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Synergistic Effect of Iron and Zinc Nanoparticles with Recommended Nitrogen Dose on Production and Grain Quality of Maize (*Zea mays* L.) Cultivars Under Drought Stress

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Abstract: Abiotic factors, such as drought, can significantly impact the vegetative growth and productivity of maize. To investigate the effects of the combined foliar application of zinc (Zn) and iron (Fe) nanoparticles with the recommended nitrogen dose (RND) on maize production and grain chemical composition under different water regimes, two field experiments were conducted in El-Ayyat city, Giza, Egypt, during the summer seasons of 2022 and 2023. This study utilized a split-split-plot experimental design with three replications. The main plots were designated to different water regimes (100, 80, 60, and 40% of estimated evapotranspiration), while the sub-plots were randomly distributed with Zn and Fe nanoparticle concentrations (0, 100, and 200 mg/L). The sub-sub-plots were randomly allocated to three maize cultivars (SC-P3062, SC-32D99, and SC-P3433). The results revealed that exposure to drought conditions resulted in a significant decline in the yield and yield-related attributes across all maize cultivars examined. Grain yield decreased by 10–50% under drought conditions. However, the foliar application of Zn and Fe nanoparticles was found to significantly improve grain yield, protein content, oil content, starch content, crude fiber, ash, and macro- and micronutrient concentrations in the maize cultivars under control and drought stress conditions. The foliar application of Zn and Fe nanoparticles at a concentration of 200 mg/L to the SC-P3433 maize cultivar led to the greatest grain yield per hectare, reaching 11,749 and 11,657 kg under the irrigation regimes with 100 and 80% total evapotranspiration, respectively. According to the assessment using the relative drought index, the SC-P3062 maize cultivar demonstrated tolerance (T) to water stress conditions. In conclusion, the foliar application of Zn and Fe nanoparticles (100–200 mg/L) effectively mitigated the negative effects of drought stress on maize plants. This approach can be recommended for farmers in arid and semi-arid regions to maintain and improve maize yield and grain quality under water-deficit conditions.

Keywords: corn; water regime; yield; protein; starch; macro- and micronutrients

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1. Introduction

Maize (*Zea mays*, L.) is one of the most widely cultivated field crops in the world. It ranks as the third most produced cereal crop, after wheat and rice. Maize is a multipurpose crop, with uses in fields including food production, animal feed, oil extraction, construction materials, and biofuel generation [1,2]. It has a high yield and is a widely cultivated agricultural commodity that exhibits a high degree of adaptability to diverse agro-climatic environments [3,4].

Abiotic stresses, such as drought, are a significant limiting factor in crop yield and productivity. This may be due to a variety of physiological and biochemical responses, including inhibited cell expansion, reduced biomass accumulation, decreased cell membrane stability, impaired osmotic adjustment mechanisms, reciprocal damage to cell membranes, disrupted metabolic activities, decreased plant vigor, dysregulation of leaf temperature, reduced stomatal conductance, and diminished photosynthetic capacity [5–11]. Drought is a major abiotic stress factor that significantly impacts maize production and productivity, especially in the developing world [12]. The drought stress conditions can lead to significant reductions in maize yield, with estimates ranging from a 12.5 to 42.0% decrease in yield [13–15]. Bouazzama et al. [16] indicated that a deficit in irrigation had a detrimental impact on the vegetative growth of the maize plants and accelerated the process of senescence in the maize leaves. Osborne et al. [17] concluded that drought stress occurring before the silking stage can have a significant impact on maize yield; it can decrease yield by 15.1 and 22.1%. Exposure to water stress can result in substantial reductions in both the yield and yield components for different maize cultivars [18]. The yield of maize can be substantially reduced if the crop experiences water deficit during the critical period from shortly before tasselling to the beginning of grain filling. The water deficits during this developmental stage can lead to decreases in maize yield of up to 90% [19]. Insufficient water availability has been identified as a primary driver of impaired growth and developmental patterns in maize [20]. Also, drought can reduce grain starch content in many crops [21,22].

Nanotechnology has emerged as a novel technological advancement that has permeated numerous facets of our modern life. In agriculture, nanomaterials can be leveraged to achieve several key objectives. Firstly, they can facilitate a reduction in the applied quantities of plant protection products. Secondly, nanomaterials can be utilized to optimize nutrient management. Lastly, the strategic deployment of nanomaterials has the potential to enhance crop yields [23]. Nano-fertilizers can be conceptualized as nanoparticles that are capable of delivering essential nutrients to facilitate plant growth. These nanomaterials possess a higher nutrient use efficiency in comparison to conventional fertilizers [24]. Nanomaterials are characterized by their extensive surface area, which enables them to harbor a substantial abundance of nutrients. As a result, the utilization of nano-fertilizers mitigates the potential adverse effects associated with the application of customized fertilizer inputs. Furthermore, nano-fertilizers can be conceptualized as nanomaterials that are capable of delivering a comprehensive array of macro- and micronutrients to crops, thereby enhancing their overall nutritional profile and growth potential. Nano-fertilizers represent a novel category of synthetic fertilizers that are characterized by the presence of readily available nutrients in the nanoscale range [25], which improves plants' ability to use nutrients [26]. Nano-fertilization techniques possess the ability to gradually provide crops with their essential nutrient requirements. This gradual and controlled release of nutrients holds significant environmental and economic implications when juxtaposed against the application of conventional chemical fertilizers [27]. The utilization of nanoparticles can lead to enhanced nutrient uptake by plants, as well as elevated concentrations of key biomolecules such as proteins and carbohydrates [28].

Zn and Fe are widely acknowledged as essential microelements that hold a pivotal role in the growth and development processes of plants. These micronutrients occupy a crucial position in a plethora of biochemical and physiological processes that occur within the complex plant system. Dhir et al. [29] and Elanchezhian et al. [30] indicated that Zn and Fe are essential nutrients that serve as integral components in the structure or activation of a diverse array of enzymatic systems. However, Chandrika et al. [31] indicated that nano-formulations of essential micronutrients, such as Zn and Fe in the form of nanocitrates, demonstrate superior performance when compared to commercially available nutrient sources. Zn is an essential micronutrient necessary for the production of chlorophyll, as well as the synthesis of carbohydrates, which are fundamental for plant growth and development [32]. Zn contributes to the biosynthesis of various plant hormones, the synthesis of cytoplasmic components, the activation and functioning of diverse enzymatic systems, and the process of protein synthesis [33,34]. Furthermore, Khan et al. [35], Lošák et al. [36], and Hafeez et al. [37] reported that Zn is involved in a variety of essential plant processes, including the biosynthesis of tryptophan. Additionally, Zn participates in the control of carbonic anhydrase activity, the activation of RNA polymerase enzymes, the stabilization of cytoplasmic membranes, and the regulation of oxidative stress through its role in superoxide dismutase enzymes. These diverse functions of Zn contribute to enhanced plant resistance to water stress, making it a critical element for maintaining plant health and productivity, especially under drought conditions. However, the application of zinc oxide nanoparticles can improve the antioxidant enzymes in maize [38]. The available evidence suggests that ZnO nanomaterials have a positive effect on maize biomass and growth, which is expressed through the acceleration of exogenous physiological processes. Choudhary et al. [39] indicated that the foliar application of zinc-based nano-fertilizers can significantly improve yield in single-cross hybrid maize varieties. Fe serves as a critical structural component in various porphyrin molecules, including cytochromes, heme proteins, Fe-S proteins, and leghaemoglobin. This essential mineral is involved in a wide range of oxidation–reduction reactions that are fundamental to cellular respiration and photosynthesis processes. Fe serves a catalytic function in the biosynthesis of chlorophyll, Additionally, Fe is a constituent element of the enzyme nitrogenase [32]. Without Fe, the process of photosynthesis cannot occur effectively [40]. Fe nanoparticles can significantly improve the Fe content in maize plants. The evidence indicates that nano-based Fe fertilizers are more effective than traditional mineral Fe fertilizers in enhancing the growth and productivity of maize [28,41].

In semi-arid regions, the limited availability of water in the soil is widely recognized as the primary limiting factor that constrains the production of crops, such as maize [42]. The combination of rising irrigation water demands and the impacts of global climate change poses significant challenges for the future of maize production. As a result, there is an increasing urgency to develop and test techniques that can improve the drought tolerance capabilities of maize cultivars [43]. However, Huang et al. [44] suggested that there is a need for more comprehensive research studies focused on developing suitable techniques that can effectively mitigate the loss of maize yield and quality caused by water deficits. Also, Alsamadany et al. [45] recommended that the available evidence supports the need for further investigation into the applications of nanoparticles to alleviate various stresses in plants. In this investigation, we will explore the synergistic role of Fe and Zn in the form of nanoparticle sprays in conferring drought stress tolerance in maize. Limited research has been conducted on the performance of maize cultivars SC-P3062, SC-32D99, and SC-P3433 under both normal and water-stressed conditions. Therefore, the objectives of this investigation were (i) to examine the yield and chemical composition of grains in three recently single-cross hybrids, SC-P3062, SC-32D99, and SC-P3433, of maize cultivars grown under drought stress; (ii) to compare and assess the sensitivity of these cultivars to water stress; and (iii) to investigate the effect of the foliar application of Fe and Zn nanoparticles with RND on these cultivars under different water regimes.

2. Materials and Methods

2.1. Experimental Site

Two field experiments were conducted in El-Ayyat city, Giza, Egypt (29°40′53.7″ N 31°13′40.8″ E), during the two consecutive summer seasons in 2022 and 2023. During these periods, the average monthly temperatures exhibited a gradual increase, rising from 25.6 and 26.0 °C in May to 30.9 °C and 31.7 °C in August and September for the first and second seasons, respectively. The maximum relative humidity levels were recorded as 44.1 and 41.4% in September and August for the first and second seasons, respectively. The total rainfall amounts were 0.004 and 0.015 for the first and second seasons, accordingly (Table 1).

Table 1. Monthly mean of climatic data at experimental site in Ayyat city and 2022–2023 seasons *.

Month	2022			2023		
	Temperature (°C)	Relative Humidity (%)	Rainfall (mm)	Temperature (°C)	Relative Humidity (%)	Rainfall (mm)
May	25.6	40.2	0.000	26.0	35.9	0.005
June	28.7	35.0	0.004	29.8	35.7	0.002
July	30.3	37.7	0.000	31.7	35.9	0.004
August	30.9	39.4	0.000	31.1	41.4	0.002
September	30.1	44.1	0.000	29.6	40.5	0.002

* Data obtained by the Central Laboratory for Agricultural Climate (CLAC), Agricultural Research Center (ARC), Egypt.

The soil mechanical analysis was conducted in accordance with the methodology described by Klute [46], while the chemical analysis followed the procedures outlined by Page et al. [47]. The soil of the experimental site during the two studied seasons is classified as sandy loam soil (Table 2). The chemical analysis of the irrigation water was carried out following the methods described by Cottenie et al. [48]. Irrigation water was obtained from a profound well found within the exploratory region, with pH 7.6–7.4 and electrical conductivity (EC) 0.52–0.65 dS m^{-1} in both seasons (Table 3). The physical and chemical properties of the experimental soil site and irrigation water during the two studied seasons were analyzed at Reclamation and Development Center Desert Soils, Faculty of Agriculture Research Park, Cairo University.

Table 2. Physical and chemical properties of soil analysis at 30 cm depth before planting at experimental site (Ayyat City).

Soil Characteristics	2022	2023	Soil Characteristics	2022	2023
Physical Analysis			Soluble Anions and Cations (mEqu/L)		
Silt %	13	15	HCO_3	1.42	1.33
Clay %	11	12	Cl	55.93	49.25
Sand %	76	73	SO_4	46.65	50.24
Fine Sand %	58	51	Ca^{++}	65.15	59.88
Coarse Sand %	18	22	Mg^{++}	15.35	16.14
Soil Type	Sandy Loam	Sandy Loam	Na^{+}	23.99	22.49
SP	28	22	K^{+}	0.21	0.19
$CaCO_3$ %	7.5	6.7	Available Nutrients (mg kg^{-1})		
Organic Matter (%)	0.35	0.41	N	45	51
Soil Bulk Density (g cm^{-3})	1.6	1.4	P	9	8
SAR	5.67	5.34	K	92	86
Chemical Analysis			Zn	55	47
pH (Paste Extract)	7.9	7.6	Mn	0.6	0.5
EC (dSm^{-1})	8.9	8.3	Fe	4	5

SP: saturation percentage; SAR: sodium adsorption ratio.

Table 3. Chemical property analysis of irrigation water at experimental site in Ayyat city.

Season	pH	EC (dSm^{-1})	Soluble Anions (meq.L^{-1})			Soluble Cations (meq.L^{-1})				SAR %
			Cl^{-}	SO_4^{-}	HCO_3^{-}	K^{+}	Na^{+}	Mg^{++}	Ca^{++}	
2022	7.6	0.52	1.53	1.68	1.79	0.12	0.68	2.08	2.12	0.48
2023	7.4	0.65	1.44	1.57	1.83	0.15	0.55	1.98	1.79	0.53

SAR: sodium adsorption ratio.

2.2. Zinc and Iron Nanoparticle Preparation

All the reagents employed in this study were of analytical-grade quality. The nanoparticles were synthesized from their respective precursors using well-established preparatory methods. Zinc in the form of zinc chloride ($ZnCl_2$) and zinc sulfate ($ZnSO_4$) was obtained from Sigma Chemical Co. (St. Louis, MO, USA), while magnetite (Fe_3O_4) was also acquired from the same source. The zinc-based nanoparticles were synthesized using an aqueous solution containing a 1:1 volume ratio of zinc chloride and zinc sulfate, employing a top-down molecular chemical method [49]. The iron nanoparticles were obtained through a similar top-down molecular chemical approach but under a pressure of 1.5 MPa in the form of FeO [50]. The synthesized nanoparticles exhibited an uncontrolled shape with a crystalline structure and a purity of approximately 98.5%. The morphology and size of the nanoparticles were characterized using a JEOL 1010 transmission electron microscope (TEM) operated at 80 kV (JEOL, Tokyo, Japan). For the TEM analysis, a drop of the nanoparticle solution was spread onto a carbon-coated copper grid and allowed to dry at room temperature. The sizes of the nanoparticles were determined directly from the figure using the Image-Pro Plus 4.5 software (Figures 1 and 2).

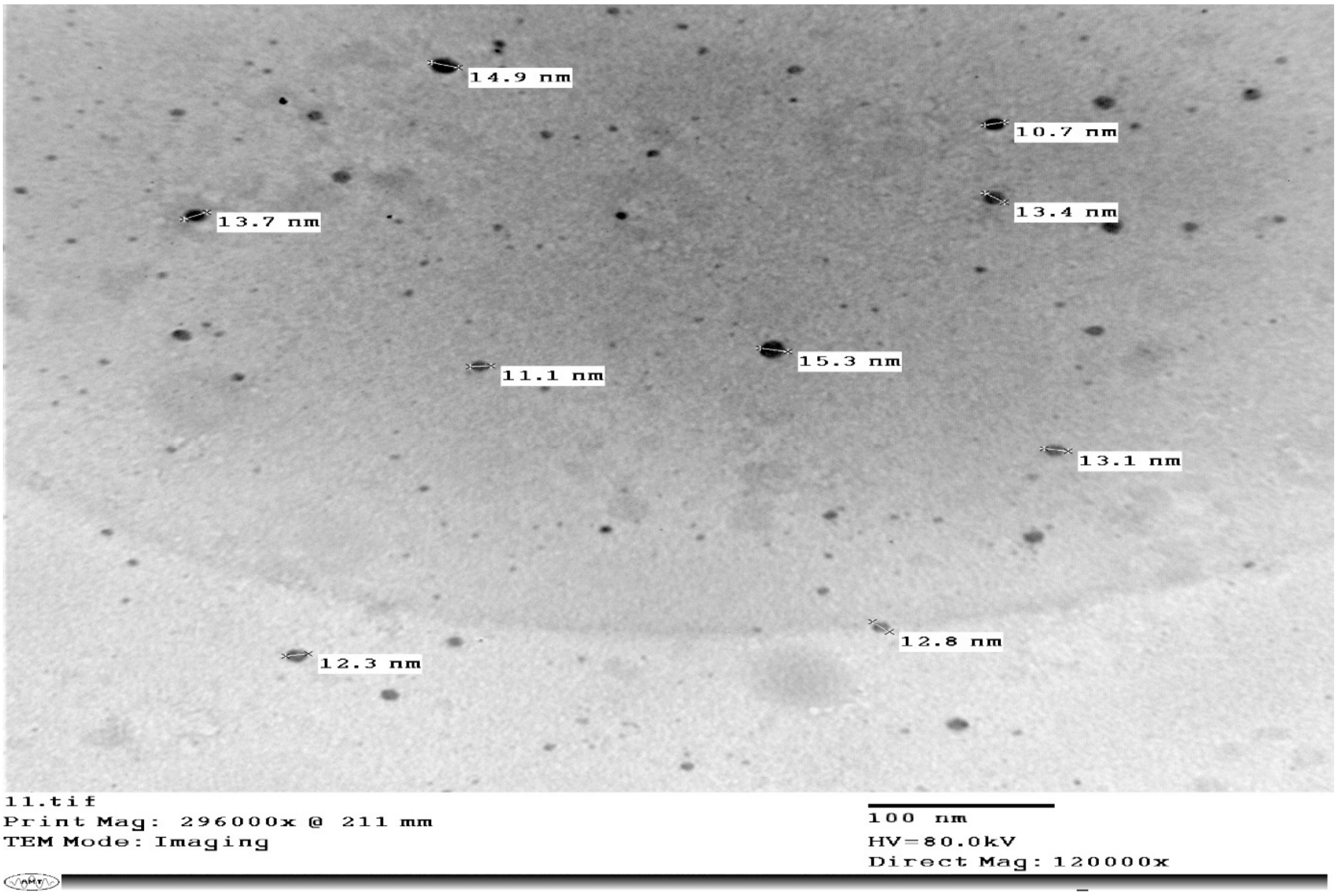

Figure 1. Transmission electron microscopy (TEM) of nano-zinc particles using 10,000× magnification.

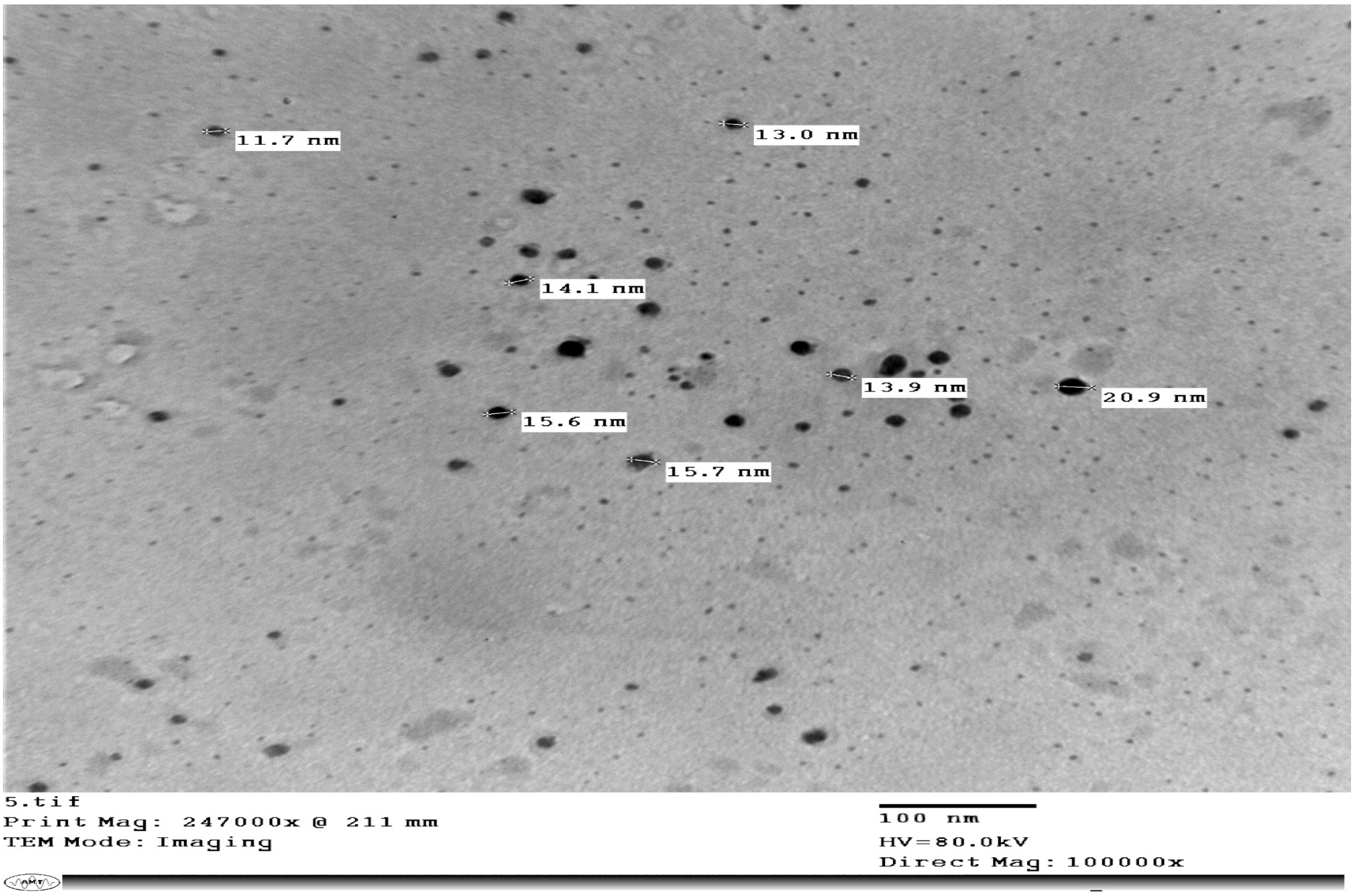

Figure 2. Transmission electron microscopy (TEM) of nano-iron particles using 10,000× magnification.

2.3. Experimental Design and Treatments

The cultivars SC-P3062, SC-32D99, and SC-P3433 were obtained from DuPont Pioneer Company, Cairo, Egypt. The genetic materials utilized in this investigation included three maize genotypes, specifically single-cross hybrids; SC-P3062, SC-32D99, and SC-P3433 were evaluated under three levels of zinc and iron nanoparticles [0 (control), 100, and 200 mg mg/L] and four water stress treatments [100 (control), 80, 60, and 40% of estimated evapotranspiration]. The irrigation interval and total amount of irrigation water applied over the entire growing season were calculated in accordance with the methods described by Allen et al. [51], as presented in Table 4. Three maize cultivars were subjected to foliar applications of Zn and Fe nanoparticles at concentrations of 100 and 200 mg/L, equivalent to approximately 50 and 100 g/ha, respectively. The nanoparticle applications were divided into three equal doses and administered at 30, 45, and 60 days after sowing. For comparison purposes, the control treatment (0 mg/L) received applications of an equal volume of distilled water. The experimental design employed in this study was a split-split-plot arrangement in a randomized complete block design with three replications. Water regimes (100, 80, 60, and 40% of estimated evapotranspiration) were assigned to the main plots, and nano-fertilizers [0 (control), 100, and 200 mg/L] were randomly distributed in the sub-plots, while the maize hybrids were randomly distributed in the sub-sub-plots.

Table 4. Water irrigation scheme of field experiments.

Date		Stage *	Net	Irrigation Levels, mm			
From	To		mm *	100%	80%	60%	40%
20-May	04-Jun	Init	153.6	219.4	175.5	188.0	125.3
10-June	10-July	Dev	795.4	1136.9	909.0	974.5	649.6
13-July	18-August	Mid	1278.5	1826.6	1461.1	1565.7	1043.8
21-August	18-Sep	End	495.4	707.5	566.1	606.4	404.3
Total uptake of water during season (m^3/ha)				3890.4	3111.8	3334.6	2223.1

mm * = milliliter of water depth, Init = initiation, Dev = development, Mid = mid-season, and End = end season.

2.4. Cultural Practices

The preceding crop in both growing seasons was faba bean (*Vicia faba* L.). The maize seeds were sown by hand in hills at a target plant density of 57,600 plants per hectare. Each individual plot consisted of 6 rows, with a row width of 70 cm and a length of 5 m. The sowing dates were 20 May and 16 May in the 2022 and 2023 growing seasons, respectively. After 20 days, the seedlings were thinned to maintain one plant per hill. Prior to sowing, a calcium superphosphate fertilizer (15.5% P_2O_5) was uniformly applied at a rate of 60 kg P_2O_5 per hectare. The recommended nitrogen dose (RND) for ammonium nitrate (33.5% N) was then added in ten equal doses at a nitrogen application rate of 360 kg N per hectare, with applications made every four days after germination. Standard agricultural practices, including weed management through two hoeing operations at 25 and 50 days after germination, were followed throughout the growing seasons. All other cultural practices were implemented as recommended by the Ministry of Agriculture, Egypt.

2.5. Data Collection

2.5.1. Agronomic Traits

At the time of harvest, ten randomly selected plants from each plot were sampled to determine the following parameters: number of leaves per plant, plant height (cm) (measured from the soil surface to the flag leaf), ear height (cm), ear weight per plant (g), grain weight per ear (g), and grain index (g) (based on 20 randomly selected ears per plot). The grain yield (kg) per hectare was measured from the entire area of each experimental unit (sub-sub-plot) and then adjusted to a moisture content of 15.5%.

2.5.2. Relative Drought Index (RDI)

The relative drought index was calculated according to Fischer et al. [52] as follows:

$$\text{STI} = \left(\text{Y}_\text{S}/\text{Y}_\text{p}\right)/\left(\overline{y}_s/\overline{y}_p\right),$$

where:

Y_S = grain yield of a given hybrid under water stress.

Y_p = grain yield of a given hybrid under non-stress.

$\overline{y}_s$ = average grain yield of all hybrids under stress.

$\overline{y}_p$ = average grain yield of all hybrids under non-stress.

When RDI $\geq$ 1, it indicates that the genotype is tolerant (T) to stress; if 0.5 $\leq$ RDI < 1, it indicates that the genotype is moderately tolerant (M); and if RDI < 0.5, it indicates that the genotype is sensitive (S).

2.5.3. Chemical Composition of Grain

The grains were manually separated from any extraneous materials and dried at a constant temperature of 65 °C. Once the grains reached a consistent weight, they were ground into a fine powder. The ground grain samples were then stored in polyethylene bags and kept in the dark at a temperature of 4 °C for chemical analyses.

Protein content was estimated using the Kjeldahl method, with a nitrogen-to-protein conversion factor of 5.75. Ash content was determined by heating the sample in a muffle furnace at 900 ± 10 °C in an oxidizing atmosphere. Crude fiber and oil content were measured using the Soxhlet extraction method. The grain samples were analyzed according to the methods described by the Association of Official Agricultural Chemists [53]. Starch content was determined through starch hydrolysis, following the procedure of Rasmussen and Henry [54].

A two-gram grain sample was subjected to combustion at 550 °C. The resulting ash was dissolved in 100 mL of 1 M hydrochloric acid (HCl) solution. The nitrogen (N) content was then determined using the micro-Kjeldahl method, as described by Jones et al. [55]. The phosphorus (P) content was quantified spectrophotometrically using the stannous chloride technique, following the procedures outlined by the Association of Official Analytical Chemists [53]. Potassium (K) was measured using a flame photometer. The concentrations of the following minerals were determined using atomic absorption spectrophotometry: calcium (Ca), magnesium (Mg), zinc (Zn), iron (Fe), manganese (Mn), sodium (Na), and chloride (Cl). The grains were digested prior to analysis as recommended by Piper [56] and as described in the AOAC Official Methods [53].

2.6. Statistical Analysis

The normal distribution of the experimental data was evaluated using the Shapiro–Wilk method [57] within the SPSS v. 17.0 statistical software package [58]. Additionally, the data were tested for any violations of the underlying assumptions required for the combined analysis of variance. This process involved separately analyzing the data for each growing season according to a split-split-plot arrangement in a randomized complete block design with three replications. Water regimes were assigned to the main plots, nano-fertilizers were randomly distributed in the sub-plots, while the maize hybrids were randomly distributed in the sub-sub-plots, followed by a combined analysis across the two seasons. The Least Significant Difference (LSD) test is a statistical method used at *p*-value = 0.05 to compare treatment means. It involves calculating the difference between pairs of means and assessing whether this difference exceeds the LSD value. If the difference surpasses the LSD value, it indicates a statistically significant variation between the means, as recommended by Snedecor and Cochran [59]. The statistical analyses were performed using the MSTAT-C software (Version 2.0) package [60].

A random linear model combined analysis over the locations for the split-split-plot design was calculated according to Snedecor and Cochran (1994) as follows:

$$Y_{ijkse} = \mu + L_e + A_j + \gamma_I + (AL)_{je} + \eta_{ije} + \beta_k + (AB)_{jk} + (BL)_{ke} + (ABL)_{jke} + K_{jke} + C_s + (CL)_{se} + (AC)_{js} + (BC)_{ks} + (ABC)_{jks} + (ACL)_{jse} + (BCL)_{kse} + (ABCL)_{jkse} + E_{ijkse}.$$

where

Y_{ijkse} = Observation in the sub-sub-plot of (L) the location	
μ = general mean.	L_e = location effect.
A_j = main plot factor "A" effect.	γ_I = rep within the location effect.
$(AL)_{je}$ = AL interaction effect.	η_{ije} = error $_{(a)}$ effect.
β_k = sub-plot factor "B" effect.	$(AB)_{jk}$ = AB interaction effect.
$(BL)_{ke}$ = BL interaction effect.	$(ABL)_{ike}$= ABL interaction effect.
K_{jke} = error $_{(b)}$ effect.	C_s = sub-sub-plot factor effect.
$(CL)_{se}$ = CL interaction effect.	(AC)js = AC interaction effect.
$(ABC)_{jks}$ = ABC interaction effect.	$(ACL)_{jse}$= ACL interaction effect.
$(BCL)_{kse}$ = BCL interaction effect.	$(ABCL)_{jkse}$ = ABCL interaction effect.
E_{ijkse} = error $_{(c)}$ effect.	

3. Results and Discussion

3.1. Agronomic Traits

The analysis revealed no significant differences between the two study years, allowing the data from both years to be combined for further evaluation. Significant differences were observed among the water regimes, nano-fertilizer treatments, and maize cultivars for various agronomic traits (Table 5). The analysis of variance presented in Table 5 demonstrated significant differences among the cultivars, water regimes, and nano-fertilizers concerning all agronomic traits examined. The mean squares related to water regimes were notably significant for every agronomic trait. Likewise, the mean squares associated with nano-fertilizers were either significant or highly significant for all traits, with the exception of ear height. Moreover, the mean squares for the cultivars were found to be highly significant across all traits. Additionally, the interaction effects among water regimes, nano-fertilizers, and cultivars displayed significant or highly significant mean squares for all agronomic traits.

Table 5. Combined analysis of variance of split-split-plot design for three maize cultivars evaluated under four water regimes and three nano-fertilizers across 2022 and 2023 seasons.

SOV	df	No. of Leaves Plant^{-1}	Plant Height (cm)	Ear Height (cm)	Ear Weight (g)	Grain Weight/Ear (g)	Grain Index (g)	Yield ha^{-1} (kg)
Season S	1	3.63	876.04	916.7 *	36,350.2 **	17,872.7 *	116.79 **	2,594,614 **
S/Reps	4	0.685	622.07	82.1	1403.3	899.39	5.19	414,595
Water A	3	5.136 *	38,732.1 **	5637.9 **	18,838 **	96,469.9 **	663.3 **	2,345,419 **
SA	3	0.617	149.78	487.33	1192.9	567.56	4.14	1,261,687
Error a	12	1.358	383.85	260.7	2468.1	1362.8	5.77	16,432.5
Fertilizer B	2	0.963	6309.1 **	343.42	6396.0 **	51,548.2 **	82.67 **	5,074,251 **
SB	2	3.352	709.5	1425.6 **	75.08	65.94	4.58	83,825.3
AB	6	1.34	310.6	187.19	5697.5 **	3297.3 **	1.64	3,719,531 *
SAB	6	0.802	237.83	127.1	1410.3	676.74	8.26	833,209
Error b	32	1.037	309.31	231.2	1282.2	671.35	5.86	137,527
Cultivars C	2	19.4 **	11,564.7 **	1471.6 **	17,713 **	12,690 **	405.21 **	3,613,423 **
SC	2	0.241	67.54	356.6 **	2.057	7.746	4.94 *	4,073,654 **
AC	6	2.82 **	684.82	951.2 **	21,588.1 **	10,488 **	32.2 *	1,608,434 **
SAC	6	0.247	183.69	173.3 **	503.03	274.32	4.14	1,346,820 **
BC	4	1.046 **	1698.9 **	270.4 **	13,001.5 **	6755.5 **	14.14 **	9,564,601 **
SBC	4	1.588 **	82.139	772.9 **	142.92	56.94	11.64 **	624,547 **
ABC	12	0.914 *	968.7 **	370.8 **	1444.5 *	747.07 **	5.2 *	1,165,143 **
SABC	12	0.418	447.73	66.26	676.41	361.88	1.79	116,339
Error c	96	0.206	348.14	29.81	509.4	271.79	2.63	102,034

* Significant at p-value 0.05, and ** significant at p-value 0.01.

Water stress resulted in a substantial decline in agronomic performance across the different cultivars, compared to the well-watered control. Additionally, drought stress significantly reduced the yield and yield components of all the evaluated maize cultivars. The foliar application of zinc (Zn) and iron (Fe) nanoparticles, however, significantly improved most agronomic traits in the different cultivars, under both the well-watered and water-stressed conditions. This included improvements in the number of leaves per plant, plant height, ear height, ear weight, and grain weight per ear, compared to the control. The extent of yield reduction under drought stress varied among the cultivars. For the SC-P3062 cultivar, yields decreased by 13.67%, 23.09%, and 49.14% under mild, moderate, and severe water stress, respectively. Similarly, the SC-32D99 cultivar experienced yield reductions of 22.60%, 23.63%, and 50.41% under 80%, 60%, and 40% of estimated evapotranspiration, respectively. The SC-P3433 cultivar exhibited yield decreases of 10.38%, 41.34%, and 50.98% under the same water regimes (Table 6).

Table 6. Agronomic traits of three maize cultivars at different levels of water regimes and foliar application of nano-fertilizers.

Water Regimes (%)	Nano-Fertilizers (mg L^{-1})	Cultivars	No. of Leaves $Plant^{-1}$	Plant Height (cm)	Ear Height (cm)	Ear Weight (g)	Grain Weight Ear^{-1} (g)	Grain Index (g)	Yield ha^{-1} (kg)
100 Irrigation	Control	SC-P3062	13.8	274.8	123.8	178.8	121.6	32.2	6561
		SC-32D99	12.5	278.5	125.2	251.7	163.6	35.0	8782
		SC-P3433	14.5	297.5	138.3	365.4	259.5	39.6	10,308
	100	SC-P3062	14.0	277.2	128.8	243.5	170.4	34.0	8228
		SC-32D99	13.3	312.8	123.5	223.2	149.5	36.0	8453
		SC-P3433	14.2	310.0	143.8	376.1	274.6	38.1	10,765
	200	SC-P3062	15.0	310.5	127.8	280.0	201.6	36.2	9369
		SC-32D99	13.3	309.5	124.0	290.6	203.4	37.3	10,461
		SC-P3433	14.7	315.0	141.5	444.6	337.9	39.2	11,749
80 Irrigation	Control	SC-P3062	14.0	275.3	128.2	163.3	111.1	29.3	5664
		SC-32D99	14.5	265.8	137.5	202.9	131.9	33.8	6797
		SC-P3433	14.5	307.5	149.3	267.0	189.5	37.5	9238
	100	SC-P3062	14.2	285.7	131.2	231.5	162.1	30.3	8135
		SC-32D99	14.0	284.2	137.3	233.2	156.2	34.1	8356
		SC-P3433	14.3	303.8	152.0	361.4	263.9	37.4	10,536
	200	SC-P3062	14.8	297.8	130.3	262.1	188.7	33.0	8915
		SC-32D99	13.2	300.0	130.5	242.5	169.8	36.7	8565
		SC-P3433	14.5	301.3	155.7	397.6	302.2	38.2	11,657
60 Irrigation	Control	SC-P3062	14.3	234.8	124.0	148.2	100.8	27.2	5046
		SC-32D99	13.3	260.5	125.0	207.2	134.7	32.8	6707
		SC-P3433	14.2	278.5	144.2	197.2	140.0	32.2	6047
	100	SC-P3062	14.7	254.2	127.3	228.7	155.1	29.0	8174
		SC-32D99	12.7	242.3	113.3	197.3	136.2	33.5	6755
		SC-P3433	14.0	295.0	141.5	248.5	181.4	32.8	6730
	200	SC-P3062	14.0	274.2	129.0	219.5	158.1	30.1	7659
		SC-32D99	12.8	261.3	120.5	188.6	132.0	33.9	6270
		SC-P3433	14.0	269.7	152.0	294.3	223.7	35.0	7269
40 Irrigation	Control	SC-P3062	14.7	211.2	99.5	106.3	72.3	22.8	3337
		SC-32D99	12.5	209.7	90.2	163.7	106.4	31.6	4355
		SC-P3433	13.8	264.2	136.2	176.5	125.3	27.6	5053
	100	SC-P3062	14.0	256.7	114.0	159.2	111.5	24.9	5389
		SC-32D99	11.8	226.3	96.7	149.8	100.3	31.1	4831
		SC-P3433	13.5	252.7	133.5	155.1	113.2	29.2	3892
	200	SC-P3062	14.5	239.5	112.3	175.9	126.6	27.9	5936
		SC-32D99	12.0	241.0	96.5	153.8	107.6	30.3	4905
		SC-P3433	14.5	260.2	153.3	193.7	147.2	29.3	5101
	$LSD_{0.05}$		0.98	20.79	17.69	42.3	30.84	3.40	1166

Drought stress significantly impacted the vegetative growth and productive performance of the evaluated maize hybrids. The reduction in the agronomic performance of maize under water stress can be attributed to various physiological mechanisms. Drought inhibits cell expansion, reduces biomass accumulation, alters cell membrane stability, impairs osmotic adjustment, and negatively impacts metabolic activities [5,6,8,11,61]. The current study found that maize grain yield decreased by 10–50% under water stress across the tested cultivars. These findings align with previous research reporting substantial yield reductions in maize under drought conditions [13–15,17,43,62]. Notably, maize yield can be reduced by up to 90% if the crop experiences water deficit from a few days before tassel emergence to the beginning of grain filling [19]. Furthermore, studies have shown that irrigation deficit can affect vegetative growth and accelerate leaf senescence in maize [16]. Water stress has also been reported to decrease grain yield and 1000-grain weight [63], as well as the number of grains per plant [64]. Overall, water deficit can lead to severe damage to the yield and yield components of maize cultivars [18].

The results showed that the foliar application of Zn and Fe nanoparticles led to a significant increase in the grain yield of the tested maize cultivars, compared to the control, under both well-watered and water stress conditions (Table 5). Under the control water regime (no stress), the grain yield of the SC-P3062 cultivar was increased by 25.41 and 42.80% when treated with 100 and 200 mg/L of Zn and Fe nanoparticles, respectively. Similarly, the grain yield of the SC-P3433 cultivar was enhanced by 11.66 and 25.40% with the same treatments. Under the mild water stress condition (80% of estimated evapotranspiration), the grain yield of the SC-P3062 cultivar was increased by 43.63 and 57.40% with 100 and 200 mg/L of Zn and Fe nanoparticle treatments, respectively. The grain yield of the SC-P3433 cultivar also showed significant increases of 14.05 and 26.19% under the same treatments. Under the moderate water stress condition (60% of estimated evapotranspiration), the grain yield of the SC-P3062 cultivar was increased by 61.99% and 51.78% with 100 and 200 mg/L of Zn and Fe nanoparticle treatments, respectively. The grain yield of the SC-P3433 cultivar showed increases of 11.29% and 20.21% under the same treatments. Even under severe water stress (40% of estimated evapotranspiration), the foliar application of Zn and Fe nanoparticles was able to significantly enhance the grain yield of the SC-P3062 cultivar by 61.49% and 77.88% with the 100 mg/L and 200 mg/L treatments, respectively. The grain yield of the SC-P3433 cultivar also showed improvements, albeit to a lesser extent, under the same treatments (Table 6).

The positive effects of the foliar application of Fe and Zn nanoparticles on plant growth have been widely reported in the literature. Several studies have demonstrated the beneficial impacts of these nanoparticles on various crop plants, including maize, under control and drought stress conditions. The enhanced growth and yield observed in the present study can be attributed to the physiological and biochemical roles of Zn and Fe in plant cells during drought stress. Zinc has been shown to increase the production of abscisic acid (ABA) in plants, which can enhance stomatal regulation and improve water use efficiency under water-limited conditions [65]. Additionally, nano-ZnO has been found to alleviate the negative effects of drought stress by improving photosynthetic carbon assimilation and mitigating the damage to mitochondria and chloroplasts in corn [61,66]. Iron, on the other hand, is a structural component of essential biomolecules involved in oxidation–reduction reactions, photosynthesis, and nitrogen fixation [32,40]. Fe nanoparticles can promote photosynthetic efficiency and nutrient absorption in plants, contributing to their enhanced productivity under stress [67–69]. Importantly, the foliar application of Fe and Zn nano-chelates has been shown to increase the number of grains per plant under stress conditions, while Fe_3O_4 nanoparticles have been reported to significantly improve 1000-grain weight and grain yield in maize under drought stress [70,71]. The results of the present study highlight the potential of the foliar application of zinc (Zn) and iron (Fe) nanoparticles as a strategy to alleviate the harmful effects of water stress on maize grain production. The findings emphasize the significance of managing Zn and Fe nanoparticles in order to enhance the productivity of maize under drought conditions. This could be attributed to the ability of these nanoparticles to improve various physiological and biochemical responses in maize plants, thereby enhancing their resilience and productivity under drought conditions.

3.2. Relative Drought Index (RDI)

The present study examined the drought tolerance of three maize cultivars, SC-P3062, SC-32D99, and SC-P3433, under varying levels of water stress (Table 7). The relative drought index (RDI) was used as an indicator of drought tolerance, with values ranging from 1.02 to 1.20 for the SC-P3062 cultivar, 0.93 to 0.99 for the SC-32D99 cultivar, and 1.04 to 0.85 for the SC-P3433 cultivar under mild (80% of estimated evapotranspiration) and severe (40% of estimated evapotranspiration) water stress conditions. Based on the RDI values, the SC-P3062 cultivar was classified as tolerant (T) to water stress, the SC-32D99 cultivar was moderately tolerant (M), and the SC-P3433 cultivar was tolerant under mild water stress conditions but moderately tolerant under moderate and severe water stress conditions. These findings suggest that the SC-P3062 cultivar was the most drought-tolerant among the three, followed by SC-P3433 and SC-32D99. Previous studies have also investigated the drought tolerance of maize hybrids under controlled environmental conditions [72]. The literature indicates that the use of drought-tolerant maize cultivars and the adoption of adaptive farming approaches can enable maize production in semi-arid regions with limited water resources, as these cultivars are less water-intensive and can maintain higher yields [73,74]. Moreover, the existing literature suggests that the RDI is an effective tool for identifying high-yielding genotypes under both normal and drought stress conditions [75]. The current study's findings on the differential drought tolerance of the three maize cultivars, as determined by the RDI, provide valuable insights into the selection and deployment of suitable genotypes in water-scarce environments.

Table 7. Mean grain yield (kg ha^{-1}) and relative drought index (RDI) for maize cultivars under water stress (data are combined across 2022 and 2023 seasons).

Hybrid	Mean				Relative Drought Index (RDI)		
	WW	80% WS	60% WS	40% WS	WW vs. 80% WS	WW vs. 60% WS	WW vs. 40% WS
SC-P3062	8052.78	7571.44	6959.78	4887.28	1.02 (T)	1.21 (T)	1.20 (T)
SC-32D99	9232.22	7906.11	6577.28	4696.89	0.93 (M)	0.99 (M)	0.91 (M)
SC-P3433	10,940.94	10,477	6681.83	4682.06	1.04 (T)	0.85 (M)	0.85 (M)
Average	9408.6	8651.5	6739.6	4755.4	1.00 (T)	1.02 (T)	0.98 (M)

WW, 80%WS, 60%WS, and 40%WS indicate well-watered, 80% water stress, 60% water stress, and 40% water conditions, respectively. T, M, and S indicate tolerant, moderately tolerant, and sensitive, respectively.

3.3. Chemical Composition of Grain

Significant differences were observed in the grain composition, except for moisture content, across the various water regimes, Zn and Fe nano-fertilizer treatments, and cultivars (Table 8). The analysis of variance presented in Table 8 demonstrated significant differences among the cultivars, water regimes, and nano-fertilizers concerning the chemical composition of grain. The mean squares for water regimes were highly significant across all aspects of grain chemical composition, while those for nano-fertilizers also showed high significance for all traits. Additionally, the mean squares for the cultivars were significant for all traits. Furthermore, the interaction effects of water regimes, nano-fertilizers, and cultivars revealed significant or highly significant differences for all components of grain chemical composition, with the exception of moisture.

Table 8. Combined analysis of variance of split-split-plot design for three maize cultivars evaluated under four water regimes and three nano-fertilizers across 2022 and 2023 seasons.

SOV	df	Moisture	Protein	Oil	Starch	Crude Fiber
Season S	1	0.077	0.047	1.477	3726.2	0.047
S/Reps	4	1.791	1.561	2.079	4169.1	0.122
Water A	3	1.321 **	20.26 **	7.172 **	8.36 **	1.178 **
SA	3	0.035 **	0.038 **	0.164 **	2.16 **	0.138 **
Error a	12	0.001	0.002	0.0001	0.058	0.001
Fertilizer B	2	0.596 **	4.14 **	0.556 **	3997 **	0.321 **
SB	2	0.386 **	0.015	0.234 **	3512 **	0.035 **
AB	6	0.263 **	0.344 **	0.087 **	5.775	0.281 **
SAB	6	0.058 *	0.682 **	1.017 **	5.651	0.597 **
Error b	32	0.021	0.013	0.016	314.29	0.001
Cultivars C	2	2.15 **	2.799 **	1.23 **	8186 **	0.645 **
SC	2	0.337	3.803 **	0.111 **	4950 **	1.323 **
AC	6	0.047	0.478 **	0.321 **	6.078	0.198 **
SAC	6	0.176	0.456 **	0.772 **	8.185	0.409 **
BC	4	1.243 **	1.987 **	0.825 **	3717 **	0.187 **
SBC	4	1.769 **	3.202 **	5.465 **	3526 **	1.282 **
ABC	12	0.114	0.53 **	0.705 **	239.45 *	0.492 **
SABC	12	0.318	1.183 **	1.18 **	28.457	0.615 **
Error c	96	0.25	0.017	0.023	87.103	0.001

* Significant at p-value 0.05, and ** significant at p-value 0.01.

The foliar application of Zn and Fe nanoparticles was found to increase the moisture, protein, oil, starch, crude fiber, and ash contents of the maize grains under both control and drought stress conditions (Table 9). Among the evaluated cultivars, SC-P3062 exhibited the highest starch content under both control and drought stress conditions. The SC-32D99 cultivar demonstrated the greatest crude fiber content in the control and moderate stress scenarios, while SC-P3433 achieved the highest protein levels across the control, moderate, and severe stress situations. Furthermore, SC-P3433 also recorded the highest ash content when subjected to the control, mild, and severe stress conditions. In terms of oil content, both SC-32D99 and SC-P3433 showed elevated values under the control and drought stress conditions. When treated with zinc and iron nanoparticles, the SC-P3062 cultivar achieved the highest starch content, at 80.67%, while SC-32D99 had the highest crude fiber content, also at 80.67%. SC-P3433 led in moisture, protein, oil, and ash contents, measuring 8.13%, 3.93%, 5.49%, and 3.83%, respectively, under the well-watered condition. Under mild stress, the SC-P3062 cultivar treated with these nanoparticles recorded the highest starch and crude fiber contents of 78.83% and 1.38%, respectively. The SC-32D99 cultivar reached the highest protein and oil contents, at 4.25% and 5.33%, respectively, while SC-P3433 had the highest moisture and ash contents, at 8.14% and 4.25%, respectively. In moderate stress conditions, the SC-P3062 cultivar, when sprayed with zinc and iron nanoparticles, achieved the highest starch content, at 80.20%. The SC-32D99 cultivar had the highest moisture, oil, crude fiber, and ash contents, measuring 8.05%, 5.05%, 0.95%, and 3.19%, respectively. SC-P3433 reached the highest protein content, at 4.92%. Under severe stress, SC-P3062 again exhibited the highest starch and crude fiber contents, at 79.52% and 0.96%, respectively, while SC-P3433 recorded the highest moisture, protein, oil, and ash contents, at 7.93%, 5.14%, 4.77%, and 3.39%, respectively.

Table 9. Grain chemical composition (%) as affected by water regime, nano-fertilizer level, and cultivar.

Water Regimes (%)	Nano-Fertilizers (mg L^{-1})	Cultivars	Moisture	Protein	Oil	Starch	Crude Fiber	Ash
100 Irrigation	Control	SC-P3062	7.96	2.89	4.68	78.76	1.13	2.24
		SC-32D99	7.86	3.45	5.39	77.94	1.03	3.65
		SC-P3433	7.68	2.92	4.96	75.27	0.90	3.37
	100	SC-P3062	7.33	3.62	4.74	80.67	0.86	1.51
		SC-32D99	7.85	2.83	4.95	76.66	1.38	3.22
		SC-P3433	8.10	3.93	5.49	74.90	1.09	3.83
	200	SC-P3062	7.71	3.51	4.82	77.61	1.00	2.06
		SC-32D99	7.55	3.85	5.10	78.23	1.05	2.27
		SC-P3433	8.13	3.65	5.13	75.82	0.81	2.54
80 Irrigation	Control	SC-P3062	7.83	2.90	5.28	78.76	0.75	2.76
		SC-32D99	7.80	3.32	4.91	78.22	1.13	4.35
		SC-P3433	7.87	3.37	5.25	74.38	1.38	3.95
	100	SC-P3062	7.37	4.06	4.89	78.83	0.86	2.44
		SC-32D99	7.64	3.52	5.11	77.26	0.55	3.44
		SC-P3433	8.04	3.58	5.61	73.91	0.99	4.52
	200	SC-P3062	7.55	3.38	4.86	76.54	1.38	2.79
		SC-32D99	7.92	4.25	5.33	77.05	0.91	3.08
		SC-P3433	8.14	4.17	4.60	75.09	0.31	3.15
60 Irrigation	Control	SC-P3062	7.57	3.86	4.83	80.19	0.55	2.41
		SC-32D99	7.33	3.95	4.34	78.15	0.88	1.84
		SC-P3433	7.37	4.79	4.09	75.34	0.43	2.87
	100	SC-P3062	7.40	4.60	4.43	80.20	0.60	2.64
		SC-32D99	7.72	4.01	5.05	77.98	0.95	3.18
		SC-P3433	7.92	4.33	4.32	74.99	0.39	1.98
	200	SC-P3062	7.52	4.24	3.82	78.14	0.65	2.05
		SC-32D99	8.05	4.16	4.62	79.02	0.91	3.19
		SC-P3433	7.99	4.92	4.52	77.47	0.71	2.97
40 Irrigation	Control	SC-P3062	7.46	4.08	4.52	78.48	0.96	3.02
		SC-32D99	7.29	4.77	4.50	78.05	1.18	2.03
		SC-P3433	7.20	4.65	4.23	72.18	1.13	1.95
	100	SC-P3062	7.19	4.89	4.41	79.52	0.96	2.06
		SC-32D99	7.38	4.37	4.39	78.61	0.85	2.79
		SC-P3433	7.89	5.46	4.66	74.4	0.51	2.26
	200	SC-P3062	7.21	4.54	3.91	77.55	0.65	1.68
		SC-32D99	7.64	4.64	4.38	77.67	0.91	2.43
		SC-P3433	7.93	5.14	4.77	75.73	0.86	3.39
	$LSD_{0.05}$		ns	1.36	1.45	2.65	0.37	0.63

ns: non-significant.

The harmful effects of water deficit on the chemical composition of grains have been well documented in the literature [21,22,76,77]. Notably, drought stress has been shown to significantly reduce starch and protein content in maize grains [78]. In the present study, the foliar application of Zn and Fe nanoparticles on maize cultivars significantly increased the moisture, protein, oil, starch, crude fiber, and ash contents of the grains under both control and drought stress conditions. These findings are in close agreement with the results reported by Linh et al. [79], who found that metal-based nanoparticles might promote plant tolerance to drought stress through the induction of drought-related gene expression. Similar positive effects of nano-microelements and nano-amino acids on important maize characteristics have been reported by Alzreejawi and Juthery [80]. Additionally, several studies have demonstrated the ability of nano-fertilizers to significantly improve grain quality [28,41,81–83]. The application of zinc oxide nanoparticles has been shown to accelerate plant development, promote yield, and fortify edible grains with essential nutrients such as Zn, thereby improving the resilience of cropping systems under drought stress [84]. Furthermore, the use of ZnO nanoparticles has been proposed as an approach for alleviating the negative effects of water stress in sorghum production [84] and maize [61,66].

3.4. Macro- and Micronutient Contents of Grain

The results of this study indicate a significant difference in the grain macronutrient contents among the different water regimes, Zn and Fe nano-fertilizers, and maize cultivars (Table 10). The analysis of variance presented in Table 10 reveals substantial differences among the cultivars, water regimes, and nano-fertilizers concerning all macronutrient contents. The mean squares associated with water regimes showed a high level of significance for every macronutrient analyzed. In contrast, the mean squares related to nano-fertilizers were highly significant for all traits except for nitrogen content. Additionally, the mean squares for the hybrids demonstrated significance across all traits. Furthermore, the interaction effects among the water regimes, nano-fertilizers, and cultivars were highly significant for all agronomic traits.

Table 10. Combined analysis of variance of split-split-plot design for three maize cultivars evaluated under four water regimes and three nano-fertilizers across 2022 and 2023 seasons.

SOV	df	N	P	K	Ca	Mg
Season S	1	0.449	0.003	0.144	0.046	0.005
S/Reps	4	1.736	0.088	1.711	0.063	0.061
Water A	3	2.291 **	0.014 **	0.023 **	0.081 **	0.011 **
SA	3	1.316 **	0.006 **	0.121 **	0.048 **	0.001 **
Error a	12	0	0	0	0	0
Fertilizer B	2	0.01	0.023 **	0.385 **	0.04 **	0.028 **
SB	2	1.814 **	0.005	0.142 **	0.011 **	0.003
AB	6	0.787 **	0.007 **	0.227 **	0.011 **	0.009 **
SAB	6	0.836 **	0.006 *	0.573 **	0.033 **	0.003 *
Error b	32	0.015	0.002	0.019	0.001	0.001
Cultivars C	2	2.414 **	0.034 **	2.063 **	0.004 **	0.018 **
SC	2	0.805 **	0.004 **	0.087 *	0.03 **	0.009 **
AC	6	1.752 **	0.006 **	0.577 **	0.027 **	0.002 **
SAC	6	1.418 **	0.01 **	0.532 **	0.047 **	0.006 **
BC	4	0.969 **	0.005 **	0.458 **	0.03 **	0.003 **
SBC	4	0.597 **	0.003 **	0.108 **	0.014 **	0.002 **
ABC	12	0.36 **	0.006 **	0.491 **	0.031 **	0.003 **
SABC	12	1.182 **	0.004 **	0.481 **	0.018 **	0.003 **
Error c	96	0.028	0.001	0.023	0.00026	0.000313

* Significant at *p*-value 0.05, and ** significant at *p*-value 0.01.

The application of zinc and iron nanoparticles to foliage significantly enhanced the contents of nitrogen (N), phosphorus (P), potassium (K), calcium (Ca), and magnesium (Mg) in grains under both normal and water stress conditions (Table 11). The findings indicate that the SC-P3062 cultivar had a higher calcium content in grains compared to the other cultivars under mild and moderate stress. Additionally, the SC-32D99 cultivar exhibited greater nitrogen and potassium levels under the well-watered (control) and mild stress conditions. It also demonstrated increased magnesium content under mild and severe stress. Conversely, the SC-P3433 cultivar consistently showed elevated phosphorus levels across the mild, moderate, and severe stress conditions. Under well-watered conditions, the SC-P3433 cultivar treated with zinc and iron nanoparticles recorded the highest levels of nitrogen, phosphorus, potassium, and calcium (3.27%, 0.31%, 2.83%, and 0.50%, respectively), while the SC-32D99 cultivar displayed the highest magnesium content (0.22%) when treated with the nanoparticles. In mild stress conditions, the SC-P3062 cultivar treated with zinc and iron nanoparticles had the highest calcium content (0.53%). The SC-32D99 cultivar achieved the highest nitrogen, potassium, and magnesium levels (3.54%, 2.65%, and 0.24%, respectively), while the SC-P3433 cultivar had the highest phosphorus content (0.28%). Under moderate stress, the SC-P3062 cultivar again showed the highest calcium content (0.42%). The SC-32D99 cultivar recorded the highest potassium content (2.68%), whereas the SC-P3433 cultivar achieved the highest nitrogen, phosphorus, and magnesium levels (3.42%, 0.32%, and 0.27%, respectively). Under severe stress conditions, the SC-P3062 cultivar demonstrated the highest potassium content (2.51%). The SC-32D99 cultivar exhibited the highest nitrogen and magnesium contents (2.37% and 0.34%, respectively), while the SC-P3433 cultivar reached the highest phosphorus and calcium levels (0.33% and 0.49%, respectively).

The results of this study indicate a significant difference in the grain micronutrient contents among the different water regimes, Zn and Fe nano-fertilizers, and maize cultivars (Table 12). The analysis of variance shown in Table 12 indicates significant differences among the cultivars, water regimes, and nano-fertilizers regarding all micronutrient contents. The mean squares associated with water regimes were highly significant for every micronutrient analyzed, a finding that also applied to the mean squares for nano-fertilizers. Additionally, the mean squares for the cultivars exhibited significant differences across all micronutrient contents. Moreover, the interaction effects involving water regimes, nano-fertilizers, and cultivars revealed highly significant differences for all micronutrient contents.

Table 11. Macronutrient contents (%) as affected by water regime, nano-fertilizer level, and maize cultivar.

Water Regimes (%)	Nano- Fertilizers (mg L^{-1})	Cultivars	N	P	K	Ca	Mg
100 Irrigation	Control	SC-P3062	2.36	0.21	1.73	0.35	0.20
		SC-32D99	2.44	0.25	2.83	0.36	0.22
		SC-P3433	2.58	0.22	2.12	0.50	0.21
	100	SC-P3062	2.46	0.28	2.00	0.47	0.20
		SC-32D99	2.15	0.24	1.93	0.38	0.22
		SC-P3433	3.27	0.23	2.83	0.38	0.21
	200	SC-P3062	2.38	0.28	2.28	0.48	0.20
		SC-32D99	2.34	0.29	2.17	0.32	0.20
		SC-P3433	2.57	0.31	2.24	0.50	0.19
80 Irrigation	Control	SC-P3062	2.56	0.20	1.85	0.38	0.17
		SC-32D99	3.54	0.20	2.57	0.48	0.20
		SC-P3433	2.32	0.21	2.14	0.35	0.18
	100	SC-P3062	2.06	0.18	1.74	0.30	0.16
		SC-32D99	2.46	0.22	2.20	0.35	0.23
		SC-P3433	2.86	0.28	2.52	0.49	0.20
	200	SC-P3062	2.11	0.27	1.93	0.53	0.23
		SC-32D99	3.54	0.25	2.65	0.45	0.24
		SC-P3433	2.43	0.26	2.11	0.35	0.19

Table 11. *Cont.*

Water Regimes (%)	Nano- Fertilizers (mg L^{-1})	Cultivars	N	P	K	Ca	Mg
60 Irrigation	Control	SC-P3062	3.21	0.26	1.78	0.30	0.16
		SC-32D99	2.98	0.26	1.99	0.30	0.18
		SC-P3433	3.30	0.32	2.51	0.30	0.18
	100	SC-P3062	2.92	0.26	1.83	0.31	0.21
		SC-32D99	2.52	0.22	2.05	0.32	0.22
		SC-P3433	3.42	0.28	2.42	0.37	0.23
	200	SC-P3062	2.82	0.21	2.28	0.42	0.19
		SC-32D99	2.64	0.32	2.68	0.34	0.29
		SC-P3433	2.95	0.32	2.43	0.40	0.27
40 Irrigation	Control	SC-P3062	2.25	0.22	2.12	0.31	0.20
		SC-32D99	2.60	0.22	1.77	0.49	0.21
		SC-P3433	2.83	0.28	2.43	0.33	0.21
	100	SC-P3062	2.68	0.25	2.51	0.34	0.22
		SC-32D99	3.16	0.27	2.01	0.31	0.22
		SC-P3433	2.87	0.28	2.19	0.28	0.22
	200	SC-P3062	2.54	0.19	1.89	0.31	0.24
		SC-32D99	3.37	0.26	2.28	0.37	0.34
		SC-P3433	3.14	0.33	2.35	0.49	0.24
	$LSD_{0.05}$		0.71	0.091	0.07	0.19	0.11

Table 12. Combined analysis of variance of split-split-plot design for three maize cultivars evaluated under four water regimes and three nano-fertilizers across 2022 and 2023 seasons.

SOV	df	Mn	Zn	Fe	Cl	Na
Season S	1	976.65	121.72	335.25	0.007	0.054
S/Reps	4	3558.7	2035.8	215.44	0.064	0.126
Water A	3	2099 **	206.7 **	44.602 **	0.003 **	0.016 **
SA	3	1289 **	52.05 **	71.058 **	0.001 **	0.045 **
Error a	12	2.338	3.357	0.003	0.0001	8.33×10^{-5}
Fertilizer B	2	981.5 **	826.9 **	400.1 **	0.034 **	0.089 **
SB	2	1091 **	52.8 *	117.1 **	0.01 **	0.03 **
AB	6	1409 **	34.24 *	23.11 **	0.007 **	0.038 **
SAB	6	1734 **	12.62	15.50 **	0.008 **	0.031 **
Error b	32	12.97	10.53	0.979	0.001	0.001
Cultivars C	2	1513 **	2394 **	1513 **	0.021 **	0.423 **
SC	2	3615 **	127.2 **	295.2 **	0.006 **	0.056 **
AC	6	1309 **	34.77 *	61.68 **	0.009 **	0.032 **
SAC	6	1625 **	134.1 **	34.52 **	0.004 **	0.043 **
BC	4	2076 **	72.5 **	57.80 **	0.01 **	0.014 **
SBC	4	708.7 **	134.4 **	6.342	0.011 **	0.056 **
ABC	12	3149 **	217.5 **	26.80 **	0.006 **	0.053 **
SABC	12	1147 **	11.61	18.57 **	0.003 **	0.029 **
Error c	96	34.36	11.897	4.436	0.000354	0.002

* Significant at p-value 0.05, and ** significant at p-value 0.01.

The application of Zn and Fe nanoparticles was found to significantly enhance the concentrations of Mn, Zn, Fe, Cl, and Na in the grains across all experimental conditions (Table 13). The results also indicate that the SC-32D99 cultivar exhibited higher grain Fe content compared to the other cultivars under well-watered (control), and mild and moderate stress conditions. Additionally, the SC-32D99 cultivar also attained higher grain Cl and Na contents under well-watered, and mild and severe stress conditions. On the other hand, the SC-P3433 cultivar consistently demonstrated higher grain Zn content across all the stress conditions, including the well-watered and mild, moderate, and severe stress conditions. Furthermore, the SC-P3433 cultivar also exhibited higher grain Mn content under mild and moderate stress conditions compared to the other cultivars. Under well-watered conditions, the SC-P3062 cultivar treated with Zn and Fe nanoparticles had the highest Mn content (162.1 ppm); the SC-32D99 cultivar treated with Zn and Fe nanoparticles had the highest Fe, Cl, and Na contents (57.78 ppm, 0.30%, and 0.60%, respectively); and the SC-P3433 cultivar treated with Zn and Fe nanoparticles had the highest Zn content (40.20 ppm). Under mild stress conditions, the SC-32D99 cultivar treated with Zn and Fe nanoparticles had the highest Fe content (58.68 ppm), while the SC-P3433 cultivar treated with Zn and Fe nanoparticles had the highest Mn, Zn, Cl, and Na contents (167.8 ppm, 44.80 ppm, 0.27%, and 0.30%, respectively). Under moderate stress conditions, the SC-32D99 cultivar treated with Zn and Fe nanoparticles had the highest Fe, Cl, and Na contents (59.03 ppm, 0.25%, and 0.28%, respectively), while the SC-P3433 cultivar treated with Zn and Fe nanoparticles had the highest Mn and Zn contents (163.0 ppm and 43.70 ppm, respectively). Under severe stress conditions, the SC-P3062 cultivar treated with Zn and Fe nanoparticles had the highest Fe content (60.50 ppm); the SC-32D99 cultivar treated with Zn and Fe nanoparticles had the highest Mn, Cl, and Na contents (157.9 ppm, 0.25%, and 0.51%, respectively); and the SC-P3433 cultivar treated with Zn and Fe nanoparticles had the highest Zn content (47.60 ppm).

Table 13. Micronutrient contents as affected by water regime, nano-fertilizer level, and maize cultivar.

Water Regimes (%)	Nano- Fertilizers (mg L^{-1})	Cultivars	Mn (ppm)	Zn (ppm)	Fe (ppm)	Cl (%)	Na (%)
100 Irrigation	Control	SC-P3062	162.4	18.40	47.15	0.14	0.13
		SC-32D99	156.4	25.68	55.38	0.30	0.21
		SC-P3433	125.0	34.70	47.55	0.16	0.14
	100	SC-P3062	125.1	16.60	45.65	0.17	0.13
		SC-32D99	146.1	26.78	55.43	0.22	0.60
		SC-P3433	189.4	40.00	49.60	0.19	0.14
	200	SC-P3062	162.1	20.26	52.35	0.19	0.17
		SC-32D99	131.2	27.38	57.78	0.30	0.30
		SC-P3433	149.1	40.20	47.70	0.19	0.17
80 Irrigation	Control	SC-P3062	120.0	16.40	45.30	0.19	0.15
		SC-32D99	147.3	22.78	55.23	0.21	0.22
		SC-P3433	159.3	34.85	45.20	0.14	0.12
	100	SC-P3062	146.9	21.35	53.35	0.15	0.15
		SC-32D99	102.5	25.98	54.68	0.21	0.20
		SC-P3433	129.0	42.90	46.05	0.26	0.16
	200	SC-P3062	132.3	23.29	55.70	0.23	0.16
		SC-32D99	120.3	26.48	58.68	0.24	0.27
		SC-P3433	167.8	44.80	48.70	0.27	0.30

Table 13. *Cont.*

Water Regimes (%)	Nano- Fertilizers (mg L^{-1})	Cultivars	Mn (ppm)	Zn (ppm)	Fe (ppm)	Cl (%)	Na (%)
60 Irrigation	Control	SC-P3062	121.6	19.50	49.95	0.16	0.12
		SC-32D99	143.3	24.73	54.18	0.19	0.25
		SC-P3433	106.4	32.65	44.95	0.13	0.13
	100	SC-P3062	160.3	22.80	55.05	0.22	0.15
		SC-32D99	135.8	30.13	54.33	0.17	0.21
		SC-P3433	148.2	42.00	52.30	0.19	0.16
	200	SC-P3062	120.2	25.21	53.65	0.23	0.15
		SC-32D99	139.0	30.98	59.03	0.25	0.28
		SC-P3433	163.0	43.70	50.15	0.23	0.16
40 Irrigation	Control	SC-P3062	145.9	23.45	49.35	0.20	0.11
		SC-32D99	116.1	24.58	58.23	0.20	0.19
		SC-P3433	130.2	34.30	43.25	0.17	0.14
	100	SC-P3062	147.9	24.85	51.90	0.23	0.16
		SC-32D99	157.9	31.33	58.03	0.20	0.17
		SC-P3433	125.8	43.20	46.15	0.17	0.15
	200	SC-P3062	146.5	27.21	60.50	0.20	0.17
		SC-32D99	130.6	34.03	59.28	0.25	0.51
		SC-P3433	143.1	47.60	48.75	0.19	0.15
	$LSD_{0.05}$		15.41	8.44	6.23	0.07	0.25

The study findings indicate that both the macro- and micronutrient contents in maize grains decreased under water stress conditions compared to normal, well-watered conditions. This suggests that the uptake of these essential nutrients was limited under water stress due to factors such as reduced cell expansion, biomass, cell membrane stability, osmotic adjustment, metabolic activities, plant vigor, leaf temperature regulation, stomatal conductance, and photosynthesis [5,6,8,9,11]. Specifically, studies have shown that water stress can lead to reduced contents of macronutrients like potassium (K), magnesium (Mg), phosphorus (P), nitrogen (N), and calcium (Ca), as well as micronutrients like manganese (Mn), copper (Cu), and iron (Fe) in maize grains [85,86]. However, the current study found that the application of Zn and Fe nanoparticles significantly improved the grain contents of several macro- and micronutrients (N, Ca, P, Mg, K, Mn, Fe, Cl, Zn, and Na) in maize under control and drought stress conditions. This may be due to the enhanced solubility, dispersion, and bioavailability of these nano-formulated mineral nutrients, which can gradually provide the crop with its essential nutrients [27,28,45,80,84,87,88].

3.5. Correlation Analysis

The correlation analysis conducted on the traits studied in maize (Figure 3A–C) revealed both positive and negative relationships among the investigated parameters. This analysis provided insights into the strength and directionality of the associations between the various traits. The correlation analysis, focusing on drought tolerance-related indices, demonstrated a positive association between yield; yield-contributing factors; moisture content; oil content; crude fiber; ash content; as well as the concentrations of phosphorus (P), potassium (K), manganese (Mn), zinc (Zn), chloride (Cl), calcium (Ca), and sodium (Na). Conversely, a negative correlation was observed between protein content; starch content; and nitrogen (N), iron (Fe), and magnesium (Mg) concentrations. These correlation patterns highlight the complex interrelationships among the physiological, biochemical, and nutritional characteristics of maize under drought stress conditions.

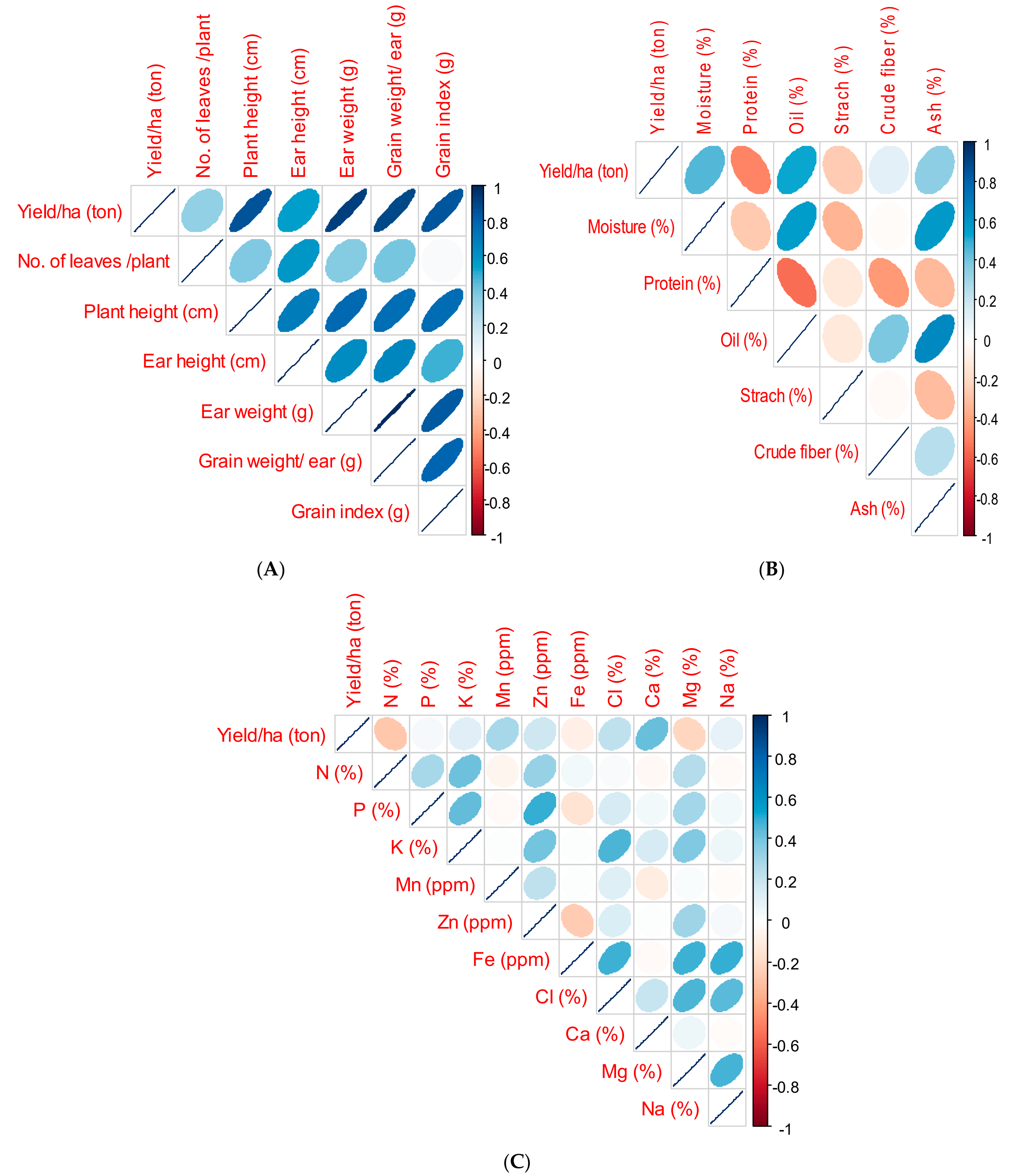

Figure 3. (**A**–**C**) A Pearson correlation analysis depicting the strength of the relationships among the parameters of maize investigated in this study.

Correlation coefficients are commonly used to measure the strength and direction of the linear relationship between independent variables [89]. Several studies have explored the correlations between maize grain yield and various agronomic traits. For instance, Yahaya et al. [90] reported a positive and highly significant correlation between maize grain yield and other agronomic characteristics. Similarly, Makore et al. [91] found that grain yield had significant positive correlations with plant height and ear height. Furthermore, studies have shown a positive and significant association between grain yield and other traits, such as 100-seed weight, ear girth, ear length, and plant height [92,93]. Abadassi [94] also reported that grain yield was highly and positively correlated with the number of grains per ear. Additionally, Teodoro et al. [95] indicated that the variables number of grains per row and weight of hundred grains are directly correlated with grain yield. Sondarava et al. [96] also found that kernel yield per plant had a significant positive association with cob weight, cob length, cobs per plant, cob girth, and kernel per row.

4. Conclusions

The synergistic application of Zn and Fe nanoparticles (100–200 mg/L) with RND significantly improved the grain yield, protein, oil, starch, crude fiber, ash, and macro- and micronutrients of maize cultivars under normal and water regimes. The research findings indicate that applying Zn and Fe nanoparticles at a rate of 100–200 mg/L could be a promising strategy for farmers in arid and semi-arid regions to maintain or improve maize crop production under water-deficit conditions. The use of these nanoparticles has been shown to effectively facilitate and alleviate the negative impacts of drought stress on maize plants. The identification of the most drought-tolerant cultivars, such as SC-P3062 and SC-P3433, which exhibited the highest grain yields under water-deficit conditions, can guide efforts to improve drought tolerance in maize. These findings can inform breeding programs and agronomic management strategies focused on developing drought-tolerant maize cultivars and improving both maize yield and grain quality under water-deficit conditions.

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