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Yield and Grain Quality of Divergent Maize Cultivars under Inorganic N Fertilizer Regimes and Zn Application Depend on Climatic Conditions in Calcareous Soil

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Abstract: The variations in temperature and rainfall patterns under climate change are threatening crop production systems, and optimizing fertilization practices is a prerequisite for sustainable cereal production. This two-year field study investigated the effects of eight treatments (T1: $P_{60}K_{60}$; T2: $P_{60}K_{60}$ + $N_{min\ spring}$; T3: $P_{60}K_{60}$ + $N_{40autumn}$ + $N_{min\ spring}$; T4: $P_{60}K_{60}$ + $N_{60spring}$; T5: $P_{60}K_{60}$ + $N_{100spring}$; T6: $P_{60}K_{60}$ + $N_{40autumn}$ + $N_{60spring}$ + Zn; T7: $P_{60}K_{60}$ + $_{N60autumn}$ + $N_{80spring}$ + Zn; and T8: $P_{60}K_{60}$ + $N_{160spring}$ + Zn) on the grain yield and quality of four divergent maize cultivars (NS-4023, NS-640, NS-6010 and NS-6030). The observations on climatic data showed substantial variations in monthly and cumulative rainfall only, which was 174 and 226 mm for 2011 and 2012, respectively, and much less than the historical cumulative rainfall of 339 mm. However, temperature during growth years showed little deviation from the historical data. The data showed that treatment and maize cultivar significantly influenced grain yield; however, grain yield remained lower in 2012 than in 2011 for each treatment and cultivar. Applying N as split doses in combination with Zn, resulted in higher grain yields than adding at once. However, the treatments and cultivars affected grain quality variables differently, including oil, thiol SH, phytate, inorganic P, soluble protein, starch, total phenol, protein, total sugars and tryptophan contents. Despite the pronounced difference in grain yields between 2011 and 2012 for each treatment and cultivar, grain quality did not always vary significantly between cultivars. Principal component analysis (PCA) revealed that the relationships between grain yield and grain quality varied significantly during 2011 and 2012. The changes in rainfall patterns at critical growth maize stages seemed to be a more important factor than temperature in regulating the response of maize cultivars in terms of grain yield and quality to various fertilization regimes in this study.

Keywords: crop rotations; maize; drought stress; fertilization; grain quality composition

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1. Introduction

Maize (*Zea mays* L.) is a cereal crop that is grown widely throughout the world in a range of agroecological environments [1]. Maize production requires the balancing of interacting factors associated with genotype, the environment, and crop management practices [2]. Optimizing mineral fertilizer management in maize production systems is critical and essential to ensure profitability, productivity and environmental sustainability [3,4].

The dynamic uptake of certain nutrients during vegetation and their role in the formation of individual plant organs is a key factor in determining the timing and manner of fertilizer application [5]. Managing nitrogen (N) and estimating the optimum mineral fertilization rate is complex because of multiple interactions that exist in the dynamic soil–plant-atmosphere system and uncertainty in weather [6]. Maximum maize yields are dependent on balanced nutrition, with N nutrition as the main nutrient limiting maize yields and grain quality [7,8]. Variation in N use efficiency (NUE) at high N-input is mainly related to variation in N uptake, whereas at low N-input, both components of NUE could play a role, specifically N utilization efficiency, i.e., grain yield/N uptake [8]. Significant interactions between the degree of N deficiency and the time of its application indicate that there is no single best time for N administration [9]. The higher amount of rainfall in June than the perennial average and N fertilization resulted in a higher maize yield compared to N application before sowing [10]. Nitrogen fertilization (40% at the same time as sowing and 60% in the spring part of the vegetation in phase 8 leaves) achieved higher corn grain yield compared to the total amount of N applied in the spring and in fertilization [11]. These authors conclude that multiple applications of N are more desirable in soils with less accessible Vetsch & Randall [12] stated that in the first year of the study, in which April and May were dry and warm with a mean daily temperature significantly higher than the perennial average, maize grain yield was 20% lower on N-treated treatments in the spring compared to the yield obtained on the variant where N was applied in the autumn, while in the other two years of the test, there were no significant differences in the yield obtained by applying N at different times.

A number of authors confirm that the uptake and accumulation of certain biogenic elements in maize and other plant species is partly under genetic control, while variations in the concentration of elements in plants are the main criterion for determining the genetic specificity of mineral nutrition [13–18]. Under conditions of deficiency of individuals or a decrease in the concentration of certain elements of mineral nutrition, different genotypes exhibit different degrees of adaptation, from which it can be concluded that the efficiency of the adoption and utilization of elements of mineral nutrition by plants is largely genetically controlled [19]. Many authors have stated that there are two ways to improve nutrient use efficiency, primarily N in maize: a more adapted fertilizer system or the sowing of better hybrids [7,20–22]. The second way to improve maize efficiency is to select genotypes that are able to absorb more nutrients (N, P and K) from soil and fertilizers (better nutrient efficiency) and better utilize them to produce higher grain yields (better nutrient utilization) [23,24]. Enhanced opportunities for the adoption, accumulation, utilization and/or reutilization of macro- and microelements can provide a basis for developing maize breeding programs for productivity and grain quality. We hypothesized that the grain yield and quality of divergent maize hybrids will depend on the N fertilization regimes. N split for various growth seasons, zinc (Zn) application and prevailing climatic conditions, primary rainfall and temperature. The objectives of this two-year field study were to evaluate the effects of N fertilization regimes along with Zn on the grain yield and quality of four divergent maize cultivars under varying rainfall and temperature conditions.

2. Materials and Methods

2.1. Experimental Site, Soil and Climate

Field trials were conducted for two years at the Experimental Station of Institute of Field and Vegetable Crops, Novi Sad, Serbia (45°20′14″ N, 19°51′44″ E, 78 m above sea level) (Figure 1).

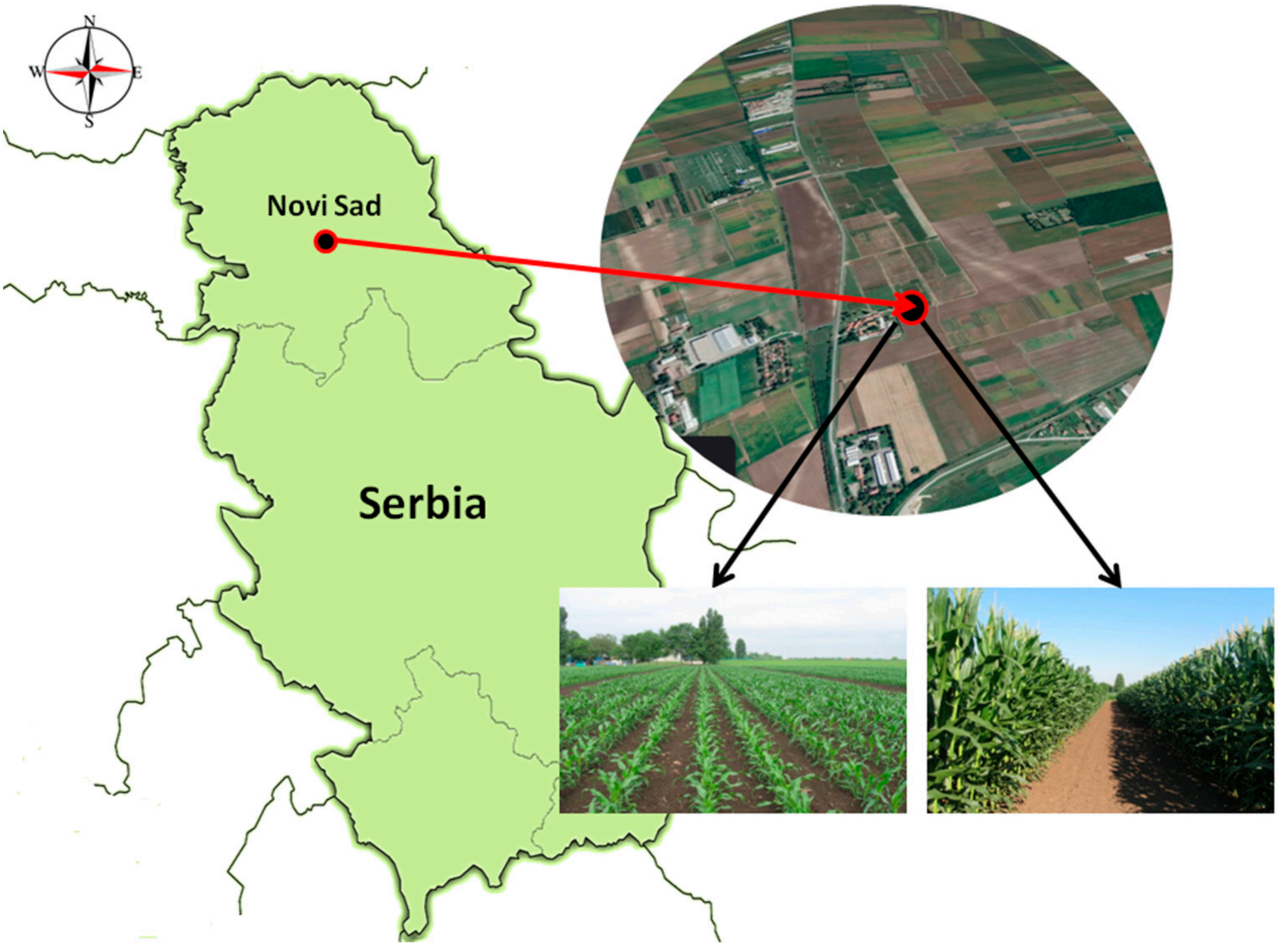

Figure 1. Location map and experimental field.

The soil at the study site is a typical calcareous chernozem in nature. Before the start of the experiment, surface (0–30 cm) and subsurface (30–60 cm) soils were sampled with augur at the end of March 2011, and the analysis showed that the surface soil was slightly alkaline and had total organic C 19.5 g kg^{-1}, total N 2.60 g kg^{-1}, available P 24.5 mg kg^{-1} and available K 27.3 mg kg^{-1} (Table 1).

Table 1. Physico-chemical properties of soil at the study site.

Depth (cm)	pH		$CaCO_3$ (%)	Total Organic C (g kg^{-1})	Total N (g kg^{-1})	AL-P_2O_5 (mg kg^{-1})	AL-K_2O (mg kg^{-1})
	KCl	H_2O					
0–30	7.60	8.63	8.24	19.5	2.60	24.9	27.3
30–60	7.98	8.67	11.88	18.4	2.67	21.1	22.5

The weather data during the growing season of both years are given in Table 2.

Table 2. Total monthly precipitation and mean air-temperatures at the experimental station during 2011 and 2012.

Year	Monthly Precipitation (mm)							Monthly Mean Air-Temperatures (°C)						
	April	May	June	July	August	September	Σ	April	May	June	July	August	September	X
2011	22.8	63.0	36.9	61.5	1.5	25.4	174.2	13.2	16.8	20.9	22.1	23.0	20.4	19.4
2012	82.8	52.2	27.5	47.7	3.5	13.1	226.8	13.0	17.5	23.0	25.2	24.6	19.8	20.5
1961–1990	47	57	83	61	55	36	339	11.4	16.6	19.6	21.1	20.6	16.9	17.7

The mean monthly air temperature in June, July and August was higher in 2011 than in 2012; however, the average temperature during the growing season in both years was slightly different. The mean monthly rainfall was generally higher in 2012, except for June and September months, whereas the cumulative rainfall in 2012 was 226.8 mm, in contrast to 174.2 mm in 2011. However, the cumulative rainfall during the experimental period remained much less than the historical rainfall, whereas the average temperature showed little deviation from the historical data (Table 2).

2.2. Experimental Design and Treatment

Four divergent maize hybrids (NS 4023, NS 640, NS 6010 and NS 6030) were sown under eight treatments representing fertilization regimes as T1: $P_{60}K_{60}$; T2: $P_{60}K_{60}$ + $N_{min\ spring}$; T3: $P_{60}K_{60}$ + $N_{40autumn}$ + $N_{min\ spring}$; T4: $P_{60}K_{60}$ + $N_{60spring}$; T5: $P_{60}K_{60}$ + $N_{100spring}$; T6: $P_{60}K_{60}$ + $N_{40autumn}$ + $N_{60spring}$ + Zn; T7: $P_{60}K_{60}$ + $N_{40autumn}$ + $N_{80spring}$ + Zn; and T8: $P_{60}K_{60}$ + $N_{160spring}$ + Zn in both years of the study. Nitrogen was split into various combinations, whereas P and K were kept constant along Zn. The experiment followed a split-plot randomized complete block design (RCBD), and each treatment had four replicates. Standard agronomic practices were followed for maize growth. The preceding crop for maize was winter wheat. Selected plots were ploughed every October up to 27–30 cm depth, and seedbed preparation was performed before sowing with heavy duty cultivators (Multi-Tiller) to 15 cm depth in March. Zinc was applied as zinc sulfate ($ZnSO_4$) in the amount of 1.0 kg ha^{-1} with foliar spraying in the fourth and sixth weeks after sowing. The crop was sown on 10 April 2011 and 18 April 2012 using a Winter Steiger AG pneumatic precision seed drill to a depth of 5 cm. The plot dimensions were 5 × 2.8 m, with an intrarow spacing of 22 cm and row spacing of 70 cm. In both years, weed control was carried out by conventional chemical methods.

2.3. Grain Yield and Quality Analysis

After maize harvest from each treatment plot, cobs were taken for grain yield and chemical analysis by using two center rows. The grain samples were prepared and ground in a mill for grain quality analysis. Protein content was estimated as the total nitrogen by the Kjeldahl method multiplied by 6.25 [25]. The soluble protein contents were determined following the method of Lowry et al. [26] with the help of alkaline Folin-Ciocakteus reagent, whereby the Berlin blue color was developed and the sample absorbance was measured at 750 µm wavelength on a spectrophotometer. The Soxhlet method was used for the determination of oil content. This method is based on the property of the fat being easily dissolved and thus extracted by means of certain organic solvents, in this case petroleum ether. Petrol ether, in addition to extra trivalent alcohol, glycerol, with related fatty acid extracts related substances such as phospholipids, sterols, waxes, pigments, essential oils and other substances, which makes the extraction fraction called "crude fat". Starch content was measured with the Ewers method by using dilute hydrochloric acid. The starch is hydrolyzed to glucose, and since glucose is optically active, this property is used for polarimetric determination of starch and total sugar by the Luff-Schoorl method. The determination of phytate (phytic acid) contents was measured spectrophotometrically according to the method of Dragičevic et al. [27] with the use of Wade's reagent, whereby Fe^{3+} is reduced to Fe^{2+} and the intensity of the purple color of the reagent is reduced, which is measured at a wavelength of 500 nm. The inorganic phosphorus contents were determined according to Dragičevic et al. [27] using a complex reagent (ammonium heptamolybdate + ammonium metavanadate), whereby yellow colour develops and absorbance was measured at 400 µm wavelength. The thiol (-SH) groups were quantified using 0.059% DTBN (2.2′-dinitro-5.5′dithiobenzoic acid) reagent, and the yellow color intensity was measured at 412 nm wavelength. The total phenol contents were measured with the help of an acidic solution of 0.1 M $FeCl_3$ and 0.008 M $K_3(FeCn)_6$, whereby a blue–green color is developed and absorbance is measured at 720 nm [28]. The tryptophan content in grain was determined by HPLC.

2.4. Statistical Analysis

Data were tested for normal distribution to meet the assumption of analysis of variance (ANOVA) test and, when needed, log-transformed prior to statistical analysis. A two-way ANOVA test was applied to study the effects of treatments and cultivars on grain yield and grain quality indicators for both years separately. Under each treatment and cultivar, differences between years were found by using an independent sample *t* test at the $p < 0.05$ significance level. Principal component analysis (PCA) was conducted for the relationships between grain yield and grain quality variables for each year. Statistical analyses were performed using SPSS for Windows software v. 19 (version 18. SPSS Inc., Chicago, IL, USA) [29].

3. Results

3.1. Oil Content and Grain Yield

Significant increases of 4.52% and 4.72% in NS-640, 4.85% and 5.36% in NS-4023, 4.66% and 5.03% in NS-6010, and 4.60% in NS-6030 were recorded by T7 in 2011 and 2012, respectively, except in NS-6030, where the increase in oil content was 5.32% at T8 in 2012. However, during 2011, the NS-4023 and NS-6010 maize cultivars reported a significant 11,231 kg ha^{-1} and 12,502 kg ha^{-1} increase in yield at T6, while for NS-640 and for NS-6030, the increase was 12,934 kg ha^{-1} and 12,738 kg ha^{-1} at T7, respectively (Figure 2).

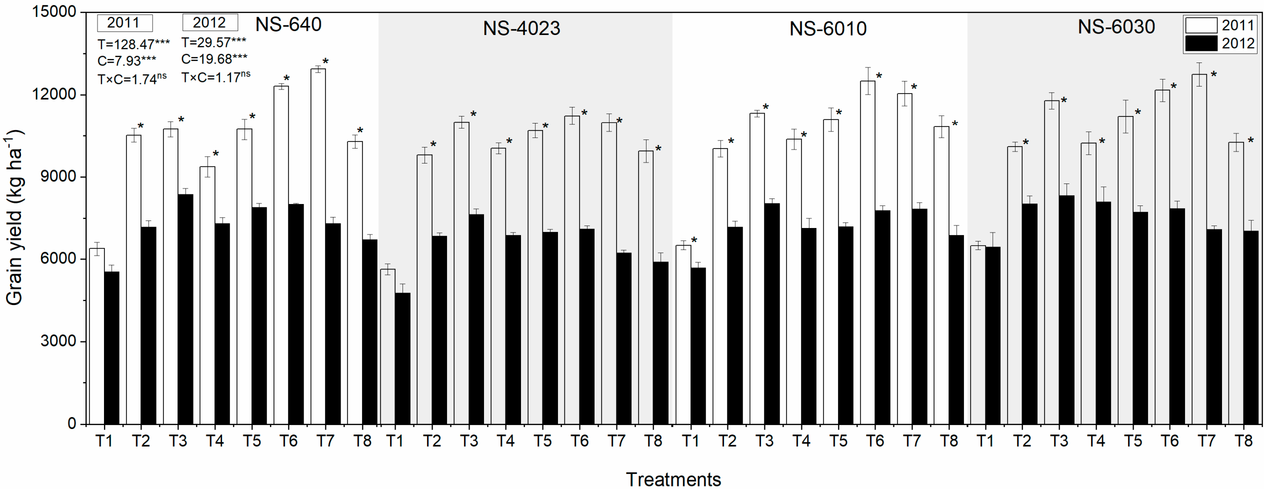

Figure 2. Fertilization effects on grain yield (kg ha^{-1}) four maize cultivars over two years. Bars show mean values of four replicates and contain standard errors of means (n = 4). For ANOVA analyses, *** show significant treatment (T), maize cultivar (C) and their interaction effects at $p < 0.001$, respectively. Each pair of bars with asterisk (*) show significant difference in grain yield between 2011 and 2012 years at $P < 0.05$. ns = non-significant effects. T1: $P_{60}K_{60}$; T2: $P_{60}K_{60} + N_{min\ spring}$; T3: $P_{60}K_{60} + N_{40autumn} + N_{min\ spring}$; T4: $P_{60}K_{60} + N_{60spring}$; T5: $P_{60}K_{60} + N_{100spring}$; T6: $P_{60}K_{60} + N_{40autumn} + N_{60spring}$ + Zn; T7: $P_{60}K_{60} + N_{40autumn} + N_{80spring}$ + Zn; T8: $P_{60}K_{60} + N_{160spring}$ + Zn.

Furthermore, the NS-4023, NS-6010, and NS-6030 maize cultivars reported increases of 7620 kg ha^{-1}, 8028 kg ha^{-1}, and 8317 kg ha^{-1} in yield at T3, respectively, during 2012, except for NS-640, where an increase of 7991 kg ha^{-1} in yield was reported by T6.

3.2. Phytate and Inorganic P

Significant variation in the grain phytate and inorganic P contents was noted under various fertilization regimes for different maize cultivars (Table 3). The fluctuations in climatic conditions variate the phytate content for different cultivars under different treatments. The phytate content of NS-640, NS-4023, NS-6010, and NS-6030 was significantly increased by 3.38, 3.39, 3.27, and 3.22 g kg^{-1}, respectively, in 2011 at T6, and in 2012, the phytate content was further increased up to 4.01 g kg^{-1} for NS-640 at T6 but 4.06, and a 3.70 g kg^{-1} increase was recorded for the phytate content of NS-4023 and NS-6030 at T1. Furthermore, during 2012, a significant increase of 3.76 g kg^{-1} in phytate content in NS-6010 was reported at T8. Inorganic P significantly varied with the changing climate. T2 reported significant increases of 1.08 and 1.16 mg kg^{-1} of inorganic P content in NS-640 and NS-6010 in 2011, respectively, while in NS-6030 and NS-4023, significant increases of 1.17 and 1.11 mg kg^{-1} of inorganic P content were noted at T7 and T8, respectively. The inorganic P of grain varied significantly with the changing temperature in 2012, and the results showed significant increases of 0.96 mg kg^{-1} (T6), 1.41 mg kg^{-1} (T1), 1.04 mg kg^{-1} (T7), and 0.92 mg kg^{-1} (T2) in the inorganic P content in grain for NS-640, NS-4023, NS-6010, and NS-6030, respectively.

Table 3. Fertilization effects on grain oil, thiol SH, phytate, inorganic phosphorus, soluble protein and starch contents of four maize cultivars over two years.

Treatments	**Oil (%)**								**Thiol SH (mmol kg^{-1})**							
	NS-640		NS-4023		NS-6010		NS-6030		NS-640		NS-4023		NS-6010		NS-6030	
	2011	2012	2011	2012	2011	2012	2011	2012	2011	2012	2011	2012	2011	2012	2011	2012
T1	3.93	4.04	**4.31**	**4.19**	3.91	4.00	4.09	4.13	**1414**	**861**	**1516**	**1657**	**969**	**1093**	**1608**	**1216**
T2	4.47	4.31	4.47	4.43	4.01	4.06	4.29	4.39	**1437**	**981**	**1544**	**1691**	**1144**	**1337**	**1906**	**1411**
T3	4.23	4.13	4.64	4.52	4.46	4.30	4.50	4.54	**1558**	**910**	**1588**	**1686**	**1186**	**1430**	**1435**	**1278**
T4	**4.10**	**4.23**	4.37	4.28	4.01	3.93	4.15	4.13	**1231**	**1037**	**1605**	**1549**	**943**	**1109**	**1540**	**1205**
T5	4.09	4.14	4.39	4.50	4.04	4.20	4.37	4.15	**1174**	**1397**	**1672**	**1621**	1099	1127	**1736**	**1063**
T6	4.50	4.62	**4.42**	**5.18**	4.22	4.69	**4.52**	**5.26**	**1738**	**1400**	**1401**	**1594**	**1263**	**1119**	**1711**	**1144**
T7	4.52	4.72	4.85	5.36	4.66	5.03	**4.60**	**5.20**	**1346**	**1298**	1572	1553	**1374**	**1236**	**1693**	**1126**
T8	**4.05**	**4.39**	4.37	4.23	4.11	4.09	**4.38**	**5.32**	**1441**	**1382**	**1640**	**1719**	**1225**	**1450**	**1679**	**1222**
ANOVA	2011: T = 7.64 ***, C = 7.63 ***, T × C = 0.69 ns 2012: T = 37.08 ***, C = 18.11 ***, T × C = 3.61 ***								2011: T = 276.62 ***, C = 5618 ***, T × C = 280.41 *** 2012: T = 346.08 ***, C = 6088 ***, T × C = 372.78 ***							
	Phytate (g kg^{-1})								**Inorganic P (mg kg^{-1})**							
	NS-640		NS-4023		NS-6010		NS-6030		NS-640		NS-4023		NS-6010		NS-6030	
	2011	2012	2011	2012	2011	2012	2011	2012	2011	2012	2011	2012	2011	2012	2011	2012
T1	**3.11**	**3.57**	**3.20**	**4.06**	**3.05**	**3.49**	**3.03**	**3.70**	**1.01**	**0.77**	**1.06**	**1.41**	**1.09**	**0.77**	**1.16**	**0.90**
T2	**3.17**	**3.56**	**3.20**	**3.84**	**3.11**	**3.63**	**3.27**	**3.07**	**1.08**	**0.80**	**0.95**	**1.14**	**1.16**	**0.85**	**1.05**	**0.92**
T3	**3.16**	**3.70**	**3.21**	**3.71**	**3.14**	**3.72**	**3.09**	**2.69**	**1.03**	**0.88**	0.96	0.99	**1.04**	**0.92**	**1.08**	**0.76**
T4	**2.99**	**3.93**	**2.92**	**3.51**	**3.05**	**3.75**	2.98	3.11	**0.89**	**0.77**	1.04	1.08	**0.97**	**0.79**	**1.03**	**0.72**
T5	**3.03**	**4.01**	**3.24**	**3.91**	**3.25**	**3.70**	**3.20**	**2.85**	**0.99**	**0.85**	**1.03**	**0.95**	0.96	0.91	**1.00**	**0.67**
T6	**3.38**	**4.01**	**3.39**	**3.93**	**3.27**	**3.68**	**3.22**	**3.04**	**1.05**	**0.96**	**1.00**	**1.05**	**1.06**	**0.95**	**1.06**	**0.87**
T7	**3.10**	**3.76**	**3.27**	**3.60**	**3.03**	**3.69**	3.02	3.09	**0.89**	**0.85**	**1.00**	**0.90**	1.02	1.04	**1.17**	**0.79**
T8	**3.27**	**3.61**	**3.32**	**3.79**	**3.17**	**3.76**	**2.78**	**2.92**	**0.93**	**0.88**	**1.11**	**1.03**	**1.01**	**0.89**	**1.10**	**0.74**
ANOVA	2011: T = 61.15 ***, C = 51.04 ***, T × C = 19.34 *** 2012: T = 41.40 ***, C = 1430 ***, T × C = 66.92 ***								2011: T = 43.14 ***, C = 136.05 ***, T × C = 42.15 *** 2012: T = 534.32 ***, C = 6872 ***, T × C = 733.90 ***							
	Soluble protein (g kg^{-1})								**Starch (%)**							
	NS-640		NS-4023		NS-6010		NS-6030		NS-640		NS-4023		NS-6010		NS-6030	
	2011	2012	2011	2012	2011	2012	2011	2012	2011	2012	2011	2012	2011	2012	2011	2012
T1	**60.1**	**35.3**	**61.4**	**40.2**	**61.7**	**36.2**	**53.7**	**39.7**	72.5	70.9	**73.3**	**70.8**	73.1	72.5	73.1	73.6
T2	**58.3**	**37.5**	**60.8**	**38.8**	**61.0**	**37.9**	**61.4**	**42.8**	73.3	73.5	73.6	73.3	73.7	73.9	73.5	73.8
T3	**62.6**	**39.0**	**60.8**	**39.1**	**62.4**	**36.5**	**60.8**	**37.6**	75.0	74.9	74.2	74.8	75.2	75.3	75.0	75.6
T4	**56.6**	**36.0**	**60.8**	**41.6**	**57.2**	**37.0**	**66.4**	**39.2**	73.2	73.3	73.6	72.9	74.0	74.1	73.9	74.4
T5	**64.4**	**38.2**	**58.1**	**32.5**	**61.5**	**38.9**	**57.5**	**41.2**	74.7	73.1	73.6	73.4	74.2	74.5	74.4	74.7
T6	**59.3**	**35.9**	**59.6**	**40.4**	**62.6**	**38.5**	**60.4**	**43.3**	74.7	75.4	74.9	74.6	74.9	74.2	75.0	77.3
T7	**59.3**	**38.0**	**59.7**	**36.1**	**58.8**	**44.1**	**55.5**	**36.5**	75.2	75.7	75.9	74.8	75.5	75.8	**75.5**	**76.3**
T8	**60.3**	**36.8**	**64.5**	**38.5**	**61.1**	**42.5**	**58.5**	**38.9**	74.8	74.5	73.7	72.1	74.7	72.7	74.6	74.5
ANOVA	2011: T = 25.02 ***, C = 22.28 ***, T × C = 46.03 *** 2012: T = 16.80 ***, C = 98.64 ***, T × C = 65.36 ***								2011: T = 4.64 ***, C = 0.28 ns, T × C = 0.19 ns; 2012: T = 20.84 ***, C = 13.46 ***, T × C = 1.48 ns							

Values of each variable are means of four replicates. For each variable under each maize cultivar, bold values indicate significant differences between years 2011 and 2012 at $p < 0.05$. For ANOVA analyses, *** show significant treatment (T), maize cultivar (C) and their interaction effects at $p < 0.05$, $p < 0.01$ & $p < 0.001$, respectively. T1: $P_{60}K_{60}$; T2: $P_{60}K_{60} + N_{min\ spring}$; T3: $P_{60}K_{60} + N_{40autumn} + N_{min\ spring}$; T4: $P_{60}K_{60} + N_{60spring}$; T5: $P_{60}K_{60} + N_{100spring}$; T6: $P_{60}K_{60} + N_{40autumn} + N_{60spring}$ + Zn; T7: $P_{60}K_{60} + N_{40autumn} + N_{80spring}$ + Zn; T8: $P_{60}K_{60} + N_{160spring}$ + Zn.

3.3. Sugar and Starch

The variations in the total sugar and starch contents of grain are presented in Tables 3 and 4.

Table 4. Fertilization effects on grain total phenol, protein, total sugars and tryptophan contents of four maize cultivars over two years.

Treatments	Total phenol (mg kg^{-1})								Protein (%)							
	NS-640		NS-4023		NS-6010		NS-6030		NS-640		NS-4023		NS-6010		NS-6030	
	2011	2012	2011	2012	2011	2012	2011	2012	2011	2012	2011	2012	2011	2012	2011	2012
T1	218	218	**124**	**245**	**163**	**309**	**242**	**402**	6.56	7.68	7.28	6.63	7.27	6.01	7.00	6.83
T2	228	265	**125**	**247**	**198**	**312**	**271**	**380**	**7.35**	**8.72**	**7.26**	**8.39**	7.72	8.25	7.80	8.07
T3	**360**	**322**	**104**	**228**	**168**	**347**	**236**	**351**	8.56	9.65	**8.16**	**9.86**	8.50	9.81	8.27	8.12
T4	**191**	**307**	**151**	**205**	**211**	**361**	**386**	**340**	7.29	8.33	6.80	7.42	7.16	7.27	6.40	7.07
T5	**156**	**236**	**138**	**205**	**169**	**355**	**260**	**357**	**8.63**	**9.93**	8.01	8.27	8.50	8.80	8.15	7.16
T6	**190**	**229**	**170**	**211**	**165**	**344**	**320**	**366**	8.35	9.67	8.14	9.44	**8.62**	**9.63**	7.97	8.86
T7	168	223	183	226	**320**	**383**	382	371	8.21	9.92	8.28	9.32	8.50	10.2	**7.95**	**8.58**
T8	**227**	**301**	**208**	**245**	**314**	**440**	**172**	**396**	**6.54**	**9.45**	**6.59**	**9.19**	6.82	8.60	**6.11**	**7.65**
ANOVA	2011: T = 89.42 ***, C = 742.62 ***, T × C = 128.13 ***; 2012: T = 12.71 ***, C = 360.22 ***, T × C = 8.74 ***								2011: T = 11.50 ***, C = 1.38 ^{ns}, T × C = 0.30 ^{ns}; 2012: T = 32.76 ***, C = 22.34 ***, T × C = 2.06 *							
	Total sugars (%)								Tryptophan (%)							
	NS-640		NS-4023		NS-6010		NS-6030		NS-640		NS-4023		NS-6010		NS-6030	
	2011	2012	2011	2012	2011	2012	2011	2012	2011	2012	2011	2012	2011	2012	2011	2012
T1	2.73	3.08	2.78	3.06	2.82	2.86	2.73	3.19	**0.048**	**0.051**	**0.051**	**0.048**	**0.047**	**0.045**	0.050	0.051
T2	3.16	3.46	2.85	3.36	3.14	3.17	3.08	3.12	**0.050**	**0.053**	**0.049**	**0.052**	**0.050**	**0.053**	0.052	0.054
T3	3.33	3.61	3.37	3.38	3.62	3.80	3.83	3.58	**0.060**	**0.063**	**0.058**	**0.063**	**0.058**	**0.060**	0.059	0.060
T4	3.63	3.83	3.57	3.32	3.47	2.90	3.30	2.88	**0.049**	**0.053**	**0.048**	**0.051**	0.050	0.052	0.052	0.052
T5	3.44	3.35	3.77	3.55	3.53	3.37	3.76	3.66	**0.057**	**0.062**	0.056	0.056	**0.055**	**0.051**	**0.056**	**0.053**
T6	3.95	3.95	3.59	3.57	3.92	4.16	3.55	3.63	**0.055**	**0.060**	**0.057**	**0.061**	**0.055**	**0.058**	**0.058**	**0.062**
T7	3.88	4.05	4.25	4.01	4.17	3.86	3.91	3.82	**0.053**	**0.061**	0.059	0.060	**0.057**	**0.062**	**0.057**	**0.060**
T8	3.76	3.68	3.28	3.04	3.37	3.09	3.09	3.10	**0.048**	**0.058**	**0.046**	**0.055**	**0.047**	**0.049**	**0.051**	**0.056**
ANOVA	2011: T = 13.20 ***, C = 0.33 ^{ns}, T × C = 0.78 ^{ns}; 2012: T = 14.24 ***, C = 1.02 *, T × C = 1.92 *								2011: T = 115.81 ***, C = 13.73 ***, T × C = 3.81 ***; 2012: T = 199.99 ***, C = 45.63 ***, T × C = 10.92 ***							

* Values of each variable are means of four replicates. For each variable under each maize cultivar, bold values indicate significant differences between years 2011 and 2012 at $p < 0.05$. For ANOVA analyses, *, *** show significant treatment (T), maize cultivar (C) and their interaction effects at $p < 0.05$, $p < 0.01$ & $p < 0.001$, respectively. ns = non-significant effects. T1: $P_{60}K_{60}$; T2: $P_{60}K_{60}$ + $N_{min\ spring}$; T3: $P_{60}K_{60}$ + $N_{40autumn}$ + $N_{min\ spring}$; T4: $P_{60}K_{60}$ + $N_{60spring}$; T5: $P_{60}K_{60}$ + $N_{100spring}$; T6: $P_{60}K_{60}$ + $N_{40autumn}$ + $N_{60spring}$ + Zn; T7: $P_{60}K_{60}$ + $N_{40autumn}$ + $N_{80spring}$ + Zn; T8: $P_{60}K_{60}$ + $N_{160spring}$ + Zn.

The sugar contents in the grain of NS-4023, NS-6010, and NS-6030 were significantly increased by 4.25%, 4.17%, and 3.91%, respectively, at T7, while the sugar content for NS-640 was increased by 3.95% at T6 in 2011. Furthermore, the change in rainfall and air temperature during 2012 showed that the sugar content in the grain of NS-640, NS-4023, and NS-6030 was increased by 4.05%, 4.01%, and 3.82%, respectively, by T7, while a sugar content of 4.16% was reported from NS-6010 at T6. The starch content was not affected by the change in climate and showed sustainability at T7 for all maize cultivars except NS-6030 by T6. Sufficient water is needed for the better utilization of inorganic fertilizer. During the experimental period, the significant rainfall is effective for the increase in sugar and starch content at the maximum addition of fertilizers with split doses (T7).

3.4. Protein and Tryptophan

The variation in total protein and soluble protein content in maize cultivars is presented in Table 4. During 2012, the total protein content in maize was significantly affected by different treatments (T) and maize cultivars, while in 2011, the protein content was not significantly affected by different cultivars. Furthermore, the interaction effect of treatments and cultivars did not have significant effects on the total protein content in 2011 but showed significant changes in 2012. The protein content was increased by 8.63 and 9.93% by T5 in the NS-540 maize cultivar. The protein content showed increases of 8.28 (T7) and 9.86 (T3) in 2011 and 2012, respectively. Furthermore, NS-6010 showed that the protein content was increased by 8.62% by T6 in 2011 and 10.2% by T7 in 2012. The total protein content under NS-6030 increased by 8.27% under T3 in 2011 and 8.88% under T6 in 2012. During 2011 and 2011, the soluble protein content significantly increased 64.4 g kg^{-1} in T5, 39.0 g kg^{-1} in T3 in NS-640, 64.5 g kg^{-1} in T8 and 41.6 g kg^{-1} in T4 in NS-4023, 62.6 g kg^{-1} in T6, 44.1 g kg^{-1} in T7 in NS-6010, and 8.27 g kg^{-1} in NS-6030. The significant variation in tryptophan for different maize cultivars under different treatments is presented in Table 4. Significant increases of 0.060% and 0.063% tryptophan were noted at T3 in NS-640, while 0.059% at T7 and 0.063% at T3 in NS-4023 were recorded during 2011 and 2012. Furthermore, during 2011 and 2012, significant increases of 0.058% and 0.059% tryptophan were noted at T3 in NS-6010 and NS-6030, respectively. In the second year (2012), due to the change in climatic conditions, a significant increase of 0.062% at T7 in NS-6010 and 0.062% at T6 was noted in NS-6030.

3.5. Total Phenol and Thiol SH

Phenol and thiol SH were significantly affected by different treatments (T), cultivars (C) and the interaction of T and C (Table 3). The total phenol content was significantly increased by 360 mg kg^{-1} and 322 mg kg^{-1} by T3 in NS-640 during 2011 and 2012, respectively. Further T8 reported a significant increase of 208 mg kg^{-1} and 245 mg kg^{-1} phenol content in NS-4023 and 314 mg kg^{-1} and 440 mg kg^{-1} phenol content in NS-6010 during 2011 and 2012.

3.6. Relationship among Biochemical Attributes and Yield

Grain biochemical variables and yield of maize were correlated (Figure 3a,b). The total protein, tryptophan, starch, total sugar, and oil contents and yield showed positive and strong correlations compared with the remaining variables. However, except for all variables, the oil content showed a positive correlation with Thiol SH in 2011 (Figure 3a). During 2012, strong positive correlations were noted among starch, total sugar, total protein, tryptophan and yield, but oil content and yield showed weaker correlations than in 2011. Moreover, negative correlations were found among inorganic phosphorus, total sugar, yield and phytate of maize, while soluble protein documented a negative correlation for all tested variables except phytate (Figure 3a).

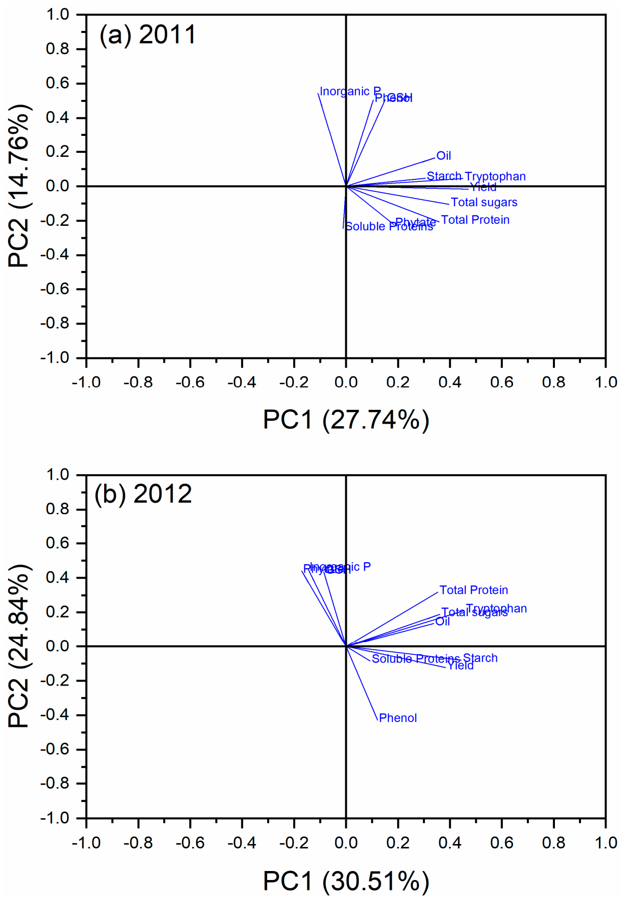

Figure 3. PCA loading plots of maize yield and grain quality parameters for the years 2011 and 2012.

Furthermore, during 2012, thiol SH, total phenol, starch, yield and inorganic P were negatively correlated (Figure 3b). Similarly, total phenol, sugar, protein and tryptophan were negatively correlated. However, strong negative correlations were noted among phytate, soluble protein, total phenol, oil, starch and yield of maize.

4. Discussion

Maximum maize grain yields are influenced by a number of factors, including N fertility, growing are influenced by season conditions, water availability, and soil conditions [30]. The proper management of fertilizer significantly enhanced crop productivity and profitability [31]. In our results, the performance of maize cultivars varies with the number of fertilizers and variation in climate. Similarly, previous studies have shown that sesame responds differently to fertilization at different sites, in different growing seasons, and between cultivars [32–34]. The deficiency or excess of N in an unfriendly environment can cause disorder in nutrition with a significant decrease in production and oil content [35]. Our results showed that T7 ($P_{60}K_{60}$ + N_{40} autumn + N_{80} spring + 1.0 kg ha^{-1} + Zn) significantly increased the oil content in all maize cultivars. Amooaghaie and Golmohammadi [36] reported that the addition of more micro (Zn, Cu, Fe and Mn) and macro (N and P) nutrients after the addition of organic fertilizer increased the oil production of *Thymus vulgaris* L. The results showed that the significant response of T6 to the phytate content of NS-640 was not changed with respect to changes in climate conditions, while the effect of treatments on the phytate content of NS-4023, NS-6010, and NS-6030 was significantly changed with respect to changes in climatic conditions in 2012 because the phytic acid contents of grain materials vary by cultivar, climatic conditions and year. The accumulation site of phytic acid in monocotyledonous seeds (wheat, barley, rice, etc.) is the aleurone layer, but maize differs from other cereals, as >80% of phytic acid is located in the germ of grain [37]. Phytic acid is known as the storage form of phosphorus in seeds and generally represents ≈1–2% of seed dry weight. Cereal grains such as maize are among the foods of plant origin that have the highest content of phytic acid [38]. An increase in phosphorus content was noted with the addition of fertilization [39]. Furthermore, Saha et al. [30] reported that the phosphorous and potassium contents in grain were higher under the NPK and FYM treatments than under the other treatments. The results of grain phytate and inorganic P content for NS-4023, NS-6010, and NS-6030 varied significantly with the changing climate during 2012, except for NS-640. It is concluded that phytate and inorganic P content in the grain of NS-640 consistently increased at T6 with the change in climate and thus reported that changing climate has no effects on phytate and inorganic P grain content of NS-640. The results showed that T7 was more effective for the significant increase in sugar contents in all maize cultivars except NS-6010 with the change in climate between years. In 2011 and 2012, the grain starch content was significantly increased by 75.2% and 75.7% in NS-640, 75.9% and 74.8% in NS-4023, and 75.5% and 75.8% in NS-6010 at T7. T6 reported 75.0% and 77.3% higher values of grain starch content in maize cultivar NS-6030. Dai et al. [40] reported that the starch and protein content in wheat was higher under normal irradiation than under water saving and rain-fed conditions. Heat stress not only decreases maize yield but also reduces the quality and content of starch [41]. Therefore, during the experimental period, there was no significant variation in the temperature between 2011 and 2012, and thus, the increase in the addition of fertilizer with sufficient rainfall increased the starch content. Furthermore, a decrease in starch content was noted from 15 days of heat stress after pollination. The increase in precipitation in 2012 and the increase in starch content compared with 2011 are further confirmed by Kaplan et al. [39], who found that sugar and soybean contents significantly increased with sufficient irrigation. Furthermore, Dai et al. [40] reported that the starch content in maize depends on planting conditions [41–43]. The grain protein content was higher in those treatments, where N was applied only in mineral form. This is due to the quick availability of nutrients to plants. Plants that received both mineral and organic fertilizer produced more protein yield per plot (Saha et al., 2008). Our results showed a large change in total protein content and soluble protein content among treatments in the second year of the experiment due to changes in climate Dai et al. [40]. The addition of fertilizer reduced the protein by 7%, antioxidant activities by 24% and antioxidant phenolic compounds by 19–71%. These reductions were due to the increasing N concentration in plants through fertilizer [44]. The influence of N on protein concentration may be worse when the concentration of essential nutrients in protein, which determines the quality of the fruits, is considered. The antioxidant components were reduced by 20–30% at fertilizer rates above 100 kg NPK ha^{-1} [45]. Furthermore, the application of combined fertilizer (NPK) with compost significantly increased N availability and enhanced proteins for growth [46,47]. The treatment of NPK and compost increased the phenolic content compared with that of the control and other treatments [48], and the addition of bio fertilizer alone or in combination with N fertilizer significantly enhanced carbohydrates, flavonoids and phenols in plants [49,50]. NS-6030 showed a significant increase of 386 mg kg^{-1} at T4 in 2011, but due to climate change in 2012, a 402 mg kg^{-1} increase in the phenol content was noted at T1. The thiol SH content significantly increased by 1738 mmol kg^{-1} and 1400 mmol kg^{-1} at T6 in NS-640 during 2011 and 2012, respectively, while T8 reported increases of 1640 mmol kg^{-1} and 1719 mmol kg^{-1} in NS-4023 during 2011 and 2012, respectively. Furthermore, thiol SH contents of 1374 mmol kg^{-1} by T7 in 2011 and 1450 mmol kg^{-1} by T8 in 2012 were reported in NS-6010, and the thiol SH content in NS-6030 was 1906 mmol kg^{-1} and 1411 mmol kg^{-1} increased by T2 in 2011 and 2012, respectively. The total phenol and thiol SH were significantly decreased with the increase in fertilization in cultivars NS-640 and NS-6030. However, the results obtained by Paschold et al. [45], showed a reduction in total phenolics and antioxidant activities in asparagus with increasing fertilization. Thus, it is concluded that cultivars NS-4023 and NS-6010 are friendly with the environment in which phenol and thiol SH were notably reduced even with the increase in fertilization. Furthermore, Mitchell and Chassy [51], reported that plants with limited N were shown to accumulate more flavonoids than those that are well supplied within organic fertilizers. Nitrogen fertility has a major role in maintaining maximum maize grain yields; however, a number of other factors limit yields even when N fertility is optimal.

5. Conclusions

We investigated the effects of eight fertilization regimes (T1: $P_{60}K_{60}$; T2: $P_{60}K_{60}$ + $N_{min\ spring}$; T3: $P_{60}K_{60}$ + $N_{40autumn}$ + $N_{min\ spring}$; T4: $P_{60}K_{60}$ + $N_{60spring}$; T5: $P_{60}K_{60}$ + $N_{100spring}$; T6: $P_{60}K_{60}$ + $N_{40autumn}$ + $N_{60spring}$ + Zn; T7: $P_{60}K_{60}$ + $N_{40autumn}$ + $N_{80spring}$ + Zn; and T8: $P_{60}K_{60}$ + $N_{160spring}$ + Zn) on the grain yield and quality of four maize cultivars (NS-4023, NS-640, NS-6010 and NS-6030) in an alkaline calcareous soil. With the exception of T1, grain yield remained significantly lower in 2012 than in 2011. We found that N applied as split doses in autumn and spring with Zn resulted in higher grain yields than when N was reduced or added as the sole application. The fertilization regimes and cultivars affected grain quality differently during both years. Despite the always significant effects of fertilization regimes on grain quality indicators, the effects of cultivars varied considerably for grain quality between 2011 and 2012. The data on average climatic conditions at the study site showed much stronger variations in monthly and cumulative rainfall than temperature in 2011 and 2012. The variations in the effects of fertilization regimes on the grain yield and grain quality of the maize cultivars might be due to changes in rainfall patterns. These treatment and cultivar effects were further evident from the different relationships between grain yield and grain quality variables in 2011 and 2012 fueled by variations in climatic conditions. The optimum impact of inorganic N fertilizer regimes and Zn application on maize yield and quality requires a strategy taking into account balanced uptake of all elements during period of vegetation and yield formation. However, our study emphasizes conducting more long-term studies to further confirm the findings from this study. Future research is still suggested to evaluate these relationships between grain nutrient concentrations and maize GY for a wider range of genotypes and crop management treatments on different soil types.

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