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Article

Innovative Controlled-Release Polyurethane-Coated Urea Could Reduce N Leaching in Tomato Crop in Comparison to Conventional and Stabilized Fertilizers

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Abstract: Large amounts of fertilizers are being used in agriculture to sustain growing demands for food, especially in vegetable production systems. Soluble fertilizers can generally ensure high crop yields, but excessive leaching of nutrients, mainly as nitrate, can be a major cause of water pollution. Controlled-release fertilizers improve the nutrient use efficiency and lower the environmental hazard, usually without affecting the production. In this study, an innovative controlled-release coated urea fertilizer was compared to conventional nitrogen (N) fertilizers and a soluble ammonium-based fertilizer containing a nitrification inhibitor, in a round table tomato cultivation. Both the water and N balance were evaluated for each treatment, along with the yield and quality of the production. The experiment was repeated in three different seasons (spring, autumn and summer-autumn) in a glasshouse to prevent the effect of uncontrolled rainfall. The results indicated that N leaching decreased by increasing the percentage of coated urea. The application of at least 50% total N as coated urea strongly reduced N leaching and improved N agronomic efficiency in comparison with traditional fertilizers, ensuring at the same time a similar fruit production. Due to reduced leaching, the total N amount commonly applied by growers could be lowered by 25% without detrimental effects on commercial production.

Keywords: nitrogen fertilizer; nitrification inhibitor; nitrogen leaching; nitrogen use efficiency; 3,4-dimethylpyrazole phosphate (DMPP)

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1. Introduction

With the rapid increase of the global population, agriculture is required to satisfy the consequent boost in food demand worldwide. For example, in 2013 the production of primary foodstuffs such as wheat and maize reached 713 and 1018 millions of metric tons, respectively, and it has been estimated that in 2050 the world requirement will be 85% higher than in 2013 [1]. Along with water, considerable amounts of fertilizers have been thus far applied to raise the yield of agricultural crops. Nitrogen (N) is the main plant macronutrient and its concentration in natural soils is often deficient to ensure adequate plant growth and crop yield [2], eventually leading to high rates of N fertilization. Over a four-decade period from 1961 to 2013, the world consumption of N fertilizers has increased from 11.3 Tg N/year to 107.6 Tg N/year [3]. The use of fertilizers has especially increased in the intensive vegetable crop production system [4–6]. In China, N fertilization for the cultivation of vegetables exceeds 1000 and 3000 kg N/ha year in the open-field and greenhouse conditions, respectively. In the same country, in 2008, 17% of the national input of N fertilizers was devoted to the vegetable cropping system [7].

The conventional fertilizers that are commonly applied by growers are highly soluble salts and are liable up to 70% N losses due to volatilization and leaching [8]. These processes have two main undesirable effects: (1) a poor fertilization efficiency because the nutrient element is driven off the root zone, making it unavailable to the plant; (2) a harmful impact on the environment, due to either greenhouse gas emissions or surface water pollution by eutrophication. Nitrogen is commonly applied as nitrate ion, or it is quickly oxidized to this form through nitrification by soil microorganisms. The supply of different N forms or the nitrification process can cause hazardous volatilization losses as ammonia, N monoxide or other N oxides that could contribute to the greenhouse effect. In addition, nitrate ion is not retained by the soil and is easily leached [6,9].

Nitrogen leaching is generally more severe with intensive greenhouse cultures than with open-field crops, as plant growth is faster under controlled conditions and N fertilization represents an effective and low-cost practice to increase the production yield [6]. In fact, several authors drew attention to the occurrence of eutrophication and water pollution in the main European districts for protected vegetable crop production, such as Spain [10], Italy [11], The Netherlands [12], Poland [13] and Greece [14]. The environmental impact associated with nitrate leaching has become a major concern all over the world. In Europe, this has led to the introduction of the Nitrates Directive [15], to limit N pollution and improve water quality. According to the directive, the Nitrate Vulnerable Zones (NVZs) are land areas where drainage water from agricultural crops can cause contamination of larger water bodies by excess nitrate [16]. Hence, the limitation of fertilizers application in agriculture represents an effective measure to counteract nitrate pollution of surface water [17]. With N overfertilization, nitrate ion can also accumulate in the edible parts of several food crops [18]. Human intake of nitrate with the diet has been related to gastric cancer [19–21] and has directed the European Union toward a restriction to the nitrate content in food as a safety measure for the consumer [22].

Based on the above considerations, many efforts have been made to rationalize N fertilization. The application of enhanced efficiency fertilizers is a functional approach to achieve this purpose by limiting nutrient amounts in soils and at the same time reducing both N leaching and N volatilization losses. Enhanced efficiency fertilizers can be divided into three subgroups [23]: (i) slow-release fertilizers, (ii) stabilized fertilizers, (iii) controlled-release fertilizers. Slow-release fertilizers contain low solubility N compounds that become available to plants only after microbial degradation. Stabilized fertilizers contain chemical inhibitors, which slow down or stop biological processes. These include urease inhibitors that hinder the hydrolysis of urea by urease enzyme, or nitrification inhibitors such as dicyandiamide (DCD), or 3,4-dimethylpyrazole phosphate (DMPP), which prevent the oxidation of ammonium ion [24]. Controlled-release fertilizers are made of an inner core and an outer layer. The former is a water-soluble fertilizer such as urea, ammonium nitrate or potassium nitrate; the latter is a coating material such as sulfur, an alkyd- or polyurethane-like resin, a thermoplastic polymer or a mineral-based inorganic material [25]. Controlled-release fertilizers can also be made by the combination of sulfur-coated urea with an additional polymer or resin coating [26,27].

Two main limitations to the use of controlled-release fertilizers are their relatively high cost, and the difficulty to develop an adequate coating for irregularly shaped fertilizers or highly soluble compounds such as urea. The controlled-release fertilizer used in this study consisted of polyurethane-coated urea granules and was manufactured using an innovative polymer coating patented technology (E-MAX) that can be employed in combination with many types of fertilizers, including hygroscopic compounds or irregularly shaped materials. The release mechanism of coated fertilizers is based on the osmosis phenomenon produced by the diffusion of water through the coating, which leads to the solubilisation of the inner fertilizer. Water transfer through the coating layer is the rate determining step and depends on the chemical structure of the polymer, the thickness of the coating layer and the temperature. Therefore, for a given polymer with a fixed thickness, the release rate should be temperature-dependent and should be assessed through the temperature regime experienced by the coated fertilizer [28,29]. Thus, the release of nutrients into the soil could be predicted and controlled over time. With the E-MAX coating technology, the thickness of the polymer layer is well below 100 µm; the coating material is evenly spread and fixed on the whole surface of discrete 2- to 4-mm-diameter particles, degrades slowly and is essentially inert in the soil after the nutrient has been released. The work was aimed at evaluating: (i) the release curve and the effectiveness of the polyurethane-coated urea in relation to the plant N requirements in different climate growing conditions; (ii) the effect of this controlled-release fertilizer on N leaching and on the yield and quality of a soil greenhouse tomato cultivation in comparison with fertilization techniques that employ a nitrification inhibitor or soluble salts.

2. Materials and Methods

Although the controlled-release fertilizer used in this study was being developed and marketed mainly for open field application, three experiments were carried out in a glasshouse at the University of Pisa on round-table tomato plants (cultivar Hybrid F1 "OPTIMA"). The use of a greenhouse equipped with lysimeters allowed for the prevention of the negative effects of uncontrolled rainfall events and made possible to easily collect, measure and analyse water drainage and N leaching, thus enabling reliable computations of both water and N balance in the different treatments. The present study was focused on the time interval of N release by the coated urea (3–4 months) rather than to the long-term agronomical effects of the treatments. Therefore, the growing period lasted from the transplanting to the harvesting of the third or fourth truss and was shorter than that of a typical greenhouse cultivation of tomato, which is generally conducted until the ripening of the fifth or sixth truss. However, the growing conditions of the experiments closely resembled those of a real cropping system and enabled the evaluation of the yield and quality of the production.

2.1. Experimental Design

Three experiments were performed under different growing conditions: Experiment 1 (spring 2015), Experiment 2 (autumn 2015) and Experiment 3 (summer–autumn 2016). In all the experiments, either the stabilized or the controlled-release fertilizer were compared with a conventional treatment (CON). The distinct N treatments and fertilizer addition programs are detailed in Table 1. The same total N dose was applied in all the treatments using different N sources: (i) the inorganic salts potassium nitrate KNO_3, calcium nitrate $Ca(NO_3)_2$, ammonium nitrate NH_4NO_3 and ammonium sulphate $(NH_4)_2SO_4$; (ii) a stabilized fertilizer containing 26% total N (7.5% as nitrate and 18.5% as ammonium), with the addition of DMPP as a nitrification inhibitor (ENTEC® 26:0:0 Nitrogen-Phosphorus-Potassium, EuroChem Agro, Cesano Maderno, Italy); (iii) an innovative controlled-release fertilizer, manufactured using the E-MAX coating technology and consisting of granules of urea fertilizer coated by a permeable and very thin polyurethane layer (Agrocote® Max; ICL Specialty Fertilizers, Heerlen, The Netherlands; Patent EP 2672813 B1). The stabilized and controlled-release fertilizers will be hereafter indicated as DMPP and CU, respectively.

The total N dose was adapted to the different climate conditions of each experiment and, as plant growth is normally slower in autumn, N fertilization was necessarily lower in Experiment 2 than in Experiment 1 (300 kg/ha against 360 kg/ha) to prevent excess leaching. A reduced total N application in the cold season is consistent with the growers' common practice. For this reason, a similar absolute amount of CU or DMPP applied as base fertilization corresponded to a different percentage of total N. For example, Table 1 shows that the DMPP dose tested in Experiment 1 was 72 kg N/ha (20% of total N) and was comparable to the DMPP amount applied in Experiment 2 (75 kg N/ha; 25% of total N). Both the N dose and the N percentage are reported in Table 1 for each fertilizer.

Table 1. Description of the fertilization treatments applied in the three experiments and total cost of fertilizers.

Treatment	Short Description	Total N Dose	Base Fertilization	Top-Dressing (Fertigation)			Total Cost of Fertilizers	Total Cost of N Fertilizers
				kg N/ha (% total N)				
		kg N/ha	kg N/ha (% Total N)	NH_4NO_3	$Ca(NO_3)_2$	KNO_3	€/ha	
				Experiment 1				
CON1	Growers' practice	360	72 (20) as $(NH_4)_2SO_4$	72 (20)	166 (46)	50 (14)	1887.04	1216.13
DMPP20	DMPP® 26.0.0	360	72 (20) as DMPP®	72 (20)	166 (46)	50 (14)	1874.51	1203.60
CU20	CU	360	72 (20) as CU	72 (20)	166 (46)	50 (14)	1875.47	1204.56
CU40	CU	360	144 (40) as CU	0	166 (46)	50 (14)	1898.95	1228.04
CU75-1	CU	360	270 (75) as CU	0	90 (25)	0	2002.21	1049.25
				Experiment 2				
CON2	Growers' practice	300	75 (25) as $(NH_4)_2SO_4$	90 (30)	75 (25)	60 (20)	1624.54	1010.04
DMPP25	DMPP® 26.0.0	300	75 (25) as DMPP	90 (30)	75 (25)	60 (20)	1611.50	997.00
CU50	CU	300	150 (50) as CU	15 (5)	75 (25)	60 (20)	1636.95	1022.45
CU75-2	CU	300	225 (75) as CU	0	75 (25)	0	1606.69	653.73
				Experiment 3				
CON3	Growers' practice	300	75 (25) as NH_4NO_3	90 (30)	75 (25)	60 (20)	1624.54	1010.04
CUred	CU reduced dose	225	150 (67) as CU	0	75 (33)	0	1475.88	522.92

The values between parentheses correspond to percentage of total N dose. CON: conventional treatment; DMPP: treatment with stabilized fertilizer; CU: treatment with coated urea. The total cost of N fertilizers and of all fertilizers were calculated using the following fertilizer prices: $(NH_4)_2SO_4$: N = 21%, 400 €/ton; NH_4NO_3 with DMPP (ENTEC 26): N = 26% 450 €/ton; coated urea (Agrocote®Max); N = 44%, 750 €/ton; KH_2PO_4: P_2O_5 = 52%, K_2O = 34%, 1760 €/ton; K_2SO_4: K_2O = 52%, 880 €/ton; $Ca(NO_3)_2$: N = 15.5%, Ca = 26%, 540 €/ton. The fertilizer prices are referred to an end-user located in Tuscany (Italy) in 2018.

For both conventional and stabilized fertilizers, the high solubility limited the amount that could be applied as base fertilization to 75 kg N/ha, to prevent detrimental salinity effects on the crop. In contrast, with the controlled-release CU fertilizer higher doses could be applied, up to 270 kg N/ha. The outcome of Experiment 1 was used to tune the conditions of the subsequent trial and, as in spring no significant effect was observed on the production with the CU20 treatment, higher CU doses were employed in autumn. In addition, at least 75 kg N/ha was applied in all the treatments as calcium nitrate. This amount was never decreased in the three experiments, to allow a sufficient calcium supply to the plants and ensure a correct calcium nutrition, preventing the occurrence of the blossom-end rot. For the CUred treatment, which employed a reduced N dose, the above amount of $Ca(NO_3)_2$ represented 33% of total N applied (Table 1).

In all the experiments, both N and water balance of the tomato culture were evaluated for each fertilization treatment. Inside the greenhouse, the plants were grown in lysimeters to enable reliable determination of water and N status in the growing system. Each lysimeter hosted four plants and consisted of a 200 L plastic tank (75 × 53 cm, height 50 cm), containing 20 L (5 cm) pumice layer at the bottom to ensure correct drainage. The pumice layer was topped off with 160 L sandy soil and peat (40 cm depth; 60:40 volume ratio; 1.2 kg/L specific weight). Along with the results of soil analyses, the main climatic parameters of the three experiments are reported in Table 2. The greenhouse heating guaranteed a minimum inner air temperature of 12.5 °C. Global radiation, air temperature, soil temperature at 15 cm depth and relative humidity (RH) were recorded every ten minutes by a climate station equipped with three different probes for soil temperature, connected to a database (Econorma, Treviso, Italy). The recorded values were used to calculate the cumulative radiation and the average daily values of RH, soil temperature and air temperature. The cumulative soil temperature was obtained by the sum of the values of daily average soil temperature recorded in each experimental period.

In each experiment, a zero-N fertilization treatment with the same levels of the other nutrients was also included for the assessment of N use efficiency. Although this is normally the control treatment in agronomic experiments, the main goal of the present study was to evaluate the effect of different fertilization strategies on the reduction of N leachate as compared with conventional fertilization. For this reason, the conventional treatment rather than the zero-N treatment was regarded as the control in our experiments.

After transplanting and until the end of the experimental period, each treatment was fertigated with nutrient solution to ensure a proper supply of all the macro- and micronutrients to the plants. Along with N, all the treatments of the three experiments received the same total amounts of phosphorus (P) and potassium (K), which were 1.4 and 12 g/plant, respectively (equivalent to 96 kg/ha P_2O_5 and 433 kg/ha K_2O). These P and K doses are commonly used by the greenhouse growers in Italy and were either applied as base fertilizers or supplied by fertigation. The total calcium supply ranged from 60 mg/L (that is the concentration in the irrigation water) to 150 mg/L. The latter value was reached only when calcium nitrate was used as a N source to prevent the occurrence of the blossom-end rot. The concentrations of the other elements in the nutrient solution were the following (mg/L): Mg 30; Na 230; Cl 320; Fe 2; B 0.27; Cu 0.24; Zn 0.29; Mn 0.55 and Mo 0.05. Depending on the treatment and on the phenological phase, different amounts of inorganic N fertilizers were added when necessary to the nutrient solution (Table 1) to achieve the same final N dose in each treatment. Specifically, NH_4NO_3 was supplied from transplanting until the blooming of the second truss, $Ca(NO_3)_2$ was employed until the ripening of the first truss and KNO_3 was added during the ripening stage, until the end of the experiment. The irrigation was generally applied twice a day, according to the climate conditions and the canopy development, in the same amount for all the treatments investigated.

The tomato plantlets were transplanted at the stage of six-seven true leaves, which in the three experiments corresponded to a different plant age (50–30 days), depending on the thermal growing conditions. Similarly, the end of the experimental period corresponded to the harvest of the fourth truss in Experiment 1 or to the harvest of the third truss otherwise.

Table 2. Climate and soil parameters measured in the three experiments. Temperature, humidity and radiation are reported as the average values inside the greenhouse during the whole experimental period. Soil parameters are reported as the initial values immediately before the beginning of each experiment.

Parameter	**Experiment 1 Spring 2015**	**Experiment 2 Autumn 2015**	**Experiment 3 Summer/Autumn 2016**
Growing period	20 March–7 July 2015	21 September 2015–28 January 2016	22 August–1 December 2016
Daily mean air temperature (°C)	22.7 ± 5.5	16.4 ± 3.9	20.4 ± 4.2
Daily mean soil temperature (°C)	22.4 ± 5.4	17.3 ± 3.9	20.7 ± 4.2
Air and soil temperature range (°C)	15–32	11–26	14–28
Cumulative average daily soil temperature (°C)	2459.9 ± 96.7	2245.8 ± 67.4	2079.1 ± 62.3
Relative humidity (%)	62.7 ± 7.7	79.6 ± 10.7	77.9 ± 11.4
Average daily global radiation ($MJ/m^2 \cdot day$)	10.5 ± 3.6	2.4 ± 0.7	5.0 ± 1.6
Cumulative global radiation (MJ/m^2)	1151.7 ± 43.8	299.9 ± 9.0	506.3 ± 15.2
pH	8.1 ± 0.1	6.8 ± 0.1	7.0 ± 0.1
Electrical Conductivity (mS/cm at 25 °C)	0.22 ± 0.08	0.29 ± 0.06	0.39 ± 0.08
Nitrate (mg NO_3^-/kg)	20 ± 2	28 ± 2	33 ± 4
Ammonium (mg NH_4^+/kg)	1.2 ± 0.2	7.0 ± 0.2	8.0 ± 0.3
Exchangeable Potassium (mg K_2O/kg)	140 ± 7	136 ± 5	129 ± 9
Exchangeable Calcium (mg Ca/kg)	2112 ± 11	2258 ± 13	2295 ± 13
Exchangeable Magnesium (mg Mg/kg)	80 ± 8	110 ± 8	91 ± 7
Assimilable Phosphorous (mg P_2O_5/kg)	76 ± 6	77 ± 6	70 ± 7
Assimilable Iron (mg Fe/kg)	388 ± 10	334 ± 16	388 ± 15
Assimilable Manganese (mg Mn/kg)	204 ± 8	215 ± 10	226 ± 11
Assimilable Zinc (mg Zn/kg)	6.0 ± 0.1	4.3 ± 0.5	6.2 ± 0.7
Assimilable Copper (mg Cu/kg)	5.9 ± 0.4	2.11 ± 0.02	3.20 ± 0.02
Soluble Boron (mg B/kg)	0.45 ± 0.04	0.21 ± 0.02	0.35 ± 0.04
Organic matter content (%)	2.31 ± 0.12	1.44 ± 0.10	4.15 ± 0.15
C/N	33.6 ± 0.6	14.0 ± 0.4	17.2 ± 0.2
Cationic Exchange Capacity (meq/100 g)	12.8 ± 1.0	11.6 ± 0.5	15.4 ± 1.1
Clay (%)	11.6 ± 0.9	6.2 ± 0.6	7.6 ± 0.8
Silt (%)	20.8 ± 1.2	20.5 ± 1.9	19.9 ± 1.1
Sand (%)	67.6 ± 2.1	73.3 ± 1.1	72.5 ± 2.2

Mean values ± standard deviation. n = 5 in Experiment 1; n = 3 in Experiment 2 and Experiment 3.

2.2. Analyses of Water, Soil, CU Granules and Plant Tissue Samples

The average values of the climate parameters (RH, air and soil temperature, cumulated global radiation) were recorded daily. Nitrogen was contained as urea in CU granules and in different chemical forms in water, soil and tissue samples. A summary of N determinations and analytical assays used can be found in Table 3.

Due to the autumn climate conditions, in both Experiments 2 and 3 the growing cycle was longer than in spring, while the crop evapotranspiration and the plant growth were strongly reduced. Therefore, an increase of the water collection period was necessary to maintain the same number of drainage samplings as Experiment 1. The cumulated drainage water was sampled from each container every 7–10 days in Experiment 1 and every 13–15 days in Experiment 2 and Experiment 3. The water samples were filtered on Whatman qualitative filter paper and analysed for the concentrations of nitrate (salicylic acid method) [30]; ammoniacal N (indophenol method) [31] and ureic N (enzymatic assay using a commercial kit; Megazyme International, Wicklow, Ireland). All the absorbance measurements were carried out using a Lambda35 UV-vis double beam spectrophotometer (Perkin Elmer, Waltham, MA, USA).

The soil samples were dehydrated at 40 °C in a ventilated oven and sieved to separate intact CU granules. The dried soil samples were extracted with water, 1 M KCl, 0.5 N $NaHCO_3$ at pH 8.5 or 1 N CH_3COONH_4 at pH 7.0, respectively, for the spectrophotometric determinations of nitrate [30], ammoniacal N [31] and available P [32] and for the assessment of exchangeable K by atomic absorption spectroscopy (AAS) [33]. In all cases, a 1:2 w/v extraction ratio was used. The total organic matter and the other soil parameters reported in Table 2 were assessed according to official methods the Italian Ministry of Agriculture and Forestry [34].

Table 3. Analytical assays used to determine nitrogen concentration in samples of water, soil, coated urea fertilizer and plant tissues in the three experiments.

Sample	Fraction of Total N	Determination	Chemical Form
Cumulated water drainage	Ureic	Enzyme kit (urease)	Urea
	Nitric	Spectrophotometric assay (nitrosalycilate method)	Nitrate
	Ammoniacal	Spectrophotometric assay (substituted indophenol method)	Ammonium + Ammonia
Soil	Ureic	Enzyme kit (urease)	Urea
	Reduced	Kjeldahl method	Organic + Ammonium + Ammonia
	Nitric	Spectrophotometric assay (nitrosalycilate method)	Nitrate
	Mineral	Nitrate + Ammoniacal N	Nitrate + Ammonium + Ammonia
	Total	Reduced + Nitrate	Organic + Nitrate + Ammonium + Ammonia
Coated urea fertilizer	Ureic	Enzyme kit (urease)	Urea
	Ammoniacal	Spectrophotometric assay (substituted indophenol method)	Ammonium + Ammonia
Plant tissues	Nitric	Spectrophotometric assay (nitrosalycilate method)	Nitrate
	Reduced	Kjeldahl method	Organic + Ammonium + Ammonia
	Organic	Reduced − Ammoniacal	N-containing organic compounds including urea
	Total	Reduced + Nitrate	Organic + Nitrate + Ammonium + Ammonia

The N amount retained by the coated urea granules was determined in all the CU treatments. At the beginning of each experiment, 2 g aliquots of the coated fertilizer were wrapped in net fabric before application to each lysimeter. Every 30 days during the cultivation period (for Experiments 1 and 2) and at the end of the cultivation period (for all three experiments), the wrappings were removed from the soil to collect the residual granules, which were gently washed with distilled water, oven-dried at 70 °C and powdered with mortar and pestle. The powder was dispersed into 200 mL distilled water and the filtered solution was analysed for the concentration of urea. For each cultivation period, the N release by the coated fertilizer was evaluated by the difference between the initial and final ureic-N amounts in the net-wrapped granules.

All the plant samples were dried in a ventilated oven at 70 °C till constant weight and ground in a mill to a fine powder. The crop yield was determined as the number and fresh weight of the fruits, which were picked weekly and divided into marketable and nonmarketable categories. To evaluate the quality of the production, four fruits from different plants were collected from each lysimeter in the middle of the harvesting period and were homogenized in a mixer. Part of each homogenized sample was oven-dried for dry matter determination; the remaining material was centrifuged, and the resulting juice was analysed for pH, EC, total soluble solids (determined by refractometry and expressed as °Brix) and total titratable acidity (determined by acid-base titration with 0.1 M sodium hydroxide and expressed as g citric acid in 100 mL juice). The shoot dry biomass production was determined at the end of each experiment. All the dry tissue samples were analysed for their contents of nitric, ammoniacal and reduced N, as described previously for soil samples.

2.3. Calculation of N and Water Balance Sheet and N Use Efficiency

A balance sheet for both water and N was computed for each treatment and experiment. Water evapotranspiration was calculated as the difference between water supply and water drainage (both measured); the leaching fraction was computed as the ratio between water drainage and water supply. The computation of N balance was based on the available amount during cultivation (initially contained in the soil or supplied through fertilization) and the amount that was actually removed (leached or absorbed by the plants) or remained in the soil at the end of the experiments. The amounts of fertilizers were weighed using a technical balance with 0.1 g precision and 1.0 kg/ha was cautiously assumed as the standard deviation for the total N applied. Soil mineral N was evaluated as the sum of nitric and ammoniacal N (Table 3) and was assessed both at the beginning (prior to base fertilization) and the end of each experiment. The total N amount of the system at the end of the experiment (N output) was evaluated as the sum of the N fractions that were absorbed by the plants, were lost by leaching, remained in the soil as mineral N or remained in the CU granules as residual urea. The final amount of urea in the soil was negligible (less than 0.1 mg/kg), due to both the controlled release by the CU fertilizer and to the fast leaching and mineralization processes that urea undergoes in soils [35]. The total N amount available during the growing period (N input) was calculated as the sum of the initial mineral amount in the soil and the amount applied with fertilizers, both as base fertilization and with fertigation (total N supplied). Based on the results of the zero-N treatments, some nitrogen use efficiency (NUE) indexes were calculated according to [36,37], using the following formulas:

$$\text{Agronomic Efficiency (AE)} = (\text{Y} - \text{Y0})/\text{F}$$

$$\text{Partial Factor Productivity (PFP)} = \text{Y}/\text{F}$$

$$\text{Apparent Recovery Efficiency by difference (REC)} = (\text{U} - \text{U0})/\text{F}$$

$$\text{Physiological Efficiency (PE)} = (\text{Y} - \text{Y0})/(\text{U} - \text{U0})$$

where Y and Y0 (g/m^2 on a fresh weight basis) are the tomato yields with and without N fertilization, respectively; F is the total N supplied (g N/m^2) and U and U0 (g N/m^2) are the N contents in fruits with and without N fertilization, respectively.

2.4. Statistical Analysis

A completely randomized design was adopted. As the statistical variability of the data was initially unknown, in Experiment 1 five replicates (lysimeters) were prudentially arranged. Based on the results of the first experiment, the number of replicates could be reasonably reduced to three in the subsequent trials to obtain an adequate statistical discrimination and limit the cost of data collection. Each replicate consisted of four tomato plants. The collected data were tested for normality and homoschedasticity by means of the Shapiro–Wilk's and Levene's test, respectively. The data were subjected to one-way ANOVA and the mean values were compared by Tukey test using the Statgraphics Plus 5.1 software (StatPoint, Inc., Herndon, VA, USA).

3. Results

For all the experiments, Table 4 reports the water balance, Table 5 shows the biomass and N distribution in different plant tissues and Table 6 reports the data concerning the yield and quality of the tomato production obtained with the different treatments. The N balance for the three experiments is reported in Table 7. Table 8 reports the NUE indexes that were calculated from the tomato yield (Y0; kg/m^2 on a fresh weight basis) and the N content of fruits (U0; g N/m^2) obtained without N fertilization (zero-N treatment).

In all the treatments, only negligible amounts of urea and ammonium (0–0.08 g N/m^2) were detected in the drainage water. Thus, N leached from the soil was almost completely in the form of nitrate ion.

In Experiment 1, the water balance was similar for the CON1, DMPP20 and CU20 treatments, while a higher water drainage and leaching fraction along with a lower evapotranspiration were observed for CU40 and CU75-1 treatments (Table 4). Both the dry biomass and the N concentration in the tissues were affected by N fertilization. Compared with CON1, all the treatments except CU20 increased the dry biomass of fruits. In addition, both CU40 and CU75-1 increased the fruit N concentration (Table 5). However, apart from slight differences in the number of fruits, the distinct treatments had no significant effect on the tomato yield or quality (Table 6).

Table 4. Effect of different fertilization strategies on the water balance.

Treatment	Water Supply (L/m^2)	Water Drainage (L/m^2)	Leaching Fraction (%)	Evapotranspiration (L/m^2)
		Experiment 1		
CON1	472.5 ± 19.2	67.5 ± 2.6 ^{b}	14.3 ± 2.2 ^{b}	405.0 ± 12.7 ^{a}
DMPP20	472.7 ± 19.4	61.3 ± 2.5 ^{b}	13.0 ± 2.9 ^{b}	411.4 ± 12.5 ^{a}
CU20	470.2 ± 20.1	66.6 ± 2.7 ^{b}	14.2 ± 2.5 ^{b}	403.5 ± 11.3 ^{a}
CU40	475.8 ± 19.1	94.6 ± 3.7 ^{a}	19.9 ± 3.4 ^{a}	381.2 ± 11.9 ^{b}
CU75-1	475.8 ± 17.7	97.8 ± 4.6 ^{a}	20.7 ±3.3 ^{a}	375,6 ± 11.0 ^{b}
		Experiment 2		
CON2	171.6 ± 9.3	38.4 ± 2.4 ^{b}	22.4 ± 1.8 ^{b}	133.3 ± 3.0 ^{a}
DMPP25	173.6 ± 7.2	39.8 ± 3.1 ^{b}	22.9 ± 2.1 ^{b}	133.8 ± 2.9 ^{a}
CU50	168.7 ± 6.9	41.7 ± 2.9 ^{b}	24.7 ± 1.9 ^{ab}	127.0 ± 3.2 ^{ab}
CU75-2	171.9 ± 8.2	46.7 ± 3.2 ^{a}	27.2 ± 2.1 ^{a}	125.2 ± 2.8 ^{b}
		Experiment 3		
CON3	321.4 ± 11.2	94.7 ± 4.7	29.5 ± 2.1	226.7 ± 6.5
Cured	326.3 ± 9.2	94.1 ± 5.6	28.8 ± 1.9	232.2 ± 5.8

Mean values ± standard deviation. In each experiment, different letters within the same column identify a significant difference ($p < 0.05$), according to Tukey test following one-way ANOVA. Mean values without any letters are not significantly different. CON: conventional treatment; DMPP: treatment with stabilized fertilizer; CU: treatment with coated urea.

Table 5. The influence of different fertilization strategies on the distribution of biomass and nitrogen in tomato tissues.

Treatment	Dry Biomass (g/m^2)			N Tissue Concentration (% Dry Biomass)		
	Leaves	Stems	Fruits	Leaves	Stems	Fruits
			Experiment 1			
CON1	179.4 ± 6.7 ^{b}	156.8 ± 10.1	717.0 ± 12.8 ^{c}	2.52 ± 0.03 ^{b}	2.25 ± 0.04 ^{ab}	2.95 ± 0.04 ^{b}
DMPP20	191.4 ± 9.4 ^{a}	155.9 ± 9.9	762.3 ± 12.5 ^{a}	2.60 ± 0.05 ^{a}	2.23 ± 0.02 ^{b}	3.04 ± 0.04 ^{ab}
CU20	194.5 ± 9.7 ^{a}	169.8 ± 9.7	714.7 ± 13.1	2.63 ± 0.04 ^{a}	2.28 ± 0.03 ^{ab}	3.00 ± 0.03 ^{b}
CU40	167.4 ± 5.3 ^{c}	155.3 ± 8.5	741.0 ± 15.1 ^{b}	2.62 ± 0.04 ^{a}	2.31 ± 0.03 ^{a}	3.10 ± 0.02 ^{a}
CU75-1	162,9 ± 5.5 ^{c}	154.8 ± 7.9	759.9 ± 13.2 ^{a}	2.68 ± 0.05 ^{a}	2.24 ± 0.03 ^{b}	3.12 ± 0.03 ^{a}
			Experiment 2			
CON2	206.6 ± 10.6 ^{a}	100.1 ± 6.7 ^{a}	195.8 ± 14.2 ^{b}	3.59 ± 0.03 ^{a}	3.00 ± 0.01 ^{ab}	3.44 ± 0.02 ^{ab}
DMPP25	189.5 ± 7.9 ^{b}	87.5 ± 6.5 ^{b}	189.9 ± 12.1 ^{b}	3.51 ± 0.02 ^{a}	3.16 ± 0.02 ^{a}	3.22 ± 0.01 ^{b}
CU50	198.4 ± 9.3 ^{ab}	85.9 ± 6.8 ^{b}	216.2 ± 14.6 ^{a}	3.46 ± 0.02 ^{ab}	2.83 ± 0.02 ^{bc}	3.49 ± 0.02 ^{a}
CU75-2	190.5 ± 8.4 ^{b}	101.0 ± 7.1 ^{a}	234.1 ± 15.2 ^{a}	3.22 ± 0.01 ^{b}	2.52 ± 0.02 ^{c}	3.60 ± 0.03 ^{a}
			Experiment 3			
CON3	191.9 ± 9.5	82.5 ± 6.1	197.6 ± 18.1	3.72 ± 0.03 ^{a}	2.61 ± 0.02	3.62 ± 0.02
Cured	184.0 ± 8.2	77.4 ± 5.8	214.4 ± 19.2	3.20 ± 0.02 ^{b}	2.72 ± 0.03	3.59 ± 0.02

Mean values ± standard deviation. For each column in each experiment, different letters identify a significant difference ($p < 0.05$), according to Tukey test following one-way ANOVA. Mean values without any letters are not significantly different. CON: conventional treatment; DMPP: treatment with stabilized fertilizer; CU: treatment with coated urea.

Table 6. The influence of different fertilization strategies on yield and quality of the tomato crop.

Fruit Production							Fruit Quality			
Treatment	**Fruit Yield (kg/m^2)**		**Fruit Amount (n° Fruits/m^2)**		**Average Fruit Weight (gFW/Fruit)**	**Fruit Dry Matter Content (%)**	**pH**	**EC (dS/m)**	**Total Soluble Solids (°Brix)**	**Titratable Acidity (g Citric Acid/100 mL)**
	Total	**Market Quality**	**Total**	**Market Quality**						
Experiment 1										
CON1	12.8 ± 0.68	9.8 ± 0.9	59.0 ± 1.4 ^{b}	39.5 ± 1.6 ^{ab}	247.8 ± 22.1	5.60 ± 0.11	4.17 ± 0.04	5.23 ± 0.20	4.65 ± 0.20	0.57 ± 0.03
DMPP20	13.8 ± 0.79	10.4 ± 1.1	63.2 ± 2.2 ^{ab}	39.2 ± 1.5 ^{ab}	265.6 ± 28.2	5.52 ± 0.09	4.14 ± 0.03	5.14 ± 0.19	4.62 ± 0.23	0.58 ± 0.04
CU20	12.7 ± 0.71	9.8 ± 0.7	59.5 ± 1.8 ^{ab}	38.5 ± 1.6 ^{b}	255.3 ± 20.5	5.63 ± 0.15	4.14 ± 0.03	5.37 ± 0.24	4.45 ± 0.21	0.57 ± 0.04
CU40	13.4 ± 0.82	10.7 ± 0.8	65.7 ± 2.1 ^{a}	43.0 ± 2.9 ^{a}	248.8 ± 20.5	5.53 ± 0.10	4.16 ± 0.04	5.28 ± 0.21	4.57 ± 0.25	0.58 ± 0.05
CU75	13.5 ± 0.87	10.8 ± 0.9	64.6 ± 1.9 ^{a}	42.2 ± 3.1 ^{a}	254.7 ± 21.1	5.63 ± 0.14	4.15 ± 0.02	5.36 ± 0.25	4.63 ± 0.22	0.59 ± 0.06
Experiment 2										
CON2	4.21 ± 0.21 ^{b}	3.80 ± 0.31 ^{b}	33.5 ± 4.1	26.3 ± 2.4 ^{b}	144.8 ± 9.7 ^{b}	4.65 ± 0.08	4.42 ± 0.03 ^{b}	6.22 ± 0.34 ^{b}	4.10 ± 0.14 ^{b}	0.40 ± 0.03
DMPP25	4.04 ± 0.23 ^{b}	3.85 ± 0.41 ^{b}	33.8 ± 3.8	25.3 ± 2.5 ^{b}	152.5 ± 10.6 ^{ab}	4.70 ± 0.11	4.41 ± 0.03 ^{b}	6.87 ± 0.32 ^{ab}	4.40 ± 0.18 ^{ab}	0.45 ± 0.04
CU50	4.70 ± 0.31 ^{ab}	4.30 ± 0.35 ^{ab}	33.8 ± 3.9	27.3 ± 2.9 ^{ab}	155.0 ± 10.3 ^{ab}	4.60 ± 0.09	4.40 ± 0.04 ^{b}	6.65 ± 0.34 ^{b}	3.98 ± 0.14 ^{b}	0.42 ± 0.03
CU75	4.99 ± 0.33 ^{a}	4.70 ± 0.35 ^{a}	37.2 ± 4.2	30.0 ± 3.1 ^{a}	156.7 ± 10.1 ^{a}	4.69 ± 0.10	4.52 ± 0.04 ^{a}	7.54 ± 0.41 ^{a}	4.50 ± 0.15 ^{a}	0.41 ± 0.04
Experiment 3										
CON3	4.39 ± 0.19	3.77 ± 0.28	38.3 ± 3.9	26.3 ± 2.5	143.6 ± 10.9	4.50 ± 0.13	3.90 ± 0.04	5.23 ± 0.25	4.47 ± 0.09	0.73 ± 0.06
CUred	4.64 ± 0.18	4.08 ± 0.31	36.0 ± 3.7	28.8 ± 2.6	141.9 ± 11.2	4.62 ± 0.15	3.86 ± 0.05	5.14 ± 0.30	4.49 ± 0.07	0.65 ± 0.07

Mean values ± standard deviation. For each parameter in each experiment, different letters identify a significant difference ($p < 0.05$), according to Tukey test following one-way ANOVA. Mean values without any letters are not significantly different. CON: conventional treatment; DMPP: treatment with stabilized fertilizer; CU: treatment with coated urea. FW: fresh weight; EC: electrical conductivity.

Table 7. Nitrogen balance for different fertilization strategies in the three experiments.

	N Distribution (kg/ha)		**Treatments**				
	Experiment 1		**CON1**	**DMPP20**	**CU20**	**CU40**	**CU75-1**
Input	Mineral soil content prior to fertilization (A)		39.2 ± 1.0	39.2 ± 1.0	39.2 ± 1.0	39.2 ± 1.0	39.2 ± 1.0
	Supplied by base fertilization (B)	soluble salt	72.0 ± 1.0 ^{c}				
		DMPP		72.0 ± 1.0 ^{c}			
		CU			72.0 ± 1.0 ^{c}	144.0 ± 1.0 ^{b}	270.0 ± 1.0 ^{a}
	Supplied by fertigation (C)		288.2 ± 2.5 ^{a}	287.5 ± 2.8 ^{a}	287.8 ± 3.1 ^{a}	216.3 ± 2.1 ^{a}	90.6 ± 1.1 ^{c}
	Total N input (I)		399.4 ± 1.8	398.7 ± 2.0	399.0 ± 2.2	399.5 ± 1.3	399.8 ± 3.0
Output	Mineral soil content after experiment (E)		40.6 ± 3.3 ^{c}	41.9 ± 4.3 ^{c}	47.3 ± 5.1 ^{c}	62.1 ± 5.8 ^{b}	72.9 ± 6.1 ^{a}
	Residual in CU granules (F)				7.9 ± 1.5 ^{c}	15.8 ± 1.9 ^{b}	29.7 ± 2.5 ^{a}
	Leached (G)		127.2 ± 8.1 ^{a}	97.8 ± 6.7 ^{b}	97.0 ± 7.1 ^{b}	57.2 ± 5.1 ^{c}	25.4 ± 3.1 ^{d}
	Plant uptake (H)		272.4 ± 12.1 ^{b}	290.3 ± 13.5 ^{a}	290.2 ± 13.1 ^{a}	290.1 ± 12.7 ^{a}	296.5 ± 15.1 ^{a}
	Total N output (O)		440.2 ± 14.1 ^{a}	430.0 ± 13.7 ^{a,b}	442.4 ± 15.1 ^{a}	425.2 ± 11.5 ^{b}	424.5 ± 12.5 ^{b}
	N output − N input (Δ)		40.8	31.3	43.4	25.7	24.7
	Relative error		9.27%	7.28%	9.81%	6.04%	5.82%
	Experiment 2		**CON2**	**DMPP25**	**CU50**		**CU75-2**
Input	Mineral soil content prior to fertilization (A)		14.9 ± 1.0	14.9 ± 1.0	14.9 ± 1.0		14.9 ± 1.0
	Supplied by base fertilization (B)	soluble salt	75.0 ± 1.0 ^{c}				
		DMPP		75.0 ± 1.0 ^{c}			
		CU			150.0 ± 1.0 ^{b}		225.0 ± 1.0 ^{a}
	Supplied by fertigation (C)		224.5 ± 2.7 ^{a}	224.5 ± 2.9 ^{a}	144.1 ± 1.7 ^{b}		74.9 ± 0.3 ^{c}
	Total N input (I)		314.4 ± 18.6	314.4 ± 18.7	309.0 ± 16.1		314.8 ± 14.5
Output	Mineral soil content after experiment (E)		100.0 ± 9.1 ^{a}	110.8 ± 8.6 ^{a}	85.8 ± 7.1 ^{b}		89.8 ± 6.8 ^{b}
	Residual in CU granules (F)				21.0 ± 2.2 ^{b}		31.5 ± 2.4 ^{a}
	Leached (G)		46.0 ± 3.1 ^{a}	42.1 ± 2.9 ^{a}	28.4 ± 1.9 ^{b}		20.0 ± 2.1 ^{c}
	Plant uptake (H)		171.4 ± 11.8 ^{a}	155.2 ± 12.4 ^{b}	168.5 ± 11.6 ^{a}		171.1 ± 12.1 ^{a}
	Total N output (O)		317.4 ± 20.1	308.1 ± 17.2	303.7 ± 18.6		312.4 ± 21.2
	N output − N input (Δ)		3.0	−6.3	−5.3		−2.4
	Relative error		0.95%	−2.04%	−1.75%		−0.77%

Table 7. *Cont.*

N Distribution (kg/ha)			**Treatments**	
	Experiment 3		**CON3**	**CUred**
Input	Mineral soil content prior to fertilization (A)		20.3 ± 1.0	20.3 ± 1.0
	Supplied by base fertilization (B)	soluble salt	75.0 ± 1.0 ^{b}	
		CU		150.0 ± 1.0 ^{a}
	Supplied by fertigation (C)		229.0 ± 17.5 ^{a}	79.0 ± 8.1 ^{b}
	Total N input (I)		324.3 ± 22.4 ^{a}	249.3 ± 23.1 ^{b}
Output	Mineral soil content after experiment (E)		122.9 ± 12.4 ^{a}	87.8 ± 8.8 ^{b}
	Residual in CU granules (F)			16.5 ± 1.8
	Leached (G)		60.8 ± 6.1 ^{a}	21.0 ± 2.2 ^{b}
	Plant uptake (H)		164.6 ± 15.4 ^{a}	156.9 ± 11.2 ^{b}
	Total N output (O)		348.3 ± 21.1 ^{a}	282.2 ± 17.5 ^{b}
	N output − N input (Δ)		24.0	32.9
	Relative error		6.89%	11.66%

Mean values ± standard deviation. For each parameter, different letters identify a significant difference ($p < 0.05$), according to Tukey test following one-way ANOVA. CON: conventional treatment; DMPP: treatment with stabilized fertilizer; CU: treatment with coated urea. I = A + B + C; O = E + F + G + H; Δ = O − I; Relative error = Δ/O.

Table 8. Nitrogen use efficiency indexes calculated from the data collected in the three experiments.

Fertilization Treatment	AE (g FW/g N)	PFP (g FW/g N)	REC (g N/g N)	PE (g FW/g N)
		Experiment 1		
CON1	306.7 ± 15.4	355.0 ± 20.3	0.54 ± 0.05 ^{b}	568.5 ± 31.9
DMPP20	333.9 ± 20.1	382.2 ± 22.2	0.58 ± 0.04 ^{a,b}	576.9 ± 40.2
CU20	303.1 ± 15.1	351.4 ± 21.5	0.57 ± 0.03 ^{b}	534.1 ± 35.1
CU40	323.9 ± 16.2	372.2 ± 26.4	0.59 ± 0.04 ^{a}	548.9 ± 21.3
CU75-1	325.3 ± 18.3	373.6 ± 25.1	0.61 ± 0.05 ^{a}	532.8 ± 19.2
		Experiment 2		
CON2	102.39 ± 8.6 ^{b}	134.3 ± 10.2 ^{b,c}	0.19 ± 0.02 ^{b,c}	537.7 ± 23.5
DMPP25	96.97 ± 5.9 ^{b}	128.9 ± 12.3 ^{c}	0.17 ± 0.02 ^{c}	568.2 ± 27.2
CU50	120.09 ± 12.5 ^{a}	152.6 ± 14.1 ^{a,b}	0.22 ± 0.03 ^{a,b}	544.9 ± 21.1
CU75-2	125.84 ± 10.6 ^{a}	157.7 ± 12.0 ^{a}	0.24 ± 0.04 ^{a}	515.0 ± 20.9
		Experiment 3		
CON3	114.8 ± 10.4 ^{b}	144.4 ± 16.1 ^{b}	0.21 ± 0.03 ^{b}	536.9 ± 21.5
CUred	163.3 ± 12.6 ^{a}	202.6 ± 20.1 ^{a}	0.31 ± 0.04 ^{a}	530.5 ± 20.1

Mean values ± standard deviation. For each index and each experiment, a different letter indicates a significant difference, according to Tukey test following one-way ANOVA ($p < 0.05$). Mean values without any letters are not significantly different. Y0: tomato yield; U0: nitrogen content in fruits; AE: agronomic efficiency; PFP: partial factor productivity; REC: Apparent recovery efficiency by difference; PE: physiological efficiency; FW: fresh weight; CON: conventional treatment; DMPP: treatment with stabilized fertilizer; CU: treatment with coated urea. The values of Y0 (kg FW/m^2) and U0 (g N/m^2)used for the calculations were, respectively 1.74 ± 0.11 and 1.73 ± 0.15 in Experiment 1; 1.00 ± 0.09 and 0.76 ± 0.08 in Experiment 2; 0.90 ± 0.07, and 0.65 ± 0.05 in Experiment 3.

Concerning the N balance (Table 7), the total N plant uptake was lower in CON1 than the other treatments. The coated fertilizer (CU40 or CU75-1) was able to reduce N leaching by about 55% or 80% as compared to the control. The same effect was observed also for the DMPP20 and CU20 treatments, although to a lower extent (about 24% reduction). The soil contained always more mineral N at the end of the experiment than at the beginning, especially with the CU treatments that decreased N loss by leaching. However, in all the treatments the N output was higher than the N supplied. The REC index was significantly higher with the CU40 and CU75-1 treatments than with the control, while no significant difference was observed for AE and PFP (Table 8).

In Experiment 2, the water balance for the DMPP25 treatment was similar to that of the control. In contrast, both CU treatments exhibited the highest leaching fraction and the lowest evapotranspiration. Moreover, the CU75-2 produced the highest water drainage (Table 4). The different fertilizers affected the distribution of both dry matter and N content among plant organs, although the dry biomass of the whole plants remained generally unchanged (Table 5). The best results for yield and fruit quality were obtained with the CU75-2 treatment (Table 6). With the CU fertilizer, the total N plant uptake resulted similar to that of the control, but higher than that of the DMPP25 treatment. In addition, the coated fertilizer reduced N leaching, determined higher values of all the agronomical indexes and, in contrast with the outcome of Experiment 1, resulted in a lower final content of mineral N in the soil compared with the other treatments. At the end of Experiment 2, about 14% ureic N was still retained by the coated fertilizer (Tables 7 and 8).

The analysis of the CU granules during and at the end of the growing period gave similar results in both Experiments 1 and 2 (Figure 1). The N release into the soil by the CU fertilizer was temperature- rather than time-dependent and the whole set of data was fitted by an exponential-type function of the cumulative daily average soil temperature (thermal sum, X) with excellent correlation ($r^2 = 0.99$, $n = 30$). Nevertheless, for N release values below 80%, the relationship could be well described ($r^2 = 0.95$; $n = 18$) by the linear function (data not shown):

$$\% \text{ N release} = 3 + 0.05203 \times X$$

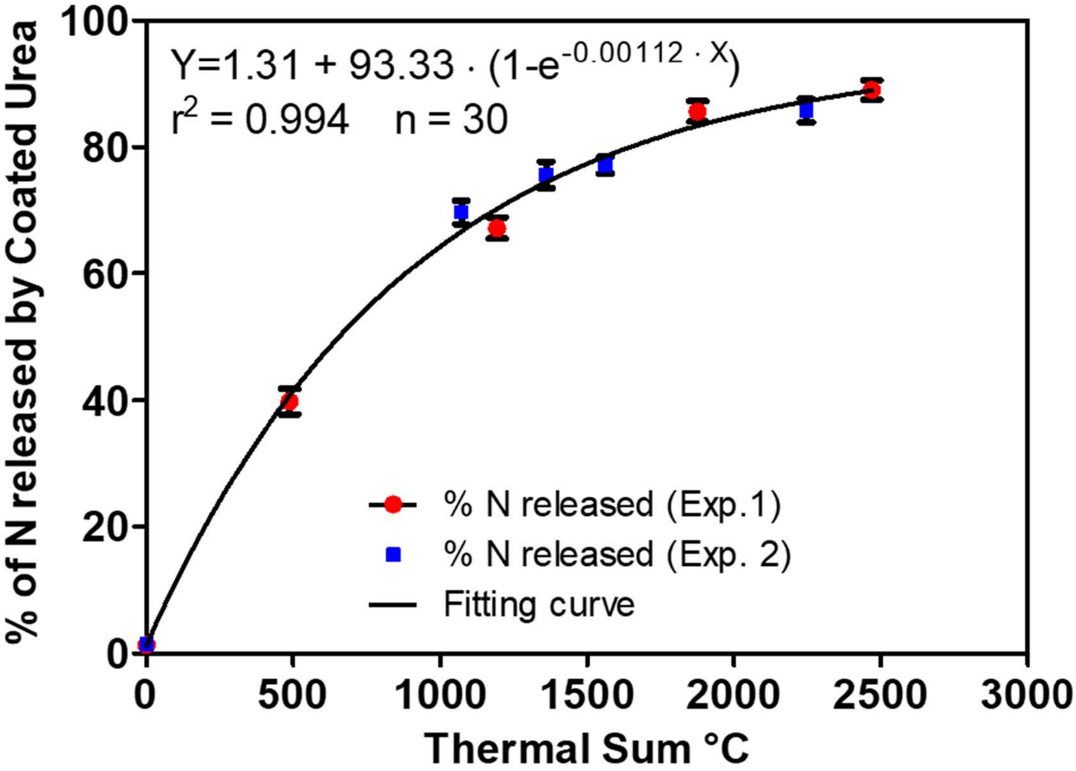

Figure 1. Percentage of N released by the granules of coated urea (CU) in Experiments 1 and 2, as a function of the cumulative daily average soil temperature (thermal sum).

In Experiment 3, the CUred treatment exhibited a similar water balance as the control (Table 4) and produced similar fruit biomass and yield, without affecting the quality parameters or the N content of the fruits (Tables 5 and 6). The amount of N leached was almost 3-fold lower with the coated fertilizer and a decrease was also observed in both plant N uptake and soil mineral N at the end of the experiment. The analysis of the CU granules recovered at the end of the trial revealed that 11% ureic N had not been released into the soil. As in Experiment 2, higher values of AE, PFP and PE indexes were obtained with the coated fertilizer (Table 8).

4. Discussion

All the treatments received the same amount of irrigation water, apart from low dissimilarities due to unavoidable inefficiencies in the irrigation system. The maximum differences in water supply were only 1.2% in Experiment 1, 3.0% in Experiment 2 and 1.5% in Experiment 3. Moreover, the leaching fraction was never lower than 13% (Table 4), which is indicative of a correct irrigation regime. With the only exception of the CUred treatment, all the treatments within the same experiment received the same total N amount.

4.1. Effect on the Crop (Yield and Quality)

Table 6 shows that in all the experiments the use of the DMPP fertilizer did not significantly affect the tomato yield compared with the control treatment. In contrast, both the CU40 and CU75-1 treatments in Experiment 1 improved the fruit amount and the CU75-2 treatment in Experiment 2 improved both the yield and the tomato quality. Although the differences were not always significant, at the highest urea doses we observed an increasing trend in all the parameters of fruit production in both Experiments 1 and 2. In each experiment, the different treatments did not affect the dry matter percentage of the fruits (Table 6) and the dry weight of the whole plants was also generally unaffected (Table 5). On the other hand, a different weight distribution among plant organs was observed with the different fertilizers; in Experiment 1, the leaf dry biomass was higher for the CON1 than for the high dose CU treatments, and the same behaviour was observed in Experiment 2, where also the N concentrations of leaf and stem tissues were higher for CON2 than for the CU75-2 treatment (Table 5). This outcome indicated a lower vegetative vigour for the CU-treated plants, which could be due to a reduced initial soil N availability and was consistent with a significantly lower evapotranspiration and a higher leaching fraction than those of the control and DMPP treatments (Table 4).

On the other hand, in Experiment 1 the application of coated urea at low concentration (CU20) produced a similar effect as DMPP20; although both treatments significantly lowered N leaching (Table 7), they determined an increase in leaf dry biomass and N concentration compared with CON1 (Table 5). Nitrogen is the main constituent responsible for vegetative growth and top dressing was initially applied as NH_4NO_3 with both treatments (Table 1). Hence, this outcome suggested that the plants vegetative behaviour was not effectively limited, due to a ready N availability in the root zone at the beginning of the growing period. In agreement with our findings, it was reported that in tomato high N levels increased plant vigour and delayed flower and fruit formation [38]. Similar results were reported also for different vegetable species, such as zucchini [39].

A limitation of plant vigour by the CU fertilizer was observed also in Experiments 2 and 3. Compared with CON2, the CU75-2 treatment increased both yield and fruit size and determined a similar N uptake; to a lesser extent, the same behaviour was observed also for the CU50 treatment, thereby suggesting that application of the coated fertilizer did not affect the plants ability to take up N from the soil. In Experiment 3, the reduction of the total N dose determined a strong decrease of N leaching compared with the control; thus, despite a slightly lower N uptake, the CUred treatment did not have any effect on the production (Tables 6 and 7).

4.2. N Use Efficiency and Agronomical Implications

In Experiment 1, all the values of the agronomical indexes were higher than the other trials, probably due to high light intensity conditions (approximately 5-fold higher than in Experiment 2) and high fruit yield during the spring season. In agreement with this outcome, [37,40] found that the REC index, which denotes the crop ability to absorb N from the soil, could be increased in processing tomato by good climatic conditions, since the crop could use more efficiently the N fertilizer available. Moreover, the lower ratio between crop N uptake and N supply that occurred in Experiments 2 and 3 could have contributed to reduce the NUE indexes as compared with Experiment 1. Several authors [37,41,42] reported that the NUE starts to decline when the N supply exceeds the crop N requirement. In all the experiments, the physiological index PE was not influenced by the type of fertilizer that was supplied to the plants (Table 8), indicating that the distinct treatments did not affect the physiological processes of N uptake and use. On the other hand, except for the CU20 treatment, in all the experiments the REC index was higher with CU than with the other fertilizers. A similar trend was observed in Experiments 2 and 3 for AE and PFP. The substantial increase of the agronomical indexes observed with the coated fertilizer can be explained by a higher fruit yield (Table 6), and in Experiment 3, by the reduction of the total N dose (Table 1). Several authors [7,43,44] reported NUE data for distinct vegetable cropping systems, either under greenhouse or in open-air conditions. With a fertilizer dose below 500 kg N/ha, the literature values of REC for greenhouse tomato ranged from 0.21 to 0.33 [7], which is in good agreement with those reported in Table 8 for Experiments 2 and 3. It was found that, along with yield and quality, the NUE was improved in potato fertilized with controlled release urea [45]. Similar results were obtained in wheat [46] and rice [47].

One possible drawback of CU application is the time gap between N release and N plant uptake [26,27]. Generally, the controlled release fertilizers are characterized by a release period, that is the time interval necessary for a fertilizer granule to release 80% of the inner nutrient at a fixed temperature (21 °C or 25 °C). Our study showed that the N release by the CU fertilizer was positively correlated with the cumulative daily average soil temperature (thermal sum) rather than with the time elapsed from transplanting both in spring and in autumn (Figure 1), despite the daily average temperature increased during the growing cycle in Experiment 1 and followed the opposite trend in Experiment 2. As expected, the crop development and the N uptake were also increased by higher temperatures in all the treatments. Therefore, the application of the CU fertilizer enabled us to effectively meet the plants nutritional needs, and our results demonstrated that the CU fertilizer could be used as the predominant N source, with simplification of the fertigation programs. However, to prevent a possible yield reduction due to calcium disorder (blossom-end rot), about 25–33% of the total N crop requirements should be beneficially satisfied by the application of calcium nitrate [48].

4.3. Effect on the Environment (N Leaching)

Compared with the conventional treatment, the use of DMPP fertilizer reduced N leaching only in Experiment 1 (Table 7), even though the nitrification inhibitor was expected to be less effective at higher temperature [49]. However, some authors [50] reported that the inhibiting efficiency of DMPP is modulated by several soil parameters acting simultaneously.

Both in Experiments 1 and 2, a lower evapotranspiration was observed for the high-dose CU treatments than for the other treatments. Because of similar irrigation, this was associated with higher values of water drainage and leaching fraction (Table 4). However, the CU treatments determined a lower N leaching (Table 7), in agreement with studies on several species, such as potato and corn [51], bell pepper [52] and rice [53]. This outcome suggested that CU application was effective in limiting N losses into drainage water. Following a similar trend with this result, a recent life cycle assessment (LCA) study on the impact of N fertilizers on the environment [8] reported the use of alternative coated N fertilizers as an effective strategy to reduce water pollution by eutrophication.

A reduced N loss by leaching with the CU fertilizer suggested the possibility to decrease the N dose commonly applied by growers. This hypothesis was tested in Experiment 3, where the CUred treatment employed -25% total N compared to the conventional fertilization. The data proved the effectiveness of the CU fertilizer, which enabled to decrease N leaching by about 65% (Table 7) without appreciable differences in tomato yield or quality (Table 6). Moreover, the results of Experiment 3 confirmed that with the CUred treatment, the combined effects of lower N supply and lower N loss allowed for the saving of considerable amounts of fertilizer, improving both economic costs and environmental impact. Specifically, in Experiment 3 the amount of fertilizer that could be saved with no influence on the production was up to 114.8 kg N/ha, that is about 30% of total N normally applied in tomato culture.

Concerning the N balance, our results showed that in Experiment 2, the plant growth was lower than expected, due to unexpectedly low light intensity in the autumn season (Table 2). In consequence, N input was higher than N output with both the stabilized and the coated fertilizer. On the other hand, both in Experiments 1 and 3, N input was always lower than N output, with a difference ranging from 24.0 to 43.4 kg N/ha. However, it is worth noting that the computation of N input reported in Table 7 did not include the N supply from soil organic matter mineralization during the growing period. This contribution could be estimated as 23 kg N/ ha in Experiment 1 and 21 kg N/ha in Experiment 3, based on literature data for mineral N release in different types of soils [54]. By adding the estimated amounts to the N input, the overestimation of N output resulted well below 5% for all the treatments.

5. Conclusions

This study confirmed the effectiveness of the CU fertilizer in reducing N leaching from the soil both in spring and autumn growing cycles. At the same time, the results showed that with CU application both tomato yield and quality were maintained or even improved compared with conventional or stabilized fertilizers. Therefore, the CU treatments could satisfy the plants N requirement, preventing at the same time excess concentration of the element in the root zone. This outcome is consistent with the expected performance of controlled-release fertilizers, which should match the nutritional needs of plants better than the soluble or stabilized fertilizers, by providing a gradual N release in the soil. In contrast, with both the CON and DMPP treatments, the high availability of soluble N in the soil promoted vegetative behaviour, with a consequent increase in water use and a possible blooming delay.

The experiments indicated that N leaching could be effectively decreased by increasing the percentage of coated fertilizer and that the decrease of N leaching ranged from 9 to 28% of total N applied.

Further work (specifically, a proper validation trial) is needed to extend the results obtained in the greenhouse to the open field growing conditions. The main outcome of this study was that the limitation of N losses achieved using the coated fertilizer enabled a reduction of N application by 25% as compared with the growers' practice, without detrimental effects on the tomato production.

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