agronomy

MDPI

Article

Comparing Soil vs. Foliar Nitrogen Supply of the Whole Fertilizer Dose in Common Wheat

Manuel Ferrari [1], Cristian Dal Cortivo [1], Anna Panozzo [1,*], Giuseppe Barion [1], Giovanna Visioli [2], Gianluigi Giannelli [2] and Teofilo Vamerali [1]

[1] Department of Agronomy, Food, Natural Resources, Animals and the Environment, University of Padua, 35020 Legnaro, Italy; manuel.ferrari@unipd.it (M.F.); cristian.dalcortivo@unipd.it (C.D.C.); giuseppe.barion@unipd.it (G.B.); teofilo.vamerali@unipd.it (T.V.)

[2] Department of Chemistry, Life Sciences and Environmental Sustainability, University of Parma, 43124 Parma, Italy; giovanna.visioli@unipr.it (G.V.); gianluigi.giannelli@unipr.it (G.G.)

* Correspondence: anna.panozzo@unipd.it

Citation: Ferrari, M.; Dal Cortivo, C.; Panozzo, A.; Barion, G.; Visioli, G.; Giannelli, G.; Vamerali, T. Comparing Soil vs. Foliar Nitrogen Supply of the Whole Fertilizer Dose in Common Wheat. *Agronomy* **2021**, *11*, 2138. https://doi.org/10.3390/agronomy11112138

Academic Editors: Krešimir Dvojković, Hrvoje Šarčević, Aleksandra Torbica and Daniela Horvat

Received: 1 October 2021
Accepted: 22 October 2021
Published: 26 October 2021

Abstract: Late-season N application through foliar spraying is recognized as an efficient agronomic practice for improving grain quality in common wheat, although the major part of N is still supplied by soil fertilization. This study assessed the impact of various N doses entirely applied by repeated foliar sprayings on wheat growth, yield and quality, in comparison with conventional soil fertilization management with a recommended dose of 160 kg N ha^{-1} as ammonium nitrate (C-M). Doses of 96, 104 and 120 kg N ha^{-1} as both UAN (urea-ammonium-nitrate) and urea applied by foliar spraying were evaluated in a 2-year field trial in Northern Italy in a silty loam soil with 1.7% organic matter. Here, it was demonstrated that the canopy greenness was similar in all treatments, with slight grain yield increases by the lowest foliar N dose vs. C-M. The higher N foliar doses mainly improved the grain protein content and both high- and low-molecular-weight glutenin subunits (HMW-GS, LMW-GS), particularly with urea. It is concluded that in our fertile soil, managing N fertilization exclusively through foliar spraying is feasible without compromising grain yield and ameliorating quality at the same time. Improved nutrient use efficiency and beneficial environmental effects are also expected by reducing the nitrogen load on the agricultural fields by 25–40%.

Keywords: ammonium nitrate; common wheat; foliar fertilization; gluten proteins; grain yield and quality; vegetational indexes; urea

1. Introduction

Foliar fertilization consists in the application—via spraying—of nutrients to the crop canopy, allowing their absorption by leaves and stems [1]. This agronomic practice was firstly applied in the early 1900s and mainly limited to micronutrient application in high-value horticultural crops such as potato and tomato [2]. However, in the last few years, it has become a standard practice for applying various nutrients in many crops [3].

Among several advantages, foliar fertilization is able to alleviate nutrient deficiency faster than soil application [2,4]. It can also be successfully used for both macro- and micronutrients, with large benefits for low-mobile elements in dry soils and with poor root growth [5–7]. Other benefits refer to the opportunity of combining the nutrient supply together with other agrochemicals such as herbicides, fungicides and insecticides, allowing labor, machinery and energy cost savings [8]. Following the high leaf absorption, improved fertilization efficiency and reduced nutrient losses are also expected, particularly with nitrogen [9].

In common wheat (*Triticum aestivum* L.), the application of nitrogen through foliar spraying is recognized as one of the most efficient agronomic tools to improve the grain protein content and the bread-making properties of flours [10–12]. However, the response of wheat depends on the fertilizer form, concentration and frequency of application, growth stage and leaf age, as well as other morphological and physiological traits [3]. As regards the chemical form, urea–ammonium nitrate (UAN), urea and ammonium sulfate (AS) are the most used in wheat [2].

Grain yield in small-grain cereals is the result of various components, such as plant density, tillering, number of spikelets per spike, number of kernels per spikelet and kernel weight. Such components are the result of the success of critical phenological stages, such as germination, tillering, stem elongation, anthesis, grain formation and filling [13]. Besides environmental conditions, the rate and timing of N applications are crucial for improving yield and grain protein content in wheat [14,15]. Early in the season, nitrogen availability stimulates the vegetative growth of wheat and enhances yields at the expense of protein accumulation in the grains. Conversely, N application at late growth stages has less influence on grain yield but better effects on grain protein accumulation [16,17]. As N is allocated faster to grains through leaf application [18], the practice of applying N solutions to the canopy is commonly used only late in the growing season, particularly at anthesis [19–21] or early milk [22], with the aim of improving flour quality and the bread-making properties [23].

Several studies have identified an optimal dose of approximately 30 kg N ha^{-1} to be used by foliar application for providing the best increase in the grain protein content [10,20]. Higher amounts, up to 60 kg N ha^{-1}, are possible, although severe leaf burning can occur under specific environmental conditions [22]. For these reasons, much of the research is focused on the effects of foliar N supply only late in the season, while very few studies have dealt with the use of foliar spraying to replace the main N dose conventionally applied to the soil by splitting it during the crop cycle [24].

Given this background, this study aimed at evaluating the effects of nitrogen fertilization supplied exclusively by foliar spraying in winter wheat, by comparing different N doses and in comparison with conventional soil fertilization. The trials were carried out across two growing seasons in Northern Italy, by comparing two types of liquid fertilizers, containing urea–ammonium nitrate (UAN) and urea, respectively. In order to minimize possible leaf phytotoxicity, the N dose was split into four applications over the spring time. Recorded parameters were: (i) normalized difference vegetation index (NDVI) and leaf chlorophyll content (as SPAD values) across the growing season; (ii) final grain yield and harvest index at harvest; and (iii) grain quality as highlighted by protein and gluten content, and gluten composition.

2. Materials and Methods

2.1. Field Trial Set-Up

The trials were conducted at the "Lucio Toniolo" experimental farm of the University of Padua at Legnaro (NE Italy, 45°21′ N, 11°58′ E, 12 m a.s.l.) during the 2018–2019 and 2019–2020 growing seasons. The soil was silty loam (fulvi-calcaric-cambisol; USDA classification) with pH 8.0, 1.7% organic matter, CEC of 11.4 cmol (+) kg^{-1} and a total N content of 1.1 g kg^{-1} (arable layer, beginning of experiment). The climatic data were provided by a meteorological station placed within the experimental farm and managed by the regional weather service center, ARPAV (Teolo, Padua, Italy).

In both years, the soil was ploughed to a depth of 0.3 m, incorporating the residues of the previous crop, and harrowed twice at 0.2 m. In order to minimize the effects of residual soil nitrogen availability on wheat growth, in both trials, sugar beet was the forecrop, receiving a low nitrogen dose during cultivation (~90 kg N ha^{-1}).

The experimental set-up consisted of a completely randomized block design with three replicates (n = 3); each plot measured 10 × 6 m (60-m^2) and included 24 wheat rows 12 cm apart. The wheat var. "Bologna" (SIS, Bologna, Italy) was sown in both trials, being a variety with high bread-making quality and one of the most widespread in Northern Italy.

In the first year, sowing took place on 22 October 2018, harvesting on 26 June 2019; in the second year, sowing took place on 28 October 2019 and harvesting on 22 June 2020, respectively. Chemical weed control was applied post-emergence with GRANSTAR®

ULTRA SX (dose 50 g ha^{-1}; a.i. thifensulfuron-methyl and tribenuron-methyl; FMC Agro Italia s.r.l.) at ZDS 32–33 (2nd–3rd node detectable). Protection against fungal diseases was ensured by two fungicide treatments, one at ZDS 37–39 (flag leaf visible) with KISHAR (dose 1 L ha^{-1}; a.i. azoxystrobin and cyproconazole; Comercial Química Massó, S.A.), and one at ZDS 65–69 (end flowering) with CARAMBA® (dose 1 L ha^{-1}; a.i. metconazole; BASF Italia s.p.a.). This last treatment was combined with the insecticide KARATE ZEON® (dose 1 L ha^{-1}; a.i. lambda-cyhalothrin; Syngenta Italia s.p.a.) in order to protect wheat against insects.

Three foliar N fertilization treatments (f) were compared with conventional soil fertilization, which was considered as a control (C-M, conventional management). Leaf application considered different amounts of N, i.e., 96, 104 and 120 kg N ha^{-1}, named F-96, F-104 and F-120, respectively, corresponding to a reduction of 40%, 35% and 25% compared with the conventional dose of 160 kg ha^{-1}.

After soil application of 32 kg N ha^{-1} at sowing in all the treatments, F-96 received the foliar application of 16 kg N ha^{-1} repeated 4 times during the crop cycle. F-104 and F-120 received an increased amount of N: 8, 16 and 32 kg N ha^{-1} in the first three applications, and the fourth at flowering 16 kg N ha^{-1} in F-104 and 32 kg N ha^{-1} in F-120 (see Table 1 for details).

Table 1. Dates and growth stages of N application (kg ha^{-1}).

Year	Date	Phenological Stage	Treatment								
			UAN					UREA			
			0N	C-M	F-96	F-104	F-120	C-M	F-96	F-104	F-120
2018–2019	20 October 2018	Pre-sowing	32 (s)	32 (s)	32 (s)	32 (s)	32 (s)	32 (s)	32 (s)	32 (s)	32 (s)
	25 February 2019	Tillering (ZDS 26)	-	58 (s)	16 (f)	8 (f)	8 (f)	58 (s)	16 (f)	8 (f)	8 (f)
	21 March 2019	Stem elongation (ZDS 37)	-	58 (s)	16 (f)	16 (f)	16 (f)	58 (s)	16 (f)	16 (f)	16 (f)
	24 April 2019	Booting (ZDS 40)	-	-	16 (f)	32 (f)	32 (f)	-	16 (f)	32 (f)	32 (f)
	7 May 2019	Flowering (ZDS 62)	-	12 (f)	16 (f)	16 (f)	32 (f)	12 (f)	16 (f)	16 (f)	32 (f)
2019–2020	22 October 2019	Pre-sowing	32 (s)	-	-	-	-	32 (s)	32 (s)	32 (s)	32 (s)
	25 February 2020	Tillering (ZDS 27)	-	-	-	-	-	58 (s)	16 (f)	8 (f)	8 (f)
	28 March 2020	Stem elongation (ZDS 37)	-	-	-	-	-	58 (s)	16 (f)	16 (f)	16 (f)
	24 April 2020	Booting (ZDS 40)	-	-	-	-	-	-	16 (f)	32 (f)	32 (f)
	7 May 2020	Flowering (ZDS 62)	-	-	-	-	-	12 (f)	16 (f)	16 (f)	32 (f)
Total N dose			32	160	96	104	120	160	96	104	120
N saving (%) vs. C-M treatment			80%	Ref.	40%	35%	25%	Ref.	40%	35%	25%

s = soil. C-M = conventional N management; F = foliar N spraying. ZDS: Zadok's Phenological Stage [25].

In the first year only, two different liquid fertilizers were compared, i.e., urea (dissolved in water) and urea–ammonium nitrate (UAN, liquid formulation). In the second year, only urea was used.

Results were compared with an absolute control receiving only 32 kg N ha^{-1} at sowing, and the conventional management C-M having two dress applications to the soil of granular ammonium nitrate (Table 1). Following the local practices, the control treatment C-M received the last application of N at flowering as foliar application with 12 kg N ha^{-1} as UAN or urea, for a proper comparison with foliar treatments with the two fertilizers.

Besides 32 kg N ha^{-1}, pre-sowing fertilization consisted of 96 kg ha^{-1} of P_2O_5 and 96 kg ha^{-1} of K_2O (as ternary fertilizer) incorporated into the soil through harrowing. No other P and K fertilizers were applied during the growing season.

As regards N fertilization, granular ammonium nitrate (27% N content) (NAC 27 N; Borealis L.A.T., Linz, Austria) was applied by hand in the conventional soil treatment C-M, while in foliar treatments, N was applied as urea (UREA 46 N; Borealis L.A.T., Linz, Austria) (solid urea dissolved in water at air temperature) and urea–ammonium nitrate (UAN, 26 % N, liquid formulation) (NSZ 26, Cifo, Bologna, Italy) (1st year). Both the fertilizers were applied through canopy spraying by using a computerized multi-sprayer plot bar IRP302 (Vignoli, Rovigo, Italy) with air induction XR flat spray nozzles (AIXR TeeJet®; TeeJet® Technologies, Springfield, IL, USA). The spraying volume was set at 430 L water ha^{-1}, with 3 bar pressure and tractor forward speed of 3 km/h to ensure adequate canopy wetting. Depending on the single N application dose, i.e., 8, 16 or 32 kg ha^{-1}, N concentration in water was 2%, 4% and 8% w/v, respectively.

2.2. Plant Analysis

Leaf chlorophyll content was indirectly revealed as SPAD (Soil and Plant Analysis Development) values, periodically collected from the beginning of stem elongation to the end of flowering with a SPAD 502 chlorophyll meter (Konica-Minolta, Hong Kong) on the last fully developed leaf (6 leaves randomly chosen per plot) at 15-day intervals throughout April and part of May in both years.

At the same time as the SPAD measurements, the Normalized Difference Vegetation Index (NDVI) of the canopy of each plot was monitored with an active handheld Greenseeker spectrometer (NTech Industries, Ukiah, CA, USA). The instrument reveals the canopy reflectance at wavelengths of 590 nm (refRED) and 880 nm (refNIR), providing a ratio value, as follows:

$$\mathrm{NDVI} = \frac{\mathrm{ref_{NIR}} - \mathrm{ref_{RED}}}{\mathrm{ref_{NIR}} + \mathrm{ref_{RED}}}$$

Additionally, shoot dry biomass was assessed at end flowering in both the growing seasons (21 May 2019; 7 May 2020), by weighting shoot biomasses of sampling areas after oven-drying (65 °C, 75 h).

2.3. Foliar Phytotoxicity

As nutrient solutions applied to plants may cause damage, defined as leaf “burning”, “scorching” or “tipping”, the possible leaf phytotoxicity was evaluated at 7 days after the last foliar application (flowering stage). Ten flag leaves of wheat were randomly taken from each plot and compared through a photographic survey, using a modified version of the method proposed by Philips and Mullins [26]. Here, data are provided for the 2nd year trial by calculating the fraction leaf length (generally the tip) with brown color.

2.4. Yield Parameters and Nitrogen Use Efficiency (NUE)

Final yield was assessed at maturity by collecting the grains in the central area of each plot (~40 m^2) by using a mini combine harvester (Wintersteiger, Ried, Austria). The harvest index (grain-to-total shoot weight ratio) was measured in a checking area of 1 m^2 in each plot, while N concentration in grain and straw was determined from these sample materials by the Kjeldahl method.

We also evaluated the thousand seed weight (TSW) by weighing 1000 kernel samples obtained from a counting machine (Numigral Seed Counter, Chopin Technologies, Villeneuve-la-Garenne, France), and the testing weight through Near-InfraRed Spectroscopy (NIRS) technology with Infratec-1241 instrumentation (Foss Analytical, Hillerød, Denmark).

Nitrogen use efficiency (NUE) and its two components (N-uptake efficiency, NUpE; N-utilization efficiency, NUtE) were calculated in accordance with Moll et al. [27]:

$$\mathrm{NUE} = \mathrm{NUpE} \times \mathrm{NUtE}$$

$$\frac{\mathrm{G_w}}{\mathrm{N_s}} = \frac{\mathrm{N_t}}{\mathrm{N_s}} \times \frac{\mathrm{G_w}}{\mathrm{N_t}}$$

G_w: grain weight (kg ha^{-1});
N_s: nitrogen supply (kg ha^{-1});
N_t: total plant nitrogen content at maturity (kg ha^{-1}).

2.5. Grain Quality

In the 2019–2020 trial, during the grain filling period from 28th May to harvest, 15 ears per plot were periodically collected and frozen at −18 °C. Subsequently, the ear samples were dried in an oven (65 °C, 48 h) and threshed with a small harvester in order to collect the kernels. Each sample was milled, and the flour analyzed for determining the N content (Kjeldahl method) and grain protein content in all the treatments. At harvest, the total grain protein content (GPC), the Zeleny index (sedimentation test) and wet gluten (at 14% humidity) were determined as main parameters for the assessment of the bread-making quality. GPC was calculated by multiplying the grain N content by 5.7, while the other parameters through Near-InfraRed Spectroscopy (NIRS) technology with Infratec-1241 instrumentation (Foss Analytical, Hillerød, Denmark).

For each treatment, the gluten protein quantification was obtained on 30 g grain samples (n = 3) gently milled with a Knifetec™ 1095 (Foss, Hillerød, Denmark), while gliadins, high-molecular-weight glutenin (HMW-GS) and low-molecular-weight glutenin subunits (LWM-GS) were extracted from refined flour following the procedure of Visioli et al. [6].

2.6. Statistical Analysis

The data from all the assessed parameters were subjected to ANOVA within Statgraphics Centurion XI software (Adalta, Arezzo, Italy). Separation of means was set at $p \leq 0.05$ with the Newman–Keuls test.

In the dataset of the 1st year, statistical analysis was performed within each fertilizer type (UAN and UREA) in order to identify the best treatment for each option.

A factorial discriminant analysis (MDA, Multigroup Discriminant Analysis with Wilks' lambda and Pillai's trace tests) and a principal component analysis (PCA) were also carried out in order to facilitate the interpretation of the large dataset from the trial. Multivariate data normality was preliminary verified by the Shapiro test. Before analysis, data were standardized by subtracting the mean and dividing the result by the standard deviation within each variable.

Correlation analysis among yield and grain quality parameters (GPC, wet gluten, testing weight, harvest index, TSW and Zeleny index) was carried out by calculating the Pearson correlation coefficients. The analyses were performed by MS Excel XLSTAT (Addinsoft, Paris, France).

3. Results

3.1. Climatic Conditions during the Trials

The climatic conditions in the two experimental seasons (2018–2019 and 2019–2020) had contrasting temperature and rainfall patterns (Figure S1). The temperature was higher than the 10-year average (1998–2019) during winter and early spring, particularly in the 2nd year. Compared to the historical mean, the average air temperature of the 1st year was lower in May (15 °C vs. 18 °C) and higher in June (25 °C vs. 22 °C); in the 2nd year, it was lower in June. As regards the precipitation, in the 1st year, high rainfall was recorded in October, and particularly in April (131 mm vs. 73) and May (201 mm vs. 91 mm). In the 2nd year, high rainfall was recorded in November and December, and particularly in June (143 mm). Wind and some lodging affected wheat in the 2nd year.

3.2. Effects on Vegetation Indices

The vegetational parameters, calculated as the seasonal average, did not show high variations related to N fertilization management during both years. In detail, in the 1st year, SPAD values decreased slightly ($p > 0.05$, n.s.) at any N dose applied by foliar spraying with both fertilizers, urea and UAN, compared with the control, C-M, except for significantly lower readings at F-96 with urea (−4% vs. C-M; $p \leq 0.05$). The same trend was observed in the 2nd year, with statistically significantly lower values in F-96 vs. F-104 (Table 2). Similarly, in the 1st year, NDVI under foliar treatments was slightly lower vs. C-M, although no statistically significant differences were revealed with both fertilizers. In the 2nd year, with urea as a foliar fertilizer, F-96 and F-120 had a significantly lower NDVI compared with C-M, being −8% and −5% vs. controls.

Table 2. Vegetational parameters: SPAD, NDVI (mean seasonal values from stem elongation to end flowering) and shoot dry weight (DW; g m^{-2}) at flowering (±S.E.; $n = 3$) in wheat plants under different foliar N fertilization treatments in a two-year field trial with UAN and urea as fertilizers. In brackets: % variation vs. each conventional management C-M. Letters: statistically significant differences among treatments within the same fertilizer (Newman–Keuls test, $p \leq 0.05$).

Year	Fertilizer	Treatment	SPAD		NDVI		Shoot DW (g m^{-2})	
2018–2019		0N	44.3 ± 1.17		0.745 ± 0.004		1359 ± 57.3	
	UAN	C-M	47.4 ± 1.01	a	0.770 ± 0.016	a	1319 ± 62.0	a
		F-96	45.7 ± 0.35	a (−4)	0.758 ± 0.021	a (−2)	1246 ± 30.6	a (−6)
		F-104	45.3 ± 0.90	a (−4)	0.736 ± 0.022	a (−4)	1414 ± 107.3	a (+7)
		F-120	46.8 ± 0.35	a (−1)	0.760 ± 0.012	a (−1)	1349 ± 73.8	a (+2)
	UREA	C-M	47.4 ± 0.29	a	0.782 ± 0.013	a	1410 ± 81.9	a
		F-96	45.7 ± 0.77	b (−4)	0.753 ± 0.019	a (−4)	1431 ± 86.3	a (+2)
		F-104	46.5 ± 0.19	ab (−2)	0.771 ± 0.017	a (−1)	1348 ± 36.1	a (−4)
		F-120	45.9 ± 0.61	ab (−3)	0.771 ± 0.010	a (−1)	1474 ± 66.7	a (+5)
2019–2020		0N	39.8 ± 1.65		0.690 ± 0.090		1371 ± 94.1	
	UREA	C-M	47.4 ± 0.16	ab	0.837 ± 0.005	a	1578 ± 188.3	a
		F-96	44.9 ± 0.37	b (−5)	0.774 ± 0.021	c (−8)	1479 ± 152.6	a (−6)
		F-104	47.6 ± 0.28	a (+1)	0.820 ± 0.007	ab (−2)	1512 ± 6.0	a (−4)
		F-120	46.4 ± 1.47	ab (−2)	0.793 ± 0.035	bc (−5)	1309 ± 66.8	a (−17)

At wheat flowering, shoot biomass was somewhat variable among N doses and fertilizer type, although no statistically significant differences were found in either year. In the 2nd year, biomass was lower than the 1st year, likely due to spring drought, with appreciable but not significant reductions by foliar treatments compared to C-M (Table 2).

3.3. Leaf Phytotoxicity

From the analysis of the flag leaf images of wheat at 7 days after the last foliar treatment (flowering) in the 1st-year trial (Figure S2), only slight burning symptoms were observable in the F-104 and F-120 treatments with both UAN and urea, while no injury was detected in the controls or the F-96 foliar treatment. On the contrary, in the 2nd year, damage was clearly noticeable in the leaf tips of sprayed plants, especially at medium and high N doses. The extent of leaf burning was considerable with the F-104 and F-120 treatments, with 21% and 26% of the leaf length burned, which were significantly higher compared to F-96 (9% of damage) and conventional management C-M (8% of damage) ($p \leq 0.05$) (Figure S3).

3.4. Grain Yield and Quality

At harvest, significant variations in productivity were detected among treatments. In the 1st year, with UAN, the medium foliar N dose (F-104) reached statistically higher productivity (6789 kg ha^{-1}) than the control C-M (+6%) and F-120 (+7%). Instead, with urea, the grain yield in F-96 and F-120 was higher than in the F-104 treatment, the latter achieving the lowest value (6193 kg ha^{-1}). In the 2nd year, results with urea were somewhat similar to the previous season as the three foliar treatments had a slight ($p > 0.05$) yield improvement, with the better increase (+11% vs. C-M, $p > 0.05$) with F-96 (Table 3).

Table 3. Productivity parameters: grain yield, harvest index (HI), thousand seed weight (TSW) and testing weight (mean ± S.E.; $n = 3$) in wheat plants under different foliar N fertilization treatments in a two-year field trial with UAN and urea as fertilizers. In brackets: % variation vs. each conventional management C-M. Letters: statistical comparisons among treatments within same fertilizer (Newman–Keuls test, $p \leq 0.05$).

Year	Fertilizer	Treatment	Yield DW (kg ha^{-1})		Harvest Index (%)		TSW (g)		Testing Weight (kg hL^{-1})	
2018–2019		0N	5570 ± 9.70		34.3 ± 0.51		28.9 ± 0.26		80.9 ± 0.73	
	UAN	C-M	6407 ± 76.5	b	35.7 ± 1.11	a	29.0 ± 0.69	a	80.5 ± 0.23	b
		F-96	6635 ± 107.1	ab (+4)	35.9 ± 0.83	a (+1)	28.8 ± 0.43	a (−1)	81.7 ± 0.38	ab (+1)
		F-104	6789 ± 76.2	a (+6)	36.8 ± 1.36	a (+3)	30.3 ± 1.26	a (+5)	82.4 ± 0.49	a (+2)
		F-120	6357 ± 121.2	b (−1)	33.7 ± 3.24	a (−6)	27.8 ± 2.39	a (−9)	80.6 ± 0.90	ab (=)
	UREA	C-M	6386 ± 41.7	ab	33.1 ± 0.96	a	27.7 ± 0.72	a	79.5 ± 0.19	b
		F-96	6527 ± 96.5	a (+2)	35.8 ± 0.69	a (+8)	29.4 ± 0.36	a (+6)	81.9 ± 0.36	a (+3)
		F-104	6193 ± 95.6	b (−3)	36.0 ± 1.47	a (+9)	29.1 ± 0.44	a (−1)	80.4 ± 0.69	b (+1)
		F-120	6524 ± 69.0	a (+2)	33.9 ± 0.62	a (+2)	28.9 ± 0.66	a (−1)	81.8 ± 0.31	a (+3)
2019–2020		0N	5914 ± 758.4		41.0 ± 1.69		35.5 ± 0.57		80.9 ± 0.56	
	UREA	C-M	6129 ± 436.0	a	39.9 ± 1.75	a	34.5 ± 0.51	a	82.5 ± 0.19	b
		F-96	6828 ± 286.8	a (+11)	44.7 ± 0.36	a (+12)	38.3 ± 0.64	a (+10)	83.2 ± 0.38	ab (+1)
		F-104	6214 ± 643.9	a (+1)	39.9 ± 3.72	a (=)	35.1 ± 2.77	a (+2)	82.8 ± 0.38	ab (=)
		F-120	6259 ± 287.7	a (+2)	41.3 ± 3.14	a (+3)	35.2 ± 1.51	a (+2)	83.8 ± 0.38	a (+1)

Harvest index was not affected by N management and doses, with slight increases reached by all the foliar thesis with both fertilizers, except for a small, non-significant reduction in F-120 with UAN (−6% vs. C-M) in the 1st year. In the 2nd year, again, minor increases were assigned to F-96 and F-120 (+12% and +3%, respectively), while F-104 was similar to the control C-M (Table 3). The HI was generally low with the wheat var. Bologna, ranging from 33.1% to 36%.

A similar response was detected for the TSW, as no significant variations were observed among N management (foliar vs. soil), doses and fertilizer type. The most relevant variation was a 10% increase with F-96 in the 2nd year with urea (Table 3). As regards the testing weight, it was generally improved by foliar N fertilization, although it was significant only for F-104 with UAN, F-96 with urea in the 1st year and F-120 with urea in both years (Table 3).

By comparing the two growing seasons, with urea as a foliar fertilizer, the parameters HI, TSW and testing weight were greater in the 2nd year, while it was the opposite for grain yield.

In the 2nd year with urea as a fertilizer, the dynamics of protein accumulation in grains were significantly affected by the treatments. The medium and the highest foliar N doses were similar, except for the first sampling date at 23 DAA (days after anthesis), and statistically higher compared to F-96 and the control C-M. These two latter had comparable protein content values in the first period, but C-M significantly increased from 30 DAA onwards. The absolute control 0N remained almost stable, with statistically lower values than all the other treatments. As a consequence, the final grain protein content (GPC) showed greater values in F-104 and F-120 (Figure 1).

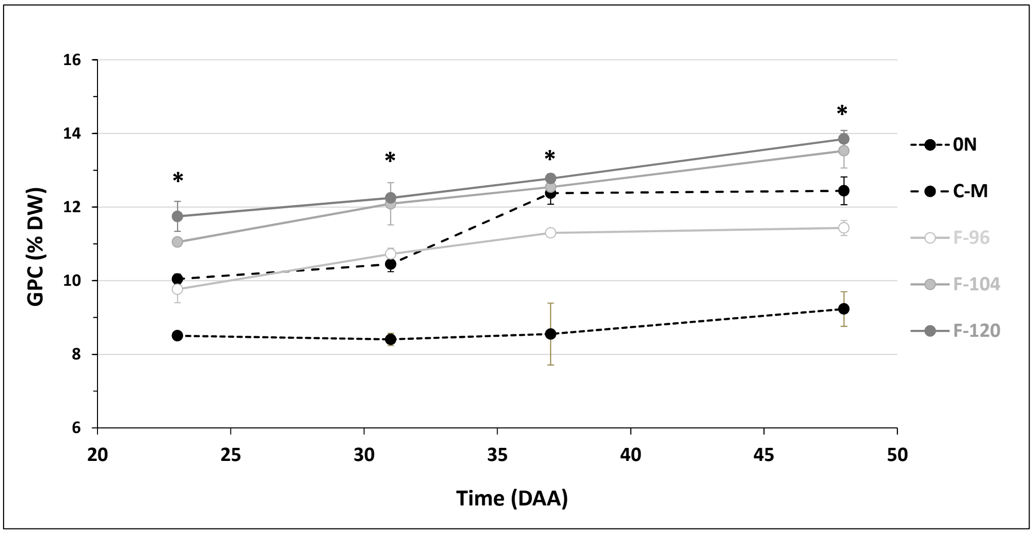


Figure 1. Dynamics of grain protein accumulation (GPC) (% ± S.E.; n = 3) in wheat over time (DAA, days after anthesis) under different foliar N fertilization treatments with urea (season 2019–2020) vs. control C-M. Asterisk (*): statistical significant differences among treatments (Newman–Keuls test, $p \leq 0.05$).

At harvest in the 1st year, no significant variations in the final GPC were detected among N treatments with UAN, whereas with urea, the treatments F-104 (14.7%) and F-120 (14.5%) were significantly higher than F-96 (13.2%) and slightly higher than controls ($p > 0.05$; n.s.). In the 2nd year with urea, F-120 had higher protein content (14.2%) compared to the other treatments, with a dose-dependent response (Table 4), thus confirming the trend of protein accumulation over the whole grain filling period.

The gluten content of grains followed the same trend of GPC. Interesting increases were found in the 1st year with F-120 with UAN (+6%) and F-104 with urea (+3%), while a moderate decrease was associated with F-96 regardless of the type of fertilizer. In the 2nd year with urea, F-104 and F-120 provided even better results (+12% and +16%, respectively; $p \leq 0.05$) (Table 4).

As regards the Zeleny index, the response was almost similar to the gluten content. In the 1st year, F-120 showed the highest increase in this index with UAN (+13% vs. C-M), and F-104 with urea (+10% vs. C-M; $p > 0.05$), while F-96 was significantly lower. In the 2nd year, F-120 with urea showed the highest improvement (+41% vs. C-M) (Table 4).

Table 4. Grain quality parameters: grain protein content (GPC), Zeleny index and wet gluten content (mean ± S.E.; $n = 3$) in *Triticum aestivum* L. under different foliar N fertilization treatments in a two-year field trial with UAN and urea fertilizers. In brackets: % variation vs. each conventional management C-M. Letters: statistical comparisons among treatments within same fertilizer (Newman–Keuls test, $p \leq 0.05$).

Year	Fertilizer	Treatment	GPC (%)		Zeleny Index (%)		Wet Gluten (%)	
2018–2019		0N	11.4 ± 0.53		33.5 ± 2.12		27.6 ± 1.31	
	UAN	C-M	14.0 ± 0.64	a	42.8 ± 5.88	a	31.4 ± 1.68	ab
		F-96	13.1 ± 0.37	a (−6)	35.9 ± 2.40	a (−16)	29.4 ± 0.80	b (−6)
		F-104	13.4 ± 0.26	a (−4)	37.9 ± 3.29	a (−11)	30.0 ± 0.61	ab (−4)
		F-120	14.5 ± 0.45	a (+4)	48.3 ± 3.40	a (+13)	33.3 ± 1.13	a (+6)
	UREA	C-M	14.3 ± 0.61	ab	44.9 ± 5.28	ab	32.5 ± 1.56	ab
		F-96	13.2 ± 0.44	b (−8)	36.7 ± 4.39	b (−18)	30.0 ± 1.10	b (−8)
		F-104	14.7 ± 0.32	a (+3)	49.2 ± 1.50	a (+10)	33.4 ± 0.61	a (+3)
		F-120	14.5 ± 0.19	ab (+1)	48.6 ± 0.80	a (+8)	32.8 ± 0.54	ab (+1)
2019–2020		0N	9.9 ± 0.41		21.6 ± 2.66		15.8 ± 0.96	
	UREA	C-M	13.2 ± 0.33	b	32.9 ± 2.66	bc	26.8 ± 1.19	b
		F-96	12.0 ± 0.15	c (−9)	29.1 ± 1.02	c (−12)	23.3 ± 0.48	c (−13)
		F-104	13.9 ± 0.35	ab (+6)	40.4 ± 5.34	ab (+23)	30.0 ± 1.27	a (+12)
		F-120	14.2 ± 0.13	a (+8)	46.3 ± 0.69	a (+41)	31.0 ± 0.23	a (+16)

Correlation analysis did not reveal significant correlations among yield and quality parameters. As expected, the main statistically positive correlation was found between GPC and wet gluten ($r = 0.97$) and the Zeleny index ($r = 0.94$). On the contrary, significant negative correlations were detected between GPC and harvest index and TSW ($r = -0.49$ and -0.50, respectively) (Table S1).

As a general observation, gluten composition was highly responsive to the N dose applied though foliar spraying, and urea allowed us to achieve better content of gluten proteins compared to UAN.

With UAN as a fertilizer, HMW-GS were significantly increased (+30%; $p \leq 0.05$) by the highest foliar N dose (120 kg ha^{-1}). Instead, with urea, no statistically significant variations were found among treatments in both years, with only slight increases in F-104 and F-120 vs. C-M (Figure 2A). The opposite response was observed for the LMW-GS content: no differences among treatments ($p > 0.05$) with UAN, and great variations with urea. In the 1st year with urea, F-120 significantly improved LMW-GS by 8% vs. C-M, and even more in the 2nd year with F-104 and F-120 (+35% and +3%, respectively) (Figure 2B).

As a consequence, total glutenins were significantly increased in F-120 with UAN (+14% vs. C-M), and in F-104 with urea in the 2nd year (+30% vs. C-M) (Figure 2C), with foliar fertilization being generally more effective than soil fertilization.

Responses in the total gliadin content were appreciable only with urea as a foliar fertilizer, particularly at medium–high N doses: increases ranged from 8% to 12% with F-104 and from 12% to 13% with F-120, depending on the year considered (Figure 2D). This led to almost a similar trend in the glutenins-to-gliadins ratio, which was slightly improved with urea and even with UAN at F-120 (Figure 2E).

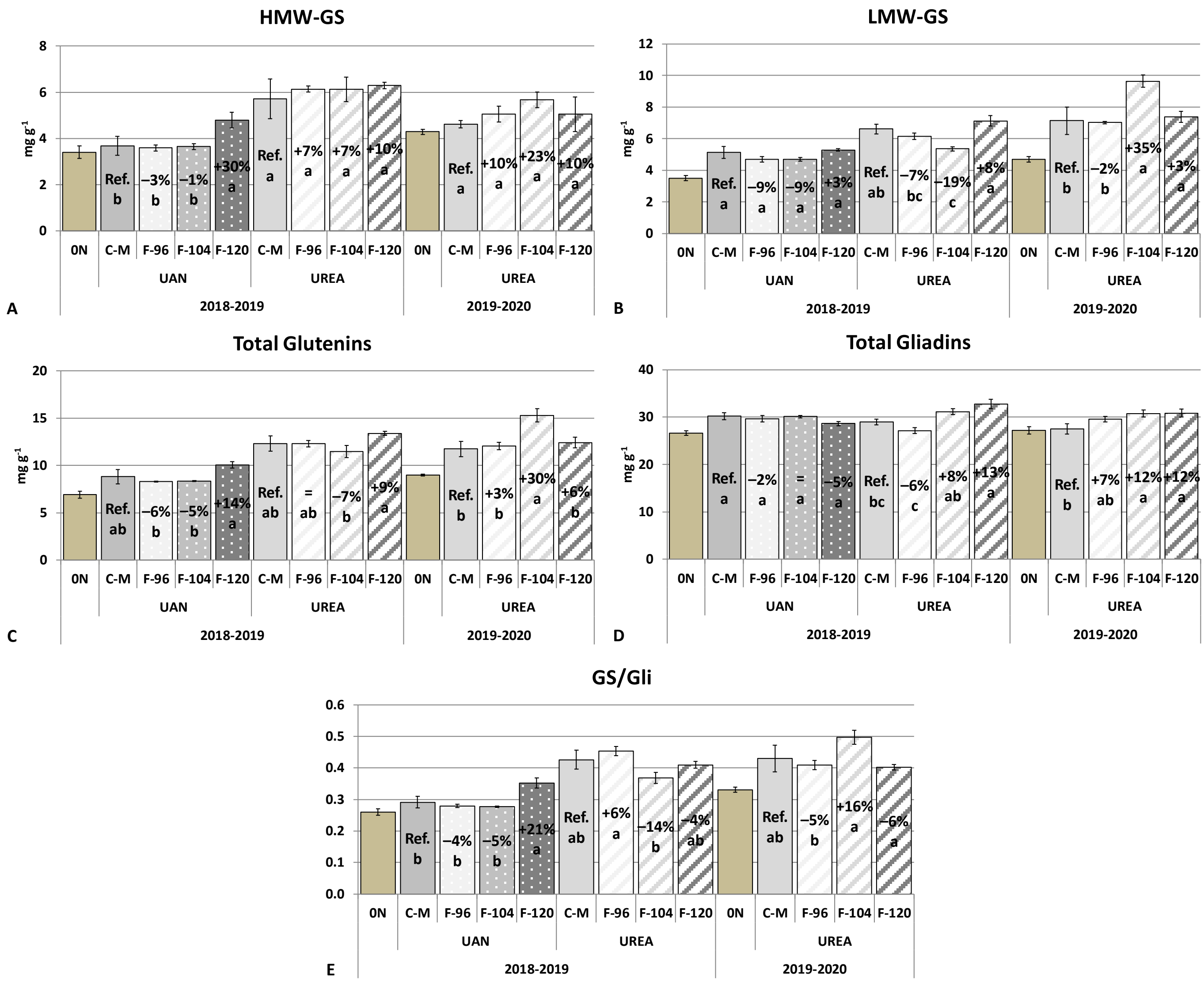


Figure 2. High-molecular-weight glutenins (HMW-GS) (**A**), low-molecular-weight glutenins (LMW-GS) (**B**), total glutenins (**C**), total gliadins (**D**) and gliadins-to-glutenins ratio (**E**) (mg g^{-1} ± S.E.; *n* = 3) in wheat grains under different foliar N fertilization treatments in a two-year field trial with UAN and urea as fertilizers. Percentages: variation vs. each conventional management C-M (Ref.). Letters: statistical comparisons among treatments within the same fertilizer (Newman–Keuls test, $p \leq 0.05$).

3.5. Nitrogen Uptake and NUE

At harvest, nitrogen accumulation followed a similar trend among treatments in both straw and grain samples. With UAN as a fertilizer, no significant variations were detected among the thesis, despite an appreciable increase with F-120 (+26% and +9% in straw and grain, respectively). On the contrary, foliar urea led to a general decrease in N straw concentration, which was often accompanied by an increase in grain N concentration in both years, particularly in the 2nd year (Figure 3).

As expected, nitrogen use efficiency improved as the N dose was reduced. Regardless of the fertilizer chosen, the best treatment was F-96 with ~70 kg grains kg^{-1} N applied, which significantly improved compared to the control C-M. Of the two components, NUE increases were mainly related to N-uptake efficiency (NUpE) improvements, this index significantly improving with foliar spraying at any N dose. N utilization efficiency (NUtE) was relatively stable, with slightly better values at high foliar N doses (Table 5).

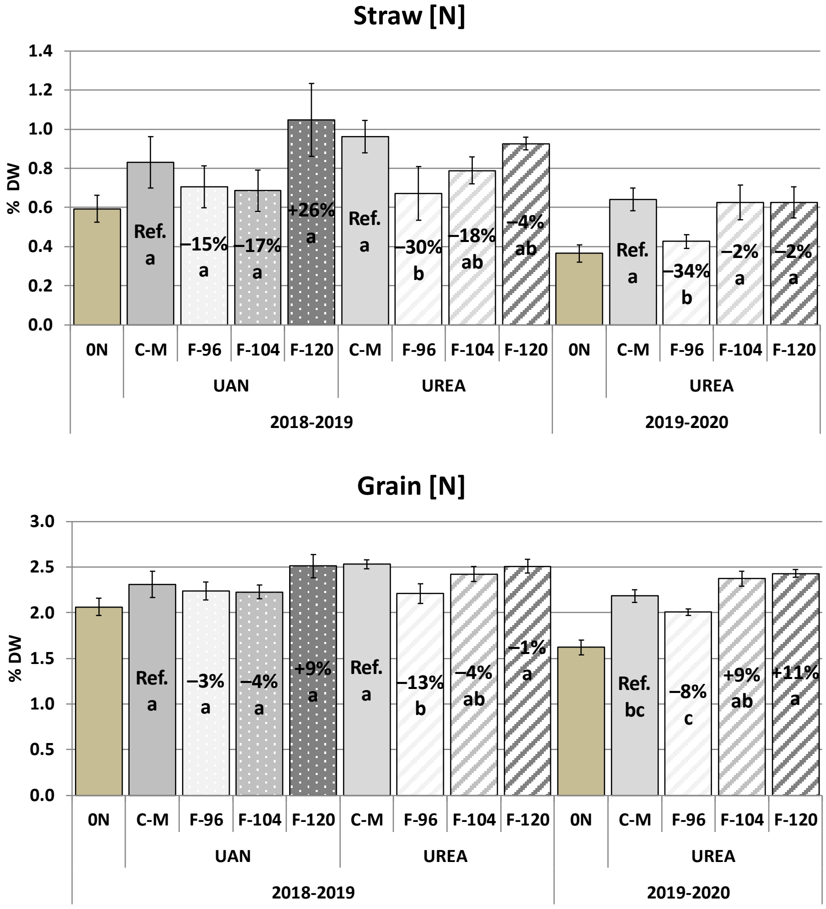


Figure 3. Nitrogen concentration in straw and grains at harvest (% DW ± SE; n = 3) of wheat under different foliar N fertilization treatments in a two-year field trial with UAN and urea as fertilizers. Percentages: variation vs. each conventional management C-M (Ref.). Letters: statistical comparisons among treatments within the same fertilizer (Newman–Keuls test, $p \leq 0.05$).

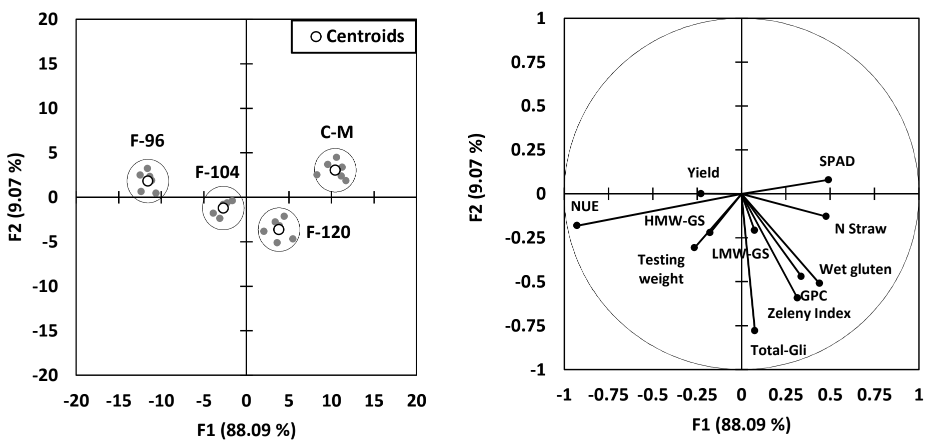
Table 5. N use efficiency (NUE), N uptake efficiency (NUpE) and N utilization efficiency (NUtE) (± S.E.; n = 3) in wheat under different foliar N fertilization treatments in a two-year field trial with UAN and urea as fertilizers. In brackets: % variation vs. each conventional management C-M. Letters: statistical comparisons among treatments within same fertilizer (Newman–Keuls test, $p \leq 0.05$).

Year	Fertilizer	Treatment	N Use Efficiency NUE kg Grains/kg N-Applied		N Uptake Efficiency (NUpE) kg N-Uptake/kg N-Applied		N Utilization Efficiency (NUtE) kg Grain/kg N-Uptake	
2018–2019	UAN	C-M	40.0 ± 0.48	d	1.39 ± 0.17	b	29.8 ± 3.64	ab
		F-96	69.1 ± 1.12	a (+73)	2.81 ± 0.19	a (+103)	24.8 ± 1.40	b (−17)
		F-104	65.3 ± 0.73	b (+63)	1.76 ± 0.18	b (+27)	37.9 ± 4.15	a (+27)
		F-120	53.0 ± 1.01	c (+32)	1.42 ± 0.14	b (+2)	38.3 ± 4.31	a (+29)
	UREA	C-M	39.9 ± 0.26	d	1.15 ± 0.15	b	35.8 ± 4.50	a
		F-96	68.0 ± 1.01	a (+70)	2.46 ± 0.04	a (+113)	27.7 ± 0.83	a (−23)
		F-104	59.6 ± 0.92	b (+49)	2.38 ± 0.49	a (+107)	27.3 ± 5.94	a (−24)
		F-120	54.4 ± 0.58	c (+36)	2.00 ± 0.14	ab (+74)	27.5 ± 1.91	a (−23)
2019–2020	UREA	C-M	38.3 ± 4.7	c	1.49 ± 0.18	b	26.1 ± 1.55	b
		F-96	71.1 ± 5.2	a (+86)	2.10 ± 0.31	ab (+41)	34.8 ± 3.32	a (+34)
		F-104	59.8 ± 10.7	ab (+56)	2.35 ± 0.20	a (+58)	25.8 ± 3.50	b (−1)
		F-120	52.2 ± 4.2	b (+36)	1.78 ± 0.11	ab (+19)	29.4 ± 0.51	ab (+13)

3.6. Principal Component Analysis (PCA) and Discriminant Analysis (DA)

PCA was performed within each fertilizer type database. With UAN, PCA identified two synthetic variables, which explained an overall variability of 99.97%, mostly attributed to the first one (F1 = 98.98%) (Figure S4). In this way, relevant variables (loadings > |0.4|) were SPAD, yield, testing weight, LMW glutenins and NUE. Following the vector direction of each variable, good correlations were established among variables plotted very close together in the graph quadrants, i.e., SPAD, GPC, wet gluten, HMW-GS, LMW-GS, Zeleny index and nitrogen content in the straw, and among yield, testing weight and NUE. Centroid positions and cluster separation in MDA summarized wheat response to different N fertilization strategies. The groups were well separated, suggesting that high N doses (conventional management included) allowed clusters to shift towards an improvement in grain quality, whereas the reduction in N dosage was related to reduced quality and improved productivity and NUE.

Considering the 2-year dataset with urea as a fertilizer, the two synthetic variables identified by PCA explained 88.09% and 9.07% of the overall variability, for F1 and F2, respectively (Figure 4). Relevant variables (loadings > |0.4|) assigned to F1 were again SPAD and NUE, and additionally GPC and straw N content. Similarly to UAN, high N doses (treatments C-M and F-120) allowed us to significantly increase the parameters related to N metabolism (i.e., SPAD, GPC, straw N content), while reduced doses to improve NUE.



Variables	F1	F2
SPAD	**0.491**	0.080
Yield	-0.228	0.001
Testing weight	-0.265	-0.307
GPC	**0.440**	**-0.510**
Zeleny Index	0.315	**-0.592**
Wet gluten	0.337	**-0.470**
N (%) Straw	**0.478**	-0.129
NUE	**-0.928**	-0.181
HMW-GS	-0.177	-0.221
LMW-GS	0.074	-0.208
Total-Gli	0.075	**-0.779**

Figure 4. Principal component analysis (PCA; top right) with variable loadings (in bold > |0.4|; bottom) and multigroup discriminant analysis (MDA; top left) in wheat under different N fertilization treatments with urea as foliar fertilizer in two years. In MDA, circles contain 100% of cases.

4. Discussion

Late-season foliar N fertilization is receiving increasing interest for improving grain protein content and flour quality in common wheat as well as semolina of durum wheat [6]. The increased impact of spring drought, with reduced nutrient uptake from the soil, and the need to improve the sustainability of wheat cultivation suggests the need to verify the possibility of entirely replacing soil N fertilization with foliar supply. The proper implementation of such management requires the investigation of the effects of different N doses, both as total amount and individual application, by taking into account possible leaf phytotoxicity. At our latitude, the heading/flowering phase of wheat is expected to occur late in spring, roughly at the beginning of May. Despite contrasting weather conditions during grain filling, with high precipitation in May of the 1st year and June of the 2nd year, poor precipitation in winter and early spring characterized both the growing seasons. This climatic pattern, despite some contrasting effects on plant and grain features (i.e., TSW and harvest index) between the two years, was a strength in our study, as foliar application can alleviate nutrient deficiency better than soil application due to poor soil moisture, providing robust information on the feasibility of this management type in real critical conditions. Indeed, the four applications of foliar N occurred during a relatively dry period, particularly in the 2nd year, while contrasting climatic conditions were recorded between the two seasons from flowering onwards. Patterns in rainfall and temperature are recognized to highly impact N management in wheat, as reported by Tedone et al. [28].

Despite the higher efficiency compared to soil fertilization, in this study, foliar N application at reduced dosages only seldom worsened the canopy greenness. Our results also indicate that reduced N doses sprayed on the canopy, although slightly altering leaf chlorophyll content and possibly photosynthesis compared to soil application, did not compromise the final yield and grain quality, similarly to what was previously reported by other authors [22,29].

Attention in leaf fertilization should be directed towards the amount of N per individual application in order to avoid any shoot/leaf phytotoxicity. Negligeable leaf injuries were recorded during the 1st year after the last spraying at flowering at any N dose, while marked leaf burning was detected in the 2nd year, particularly with the highest dose of 32 kg N ha^{-1} (treatment F-120), probably due to the higher air temperature in May 2020 (+3 °C vs. May 2019). This confirms the relevant role of climatic conditions and previous observations on possible leaf impairments [3,8]. However, damage of the flag leaf tips seems to be well tolerated by wheat, as confirmed by the appreciable yield and grain quality improvements reached by all foliar treatments, regardless of the fertilizer choice between UAN and urea. This is in agreement with the findings of several authors [11,24,26], while other studies [15,30] reported a higher threshold, i.e., 40 kg ha^{-1} as a single application between stages ZDS 39 (flag leaf visible) and ZDS 73 (early milk development), without compromising productivity.

In our study, many agronomic parameters, such as yield, harvest index and TSW, were preserved under low N doses supplied by foliar spraying, suggesting that this approach to fertilization in wheat is feasible, as indicated by the previous literature [24,31]. Our experimental soil had a relatively good fertility, with 0.11% N and 1.7% organic matter, which could have prevented a correct evaluation of N shortage compared to common practice. However, we exclude this possibility, as the grain yield of the absolute control 0N, although appreciable in both years, was accompanied by compromised SPAD and NDVI, together with other parameters related to N metabolism, thus highlighting the detrimental conditions due to N deficiency. The small variations among different N doses for the vegetational indexes and various agronomic parameters were somewhat unexpected in this research. Some studies found significant variations in productivity among various foliar treatments [29], although yield response is highly variable, depending on fertilization timing and environmental conditions [8,32].

Some authors reported increased grain protein content (GPC) under raising temperatures [33,34], and this is in agreement with our results in the 1st year, with a hotter June during seed filling. However, the most interesting result was a stimulation in GPC and gluten content, together with an amelioration of gluten composition (increased HMW- and LMW-GS) by N fertilization exclusively by foliar spraying, as found by Rossmann et al. [23]. The most recent studies agree in assigning to foliar fertilization timing an essential role, as late-season supply, between booting and heading, is more efficient in increasing GPC and bread-making properties than early applications, as occurred in our F-120 treatment [11,14,35]. In this regard, it is thought that early foliar application can stimulate leaf metabolism and its role as a sink, whereas, after pollination, the absorbed N is mainly redirected to the growing kernels. We also suggest that small amounts of foliar nitrogen at heading, as in our F-96 treatment, are insufficient to significantly improve grain quality, probably due a moderate cumulated deficiency from previous growth stages [23,36].

In this way, it is advisable to set up a foliar fertilization protocol with increasing rates over the growing season in order to sustain the increasing N demand of the crop and reach adequate standard quality of the flour. This also serves to delay leaf senescence and extend the duration of the grain filling period [37].

Compared to soil applications, where nitrogen is solubilized in the soil water solution and intercepted by plant roots, benefits of foliar fertilization are linked to high absorption efficiency and mobility across plant tissues. High grain N generally derives from retranslocation from leaves rather than new uptake. When the N requirements of developing kernels exceed the supply capacity of roots, the resulting N deficit triggers leaf protein catabolism and the transfer of the resulting nitrogen to the seeds [38], and this was observed in our foliar treatments, as highlighted by the lower N content in straw at harvest.

From an environmental point of view, foliar fertilization is expected to increase NUE greatly, and this was confirmed in our study, with a decreasing hierarchy among treatments as the amount of nitrogen increased. The best treatment was F-96, with 68–71.1 kg of grains per kg of supplied N, while the net productivity of N supplied with the conventional soil fertilization was very low. This result mainly depended on improvements in N uptake efficiency, although there was seldom an increase in N utilization efficiency, as in the 2nd year with F-96 and urea as a fertilizer. We preliminarily ascertained that the fraction of liquid N fertilizer retained by the wheat canopy at common irroration volumes (~400 L ha^{-1}) ranged from 50% (tillering) to 95% (flowering stage). As a consequence, the overall N leaf retention was estimated to be generally very high, 76%, 82% and 85% in F-96, F-104 and F-120, respectively. Great environmental benefits are therefore expected by managing the whole N fertilization by foliar applications.

As regards the two fertilizers, i.e., UAN and urea, many agronomic and qualitative parameters of the grains were better improved with urea compared to UAN. We suspect that a prevailing assimilation of nitrates and ammonium compared with urea may occur within leaves, as they act mainly as sinks. However, it cannot be excluded that urea can be absorbed by leaves better than ammonium nitrate as a consequence of the higher permeability of the leaf cuticle to urea (10 to 20 times) compared to inorganic ions [3,39]. However, other authors reported no variations in GPC and quality related to the fertilizer choice, with changes in gluten composition mainly affected by fertilization timing and methods [37].

From an economic point of view, the foliar fertilization protocol here proposed required one additional application compared to local conventional soil fertilization management, as the others can be combined with agrochemical applications (e.g., herbicides, fungicides and insecticides), with only slightly higher application costs [36]. A bottleneck to the broad introduction of this technique could be represented by the higher cost of the liquid nitrogen form, which is 4–5 times higher than solid granular fertilizers. However, this can be mitigated by preparing nutrient solutions directly on the farm using technical urea with low biuret content. In any case, the higher economic costs associated with foliar fertilization could be compensated by agronomic advantages under dry periods, and environmental benefits linked to reduced N leaching under high rainfall.

5. Conclusions

Foliar N fertilization with reduced doses has the potential to maintain high yield and quality standards in common wheat, the performance being comparable with conventional soil fertilization with granular fertilizers or even slightly higher in our specific environment with a fertile soil. The small amount of N reaching the soil with foliar fertilization sustains high N absorption and use efficiency by wheat. It would also be expected to lead to improvements in the bread-making properties of flour, related to the better grain protein content and amelioration of gluten composition, depending on the N dose. It is concluded that the implementation of a fertilization protocol based exclusively on foliar applications should consider an increasing dose of N as the growing stages proceed, using preferentially urea as a fertilizer. While weather conditions may moderately affect the agronomic results, relevant beneficial environmental effects are expected by reducing the nitrogen load on the fields by 25–40%. There surely is large scope for optimizing the foliar fertilization protocol, by considering further growing seasons and climatic conditions, as well as various soil conditions and crop management strategies (e.g., forecrop, soil tillage, variety choice).

Supplementary Materials: The following are available online at https://www.mdpi.com/article/10.3390/agronomy11112138/s1. Figure S1: Monthly mean temperatures (A) and precipitation (B) across the two growing cycles of wheat at the experimental farm of the University of Padua (Legnaro, Italy). Figure S2: Photographic survey on 10 flag leaves randomly taken from each thesis at 7 days after the last N foliar application (flowering stage) during the 1st year (14 May 2019) (A) and 2nd year (13 May 2021) (B) trial. Figure S3: Fraction of burned leaf length (% $\pm$ S.E.; n = 3) in wheat under different foliar N fertilizations in 2019–2020 (2nd year) with leaf spraying (F) at various N doses supplied as urea. Inside bars: % variation vs. conventional management C-M. Letters: significant differences among treatments (Newman–Keuls test, $p \leq 0.05$). Figure S4: Principal component analysis (PCA, top right) with variable loadings (in bold > $|0.4|$); bottom) and multigroup discriminant analysis (MDA; top left) under different N fertilization treatments with UAN as foliar fertilizer. In MDA, circles contain 100% of cases. Table S1: Pearson correlation coefficients among yield and quality parameters in wheat under different foliar N fertilization treatments and conventional soil fertilization in a two-year field trial with UAN and urea as fertilizers.

Author Contributions: Conceptualization, T.V.; methodology, T.V., M.F., C.D.C., G.V. and G.G.; software, M.F., C.D.C. and G.B.; validation, T.V. and M.F.; formal analysis, M.F. and C.D.C.; investigation, M.F. and C.D.C.; resources, T.V.; data curation, M.F., C.D.C. and A.P.; writing—original draft preparation, M.F.; writing—review and editing, C.D.C., T.V. and A.P.; visualization, T.V.; supervision, T.V.; project administration, T.V.; funding acquisition, T.V. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by East Balt Italy S.R.L. with the project "Application of foliar fertilization and precision fertilization techniques in common wheat".

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: The data presented in this study are available on request from the corresponding author.

Acknowledgments: The authors wish to thank Adriano Massignan and Diego Rossi for helping with data collection.

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

References

1. Kuepper, G. *Foliar Fertilization*; NCAT Agriculture Specialist; ATTRA Publication# CT13; Academia: San Francisco, CA, USA, 2013.
2. Fageria, N.K.; Filho, M.B.; Moreira, A.; Guimarães, C.M. Foliar Fertilization of Crop Plants. *J. Plant Nutr.* **2009**, *32*, 1044–1064. [CrossRef]
3. Fernández, V.; Sotiropoulos, T.; Brown, P. *Foliar Fertilization: Scientific Principles and Field Practices*, 1st ed.; International Fertilizer Industry Association (IFA): Paris, France, 2013.
4. Niu, J.; Liu, C.; Huang, M.; Liu, K.; Yan, D. Effects of Foliar Fertilization: A Review of Current Status and Future Perspectives. *J. Soil Sci. Plant Nutr.* **2021**, *21*, 104–118. [CrossRef]
5. Alshaal, T.; El-Ramady, H. Foliar application: From plant nutrition to biofortification. *Environ. Biodivers. Soil Secur.* **2017**, *1*, 71–83. [CrossRef]
6. Visioli, G.; Bonas, U.; Dal Cortivo, C.; Pasini, G.; Marmiroli, N.; Mosca, G.; Vamerali, T. Variations in yield and gluten proteins in durum wheat varieties under late-season foliar versus soil application of nitrogen fertilizer in a northern Mediterranean environment. *J. Sci. Food Agric.* **2018**, *98*, 2360–2369. [CrossRef] [PubMed]
7. Barraclough, P.B.; Haynes, J. The effect of foliar supplements of potassium nitrate and urea on the yield of winter wheat. *Nutr. Cycl. Agroecosyst.* **1996**, *44*, 217–223. [CrossRef]
8. Gooding, M.; Davies, W.P. Foliar urea fertilization of cereals: A review. *Nutr. Cycl. Agroecosyst.* **1992**, *32*, 209–222. [CrossRef]
9. Abad, A.; Lloveras, J.; Michelena, A. Nitrogen fertilization and foliar urea effects on durum wheat yield and quality and on residual soil nitrate in irrigated Mediterranean conditions. *Field Crop. Res.* **2004**, *87*, 257–269. [CrossRef]
10. Bly, G.A.; Woodard, H.J. Foliar nitrogen application timing influence on grain yield and protein concentration of hard red winter and spring wheat. *Agron. J.* **2003**, *95*, 335–338. [CrossRef]
11. Woolfolk, C.W.; Raun, W.R.; Johnson, G.V.; Thomason, W.E.; Mullen, R.W.; Wynn, K.J.; Freeman, K.W. Influence of late-season foliar nitrogen applications on yield and grain nitrogen in winter wheat. *Agron. J.* **2002**, *94*, 429–434.
12. Arif, M.; Chohan, M.A.; Ali, S.; Gul, R.; Khan, S. Response of wheat to foliar application of nutrients. *J. Agric. Biol. Sci.* **2006**, *1*, 30–34.
13. Hay, R.K.M. Physiological control of growth and yield in wheat: Analysis and synthesis. In *Crop Yield: Physiology and Processes*; Smith, D.L., Hamel, C., Eds.; Springer Science & Business Media: Berlin/Heidelberg, Germany, 1999; pp. 1–38.
14. Dick, C.D.; Thompson, N.M.; Epplin, F.M.; Arnall, D.B. Managing Late-Season Foliar Nitrogen Fertilization to Increase Grain Protein for Winter Wheat. *Agron. J.* **2016**, *108*, 2329–2338. [CrossRef]
15. Powlson, D.S.; Poulton, P.R.; Møller, N.E.; Hewitt, M.V.; Penny, A.; Jenkinson, D.S. Uptake of foliar-applied urea by winter wheat (*Triticum aestivum*): The influence of application time and the use of a new15N technique. *J. Sci. Food Agric.* **1989**, *48*, 429–440. [CrossRef]
16. Wang, Z.-H.; Li, S.-X.; Malhi, S. Effects of fertilization and other agronomic measures on nutritional quality of crops. *J. Sci. Food Agric.* **2008**, *88*, 7–23. [CrossRef]
17. Brown, B.D.; Petrie, S. Irrigated hard winter wheat response to fall, spring, and late season applied nitrogen. *Field Crop. Res.* **2006**, *96*, 260–268. [CrossRef]
18. Wuest, S.B.; Cassman, K.G. Fertilizer-nitrogen use efficiency of irrigated wheat: II. Partitioning efficiency of pre-plant versus late-season application. *Agron. J.* **1992**, *84*, 689–694. [CrossRef]
19. Wyatt, E.C.; Bushong, J.T.; Macnack, N.E.; Mullock, J.L.; Taylor, R.; Raun, W.R. Influence of Droplet Size of Foliar-Applied Nitrogen on Grain Protein Content of Hard Red Winter Wheat. *Crop. Forage Turfgrass Manag.* **2017**, *3*, 1–10. [CrossRef]
20. Ransom, J.; Simsek, S.; Schatz, B.; Eriksmoen, E.; Mehring, G.; Mutukwa, I. Effect of a Post-Anthesis Foliar Application of Nitrogen on Grain Protein and Milling and Baking Quality of Spring Wheat. *Am. J. Plant Sci.* **2016**, *7*, 2505–2514. [CrossRef]
21. Wuest, S.B.; Cassman, K.G. Fertilizer-nitrogen use efficiency of irrigated wheat: I. Uptake efficiency of preplant vs. late-season application. *Agron. J.* **1992**, *84*, 682–688. [CrossRef]
22. Turley, D.B.; Sylvester-Bradley, R.; Dampney, P.M.R. *Foliar-Applied Nitrogen for Grain Protein and Canopy Management of Wheat*; Home-Grown Cereals Authority (HGCA): London, UK, 2001; Review 47.
23. Rossmann, A.; Buchner, P.; Savill, G.P.; Hawkesford, M.J.; Scherf, K.A.; Mühling, K.H. Foliar N application at anthesis alters grain protein composition and enhances baking quality in winter wheat only under a low N fertiliser regimen. *Eur. J. Agron.* **2019**, *109*, 125909. [CrossRef]
24. Readman, R.J.; Kettlewell, P.S.; Beckwith, C.P. Effects of spray application of urea fertilizer at stem extension on winter wheat yield. *J. Agric. Sci.* **2002**, *139*, 1–10. [CrossRef]
25. Zadoks, J.C.; Chang, T.T.; Konzak, C.F. A decimal code for the growth stages of cereals. *Weed Res.* **1974**, *14*, 415–421. [CrossRef]
26. Phillips, S.B.; Mullins, G.L. Foliar Burn and Wheat Grain Yield Responses Following Topdress-Applied Nitrogen and Sulfur Fertilizers. *J. Plant Nutr.* **2004**, *27*, 921–930. [CrossRef]
27. Moll, R.H.; Kamprath, E.J.; Jackson, W.A. Analysis and Interpretation of Factors Which Contribute to Efficiency of Nitrogen Utilization 1. *Agron. J.* **1982**, *74*, 562–564. [CrossRef]
28. Tedone, L.; Ali, S.A.; Verdini, L.; De Mastro, G. Nitrogen management strategy for optimizing agronomic and environmental performance of rainfed durum wheat under Mediterranean climate. *J. Clean. Prod.* **2017**, *172*, 2058–2074. [CrossRef]
29. Khan, P.; Memon, M.Y.; Imtiaz, M.; Aslam, M. Response of wheat to foliar and soil application of urea at different growth stages. *Pak. J. Bot.* **2009**, *41*, 1197–1204.

30. Walsh, O.S.; Christiaens, R.J. Relative Efficacy of Liquid Nitrogen Fertilizers in Dryland Spring Wheat. *Int. J. Agron.* **2016**, *2016*, 6850672. [CrossRef]
31. Phillips, S.B.; Chen, J.; Raun, W.R.; Johnson, G.V.; Cossey, D.A.; Murray, D.S.; Westerman, R.B. Winter wheat and cheat seed response to foliar nitrogen applications. *J. Plant. Nutr.* **1999**, *22*, 1541–1549. [CrossRef]
32. Varga, B.; Svečnjak, Z. The effect of late-season urea spraying on grain yield and quality of winter wheat cultivars under low and high basal nitrogen fertilization. *Field Crop. Res.* **2006**, *96*, 125–132. [CrossRef]
33. Rao, A.C.S.; Smith, J.L.; Jandhyala, V.K.; Papendick, R.I.; Parr, J.F. Cultivar and Climatic Effects on the Protein Content of Soft White Winter Wheat. *Agron. J.* **1993**, *85*, 1023–1028. [CrossRef]
34. Johansson, E.; Prieto-Linde, M.L.; Svensson, G.; Jönsson, J. Influences of cultivar, cultivation year and fertilizer rate on amount of protein groups and amount and size distribution of mono- and polymeric proteins in wheat. *J. Agric. Sci.* **2003**, *140*, 275–284. [CrossRef]
35. Ottman, M.J.; Doerge, T.A.; Martin, E.C. Durum Grain Quality as Affected by Nitrogen Fertilization near Anthesis and Irrigation During Grain Fill. *Agron. J.* **2000**, *92*, 1035–1041. [CrossRef]
36. Blandino, M.; Vaccino, P.; Reyneri, A. Late-Season Nitrogen Increases Improver Common and Durum Wheat Quality. *Agron. J.* **2015**, *107*, 680–690. [CrossRef]
37. Blandino, M.; Visioli, G.; Marando, S.; Marti, A.; Reyneri, A. Impact of late-season N fertilisation strategies on the gluten content and composition of high protein wheat grown under humid Mediterranean conditions. *J. Cereal Sci.* **2020**, *94*, 102995. [CrossRef]
38. Mengel, K.; Kirkby, E.A.; Kosegarten, H.; Appel, T. Nitrogen. In *Principles of Plant Nutrition*; Mengel, K., Kirkby, E.A., Eds.; Kluwer Academic Publishers: Dordrecht, The Netherlands, 2001; pp. 397–434.
39. Patil, B.; Chetan, H.T. Foliar fertilization of nutrients. *Marumegh* **2018**, *3*, 49–53.