Bulgarian Journal of Agricultural Science, 29 (No 2) 2023, 304–311

Agronomic response of maize hybrids to foliar fertilization with nanosized zinc hydroxy nitrate

E. Kolentsova[1*], A. Mitkov[2], N. Nguyen[1], T. Tonev[2], K. Ivanov[1]

[1] *Agricultural University, Faculty of Plant Protection and Agroecology, Department of Chemistry and Phytopharmacy, 4000 Plovdiv, Bulgaria*
[2] *Agricultural University, Faculty of Agronomy, Department of Farming and Herbology, 4000 Plovdiv, Bulgaria*
[*] *Correspondence:* elitsa_kolentsova@abv.bg

Abstract

Kolentsova, E., Mitkov, A., Nguyen, N., Tonev, T. & Ivanov, K. (2023). Agronomic response of maize hybrids to foliar fertilization with nanosized zinc hydroxy nitrate. *Bulg. J. Agric. Sci., 29 (2)*, 304–311

Recently, nanotechnology has offered the practice of a new generation of foliar fertilizers containing nanoparticles. One of the most promising zinc-containing foliar fertilizers is zinc hydroxy nitrate. Along with this, important aspects of its application in practice, such as the number and timing of sprays and the agronomic response of different maize hybrids, remain understudied. The objective of this study was to investigate the agronomic responses of maize hybrids to foliar fertilization by zinc in the form of zinc hydroxy nitrate suspension. Grain yield and its components were used as evaluation criteria. A total of ten hybrids from three maturity groups (FAO 400, 500 and 600/700) were tested. Considerable differences were found between the groups for the grain yield parameters. Furthermore, a significant effect of Zn application was observed for grain yield, which increases up to 12.2% for P0216 FAO 480. The best effect is obtained by double spraying at 4–5 fully emerged leaf and 8–9 fully developed leaf. The most sensitive to foliar zinc fertilization are the hybrids from the early maturity group FAO 400. No direct correlation was found between foliar zinc fertilization and protein, fat and starch content in the maize grains. The preparation of the zinc hydroxide nitrate with composition $Zn_5(OH)_8(NO_3)_2 \cdot 2H_2O$ was performed by pouring a NaOH solution into $Zn(NO_3)_2 \cdot 6H_2O$ under vigorous stirring. All samples were characterised in detail by thermal analysis, X-ray diffraction, scanning electron microscopy, and inductively coupled plasma (ICP) mass spectrometry to determine their physicochemical properties, morphology and content. The field experiment was conducted in four variants, three repetitions for each hybrid. It was concluded that the synthesised zinc hydroxy nitrate has potential as a successful long-term foliar fertilizer.

Keywords: crop production; foliar fertilizer; maize hybrids; zinc hydroxy nitrate synthesis

Introduction

Maize is an important cereal crop with significant economic value in livestock and poultry production (Harris et al., 2007; Ning 2013) and processed for many industrial products for human consumption (Ortiz-Monasterio et al., 2007). The average global grain yield of maize has increased by 25% in the past 20 years compared with the previous 50 years, which relied on improved genetic and cultural practices (Ciampitti & Vyn, 2012). Among the main factors contributing to grain yield, the balanced supply of nutrients and the creation of new highly productive varieties are the most important.

Besides nitrogen and phosphorus deficiency, many crops suffer from zinc deficiency (Rashid & Ryan, 2004). Zinc deficiency is a significant risk factor for global agriculture and human health (Cakmak, 2009; Chasapis, 2017). This is so because zinc is an essential micronutrient, equally important for all life forms – for plants, animals, and humans (Alloway, 2008; Cakmak, 2009). The application of zinc as a fertilizer for increasing crop yields is a common practice. Still, maize farmers often do not implement this practice (Armani et al., 1999), leading to continuously declining yield wherever zinc deficiency occurs.

Along with changes in management techniques, creating new maize hybrids with improved characteristics contributes substantially to solving the problems with grain yield and quality (Duvick, 2005). According to Dwyer and Tollenaar (1989), the genetic contribution ranges from 33 to 79%. It's well known that the new maize varieties accumulate more post-silking dray matter than old varieties, which contributes significantly to the greater grain yield of new varieties (Rajcan & Tollenaar, 1999; Tollenaar & Wu, 1999; Echarte et al., 2008).

Many papers are devoted to the response of maize hybrids to soil fertilization, climate change and stress (Ahmad et al., 2009). To a lesser extent, soil fertilisation with zinc on the yield and quality of different maise varieties has been investigated (Hegyi et al., 2007; Echarte et al., 2008). There is a lack of information in the scientific literature about the specific response of maize hybrids with different ripening periods to foliar zinc fertilization. The physiological and molecular mechanisms of zinc deficiency tolerance are just beginning to be understood (Hacisalihoglu et al., 2003). Sadeghzadeh (2013) reported that plant genotypes vary widely in their tolerance to soils with low plant-available Zn concerning both Zn uptake and utilisation.

Recently, nanotechnologies have offered the practice of a new generation of fertilizers containing nanoparticles. Zinc-containing fertilizers typically contain nanosized ZnO (ZnO-NPs) and are used for soil and foliar fertilization with undeniable agronomic effect. (Bala et al., 2019; Song et al., 2020). However, using ZnO-NPs as a soil fertilizer is controversial due to its negative impact on soil, terrestrial and aquatic animals. (Rajput et al., 2018) have presented a detailed analysis of the effects of ZnO-NPs on soil, plants, and animals. Their study demonstrated changes in soil properties (porosity, hydraulic conductivity and humic substances), soil bacterial communities, and inhibition of enzymatic activities. This draws attention towards environmentally friendly use of zinc-containing nanomaterials, mainly as foliar fertilizers. One of the most promising zinc-containing foliar fertilizers is zinc hydroxy nitrate.

The objective of the study was to investigate the agronomic responses of maize hybrids from different maturity groups to foliar fertilization by zinc in the form of zinc hydroxy nitrate suspension. The evaluation was performed based on grain yield and its components.

Materials and Methods

Materials

The investigation was carried out in 2019 on ten of the most common maize hybrids, belonging to three maturity groups: early maturity group – P0023 (FAO 450), P20217 (FAO 480), P0217 (FAO 490); medium maturity group – P0704 (FAO 520) and P0937 (FAO 580) and medium-late maturity group – P1241 (FAO 620), P1049 (FAO 620), P1535 (FAO 650) and P2105 (FAO 700). Corteva Agriscience™ provided all seeds for the experiment.

Nanosized zinc hydroxy nitrate (ZnHN) suspension with a zinc content of 12.2% was used as a foliar fertilizer.

Methods

Synthesis of zinc hydroxide nitrate: The preparation of the $Zn_5(OH)_8(NO_3)_2 \cdot 2H_2O$ (ZnHN) was performed by pouring 3.6 M sodium hydroxide solution into 3.6M $Zn(NO_3)_2 \cdot 6H_2O$ under vigorous stirring at 60°C for 10 minutes. The initial OH/Zn molar ratio was 1.6. The white precipitate was characterised by thermal analysis – differential thermal analysis (DTA), differential thermal gravimetry (DTG), and thermal gravimetry (TG), X-ray diffraction, scanning electron microscopy (SEM), transition electron microscopy (TEM), and inductively coupled plasma (ICP) spectrometry. More details on the ZnHN synthesis, morphology and physicochemical properties are presented elsewhere (Ivanov et al., 2017).

Field experiment: The field experiment was conducted at the Research Farm, Agricultural University, Bulgaria (Figure 1) in four variants, three repetitions for each hybrid: Variant I – single spraying at the end of May (4–5 fully emerged leaf); Variant II – double spraying at the end of May (4–5 fully emerged leaf) and at the end of Jun (8–9 fully developed leaf); Variant III – single spraying at the end of Jun (8 – 9 fully developed leaf) and Variant IV – control (no spraying with zinc-containing fertilizer).

The size of the harvesting plots was 60 m^2. Two litres of suspension containing 8.0 g l^{-1} zinc hydroxy nitrate (4.2 g Zn $plot^{-1}$, recalculated 700 g Zn ha^{-1}) was used in every spraying. The base fertilization (NPK 15:15:15 – 500 kg ha^{-1} pre-sowing and 500 kg ha^{-1} ammonium nitrate at 6–7 fully emerged leaf) and drip irrigation were the same for all variants. Weed control was carried out using Click combi 2.5 l ha^{-1} applied after sowing before the emergence of the crop and weeds and a mixture of Equip SK 2.5 l ha^{-1} and Laudis OD 2.0 l ha^{-1} at 6–7 fully emerged leaf.

Before planting, surface soil samples (0–20 cm depth) from each harvesting plot were collected, air-dried, mixed and analysed for the selected physicochemical properties in

Fig. 1. Pictures of the corn plants at the beginning and end of the experiment

the university laboratory, which is accredited under БДС EN ISO/IEC 17025/AC:2006 for soil and plant analyses (Table 1). The results showed that the soil in this research area was alluvial with an alkaline pH (7.88) and low organic matter content (1.60%). It is characterised by a low content of available Fe (7.40 mg kg^{-1}), medium content of available N (41.45 mg kg^{-1}), P (41.86 mg kg^{-1}), K (202.70 mg kg^{-1}) and Mn (13.62 mg kg^{-1}) and high content of Cu (2.24 mg kg^{-1}) compared to the average range of these elements in Bulgarian soils. The content of available Zn was 3.35 mg kg^{-1} and can be classified as a medium according to the MAAF 1998 classification (Papadopoulos et al., 2009).

After harvesting, the cobs were air-dried and weighed. Random samples of grain were mixed, milled and analysed for protein, fat and starch.

No visible symptoms of zinc deficiency were observed throughout the growth period, both for the control and for all variants. No diseases or pests with an economically significant density were found.

Statistical analysis was performed using one-way ANOVA (for $P < 0.05$). Based on ANOVA results, a Tukey's test for the main comparison at a 95% confidence level was applied.

Results and Discussion

Preparation and characterization of ZnHN: The preparation of nanosized $Zn_5(OH)_8(NO_3)_2{\cdot}2H_2O$ with sheet-like form and thickness in the range 50–80 nanometers is illustrated in Figure 2c. The thermal decomposition of Zn_5HN is a four-step process (Table 2) occurring in the temperature range of 75 to 300°C (Figure 2b). It leads to a weight loss of 33.12%, which is very close to the theoretical one (34.67%).

Table 1. Soil properties and total and available N, K, P, Mn Cu, Fe and Zn concentrations

Soil test parameter	Test level	Test rating
Soil pH (1:5)	7.88 ± 0.02	Alkaline
Electrical conductivity (μS cm^{-1})	520	–
Organic matter (%)	1.60	Low
(Nutrients mg kg^{-1})		
Nitrogen (available, 1,0% KCl)	41.45 ± 2.12	Medium
Potassium (EPA 3051)	49,470.2 ± 27.4	Medium
Potassium (available, 2 N HCl) (K_2O)	202.70 ± 7.43	Medium
Phosphorous (P_2O_5) (available)	41.86 ± 2.20	Medium
Manganese (EPA 3051A)	162.10 ± 3.20	Medium
Manganese (available, DTPA)	13.62 ± 0.30	Medium
Copper (EPA 3051A)	15.22 ± 0.38	Medium
Copper (available, DTPA)	2.24 ± 0.08	High
Iron (EPA 3051A)	10,970.0 ± 270	Medium
Iron (available, DTPA)	7.40 ± 0.06	Low
Zinc (EPA 3051A)	85.24 ± 1.02	Low
Zinc (available, DTPA)	3.35 ± 0.10	Medium

The XRD pattern is identified as zinc hydroxide nitrate with composition $Zn_5(OH)_8(NO_3)_2{\cdot}2H_2O$ (JCPDS card 72-0627). The strongest peak at $2\theta = 9.2°$ and other characteristic peaks at 2θ = 18.4, 34.6, 35.4, 46.8, and 47.4° confirm the formation of pure well-crystallized compound.

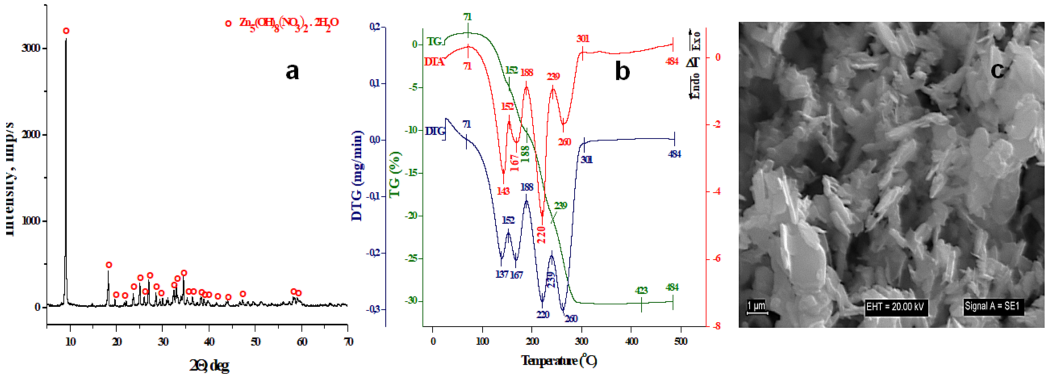

Fig. 2. X-ray pattern (*a*), Simultaneous DTA, DTG and TG curve (*b*) and SEM image (*c*), of a typical sample of ZnHN

Table 2. Average yield and yield component data for maize hybrids in maturity group FAO 600/700

Hybrid	Variant*	Corn in cob, %	Moisture, %	Yield, t ha^{-1}	% Versus control
P2105 FAO 700	1	88.25	17.2	1.78	101.4
	2	88.15	17.1	1.83	104.1
	3	87.94	17.4	1.80	102.5
	4	86.98	17.3	1.76	–
P1535 FAO 650	1	89.32	16.9	1.77	102.9
	2	88.38	16.7	1.80	104.5
	3	88.77	16.6	1.76	102.0
	4	88.73	16.8	1.72	–
P1241 FAO 620	1	88.85	16.1	1.71	104.8
	2	89.92	16.1	1.78	109.7
	3	88.81	15.9	1.67	102.1
	4	88.65	15.8	1.63	-
P1049 FAO 620	1	89.53	16.1	1.73	105.0
	2	88.77	15.7	1.79	108.4
	3	88.72	15.9	1.72	104.0
	4	88.34	15.8	1.65	–
P1063 FAO 600	1	88.32	15.3	1.67	103.3
	2	88.58	15.2	1.70	105.2
	3	88.58	15.5	1.63	101.2
	4	88.32	15.6	1.61	–
Average for the group		88.60 ± 0.61	16.25 ± 0.69	1.73± 0.07	103.59 ± 2.63

***Impact of foliar fertilization by ZnHN suspension on the grain yield components*:** Tables 2–4 present the impact of zinc hydroxy nitrate application on the grain yield, grain moisture content and the part of the corn in the cob for the hybrids from the three maturity groups.

Significant differences ($p < 0.05$) in grain yield between different maturity grope hybrids were observed. The average yield and standard deviation for all variants, including control, for the early maturity group, was 1.34 ± 0.08 t ha^{-1}. For the medium and medium-late maturity groups, the results were 1.55 ± 0.07 and 1.73 ± 0.07 t ha^{-1}, respectively. The results obtained confirm that short-season hybrids (group FAO 400) have significantly less genetic yield potential compared to medium (group FAO 500) and long-season (group FAO 600/700) hybrids. This shortcoming of short-season hybrids is largely offset by more favourable values of stability parameters (Djurovic et al., 2014). The yields of the different hybrids within the same group also differ, although to a much lesser extent.

Presented in Tables 2–4, results allow drawing definite conclusions about the effect of foliar fertilization with ZnHN on the yield of hybrids from different maturity groups. Com-

Table 3. Average yield and yield component data for maize hybrids in maturity group FAO 500

Hybrid	Variant*	Corn in cob, %	Moisture, %	Yield, t ha^{-1}	% Versus control
P0937 FAO 580	1	89.34	14.9	1.60	102.1
	2	89.31	14.7	1.64	105.0
	3	89.06	14.7	1.58	101.3
	4	89.38	14.8	1.56	–
P0704 FAO 520	1	86.32	14.1	1.51	106.0
	2	86.47	13.7	1.59	111.3
	3	86.82	13.9	1.49	104.3
	4	86.67	13.8	1.43	–
Average for the group		87.92 ± 1.45	14.33 ± 0.50	1.55 ± 0.07	105.0 ± 3.56

Table 4. Average yield and yield component data for maize hybrids in maturity group FAO 400

Hybrid	Variant*	Corn in cob, %	Moisture, %	Yield, t ha^{-1}	% Versus control
P0217 FAO 490	1	89.92	12.8	1.44	106.2
	2	89.11	12.6	1.49	109.4
	3	89.26	12.4	1.43	104.8
	4	89.62	12.7	1.36	–
P0216 FAO 480	1	89.08	12.5	1.34	107.9
	2	88.26	12.6	1.40	112.2
	3	88.54	12.8	1.32	106.3
	4	88.44	12.5	1.24	–
P0023 FAO 450	1	89.01	12.2	1.23	106.6
	2	88.11	12.4	1.33	110.3
	3	88.38	12.1	1.23	104.8
	4	88.78	12.0	1.21	–
Average for the group		88.88 ± 0.56	12.47 ± 0.26	1.34 ± 0.08	107.61 ± 2.55

pared to the control, the average yield increase for the hybrids from the FAO 400 maturity group was 7.61 ± 2.55%. For the FAO 500 maturity group and the FAO 600/700 maturity group, the increase was 5.0 ± 3.56% and 3.59 ± 2.63%. It is due to the different periods of maize phenophases in which the plant‘s reproductive organs are formed. In the early hybrids of the FAO 400 maturity group, this period was drawn forward when plant development conditions were less favourable. During this period, the temperature is relatively low, and the root system is underdeveloped. At this time, the supply of nutrients, including zinc, is insufficient to meet the plant‘s needs. Zinc feeding during this period is of great importance and plays an essential role in forming the reproductive organs of maize. This understanding was confirmed by our study on application of Zn-containing foliar fertilisers for recovery of the grain productivity potential of Zn-deficient maize plants (Ivanov et al., 2021). The physiological status of the plants and the dynamic of zinc and micro- and macroelements concentration in plant organs were monitored. The influence of foliar zinc fertilization by ZnHN on yield and grain structural components has been determined. It was established that zinc fertilization throughout the initial growth stages plays a decisive role in the formation of the reproductive organs of maize plants. Foliar zinc fertilizers can entirely recover the physiological performance of plants grown under conditions of zinc deficiency.

The application of foliar fertilizer is extremely suitable as its absorption is much faster than from the soil. The advantage of ZnHN is that its nanoscale crystals remain on the leaf surface for a long time and act as a reservoir for zinc delivery over a long period (Li et al., 2016).

Apart between the different maturity groups, there is a difference between the variants within each group. The highest yields were recorded in all three maturity groups after double treatment of the plants at 4–5 fully emerged leaf and 8–9 fully developed leaf. Most significant is the increase in yield after double treatment of P0216 hybrid by FAO 480 maturity group (12.2%). A single treatment at 8–9 fully developed leaf also has a positive effect, but it is less pronounced in all hybrids.

In our previous study (Ivanov et al., 2019), a significantly higher increase in maize yield (up to 23.19%) was found after double spraying with ZnHN suspension. The reason for the difference is that for this experiment, a very early maturity hybrid Pr 9241, group 370 according to FAO was selected, with excellent qualities (high ecological flexibility) and acclimatisation to the area of research and the content of available zinc in the soil was lower (2.82 ± 0.10 mg kg^{-1}).

The results for grain moisture content at maturity are quite different too. The average value and standard deviation for all variants, including control, was 12.47 ± 0.26% for the early maturity group. For the medium and medium-late maturity groups, the results were 14.33 ± 0.50% and 16.25 ± 0.69% respectively. The differences between the hybrids within the groups as well as between the treated plants and the controls were negligible. There is no noticeable relationship between the number and time of treatment with zinc hydroxy nitrate and this indicator's values.

The data for the part of the corn in the cob at maturity is quite different from that for yield and grain moisture. All variants' results varied within a narrow range of 86.98 for hybrid P2105 FAO 700 (control) to 89.92 for the same hybrid (double treated). Despite the significant ($p < 0.05$) differences in yields and moisture, the reason for this result is the larger grains and larger cobs of the hybrids from later maturity groups.

Impact of foliar fertilization by ZnHN suspension on the grain structural components: Tables 5 and 6 present the impact of ZnHN application on the content of the main grain structural components (protein, fat and starch). The results of Variant 2 (double treatment at 4–5 fully emerged leaf and 8–9 fully developed leaf) and the control for each hybrid were compared.

Presented in Tables 5–7, results show that the differences in the values of grain structural components of the hybrids from the different maturity groups are smaller than those of the yield and its components. Protein, fat and starch content varied within a narrow range, with differences between maturity groups not significant ($p < 0.05$).

The average protein content in the hybrids from the maturity group 400 was highest – 7.05 ± 0.85%. For the hybrids from maturity group 500 and maturity group 600/700, these values are 6.41 ± 0.09 and 6.61 ± 0.28%, respectively. The differences between the variants within the maturity groups 400 and 500, as well as between controls and variants, are noticeable but slightly pronounced.

The same trends, but a little more pronounced, are also observed with fat content. Its highest content was in hybrids of maturity group 400 (2.60 ± 0.74%), followed by maturity group 500 (2.28 ± 0.19%) and maturity group 600/700 (1.82 ± 0.31%). There is a difference in the hybrids' values within all three groups, which is most pronounced in the maturity group 400 – 49.7% difference between the controls of the hybrids P0217 FAO 490 and P0023 FAO 450.

The average starch content in the hybrids from the maturity group 600/700 was highest – 70.69 ± 1.54%. For the hybrids from maturity group 500 and maturity group 400, these values are 68.66 ± 1.17% and 68.82 ± 2.51%, respectively. All values are very close without noticeable trends within and between groups. The protein, fat and starch content values shown in Tables 5–7 are typical for the hybrids tested and do not allow a reasoned conclusion for the noticeable effect of zinc hydroxy nitrate foliar fertilization on these components.

It can be summarised that the impact of foliar zinc fertilization on protein, fat and starch content in the grains of the hybrids investigated is negligible. In this case, critical factors for the grain structural components content are climate and soil properties. This conclusion was also reached by Ahmad et al. (2009), who examined growth, yield and quality parameters of three maize hybrids (Pioneer-30D55, Pioneer-3062 and Pioneer-3012) at different levels of potas-

Table 5. Average data for grain structural components of maize hybrids in maturity group FAO 600/700

Hybrid	Variant*	Protein content, %	Fat content, %	Starch content, %
P1063 FAO 600	2	6.45	1.60	71.78
	4	6.39	2.33	71.78
P1041 FAO 620	2	6.57	1.68	70.42
	4	6.81	2.21	70.42
P1249 FAO 620	1	6.76	1.60	73.13
	2	6.47	1.53	71.78
P1535 FAO 650	1	7.22	2.21	69.07
	2	6.20	1.76	70.42
P2105 FAO 700	1	6.59	1.75	70.42
	2	6.61	1.52	67.71
Average for the group		6.61 ± 0.28	1.82 ± 0.31	70.69 ± 1.54

Table 6. Average data for grain structural components of maize hybrids in maturity group FAO 500

Hybrid	Variant*	Protein content, %	Fat content, %	Starch content, %
P1063 FAO 600	2	6.51	2.53	69.07
	4	6.45	2.11	67.71
P1041 FAO 620	2	6.38	2.32	67.71
	4	6.31	2.14	70.13
Average for the group		6.41 ± 0.09	2.28 ± 0.19	68.66 ± 1.17

Table 7. Average data for grain structural components of maize hybrids in maturity group FAO 400.

Hybrid	Variant*	Protein content, %	Fat content, %	Starch content, %
P1063 FAO 600	2	6.51	2.53	69.07
	4	6.45	2.11	67.71
P1041 FAO 620	2	6.38	2.32	67.71
	4	6.31	2.14	70.13
Average for the group		6.41 ± 0.09	2.28 ± 0.19	68.66 ± 1.17
Hybrid	Variant*	Protein content, %	Fat content, %	Starch content, %
P0023 FAO 450	2	7.76	3.45	66.16
	4	8.46	3.60	65.34
P0216 FAO 480	2	6.57	2.31	71.49
	4	6.63	2.19	70.42
P0217 FAO 490	1	6.40	2.22	69.07
	2	6.49	1.81	70.42
Average for the group		7.05 ± 0.85	2.60 ± 0.74	68.82 ± 2.51

sium fertilization (0, 100, 150, 200 and 250 kg ha^{-1}). These authors have found that the effect of maize hybrids and levels of potassium application on crude starch, oil, and protein content in grains is non-significant.

Conclusions

The agronomic response of maize hybrids to foliar fertilization with zinc hydroxy nitrate in the form of nanosized suspension was investigated. Based on the results obtained, we can conclude that the synthesised zinc hydroxy nitrate has indubitable potential as a successful long-term foliar fertilizer. A significant positive effect on grain yield up to 12.2% for variants compared to those of the controls was found. The best result is obtained by double spraying at 4–5 fully emerged leaf and 8–9 fully developed leaf. The most sensitive to foliar zinc fertilization are the hybrids from the early maturity group FAO 400. No direct correlation was found between foliar zinc fertilization and protein, fat and starch content in the maize grains. The critical factor of determining the yield and yield components is the maturity season of the hybrids.

Acknowledgements

This work was supported/(partially supported) by the Bulgarian Ministry of Education and Science under the National Research Programme „Healthy Foods for a Strong Bio-Economy and Quality of Life“ approved by DCM № 577 / 17.08.2018.

References

Ahmad, M., Riaz, A., Ishaque, M. & Malik, A. U. (2009). Response of maize hybrids to varying potassium application in Pakistan. *Pak. J. Agric. Sci., 46(3),* 179–184.

Alloway, B. J. (2008). Zinc in Soils and Crop Nutrition. *2nd Ed., IZA and IFA,* Brussels, Belgium and Paris, France.

Armani, M., Westfall, D. G. & Peterson, G. A. (1999). Influence of water solubility of granular zinc fertilizers on plant uptake and growth. *J. Plant Nutr, 22*, 1815–1827.

Bala, R., Kalia, A. & Dhaliwal, S. S. (2019). Evaluation of efficacy of ZnO nanoparticles as remedial zinc nano fertilizer for rice. *J. Soil Sci. Plant Nutr*., *19(2),* 379-389.

Cakmak, I. (2009). Enrichment of fertilizers with zinc: An excellent investment for humanity and crop production in India. *J. Trace Elem. Med Bio, 23(4),* 281–289.

Ciampitti, I. A. & Vyn, T. J. (2012). Physiological perspectives of changes over time in maize yield dependency on nitrogen uptake and associated nitrogen efficiencies: a review. *Field Crops Res., 133*, 48–67.

Chasapis, C. T., Loutsidou, A. C., Spiliopoulou, C. A. & Stefanidou, M. E. (2012). Zinc and human health: an update. *Arch. Toxicol., 86(4),* 521–534.

Djurovic, D., Madic, M., Bokan, N., Stevovic, V., Tomic, D. & Tanaskovic, S. (2014). Stability parameters for grain yield and its component traits in maize hybrids of different FAO maturity groups. *J. Cent. Eur. Agric.,* 15(4), 199–212.

Duvick, D. N. (2005). The contribution of breeding to yield advances in maize (*Zea mays* L.). *Adv. Agron., 86*, 83–145.

Dwyer, L. M. & Tollenaar, M. (1989). Genetic improvement in photosynthetic response of hybrid maize cultivars, 1959 to 1988. *Can. J. Plant Sci., 69(1),* 81–91.

Echarte, L., Rothstein, S. & Tollenaar, M. (2008). The response of leaf photosynthesis and dry matter accumulation to nitrogen supply in an older and a newer maize hybrid. *Crop Sci., 48*, 656–665.

Hacisalihoglu, G., Hart, J. J., Wang, Y., Cakmak, I. & Kochian, L.V. (2003). Zinc efficiency is correlated with enhanced expression and activity of Cu/Zn superoxide dismutase and carbonic anhydrase in wheat. *Plant Physiol., 131*, 595–602.

Harris, D., Rashid, A., Miraj, G., Arif, M. & Shah, H. (2007). On-farm seed priming with zinc sulphate solution–A cost-effective way to increase the maize yields of resource-poor farmers. *Field Crops Res., 110*, 119–127.

Hegyi, Z., Pók, I., Szőke, C. & Pintér, J. (2007). Chemical quality parameters of maize hybrids in various FAO maturity groups as correlated with yield and yield components. *Acta Agron. Hung., 55(2),* 217–225.

Ivanov, K., Kolentsova, E., Nguyen, N., Peltekov, A. & Angelova, V. (2017). Synthesis and stability of zinc hydroxide nitrate nanoparticles. *Bulg. Chem. Commun., 49*, 225–230.

Ivanov, K., Tonev, T., Nguyen, N., Peltekov, A. & Mitkov, A. (2019). Impact of foliar fertilization with nanosized zinc hydroxy nitrate on maize yield and quality. *Emir. J. Food Agric., 31(8),* 597–604.

Ivanov, K., Vasilev, A., Mitkov, A., Nguyen, N. & Tonev, T. (2021). Application of Zn-containing foliar fertilisers for recovery of the grain productivity potential of Zn-deficient maize plants. *Ital. J. Agron.*, *16,* 1759.

Li, P., Du, Y., Huang, L., Mitter, N. & Xu, Z. (2016). Nanotechnology promotes the R&D of new-generation micronutrient foliar fertilizers. *RSC Adv., 6(73),* 69465–69478.

Ning, P., Li, S., Yu, P., Zhang, Y. & Li, C. (2013). Post-silking accumulation and partitioning of dry matter, nitrogen, phosphorus and potassium in maize varieties differing in leaf longevity. *Field Crops Res., 144*, 19–27.

Ortiz-Monasterio, J. I., Palacios-Rojas, N., Meng, E., Pixley, K., Trethowan, R. & Peña, R. J. (2007). Enhancing the mineral and vitamin content of wheat and maize through plant breeding. *J. Cereal Sci., 46,* 293–307.

Papadopoulos, F., Prochaska, C., Papadopoulos, A. K., Eskridg, K. & Kalavrouziotis, I. (2009). Mn and Zn micronutrients concentrations in acidic soils and source identification using multivariate statistical methods. *Commun. Soil Sci. Plant Anal., 40(15–16),* 2357–2371.

Rajcan, I. & Tollenaar, M. (1999). Source: sink ratio and leaf senescence in maize. I. Dry matter accumulation and partitioning during grain filling. *Field Crops Res., 60*, 245–253.

Rashid, A. & Ryan, J. (2004). Micronutrient constraints to crop production in soils with Mediterranean-type characteristics: A Review. *J. Plant Nutr., 27*, 959–975.

Rajput, V. D., Minkina, T. M., Behal, A., Sushkova, S. N., Mandzhieva, S., Singh, R., Movsesyan, H. S. (2018). Effects of zinc-oxide nanoparticles on soil, plants, animals and soil organisms: a review. *Environ. Nanotechnol. Monit. Manag., 9*, 76-84.

Sadeghzadeh, B. (2013). A review of zinc nutrition and plant breeding. *J. Soil Sci. Plant Nutr.*, *13(4),* 905–927.

Song, U. & Kim, J. (2020). Zinc oxide nanoparticles: a potential micronutrient fertilizer for horticultural crops with little toxicity. *Hortic. Environ. Biotechnol.*, *61(3),* 625-631.

Tollenaar, M. & Wu, J. (1999). Yield improvement in temperate maize is attributable to greater stress tolerance. *Crop Sci., 39*, 1597–1604.

Received: **August, 31, 2021**; *Approved:* **November, 23, 2021**; *Published:* **April, 2023**