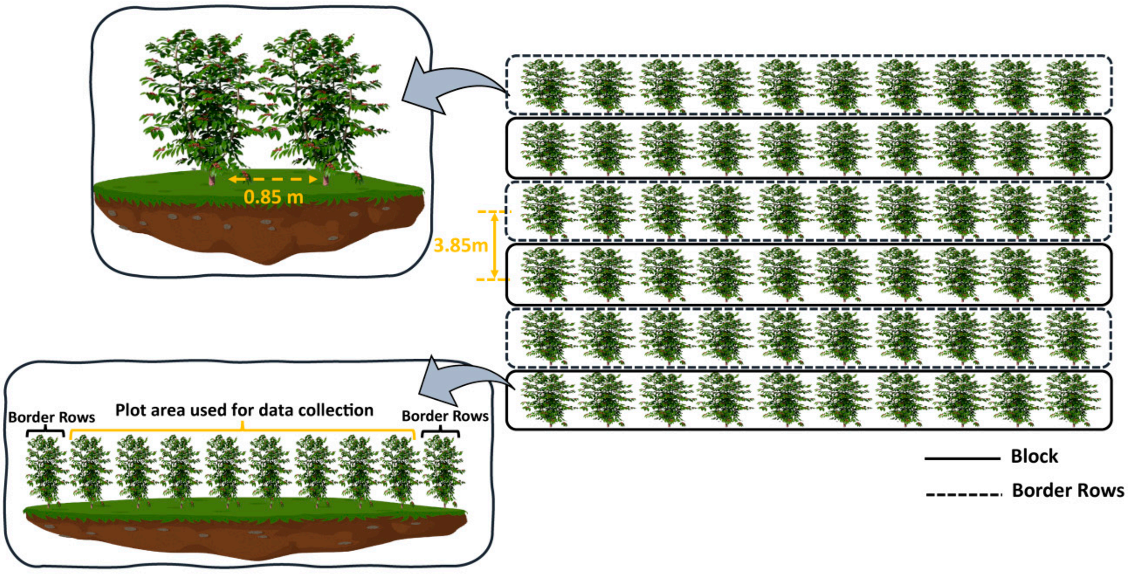

Figure 1. Sketch of the experimental plot in the field.

In each crop year, the fertilization with UCon and UNBPT was parceled out into 3 applications at intervals of approximately 30 days. The other fertilizers were applied a single time at the same time as the first fertilizer application of UCon and UNBPT. The first application (of UCon and UNBPT) and the single application (of EMax41, EMax43, Blend41, and Blend43) were always in November of each crop year.

The crop treatments (such as liming and fertilization with K, P, and micronutrients) were the same for all the treatments, meeting the needs of the experimental area according to the recommendations of [41]. The P, K, and N (focus of this study) fertilizers were applied on the surface (without incorporation in the soil) under the canopy of the coffee plants. Complementary fertilization with micronutrients (Zn, Mn, and B) was carried out through foliar application of zinc sulfate, manganese sulfate, and boric acid at a rate of 6 kg ha^{-1} year^{-1}, divided into three applications. In the field, the following factors were monitored: rainfall, mean daily soil temperatures (with a LogTag® Analyzer UTRIX-16 data logger), as well as soil moisture (by soil volumetric water content) [42] throughout the period of the trials in the two agricultural crop years.

2.4. Testing of N Release from the Fertilizers under Field Conditions and Laboratory Conditions

The release of N from the fertilizers EMax41, EMax43, Blend41, and Blend43 was monitored both in the field and in the laboratory. In the field, the study was conducted in plots with an application rate of 300 kg N ha^{-1} in both crop years, 2017–2018 and 2018–2019. The aim was to assess the impact of edaphic and climatic conditions in the cultivation field on N release. In the laboratory, the study aimed to examine N release in distilled water at 25 °C.

For field experiments, approximately 40 g of fertilizer were placed in nylon bags with a mesh size of 1.8 mm. For each agricultural year, ten bags of each treatment were placed in each plot, simulating row-crop fertilization by distributing them on the surface under the canopy of coffee plants and within leaf debris. To quantify the remaining N, the bags were collected at 7, 14, 28, 42, 56, 77, 98, 126, 154, and 196 days after fertilization (DAF). The bags were opened, and samples were ground. The residual N was quantified using the Kjeldahl method [43].

To test N release in the laboratory, the IOS 21263:2017 methodology was followed [33]. Samples containing 10 g of fertilizer were placed in “microtulle” fabric and tied in five replications. These samples were then incubated in 500 mL of distilled water at 25 °C in a controlled chamber. Solution aliquots were collected after 1, 7, 14, 28, 42, 56, 77, 98, 126, 154, and 196 days of incubation (DAI) to determine the released N quantity over time. During each collection, the water was replaced with freshly acclimatized water. The released N content was determined using the Kjeldahl method [43].

The results from each collection (both field and laboratory) were subtracted from the total N content of the fertilizer, and release curves were plotted over the 196 days. A comparison was made between the results of N release tests in the field (for both crop years) and in the laboratory to allow the prediction of field results based on laboratory information. Further details are presented in the corresponding section.

2.5. Ammonia (N-NH_3) Volatilization

Losses of N-NH_3 were monitored using the semi-open PVC collector method [44]. Bases with collectors were installed in all plots, including both control plots (without fertilization) and those where fertilizers were applied at a rate of 300 kg N ha^{-1}. In the fertilized plots, proportional amounts were applied to each base. Two laminated foam sponge disks were placed in each collector, with the lower disk immersed in a solution of phosphoric acid (concentration 85%—60 mL L^{-1}) and glycerin (50 mL L^{-1}), capable of capturing volatilized N-NH_3. The sponges were exchanged at each collection (Table S2), at which time the chambers were then rotated among the corresponding bases. The objective of the rotation was to reduce the spatial variability of the ammonia emission and allow a greater effect from the climatic variations, as suggested by Souza et al. [22].

In both crop years (2017–2018 and 2018–2019), the N-NH_3 losses were quantified daily in the first six days after the N fertilization applications (after each parceled application of the UCon and UNBPT ureas and after the single application of the other N fertilizers), and after that point, losses were quantified on pre-defined dates (Table S2). The sponges from the control plots (with zero fertilizer application) were collected at the same times.

In the laboratory, the solution from the sponges was extracted through filtering and extraction with distilled water. Aliquots of 20 mL were removed from the extract obtained for the determination of the N content (by the Kjeldahl method) [43]. The values obtained through the control treatment were discounted from the results of each collection. The resulting cumulative loss was obtained by the sum of the daily losses up to the last.

2.6. Coffee Bean Yield

The coffee bean yield was determined in the two consecutive crop years of the treatments that composed the 6 × 4 factorial arrangement described in Section 2.3. Coffee fruit was harvested by manual stripping, which began when the percentage of unripe fruit was less than 20%. The yield in the part of the plot used for data collection (eight plants) was quantified based on liters of uncleaned coffee fruit from the field (a mix of cherry, unripe, and dry fruit). After this was harvested, a representative 4-L sample was removed from the total production of each plot. This sample was dried on a coffee drying yard until reaching a moisture content near 110 g water kg^{-1}, at which time the yield of the plot was determined. The data obtained were used in the calculation of the final yield, with the results of the part of the plot used for data collection extrapolated to the density of 3056 coffee plants per hectare.

2.7. Statistical Analyses

Analysis of variance was carried out on the data of cumulative volatilization (in % and in kg $N\text{-}NH_3$ ha^{-1}), of coffee bean yield, and of soil nitrogen using the Sisvar version 5.7 software [45] after the data had passed through the normality test (Shapiro–Wilk test) and homoscedasticity of variance test (Bartlett test) using the R software [46]. In cases of significant effects of fertilizers and soil stratification depths by the F test ($p < 0.05$ and 0.08), the mean values were clustered by the Scott–Knott test at the same level of significance. Regression analysis was used in significant cases between application rates. The criteria of significance of the model (F test), of its coefficients (t test), and the value of the coefficient of determination were used together for the selection of the equations.

The N release pattern and ammonia volatilization pattern were evaluated by non-linear regression analysis, adjusting the data to a logistic equation model (1):

$$Y_i = \left[\frac{\alpha}{1 + \exp^{k(\beta - daai)}}\right] + E_i, \tag{1}$$

where Y_i is the i-th observation (of cumulative N release (%) or of cumulative loss of $N\text{-}NH_3$ (%)), with $i = 1.2 \ldots n$; daai is the i-th day after the application; α is the asymptotic value, which can be interpreted as the maximum cumulative release of N (MCR) and/or cumulative loss of $N\text{-}NH_3$ (CL); β is the abscissa of the inflection point and indicates the day on which the maximum MCR or CL occurs; k is the earliness index, and the higher its value, the shorter the time necessary to reach the MCR or CL (α); and E_i is the random error associated with the i-th observation, under the supposition that it is independent and identically distributed according to a standard of mean value of zero and constant variance $E \sim N\left(0, 1\sigma^2\right)$. For the estimate of maximum daily release (MDR) of N or of maximum daily loss (MDL) of $N\text{-}NH_3$ (MDL) (the highest amounts that occurred in a single day), that is, for determination of the inflection point of the curve, the following equation was used (2):

$$MDL \ or \ MDR = k \times \left(\frac{\alpha}{4}\right) \tag{2}$$

The day of release of 75% of the N in the fertilizer was calculated using Equation (3):

$$\Gamma 75\% = b - \frac{\ln\left(\frac{a-75}{75}\right)}{k} \tag{3}$$

With the aim of comparing the methods of testing N release in the field (for the two crop years 2017–2018 and 2018–2019) and in the laboratory (monitoring in 2017–2018), simple linear regression was used, with the equation selected by the value of the coefficient of determination. The dataset obtained at collection times that were the same for the three trials (7, 14, 28, 42, 56, 77, 98, 126, 154, and 196 DAF and DAI) was adopted as a reference.

3. Results

3.1. CRF Coating Thickness and Uniformity

The fertilizers EMax*41* and EMax*43* exhibit uniform thicknesses of 56.93 µm (standard deviation: ±7.93) and 29.67 µm (standard deviation: ±2.85), respectively, as shown in Figure 2.

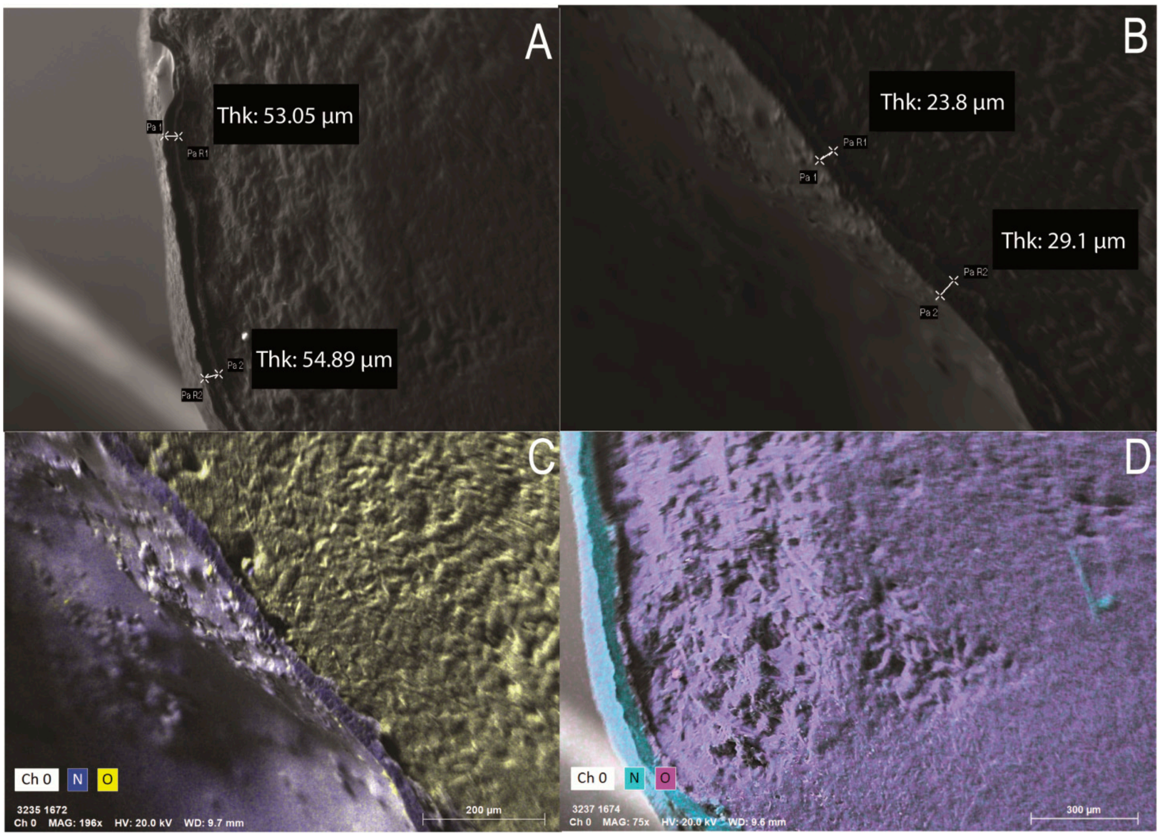

Figure 2. Scanning electron micrograph (SEM) of the fertilizers coated by the E-Max polymer, with 41% and 43% N, made to observe the thickness and uniformity of the coating. Stereomicroscope image capture. In figures (**A**,**C**)—external view in cross section of the coated urea granule with 41% N (fertilizer called EMax41 in our study); the coating is seen in the figure; (**B**,**D**)—external view in cross section of the coated urea granule with 43% N (called EMax43); the coating is seen in the figure.

3.2. Climate Monitoring in the Field Study

Cumulative rainfall was 1332 mm in the 2017–2018 crop year and 1124 mm in the 2018–2019 crop year after the N fertilization applications (Table S3) in a period of approximately 200 days of study regarding N release and volatilization of N-NH_3 from the fertilizers. The greatest effect of the rain occurred in the first six days after the fertilizer applications, with accumulations of 169 and 30 mm per crop (in 2017–2018 and 2018–2019) in the total of the three parceled applications (Table S3). This represents, in the order of the 2017–2018 and 2018–2019 crops, an average of 56 and 5 mm every six days after the fertilization with U*Con* and U*NBPT* (of concomitant applications). At that time, the mean temperature and moisture content of the soil were 20.7 °C and 21.3% (in 2017–2018) and 21.1 °C and 19.2% (in 2018–2019), respectively. These data therefore indicate more expressive water limitations in 2018–2019. A suitable range of rainfall for the coffee crop is from 1200 to 1800 mm a year [47].

3.3. N Release from the Fertilizers

The N release dynamics of the fertilizers followed a logistic model, except for EMax*43* in the 2017–2018 crop year, which had N release at around the 56th DAF greater than that of Blend*41*. The fertilizers maintained similarity between the patterns of N release in the field and in the laboratory (Figure 3; Table 1). The cumulative N released with EMax*41* always remained below EMax*43*, just as occurred with Blend*41* in relation to Blend*43*. In the same way, the N release from Blend*41* and Blend*43* was always greater than that of the individual application with 100% of the respective CRF (EMax*41* or EMax*43*) (Table S4).

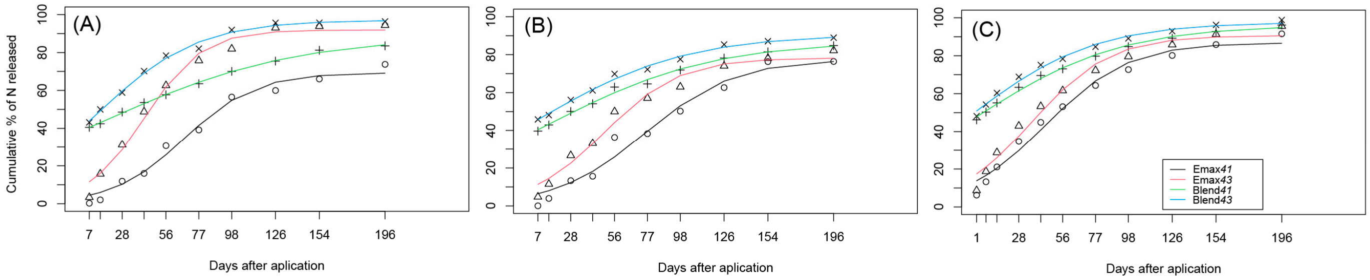

Figure 3. Percentage modeled of cumulative N release with nitrogen fertilizers on the soil surface under the coffee plant canopy in the field [crop years: 2017–2018 (**A**) and 2018–2019 (**B**)] and under immersion in distilled water at 25 °C in the laboratory (**C**). Fertilizers (40 g)—EMax*41*: urea E-Max 41%, EMax*43*: urea E-Max 43%, Blend*41*: mixture of urea with N-(n-butyl) thiophosphoric triamide (NBPT) and EMax41, and Blend*43*: mixture of urea with N-(n-butyl) thiophosphoric triamide (NBPT) and EMax43. Equations can be found in Table S4.

Table 1. Parameters of the regression adjusted to N release from the fertilizers (in the field: 2017–2018 and 2018–2019 crop years, and in the laboratory: in distilled water under controlled conditions), and parameters of the regression adjusted to the cumulative losses of N-NH_3 by volatilization (2017–2018 and 2018–2019 crop years).

PARAMETERS OF THE REGRESSION ADJUSTED TO N RELEASE						
	^{2} Parameter					^{3} MDR
^{1*} Fertilizer	α	Γ75%	β	k	R^2	
	(%)	(Day)		-	-	(% day^{-1} of N)
FIELD						
---------- *2017–2018 Crop year* ----------						
EMax*41*	69.33	PNA	67.83	0.04	0.98	0.76
EMax*43*	91.87	70.10	42.64	0.05	0.99	1.25
Blend*41*	88.54	121.66	17.52	0.02	0.99	0.36
Blend*43*	97.07	52.09	13.11	0.03	0.99	0.76
---------- *2018–2019 Crop year* ----------						
EMax*41*	77.51	173.13	75.86	0.03	0.97	0.68
EMax*43*	78.29	125.18	49.80	0.04	0.98	0.81
Blend*41*	87.12	109.91	14.62	0.02	0.99	0.42
Blend*43*	90.80	80.62	6.32	0.02	0.99	0.46
LABORATORY						
EMax*41*	86.87	94.13	45.21	0.04	0.98	0.82
EMax*43*	90.64	75.74	36.71	0.04	0.98	0.91
Blend*41*	96.19	59.76	1.60	0.02	1.00	0.53
Blend*43*	97.68	45.17	−2.27	0.03	0.99	0.62

Table 1. *Cont.*

PARAMETERS OF THE REGRESSION ADJUSTED TO THE CUMULATIVE LOSSES OF N-NH$_3$ BY VOLATILIZATION										
		Parameter								
		α		β	k	R^2	[3] MDL		[5] Reduction in losses of N-NH$_3$ in relation to UCon	Delay in MDL in relation to the mean *b of* UCon
[1] Fertilizer	[4] Parceled application	(kg N-NH$_3$ ha^{-1})	(% of N-NH$_3$)	(Day)	-	-	(kg N-NH$_3$ ha^{-1} day^{-1})	(% day^{-1} of N-NH$_3$)	%	(Day)
		---------- *2017–2018 Crop year* ----------								
U*Con*	1	29.56	29.56	3.84	0.63	0.98	4.67	4.67	-	-
	2	11.93	11.93	3.21	0.84	0.97	2.51	2.51	-	-
	3	14.64	14.64	1.02	0.74	0.89	2.69	2.69	-	-
	§ 3 AP	56.13	18.71	2.69	-	-	3.29	1.10	-	-
U*NBPT*	1	8.09	8.09	9.90	0.47	0.98	0.95	0.95	72.63	6.06
	2	9.21	9.21	5.24	0.54	0.96	1.25	1.25	22.80	2.03
	3	5.26	5.26	2.93	0.24	0.94	0.32	0.32	64.07	1.91
	§ 3 AP	22.56	7.52	6.02	-	-	0.84	0.28	59.81	3.43
EMax*41*	Single	18.89	6.29	54.14	0.05	0.99	0.23	0.08	66.35	51.45
EMax*43*	Single	50.97	16.20	30.20	0.07	0.99	0.87	0.29	9.19	27.51
Blend*41*	Single	34.75	11.58	23.55	0.07	0.96	0.63	0.21	38.09	20.86
Blend*43*	Single	57.52	19.18	25.05	0.09	0.99	1.26	0.42	−2.48	22.36
Fertilizer	Parceled application	---------- *2018–2019 Crop year* ----------								
U*Con*	1	33.66	33.66	2.52	0.90	0.99	7.54	7.54	-	-
	2	32.82	32.82	2.55	0.92	0.98	7.52	7.52	-	-
	3	24.44	24.44	1.72	0.64	0.99	3.93	3.93	-	-
	§ 3 AP	90.92	30.31	2.26	-	-	6.33	2.11	-	-
U*NBPT*	1	33.05	33.05	5.27	0.59	1.00	4.86	4.86	1.81	2.75
	2	25.06	25.06	4.73	0.60	1.00	3.74	3.74	23.64	2.18
	3	25.50	25.50	2.86	0.51	1.00	3.29	3.29	−4.34	1.14
	§ 3 AP	83.61	27.87	4.29	-	-	3.96	1.32	8.04	2.03
EMax*41*	Single	35.87	11.96	35.36	0.05	0.99	0.42	0.14	60.55	33.10
EMax*43*	Single	48.84	16.28	24.30	0.06	0.98	0.79	0.26	46.28	22.04
Blend*41*	Single	49.57	16.52	12.39	0.08	0.93	1.05	0.35	45.48	10.13
Blend*43*	Single	62.02	20.68	12.72	0.09	0.94	1.38	0.46	31.79	10.46

[1]* Fertilizer (40 g). [1] Fertilizer—UCon: conventional urea. UNBPT: urea with N-(n-butyl) thiophosphoric triamide (NBPT). EMax41: urea E-Max 41%. EMax43: urea E-Max 43%. Blend41: mixture of urea with N-(n-butyl) thiophosphoric triamide (NBPT) and EMax41. Blend43: mixture of urea with N-(n-butyl) thiophosphoric triamide (NBPT) and EMax43. [2] Parceled application—application of 300 kg N ha^{-1} in a single application or in three separate applications of 100 kg N ha^{-1}. § 3 AP—Result of three applications—calculation based on the total of the three parceled applications: 300 kg N ha^{-1}. [3] Parameters—α: asymptotic value that represents the maximum cumulative loss of N-NH$_3$. β: abscissa of the inflection point, indicates the day on which the maximum loss by volatilization occurs. K: earliness index, which indicates the time necessary to reach the maximum cumulative loss (α). [4] MDL: maximum daily loss (greatest loss of N-NH$_3$ that occurred in a single day), that is, the inflection point of the curve, calculated by the equation $MDL = k \times \left(\frac{\alpha}{4}\right)$. Values and percentages are calculated based on the same amount of each application described in '2'. [5] Comparison between results with the amount of 300 kg N ha^{-1}. Modeling equations are shown in Table S4. [2] Parameters—α: asymptotic value that represents the maximum N release. Γ75%: day on which cumulative release of 75% of the total amount of N occurs; PNA means that this percentage of release was not achieved. β: abscissa of the inflection point, indicating the day on which maximum N release occurs. K: earliness index, which indicates the time necessary to reach the maximum cumulative release (α). MDR: maximum daily release (greatest N release that occurred in a single day), that is, the point of inflection of the curve, calculated by the equation $MDR = k \times \left(\frac{\alpha}{4}\right)$.

In general, N was released nearly immediately at the beginning of the evaluations, with some fertilizers already beginning with the maximum daily release (Figure 3; parameter β of Table 1). The estimated N release from the treatments Emax*41*, Emax*43*, Blend*41*, and Blend*43* in seven days in the field was 5.5, 11.5, 40.4, and 44.8%, respectively (mean percentage from the two crop years, 2017–2018 and 2018–2019). The high rate of N release from the blends in the first week after fertilization was certainly determined by the soluble fraction (urea treated with NBPT) that composed 40% of these fertilizers.

The cumulative release in 196 days was in the following sequence of fertilizers: EMax*41* (total percentage of N released in this period: 77.9%) < EMax*43* (86.9%) < Blend*41* (90.6%) < Blend*43* (95.2%), with peaks occurring at 57, 46, 16, and 10 days, respectively, after nitrogen fertilization in the field (parameter β of Table 1). The blended fertilizers (Blend*41* and Blend*43*, with results in that order) exhibit N release 8.7% and 12.7% greater than that of the corresponding CRF in individual application (100% EMax*41* or EMax*43*). Peaks of N release (MDR) occurred earlier in the laboratory than in the field, estimated at 11 days earlier for fertilizers EMax*41* and EMax*43* and at least 8 days earlier for both blends (Blend*41* and Blend*43*). Regardless of the experimental condition (field or laboratory), maximum N release in the MDR ranged from 0.4 (for Blend*41*) to 1% (for the other sources) (maximum daily release—MDR; Table 1).

The time necessary for the release of 75% of the N in the field (for both crop years) and in the laboratory was estimated at 70, 125, and 76 days, respectively, with EMax*43*; at 122, 110, and 60 days with Blend*41*; and at 52, 81, and 45 days with Blend*43*. In the 2017–2018 crop year, EMax41 did not achieve maximum release within the 196-day interval; however, in the 2018–2019 crop year, 75% of the N was released in 173 days in the field and in 94 days in the laboratory test.

Based on fitting the mean data of the crop years to the logistic model, the respective rate of N release in the intervals of 30, 60, and 90 days after the beginning of the trials and at 196 days of the study (end of collection of the test of N release) was as follows: for EMax*41*—12%, 29%, 49%, and 73%; for EMax*43*—27%, 57%, 76%, and 85%; for Blend*41*—49%, 60%, 69%, and 84%; and for Blend*43*—59%, 74%, 83%, and 93%. These results will be related to those expected in three parceled applications with U*Con* and U*NBPT* in coffee, which will be discussed at the end of Section 4.1.

Linear Regression between Tests of N Release in the Laboratory and in the Field

The model adequately predicted the association between N release from nitrogen fertilizers in both the laboratory and the field ($p \leq 0.05$; $R^2 > 0.96$) (Figure 4). This allows estimation of the response of N release in the field based on laboratory results. The negative values of the α parameter indicate that the results observed in the laboratory are higher than those estimated in the field.

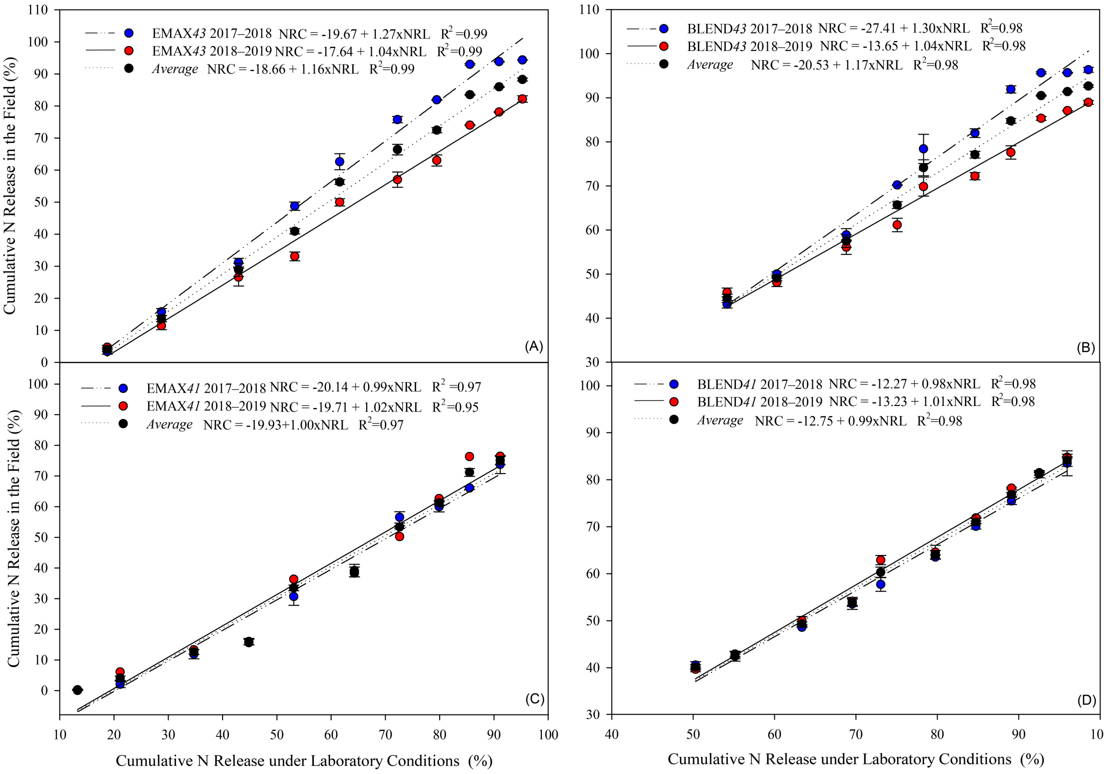

Figure 4. Linear regression of data on N release from fertilizers applied to coffee in the field in two crop years and in the mean of the crop years in relation to the results from the laboratory (in distilled water at 25 °C) (**A**–**D**). NRC: nitrogen release in the crop field; NRL: nitrogen release in the laboratory.

3.4. Ammonia (N-NH$_3$) Volatilization

The types of fertilizer affected losses of N-NH$_3$ ($p < 0.05$) (Figure 5 and Figure S1; Table 1), with their effects dependent on the soil and climate conditions (Table S3), which particularly impacted the U*Con* (in the two crop years), U*NBPT*, EMax*41*, and Blend*41* treatments (the last three in 2018–2019).

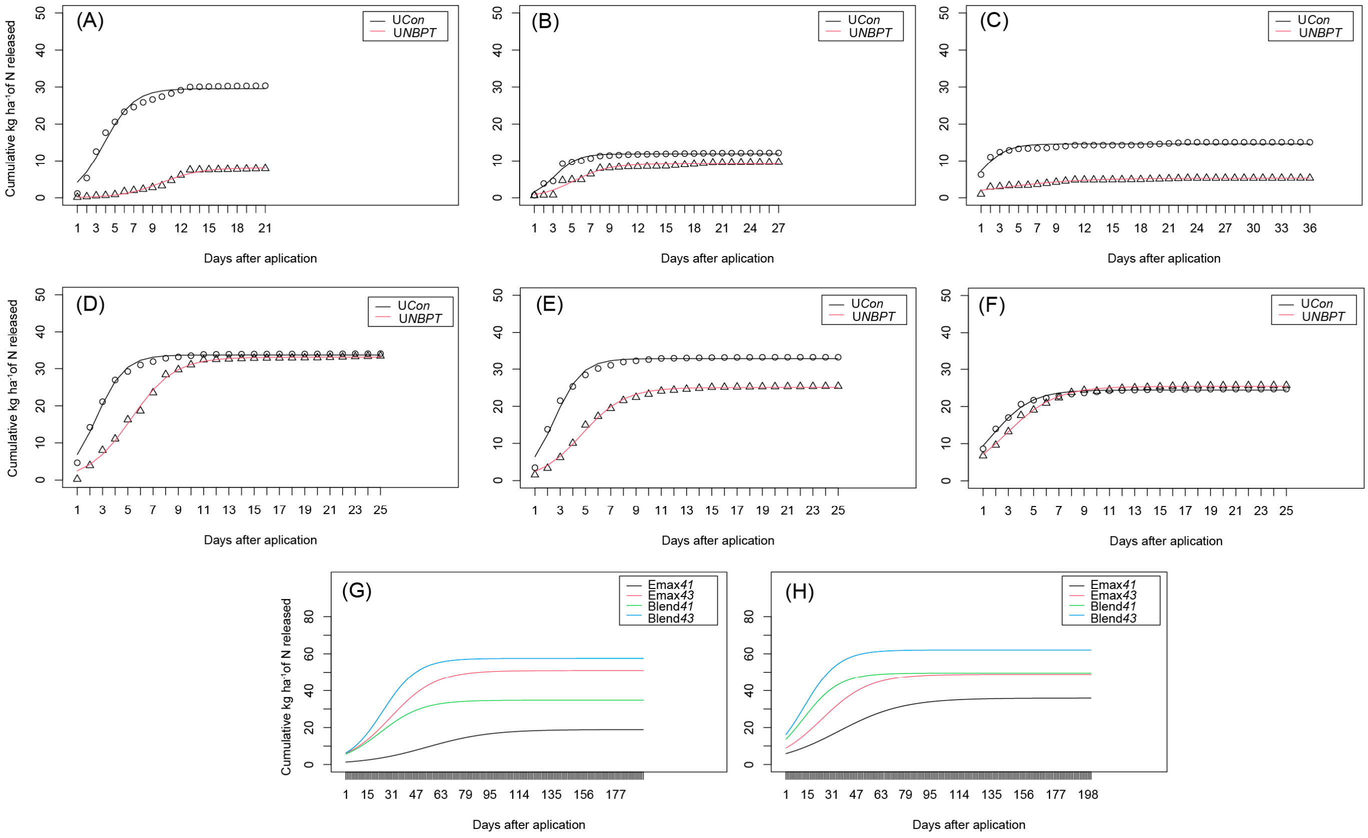

Figure 5. Cumulative volatilization through parceled application of U*Con* and U*NBPT* (**A**–**F**) and through single application for controlled-release fertilizers and blends (**G**,**H**) in two agricultural crop years with arabica coffee (2017–2018 crop year—diagrams (**A**–**C**,**G**); 2018–2019 crop year—diagrams (**D**–**F**,**H**). Equations can be found in Table S4.

The urea EMax*43* and the Blend*43* show stability in losses of N-NH$_3$ (represented by cumulative data), and the environmental conditions acted nearly exclusively to make their peaks of volatilization occur earlier (cf. parameters of the logistic model and estimated losses shown in Table 1). The mean cumulative loss in two crop years with EMax*43* and with Blend*43* was 49.9 and 42.2 kg N-NH$_3$ ha^{-1}, respectively. The maximum daily loss values for EMax*43* (0.3% of the amount applied) and for Blend*43* (0.5%) in 2018–2019 were 5.9 and 12.3 days earlier than the occurrences recorded on 30.2 and 25.1 DAF, respectively, in the previous crop year (Table 1).

There was a decline in cumulative losses of N-NH$_3$ modeled (Table 1), according to the following sequence: in the 2017–2018 crop year—U*Con* (18.7%) = Blend*43* (18.2%) = EMax*43* (16.2%) > Blend*41* (11.6%) > U*NBPT* (7.5%) = EMax*41* (6.3%); and in the 2018–2019 crop year—U*Con* (30.3%) > U*NBPT* (27.9%) > Blend*43* (20.7%) > Blend*41* (16.5%) = EMax*43* (16.3%) > EMax*41* (12.0%). That is, in the average of two crop years, the greatest loss occurred from U*Con* (24.5%) and the smallest loss from EMax*41* (9.1%); the latter mitigated N-NH$_3$ emissions by an average of 63.5% in relation to U*Con* (Table 1). However, other fertilizers also reduced these losses by more than 30%, and they delayed the peaks of volatilization in relation to U*Con* by at least 2.0 and 3.4 days (minimum in each crop year) and up to 33.1 days (in 2018–2019) and 51.4 days (in 2017–2018). This is the case of Blend*41* in the two crop years (reductions of 38.1% and 45.5% in these losses), of U*NBPT* (59.8%) in 2017–2018, and of EMax*43* (46.3%) and Blend*43* (31.8%) in 2018–2019.

In comparison with U*Con*, the following reductions per hectare occurred in the 2017–2018 crop year: 66.4% with EMax*41*; 59.8% with U*NBPT*; 38.1% with Blend*41*; and 9.2% with EMax*43*. In that crop year specifically, there was no significant difference between the cumulative losses modeled with the data from U*Con* and Blend*43*. In the subsequent crop year, the reduction per hectare was 60.6% with Emax*41*; 46.3% with Emax*43*; 45.5% with Blend*41*; 31.8% with Blend*43*; and 8% with U*NBPT* (Table 1).

The cumulative loss of N-NH_3 from the U*Con* in 2017–2018 and 2018–2019 was estimated at 18.7% and 30.3%. That is equivalent to the total eliminated in three parceled applications per crop year; each fertilizer application of 100 kg N ha^{-1} crop $year^{-1}$ eliminated, on average, 31.60, 22.40, and 19.50 kg N-NH_3 ha^{-1} (parameter α—which represents the maximum cumulative loss of N-NH_3; Table 1). There tended to be smaller losses in the third parceled application, a period that accounted for 50% of all the rainfall that occurred in the six days that followed the fertilizer applications in both crop years (Table S3). The maximum daily loss of N-NH_3—MDL from U*Con* occurred from 1 to 3.8 DAF in the 2017–2018 crop year (~2.7 DAF) and from 1.7 to 2.6 DAF in the 2018–2019 crop year (~2.3 DAF) (parameter β of parceled applications 1, 2, and 3 of the nitrogen fertilizer), when around 1.7% of the amount applied in the crop year was volatilized (Table 1).

The losses associated with the U*NBPT* in 2017–2018 and 2018–2019 represented 7.5% and 27.9% of the total amount of each crop year. In the first parceled fertilizer application of 2017–2018, the U*NBPT* delayed the MDL of the U*Con* (parameter β) by up to six days, reducing the MDL by 75% in relation to the U*Con* (Table 1). In 2018–2019, the mean delay in peak emissions from the parceled applications with the U*NBPT* was two days, and the reduction in the MDL in relation to that of U*Con* was 37%.

With EMax*41*, the losses represented 6.0% in 2017–2018 and 12.0% in 2018–2019 (Table 1). The MDL (0.08%) in 2017–2018 occurred at 54 DAF, which is a delay of 19 days in relation to the same occurrence in the 2018–2019 crop year when 0.14% was eliminated. That is equivalent to the total ammonia emissions eliminated in three parceled applications per crop year. The response of Blend*41* was similar to that of EMax*41*. In that case, there was volatilization of 37.80 and 49.60 kg N-NH_3 ha^{-1} in the crop years and a delay of 11 days in the MDL of 2018–2019 in relation to that of 2017–2018, and a 45% reduction in the amount volatilized in a single day (0.60 compared to 1.10 kg N-NH_3 ha^{-1} in 2018–2019).

A comparison between CRFs and their respective blends in 2017–2018 and in 2018–2019 shows the following results: between EMax*41* and Blend*41*, N-NH_3 volatilization was 84% and 38% greater for Blend*41* compared to EMax*41* in the respective crop years, as well as MDL that was 31 and 23 days earlier in the respective crop years, and 2.6 times greater for Blend*41* in the mean of the two crop years. Between EMax*43* and Blend*43*, volatilization was 13% and 27% greater for Blend*43*, and its MDL occurred 5 and 12 days earlier. Furthermore, Blend*43* resulted in N-NH_3 losses that were 1.4 and 1.8 times greater. A comparison between the blends shows losses that were 66% and 25% higher for Blend*43* compared to Blend*41*. The MDL of Blend*43* was 1.5 days earlier in 2017–2018 and 0.3 days earlier in 2018–2019, and the MDL was 2 and 1.3 times greater than that of Blend*41.*

3.5. Coffee Bean Yield

On average, coffee bean yield was 3354 kg ha^{-1} in 2017–2018 and 872 kg ha^{-1} in 2018–2019, and these results were affected by the interaction between nitrogen fertilizer technologies (NF) and nitrogen application rates (NAR). In the absence of NF (zero rate), the mean yield was 3020 kg ha^{-1} in 2017–2018 and 610 kg ha^{-1} in 2018–2019 (Figure 6; Table S5).

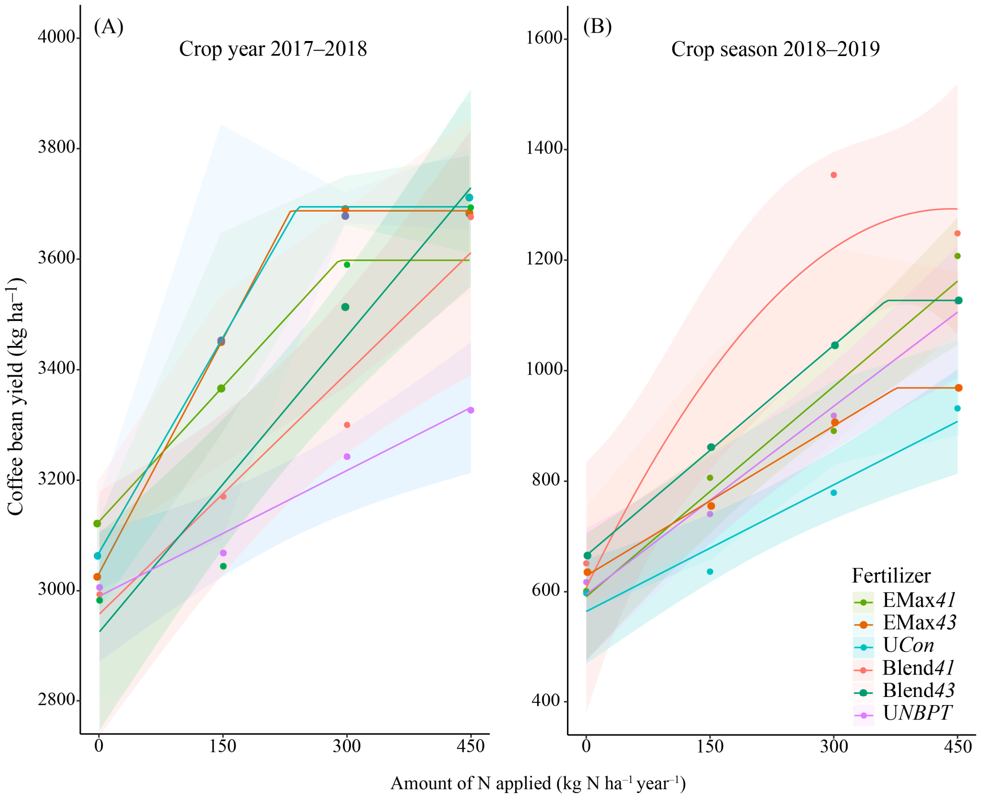

Figure 6. Coffee bean yield according to type of nitrogen fertilizer and N application rates for 2017–2018 (**A**) and 2018–2019 crop years (**B**).

In general, there was a linear increase in yield with an increasing supply of N from the fertilizers. In some cases (in 2017–2018—with U*Con*, EMax*41*, and EMax*43*; and in 2018–2019—with EMax*43* and Blend*43*, which will be detailed below), this linearity reached a plateau, with no increase in yield from an increase in the amount of N applied. The most expressive effect of supplying N in relation to the absence of fertilization was in the 2018–2019 crop year (mean increase of 75%), in which yields more than doubled (as in Blend*41*) from the application of the nutrient on the soil. In 2017–2018, the same comparison led to a mean increase of 20%.

In 2017–2018, every 150 kg N ha^{-1} added through U*Con*, U*NBPT*, EMax*41*, EMax*43*, Blend*41*, and Blend*43* led to increases in coffee bean yield of 390, 114, 244, 410, 218, and 268 kg ha^{-1}, respectively, raising the initial yields from the range of 2920 to 3122 kg ha^{-1} (results from zero application) to 3330 to 3695 kg ha^{-1} (Figure 6A; Table S5). The gains from U*Con*, EMax*41*, and EMax*43* were stabilized at the application rates of 243, 292, and 237 kg N ha^{-1}, respectively, at which point the maximum yields were achieved at 3695, 3597, and 3686 kg ha^{-1}.

In 2018–2019, likewise, with every N increase of 150 kg ha^{-1}, the coffee bean yields increased through the use of U*Con*, U*NBPT*, Emax*41*, Emax*43*, and Blend*43*, as follows: 115, 170, 190, 136, and 190 kg ha^{-1}, respectively (Figure 6B; Table S5). Applications of up to 450 kg N ha^{-1} through U*Con*, U*NBPT*, and EMax*41* brought about coffee bean yields of 908, 1106, and 1162 kg ha^{-1}, which represents increases of 61, 85, and 96% in relation to the zero-application rate (with values from 564 to 972 kg ha^{-1}). With EMax*43* and Blend*43*, coffee bean yields of 967 and 1125 kg ha^{-1} were obtained in a linear plateau response, without significant increase in yield from N application rates greater than 375 and 363 kg ha^{-1}, respectively. At these amounts, the initial coffee bean yield (without fertilization) of 628 and 665 kg ha^{-1} were raised by 54% and 69%.

The highest coffee bean yield in the latter crop year (1294 kg ha^{-1}) occurred with Blend*41* at the N rate of 443 kg ha^{-1}, tending toward a gradual decrease in these values with up to 450 kg ha^{-1} of N (Figure 6B; Table S5). The yield result from the fertilizer at this optimal application amount represents 2.14 times that obtained at the zero amount (637 kg ha^{-1} of coffee bean yield).

4. Discussion

4.1. N Release

Already at the beginning of the experiments (field and laboratory), the values of N release from the blends were higher than those from the pure CRFs. That is because the physical mixtures had 40% of their composition consisting of urea with N-(n-butyl) thiophosphoric triamide (NBPT), which is a fraction of high solubility in water [29]. That characteristic would be responsible for the immediate peak in N release for the blends in the laboratory, as this portion is already totally dissolved in the first hours. The parameter β of the model (from −2 to 2) confirms this information. In the field, dissolution of the soluble fraction is also accelerated. In the CRFs, this occurs in a more gradual manner because the fertilizer grains are surrounded by a polymer coating [25,34,48,49]. For that reason, there is control of nutrient release for a longer period [29,31], which is advantageous for the coffee plant as it requires N throughout its cycle [50]. In the case of the E-Max ureas (of 41% and 43% N), the interval of the day of maximum N release occurred up to the fortieth day in the laboratory.

Among the various factors that affect the N release rate from a CRF, the following are prominent: differences in the type of material, thickness, and permeability in the coating layer and ruptures in it, and the response of the coating material to the external environmental conditions [10,25,26,28,29,31,32].

The urea E-Max 43% has a uniform coating and thickness of approximately 30 µm, an amount of coating less than that of the urea E-Max 41% (56.93 µm); the latter, consequently, had greater longevity. E-Max 43% has 2% more N at the core of the granule, which, added to the lesser physical barrier of impediment to N release, allows greater concentrations of the nutrient to be released in a shorter period of time.

The longevity of a CRF is indicated by the time necessary to reach a cumulative N release of 75% at rest in water at 25 °C (or the temperature specified by the manufacturer) [33]. According to the manufacturer, the N release from E-Max 41% is estimated at 150–180 days in the soil, whereas from E-Max 43%, this occurs in a shorter time, from 90 to 120 days. Our results show the effect of environmental conditions on these fertilizers. Under higher moisture and temperature conditions, N release occurred earlier than that foreseen by the manufacturer, 17 days earlier for E-Max 43% (data from the 2017–2018 crop year and from the laboratory) and 56 days earlier for E-Max 41% (in the laboratory). That is, the N releases occurred at 70 and 76 days for EMax43 in the field in the 2017–2018 crop year and in the laboratory, and at 94 days for EMax41. The IOS 18644:2016 standard [51] foresees a variation of ±20% in the longevity stipulated by the manufacturer as acceptable.

The mean soil temperature while the experiments were carried out was 20.9 °C, while the distilled water in the laboratory was maintained at a constant temperature of 25 °C. This accelerated the release of N in the laboratory, possibly due to the effect on the permeability of the E-Max polymer. In the field, the volume of rainfall apparently intensified N release. This release was accelerated in the first crop year, with rainfall of around 1300 mm (200 mm more than that of the following crop year).

It should be clarified that the effect of rain on fertilizers in coffee fields in production is more limited since the amount of rain striking the ground is greater between the rows than under the coffee plant canopy (the region in which the fertilizers are applied). Regardless of the variations, there was equivalence in the patterns of cumulative N release under both experimental conditions (laboratory and field), with a peak lower than 1% and the release of 75% of N delayed most with E-Max 41% and the fertilizer blend derived from it (Blend41).

Tests of N release in the laboratory represent a useful tool for determining the N-release rate curve of CRFs [52]. Evaluation of fertilizer performance in the field is also important [28]. Our results indicated similarity in the cumulative release pattern of the four fertilizers that involved CRFs (pure or in mixtures), whether in the field or in the laboratory. Based on them, we present a reliable regression model that allows prediction of the results in the field based on laboratory information, which may be useful for application in new studies involving CRFs.

In our study, the application of conventional urea and urea treated with NBPT was parceled at three 30-day intervals. The lower values of N release from E-Max 41% (12% of N) in the first 30 days are related to its longevity (150–180 days). For that reason, the presence of urea treated with NBPT is so important to the initial availability of N in the blend that contained EMax41 (49%). An analogous response was that of Blend43 (59%) in relation to the response of the CRF EMax43 (27%); furthermore, this blend had the greatest release of N among the treatments.

There was a mean N release of 63% in 60 days and of 76% in 90 days with E-Max 43% and with the blends with EMax41 and EMax43 (Blend41 and Blend43). These values would be near those that are applied with conventional sources (urea and urea treated with NBPT). The N release from Blend43 was greater than that from the others; for E-Max 41%, the same interval was sufficient for the release of around half of that supply, 29% in 60 days, and of less than half at 90 days, 49%. At the end of 196 days (data from the last collection), EMax41 still had residual N of 26%; Blend41 had 15%; and EMax43 had 7%. These values indicate that Blend41 led to better availability of N supply compared to the controlled-release source, due to the higher rates of nutrient release coinciding with the crop cycle and in a manner nearer to the values applied for the parceled application sources. Blend41, moreover, had a response more similar to EMax43. This adjustment is interesting because of the tendency to lower the cost of the blend in relation to the cost of the CRFs in individual applications.

The N uptake rate in the arabica coffee plant follows a double sigmoid pattern, where the peaks occur in the stages of rapid expansion and maturation [50]. In comparison of the CRF values with those of the parceled applications with UCon and UNBPT, better synchronism of N availability is observed in the use of EMax43, Blend41, and Blend43 and, in a more significant way, in the use of the blends, because in the interval of the first parceled application, they exhibit higher values than those estimated for the CRFs. The dynamics of the fit of nutritional needs associated with blends are positive, with greater initial N release coinciding with the expressive demand of the coffee plant in this phase and gradual release after that, meeting the nutritional demand in other phases.

4.2. Ammonia (N-NH_3) Volatilization

The ammonia emissions were lower in the first crop year because there was considerable rainfall volume for the incorporation of the N released from the fertilizers. In 2018–2019, the rainfall after fertilization did not exceed an average of 5 mm in the cumulative amount of the first six days (the period in which volatilization is most critical [5]); in the previous crop year, this average volume was 56 mm. Furthermore, in 2018–2019, fertilization occurred predominantly on wet soil (19.2% in the first six initial days) and drying soil, which favored dissolution of the more soluble sources (urea and that treated with NBPT) and partial hydrolysis on the soil surface. That is, there was sufficient moisture to begin hydrolysis of the urea, but it was insufficient for its incorporation in the soil.

Under dry soil conditions, the rate of hydrolysis of urease—the hydrolytic enzyme that catalyzes the urea—is low; however, it gradually increases as the moisture content approaches 20% [5], and that maximizes N-NH_3 losses. For that reason, the mean peak of NH_3 loss from urea (around 2% of total fertilization and of 8%, 8%, and 4% from fertilization in parceled applications 1, 2, and 3) occurred a little more than two days after fertilization in 2018–2019 and reached, in the cumulative amount in the crop year, a loss of 30% in relation to the total N applied (~91 kg N-NH_3 ha^{-1}). These numbers were not greater still only because of the occurrence of rain in the first two days after the third parceled application of the fertilizer ($\sum$17 mm).

It is difficult to predict ideal climate conditions for the application of urea. However, the efficiency of this fertilizer will be enhanced if it is applied under suitable climate conditions [53]. This apparently minimized loss by 40% in 2017–2018 (~19% of the N applied) in relation to 2018–2019, but it does not lessen the considerable susceptibility of the source to losses in any application in the coffee crop. On average, in the two years, around 25% of all the N applied through urea was lost.

According to the literature, on average, for every three applications of urea, one is lost through volatilization (~30%) [9,10,22]. In coffee, there is no mechanical incorporation of any of the N sources in order to avoid damage to the root systems of the plants. In addition, coffee has a natural senescence of leaves, favoring the high deposition of plant residue under the plant canopy. This limits the penetration of rainwater and its contact with the fertilizer [3]. Also, in a certain way, the plant tends to restrict the deposition of rain under the canopy, limiting the incorporation of the urea by moisture. For that reason, finding sources that reduce N-NH_3 emissions and maintain adequate availability of N in the soil is a challenge for minimizing ammonia losses and improving efficiency in the use of urea in coffee growing.

Higher losses of N-NH_3 from urea are associated with the absence of additives or technologies for controlling solubility and the rate of hydrolysis. The use of urease inhibitors, such as NBPT, is an effective manner of reducing these losses [5,19,20,54]. These additives block the active sites of the urease, temporarily inactivating them, thus retarding the beginning and speed of hydrolysis of the urea. As losses of N-NH_3 normally occur in the days immediately after fertilization, the NBPT has a relatively short protection time. Consequently, the ideal situation is that some incorporation from rainwater or irrigation occurs while the inhibitory potential of the NBPT is still high.

We see reductions of 60% in the volatilization of N-NH_3 when there was a significant volume of rain in the first few days after fertilization with urea treated with NBPT (56 mm within the interval of the six first days after fertilization in 2017–2018). The NBPT molecule delayed the peak loss of N-NH_3 from the urea by up to six days in the first parceled application of the fertilizer, maintaining an average delay of 3.4 days over the entire 2017–2018 crop year. The effectiveness of the NBPT was confirmed not only by the delay in the MDL, but also by the reduction in the loss of N-NH_3 by 75% in the MDL compared to the MDL of the urea. This was a situation in which the use of the urease inhibitor was efficient. Nevertheless, even when it is degraded before the rain, a reduction in the loss of N-NH_3 is generally observed [5,19]. This is what occurred in 2018–2019, when there was a reduction of 8% in cumulative loss of N-NH_3 due to the NBPT, as well as an average delay of two days in the MDL in relation to urea.

The CRFs also mitigated losses in relation to urea. They ensured control of volatilization (from 9% to 66% more than UCon) and a longer period until the MDL (from 22 to 51 days). As they release N gradually, it is less susceptible to losses in the first few days after application [10]. That was especially the case with urea E-Max 41%, with only 9.1% cumulative loss over two crop years (mean value in relation to the N applied) and MDL occurring between 35 and 54 days after fertilization. This represents a reduction of 63.5% in relation to losses from urea and a delay of up to 52 days in MDL. For that reason, CRFs minimize environmental risks related to ammonia emissions from N fertilizers [31,34,35].

Urea E-Max 43% shows stability in the volatilization values in the two crop years (~16% of the N applied), but also greater loss of N-NH_3 (~7% more) and an earlier MDL (~25 days) in relation to the MDL of E-Max 41%. This last result is consistent with that described in N release, where higher N release values occurred in E-Max 43% of lesser longevity. This same E-Max 43% fertilizer shows efficiency in the mitigation of losses in relation to urea (reduction near 28% in the two crop years), providing N over a longer period than conventional fertilizer.

The high cost per unit of N has hindered adoption of formulations with 100% CRFs in agriculture [17,25,34], but the strategy of a physical mixture between urea with NBPT and E-Max 41% (constituting Blend41) appears to be feasible for use, diluting the cost of the

CRF through the blends. This combination reduced the cumulative volatilization of N-NH_3 by 42% compared to urea, losing less than 0.5% of the N applied in the MDL, which was recorded 16 days after that MDL of urea. Total cumulative volatilization with the blend represented 11% and 16% of the N from the single application, which is well below the mean loss from rea (~24.5%). In terms of reduction of losses by volatilization, Blend41 was exceeded only by the CRF E-Max41 (~9.1%).

According to estimates from [55], practices of mitigation such as moderate replacement of urea, the use of fertilizers of greater efficiency, incorporation of N fertilizers in the soil, and appropriate irrigation can reduce the emissions of N-NH_3 by 18–71% (4.5–17.6 Tg N year^{-1}). To achieve this 71% reduction, however, it will be necessary to conciliate all these practices, which we know is not so simple. The most feasible suggestion (and one that should be prioritized) is the replacement of urea with alternatives that optimize N-use efficiency. This is the consensus in the study of [55]. Based on our results, something possible can be adapted to coffee.

4.3. Coffee Bean Yield

In this study, N demand was in different degrees as a result of the climate conditions of the time periods, the yield potential of the coffee plants, and especially soil nutrient reserves. The greatest responses to the fertilizers and the N amounts applied occurred in terms of consolidation of the management strategy, that is, in the second crop year, when the history of previous fertility was neutralized. For that reason, the mean yield increase rose from 20% in the first crop year to 75% in the second. This increase is based on a comparison between the treatment with fertilizers and the treatment free of fertilization.

The higher yield in the first crop year is related to the biennial nature of coffee yields. This is a characteristic inherent to *Coffea arabica* L., which completes a phenological cycle in two years [56,57]. It exhibits a succession of vegetative and reproductive phases in this period, continually requiring N.

Data show that volatilization was relatively low in the first year and the soil had high initial N reserves (stocks of 14.30 Mg total N ha^{-1} in the 0–60 cm layer and of 380 kg mineral N ha^{-1} in the 0–60 cm layer; Table S1), and that may explain the yield from urea in 2017–2018 (even with volatilization of around 20% of the N applied). The good soil reserves would explain the fact that what are considered low application rates (236 kg N ha^{-1}) were sufficient to obtain high yields (in the following crop year, the demand was at least 363 kg N ha^{-1}). For that reason, there was an increase of 2.6 kg of coffee beans ha^{-1} for every kilogram of N-urea supplied on the hectare in 2017–2018, and the yield stabilized at the application rate of 243 kg N ha^{-1} crop year^{-1}. With the same amount of N, the urea application produced 522, 177, 386, and 337 kg ha^{-1} of coffee beans more than the urea treated with NBPT, E-Max 41%, and the blends with the ureas, E-Max 41% and 43%, respectively. However, in the following crop year, when volatilization reached 30% of the N applied, the increase from the application of kilograms of N-urea on the hectare did not come to 0.8 kg ha^{-1} of coffee beans (that is, 3.25 times less than in the previous crop year).

Generally, soils growing coffee are quite buffered in regard to N supply, and there are losses because of the significant stocks of N in the plants and in the soil. Because of that, results (positive or negative) in nutrition, yield, and coffee bean quality do not always appear in the short term [3]. That explains what occurred in the first crop year. However, care must be taken so that a reduction in the amount of fertilizer applied does not cause undesirable exploitation of the N stock and of soil organic matter, often built up over many years in areas growing coffee with standard application of the mineral fertilizer 20–05–2020. On the contrary, mechanisms able to maintain nutrient reserves should be used so that these reserves are not depleted in coffee fields and soil fertility is not impaired in the mid- to long-term [3,57,58].

Results show that consumption of N stocks occurred with perceptible reflections in the 2018–2019 crop year. The worse agronomic results in the non-fertilized treatment confirm this. The demand for fertilizers with higher N application rates increased in that crop year.

In that scenario, with a supply of N of up to 450 kg ha^{-1}, yields with the urea treated with NBPT rose by 85% and with E-Max 41% by 96%. Application of 375 kg N ha^{-1} with E-Max 43% was necessary to increase the initial yield by 54%, which subsequently stabilized at a plateau. It should be emphasized that with the same 375 kg N ha^{-1}, E-Max 41% produced 100 kg ha^{-1} of coffee beans more than E-Max 43%, and it even had the potential to produce 95 kg ha^{-1} of coffee beans more with an additional 75 kg N ha^{-1} (when it reaches the maximum application studied, 450 kg N ha^{-1}). That represents from 1.7 to 3.3 60-kg bags of coffee beans per hectare. This comparative increase between the E-Max fertilizers confirms the importance of extending the period of N supply over the coffee cycle. This extension is promoted by the increase in the longevity of a CRF.

The amount of N supplied and the synchronization of the supply with the phenological stages are important for meeting the nutritional needs of the coffee plant [1,50]. This is one of the purposes of the CRF technology, which aims at releasing nutrients in synchronization with the uptake curve of the crop over its cycle [28].

The adoption of blends of urea with NBPT and CRF has now brought about good yield responses. That is because the stabilized fertilizer supplied N to meet the immediate demand of the coffee plant, while the CRF released N gradually in the mid- to long-term, with both technologies favoring a reduction in NH_3 losses along with improvements in the nutrition and yield of the coffee plant. In the last crop year, the blend with E-Max 43% increased the initial yield of the treatment by 169 kg ha^{-1} of coffee beans (~70%). There were no advantages in increasing the application over the level of 363 kg N ha^{-1}, since the coffee bean yield remained stable at 1125 kg ha^{-1}. The blend with E-Max 41% at the same N amount (363 kg N ha^{-1}) yielded nearly 670, 430, and 150 kg ha^{-1} more than the absence of fertilization, fertilization with urea, and fertilization with the blend with E-Max 43%, respectively. In comparison with the fertilizer in the proportion of 100% urea with NBPT, the increase in coffee bean yield was 265 kg ha^{-1}; and in 100% CRF E-Max 41%, the increase was 221 kg ha^{-1}. That corresponds to 11.1, 7.2, 2.4, 4.4, and 3.7 more bags of commercial coffee beans per hectare, respectively. And this mean value can be further increased with up to 443 kg N ha^{-1} through the blend. This is an extra yield achieved by the adoption of a technology that even aggregates other economic and environmental benefits [37,59].

Among the benefits of using blends such as urea with CRF is a reduction in the number of application operations. Single application saves work and time compared to parceled application of urea, and that can reduce production costs and possibly problems from soil compaction [34,60].

Regarding possible reduction in N application from blends with E-Max 41% from 450 to 443 or even to 363 kg N ha^{-1} (reduction to 80% of the application rate, with results that even exceeded those of the other fertilizers in 2018–2019), would not compromise the coffee yield in the 2018–2019 crop year, although they could bear consequences for soil N stocks. That, however, would not be something restricted to this blend.

5. Conclusions

The N release dynamics of nitrogen fertilizers containing CRF were similar in the field and in the laboratory. The cumulative N released from E-Max 41% always remained below that from E-Max 43%, just as occurred with Blend*41* in relation to Blend*43*. We presented a reliable regression model that allows prediction of field results based on laboratory information, which may be useful for application in new studies involving CRFs.

The fertilizer technologies mitigated the N-NH_3 emissions in relation to those from urea (of volatilization near 25%). In the mean of the two consecutive crop years, the equivalent mitigation potential was in the following decreasing order: urea E-Max 41 (63%) > Blend*41* (43%) > urea E-Max 43 (32%) > U*NBPT* (28%) > Blend*43* (19%).

There was an effect of fertilizer management with different types of fertilizers and N application rates on the results of hulled coffee bean yield. The mean increase in yield rose from 20% in the first crop year to 75% in the second, with more expressive results with fertilizers containing CRF and, above all, with Blend*41* at application rates of up to 443 kg ha^{-1} $year^{-1}$.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/soilsystems7040083/s1, Figure S1. Daily volatilization per parceled application of U*Con* and U*NBPT* (A) and per single application for controlled-release fertilizers and blends (B), with rainfall (C) in two agricultural crop years with arabica coffee; Table S1. Chemical and physical characterization of the soil of the experimental area before setting up the experiments, in October 2017; Table S2. Date of removal of sponges for evaluation of volatilized N-NH_3; Table S3. Rainfall and soil moisture and temperature in the first 6 days after single application of the fertilizer or after parceled applications of the fertilizer; Table S4. Regression of the logistic model for data on N release in the laboratory and field in two consecutive crop years (2017–2018 and 2018–2019) and for data on N-NH_3 volatilization in the field in the same crop years; Table S5. Regressions of coffee bean yield according to type of nitrogen fertilizer and application rates.

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