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Zinc loading in urea-formaldehyde nanocomposites increases nitrogen and zinc micronutrient fertilization efficiencies in poor sand substrate

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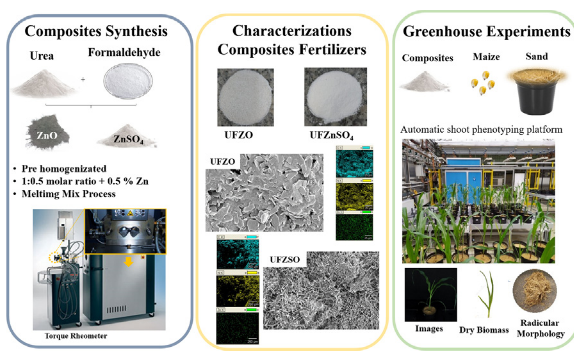
HIGHLIGHTS

- Up to 50 % of the total N application is lost by volatilization;
- Nanocomposite loaded with $ZnSO_4$ or ZnO for co-application of Zn and N, can reduce the N losses;
- Integrated system for an easy application of N and Zn in an optimized manner;
- Root morphology is altered in the presence of the fertilizer nanocomposite;
- N uptake has risen potentially in the presence of the urea: urea-formaldehyde matrix loaded with Zn.

GRAPHICAL ABSTRACT



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ABSTRACT

Agricultural output needs significant increases to feed the growing population. Fertilizers are essential for plant production systems, with nitrogen (N) being the most limiting nutrient for plant growth. It is commonly supplied to crops as urea. Still, due to volatilization, up to 50 % of the total N application is lost. Slow or controlled release fertilizers are being developed to reduce these losses. The co-application of zinc (Zn) as a micronutrient can increase N absorption. Thus, we hypothesize that the controlled delivery of both nutrients (N and Zn) in an integrated system can improve uptake efficiency. Here we demonstrate an optimized fertilizer nanocomposite based on urea:urea-formaldehyde matrix loaded with $ZnSO_4$ or ZnO. This nanocomposite effectively stimulates maize development, with consequent adequate N uptake, in an extreme condition – a very nutrient-poor sand substrate. Our results indicate that the Zn co-application is beneficial for plant development. However, there were advantages for ZnO due to its high Zn content. We discuss that the dispersion favors the Zn delivery as the nanoparticulated oxide in the matrix. Concerning maize development, we found that root morphology is altered in the presence of the fertilizer nanocomposite. Increased root length and surface area may improve soil nutrient uptake, potentially accompanied by increased root exudation of essential compounds for N release from the composite structure.

1. Introduction

Global food security is of particular concern as the world population is expected to increase in the next decades (FAO - Food and Agriculture Organization of the United Nations, 2017). Therefore, the agricultural output will need to expand to feed the growing population significantly.

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However, production gains should be achieved on already existing farmland to avoid further deforestation and land-use conflicts. In this regard, fertilizers are indispensable components of plant production systems for supplying nutrients that are essential for proper crop development. Nitrogen is the most limiting essential nutrient for plant growth and is commonly provided to crops as urea. Nevertheless, almost half of the applied amount is lost to the atmosphere, contributing to atmospheric greenhouse gas emissions, in addition to run-off and leaching resulting in the pollution of both aquifers and surface water bodies (Dimkpa et al., 2020). To tackle these issues, research on nitrogen-based fertilizers has mainly focused on developing slow or controlled release fertilizers (Dhakal et al., 2020; Dimkpa et al., 2020).

The use of urea:urea-formaldehyde polymers (UF polymers) as N fertilizers has been proven an excellent option to overcome urea losses, as this material can deliver nutrients at a controlled rate, avoiding fast hydrolysis in soil (Giroto et al., 2021; Giroto and Ribeiro, 2018; Guo et al., 2018; Xiang et al., 2018; Zhang et al., 2020). Although most studies addressed macronutrient management, there are strong indications that micronutrient deficiencies significantly limit crop productivity (Kihara et al., 2017; Vanlauwe et al., 2015). Micronutrient deficiencies have been observed worldwide (Kihara et al., 2017), and zinc (Zn) deficiency is considered to be the most common (Alloway, 2009; Cakmak, 2008; Cakmak et al., 1994; Hacisalihoglu, 2020; Rodella et al., 2017; Sadeghzadeh and Rengel, 2011). Zn is required by all living organisms in small concentrations, playing an essential role in enzymatic reactions and metabolic activities, especially in nitrogen metabolism (Cakmak, 2008; Sadeghzadeh and Rengel, 2011).

N fertilization is also affected by Zn application. For instance, experiments in forage have indicated that Zn can increase the absorption of N from urea (Gonzalez et al., 2019; Guimarães et al., 2016). A significant increase in total N uptake was observed even as simply urea:$ZnSO_4$ (1.17 g Zn kg^{-1} urea) physical mixture. Several Zn forms have been used as fertilizers, including Zn sulfate ($ZnSO_4$) and Zn oxide (ZnO) (McBeath and McLaughlin, 2014). These Zn sources can be obtained in combination with granular nitrogen, with no need for extra labor or machinery, or additional application infrastructure (Joy et al., 2015; Mortvedt and Giordano, 1969). Recently, Giroto et al. (2021) have tested the Zn loading (sulfate or oxide) in urea-formaldehyde (UF) polymers as multi-nutrient composite fertilizers. It was observed that the polymer structure was affected by Zn addition during the composite synthesis, with no dependence on a specific Zn source. Moreover, the Zn sources featured different solubilization behaviors in the water release test. This previous study proved the feasibility of the production and application of UF loaded with Zn used as slow-release fertilizers, showing the beneficial effects for both nutrients, i.e., reducing N volatilization and increasing Zn bioavailability (Giroto et al., 2021).

Thus, we hypothesize that the controlled delivery of both nutrients (N and Zn) in an integrated system – e.g., a granule comprising them in an organized manner – can increase their uptake efficiency and, as a consequence, favor the plant development. We demonstrate that an optimized nanocomposite fertilizer composed of urea:urea-formaldehyde matrix loaded with $ZnSO_4$ and ZnO effectively stimulates the early growth of maize (*Zea mays* L.) when grown in a sandy substrate without distinct nutrient concentrations and no organic matter.

2. Materials and methods

2.1. Preparation and characterization of the composites fertilizers

Composite fertilizers based on urea:urea-formaldehyde (UF) matrix were prepared as described by Giroto et al. (2021). The samples were synthesized by the melting-mix process using a torque rheometer (Polylab RHEODRIVE Rheomix mixer and OS4, Thermo Fisher Scientific, Waltham, MA, USA) under 60 rpm and 90 °C for 10 min. Urea (Sigma-Aldrich, USA) was previously milled to a size range ≤ 300 μm, using a TE-330 hammer mill, Technal, Brazil), paraformaldehyde (Sigma-Aldrich, USA), and zinc sources (ZnO or $ZnSO_4$, both Synth, Brazil) was used in powder form as obtained. All sources were firstly pre-homogenized in a plastic bag and then inserted into the rheometer. Pure UF was synthesized to be used as the N fertilizer control without Zn loading, prepared following a molar ratio of 1:0.5 between urea and paraformaldehyde (Giroto and Ribeiro, 2018). The same procedure was applied to prepare the UFZn composites, adding the Zn source at the proportion of 0.5 wt.-%. The samples were kept in an oven at 80 °C for six hours and stored after cooling. The molecular structure of the composite is illustrated in Fig. 1. The samples were named UFZO for the composite with zinc oxide and UFZS for zinc sulfate.

The morphology of the composites was characterized by scanning electron microscopy (SEM) and energy-dispersive X-ray analysis (EDX) with a JSM6510 microscope (JEOL) using the secondary electron mode. The chemical composition was verified for both nitrogen and zinc, as can be seen in the Supplementary Material, Table S1. Nitrogen elementary analysis was conducted in a PerkinElmer 2400 Series II CHNS/O Elemental Analyzer (PerkinElmer, Norwalk, CT, USA), and Zn determination was conducted with an atomic absorption spectrometer (PerkinElmer PinAAcle 900 T, Norwalk, CT, USA).

2.2. Greenhouse experiment

2.2.1. Maize cultivation setup

A greenhouse experiment was carried out to evaluate the fertilizer performance of the UFZn composites in a sand substrate-plant system. We aimed to determine the effectiveness of the controlled release of N by the composites in supplying the micronutrient Zn, compared to ammonium nitrate plus zinc sulfate and a control treatment without fertilization.

The experiment was carried out for 6 weeks from February to March 2020 under controlled greenhouse conditions at the Forschungszentrum Jülich GmbH, IBG-2: Plant Sciences, Germany (50°54′36" N, 6°24′49″ E). To evaluate the combined effects of Zn co-granulated in an N fertilizer, the following treatments were included: i) negative control with no N and Zn fertilizer; ii) positive control with highly soluble fertilizers, i.e., ammonium nitrate (AN) and zinc sulfate (ZS); iii) pure urea (Ur) and iv) pure UF polymer (UF), v) Ur with the addition of ZS, vi) UF with the addition of ZS, vii) UFZO, and viii) UFZS. Treatments with pure Ur and UF were investigated to evaluate their effectiveness as such, without Zn addition. An N proportion of 200 mg kg^{-1} (or 400 kg/ha) of the sand substrate was fixed for all treatments. To achieve an equal amount of Zn (3 mg kg^{-1} of the sand substrate), zinc sulfate was added to the treatments where needed (Supplementary Material Table S1). Phosphorus (P, 200 mg kg^{-1}), potassium (K, 150 mg kg^{-1}), calcium (Ca, 50 mg kg^{-1}), magnesium (Mg, 1.5 mg kg^{-1}), copper (Cu, 3 mg kg^{-1}), manganese (Mn, 4 mg kg^{-1}) and molybdate (Mo, 0.15 mg kg^{-1}) were also supplemented according to Malavolta et al. (1997).

Nutrient-poor sand was selected because of its significantly low organic matter content and low urease activity (2.9 mg urea N hydrolyzed kg^{-1} sandy substrate h^{-1}) (Tabatabai and Bremner, 1972), and to reduce biological activity that might interfere with urea availability. The sand (characterization given in Supplementary Material, Table S2) was first dried at room temperature and sieved to remove any possibility of coarse particles or plant residues. Pots of 5 l were then half-filled with sand, followed by the addition of nutrient solution with a total of 15 replicates for each treatment. Fertilizers were applied approx. 7 cm below the sand surface, as shown in Fig. 2a. Finally, the pots were filled up with a total of 5 kg of sand.

Maize seeds (*Zea mays* L. "Badischer Gelber", Kiepenkerl-Bruno Nebelung GmbH, Germany) were pre-germinated in the same sand substrate and seedlings were transplanted after 5 days exactly above the fertilizer placement, ensuring the maximum accessibility of the fertilizer by the plant roots. Per pot, two seedlings were added, and after seven days of growth, one plant was removed, allowing only one plant to grow undisturbed. Pots were positioned in a completely randomized design on three tables of the Screen-House automated shoot phenotyping platform (Fig. 2b and c), as described in full by Nakhforoosh et al. (2016).

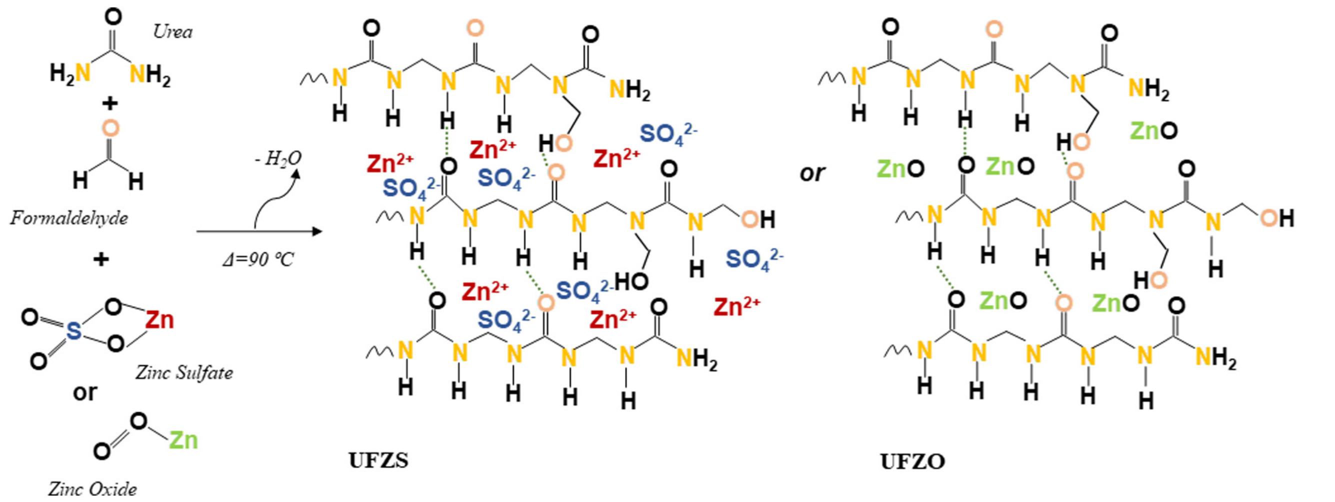


Fig. 1. Preparation of urea:urea-formaldehyde (UF) zinc composites (generic structure). Urea reacts with formaldehyde forming UF polymers loaded with zinc from zinc sulfate or zinc oxide between the UF polymer chains (UFZS and UFZO, respectively).

2.2.2. Plant growth conditions

Plants were grown under natural light during the day; additional assimilation lighting was supplied by mercury lamps (SON–T AGRO 400, Philips) whenever natural light intensity was below 400 mmol s^{-1} m^{-2}, providing a total daily light period of 16 h. The average temperature during the experiment was 19 °C during the day and 17 °C at night, with a relative humidity of 60 % during the day and 50 % at night. To avoid table microclimate or border effects, automated randomization of pot position was conducted twice per week (Robles-Aguilar et al., 2020). Watering was adjusted to maintain the substrate water content at 50 % of its water holding capacity, determined by weighing each pot every second day on the automated weighing and watering platform (Fig. 2d). Plants were harvested after six weeks of growth. All the plants were in the same development stage (V-stage) on harvesting.

2.2.3. Data collection on plant performance and nutrient uptake

Images of maize shoots were taken after six weeks of growth and before the harvest in the automated shoot phenotyping platform Screen-House (Fig. 2e). Shoot front view images taken at 0°, 90°, 180°, and 270° were used to obtain the projected shoot area for each treatment replicate. The color segmentation of the photos was obtained by in-house developed software at IBG-2: Plant Sciences, Forschungszentrum Jülich, with the following threshold settings in the HSB color space: Hue from 38.25 to 127.5, Saturation from 51.4 to 255.0, and Brightness from 19.57 to 255.0. The software provides the projected shoot area in pixels, converted to cm^2 (1 cm^2 = 1 / $(89)^2$ pixel).

After harvest, shoots were dried at 65 °C in a forced-draft oven until dry weights were constant. Shoot dry biomass was determined, and subsequently, samples were homogeneously ground to a size range of 2 mesh, using a TE-330 hammer mill. All root samples were stored in a 50 % (*v*/v) ethanol/water solution. Roots were then carefully washed to remove the attached substrate before scanning to determine the parameters mentioned below (Epson Expression Scan 1680, WinRHIZO STD 1680, Long Beach, Canada). Data for several root traits, such as total root length, root surface area, root diameter, and diameter class length (DCL, root length within a diameter class), were obtained using WinRHIZO V.2009 software (Regent Instruments Inc., Quebec, Canada). The average root length was divided into two diameter classes: ($0 < d \leq 1$) and ($1 < d \leq 2$) increments from root images for each root section. The following parameters were based on observed and computed data: root-to-shoot mass ratio (root dry mass/shoot dry mass), and relative diameter class length (rDCL) = DCL / root length (yielding a proportion of root length to normalize disparity between plants of different sizes) as described by Robles-Aguilar et al. (2019).

After root measurements, all samples were dried at 65 °C in a forced-draft oven until dry weights were constant and subsequently homogeneously ground to a size range of 2 mesh, using a TE-330 hammer mill

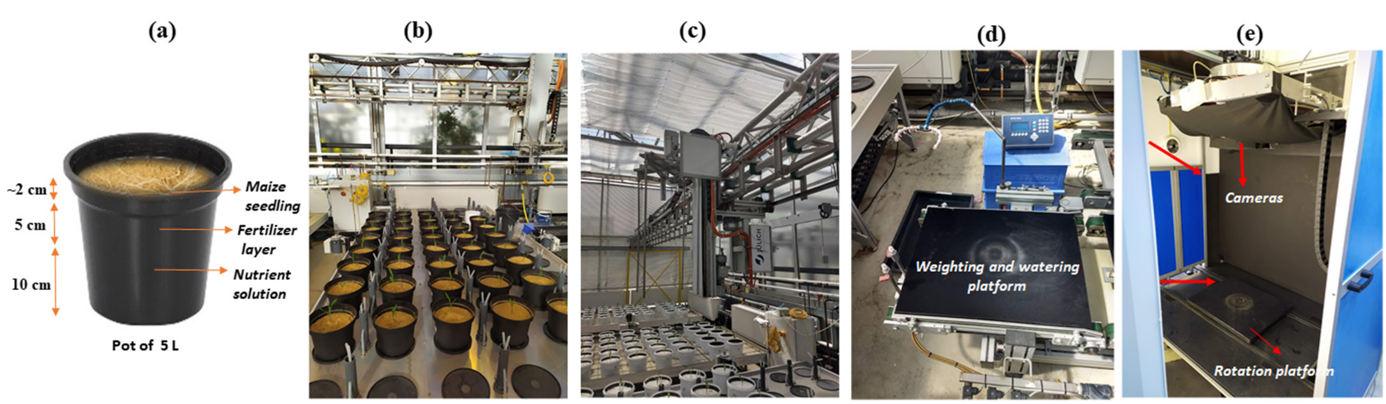
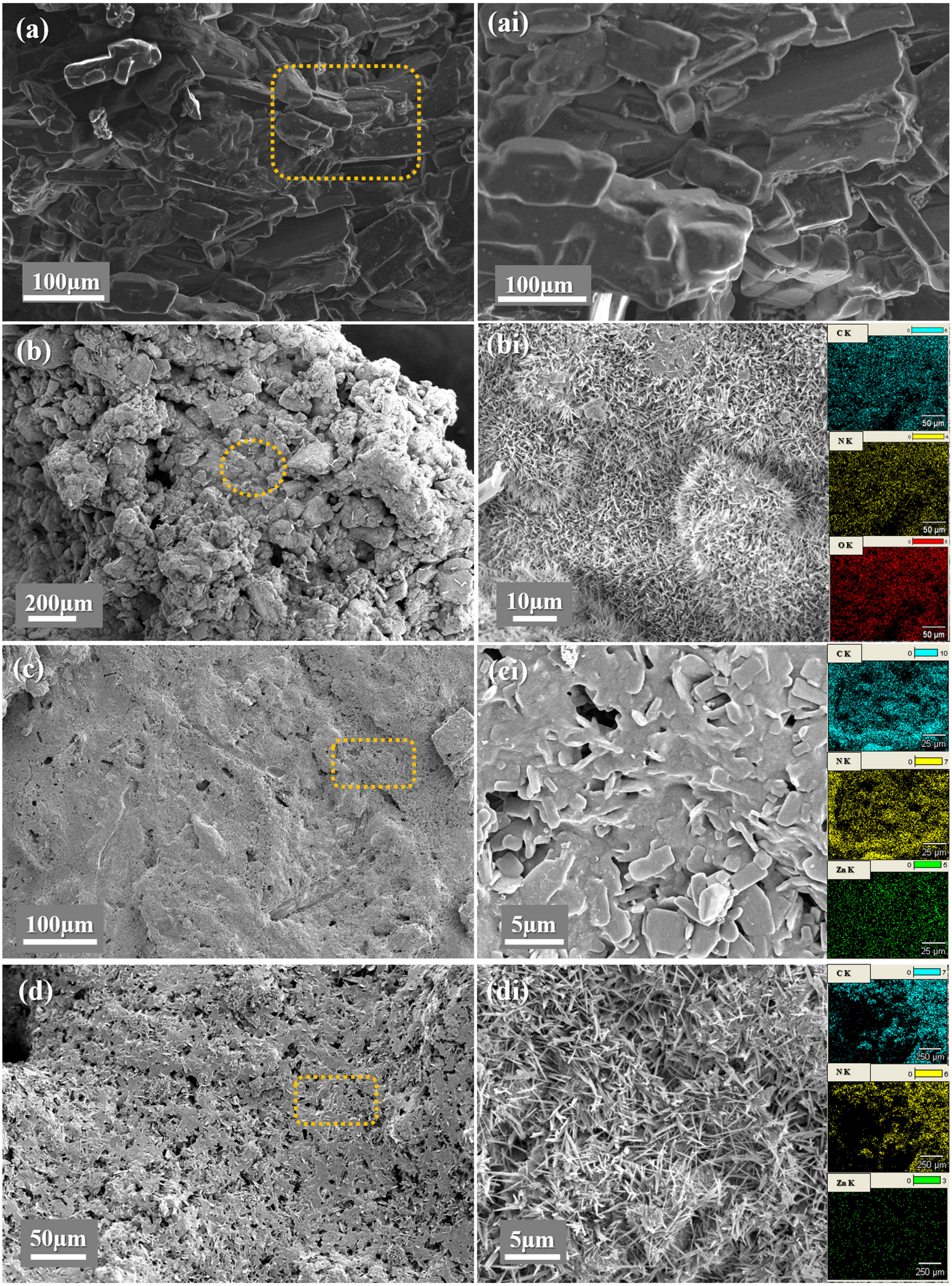


Fig. 2. Greenhouse fertilizer efficiency experiment in the ScreenHouse automated shoot phenotyping facility. (a) Pot-setup scheme with a fixed layer of fertilizer approx. 7 cm below the surface, and the maize seedling approx. 2 cm below the surface; (b) randomized pot distribution on the tables; (c) robotic arm carrying the pots to (d) the weighing and watering platform, and to (e) the imaging chamber with three cameras (top view, side views at 45° and 90°) and a rotation platform.


(a)
100µm
(ai)
100µm
(b)
200µm
(bi)
10µm
C K
N K
O K
50 µm
(c)
100µm
(ci)
5µm
C K
N K
Zn K
25 µm
(d)
50µm
(di)
5µm
C K
N K
Zn K
250 µm

(Tecnal, Brazil). Samples of 100 mg of the powdered and homogenized shoot were digested with 3 ml HNO_3, and 2 ml H_2O_2 in the microwave at full power for 10 min and made up a total volume of 14 ml. The samples were then analyzed for entire Zn content by ICP-OES (ThermoScientific, iCAP6500, USA). The N content was determined by elemental analysis (VarioELcube, Elementar, Germany).

Based on the accumulated dry mass shoot or root and N and Zn content, the uptake of these nutrients was estimated, and thus, the apparent N and Zn recovery efficiency (RE) was estimated using Eq. (1):

$$\mathrm{RE}\ (\%) = \frac{(\mathrm{U1} - \mathrm{U0})}{\mathrm{F}} \times 100 \tag{1}$$

where F is the amount of fertilizer (N or Zn) soil-applied, U1 is the total plant N or Zn uptake in biomass in an experimental pot that received N or Zn fertilizers, and U0 is the total N uptake in biomass in an experimental pot unfertilized N and Zn (control).

2.2.4. Nutrients remaining in the soil after harvest

After plant harvesting, substrate samples were collected, air-dried, and homogeneously sieved to investigate the remaining nutrients. Total N was extracted by the Kjeldahl method (Embrapa, 2011). The amount of mineral N (NH_4^+ and NO_3^-) was analyzed by soil extraction using KCl (Synth, Brazil) solution (1 mol l^{-1}), with a ratio of 10:1 for extractant and sand. To inactivate the urease enzyme, a solution of 5 mg l^{-1} of phenyl-mercuric acetate (Sigma-Aldrich, USA) was added at the extraction stage as described by Tabatabai and Bremner (Tabatabai and Bremner, 1972). The suspension was stirred for one hour, filtered, and stored in a refrigerator (5 °C) until further analysis. The mineral N extracted (NH_4^+ and NO_3^-) were analyzed colorimetrically according to Kempers and Zweers (Kempers and Zweers, 1986).

Available Zn in the sand was extracted using 5 g of the substrate with 25 ml of extraction solution under agitation for 5 min. Sand extracts (5:1 solution/sand ratio) were obtained using a Mehlich-1 (0.05 mol l^{-1} hydrochloric acid (Vetec, Brazil) plus 0.0125 mol l^{-1} sulfuric acid (Synth, Brazil) solution (De Campos Bernardi et al., 2002). The clear supernatant obtained after sedimentation was analyzed inductively to determine solubilized Zn using ICP-OES (ThermoScientific, iCAP6500, USA).

2.3. Statistical analysis

Differences among treatments in shoot and dry root biomass, projected shoot area, nutrient uptake, and root morphological traits were assessed by one-way analysis of variance (ANOVA). Normality and homogeneity of variance were tested using R Statistics software. Pairwise differences among treatments were compared by Tukey's test ($p < 0.05$).

3. Results and discussion

3.1. Characterization of UFZn composites

The surface morphologies of urea (a, ai), pure UF polymer (b, bi), and composites (c-di) are shown in Fig. 3. Urea exhibits irregular tetragonal crystal shapes while the UF polymer shows acicular crystals. The segregation of micronutrient particles when mixed in granules with other sources, e.g., monoammonium phosphate (MAP) or diammonium phosphate (DAP), is favored by differences in particle sizes (Rodella and Chiou, 2009; Santos et al., 2018). The images in Fig. 3 (ci) and (di) reveal that both $ZnSO_4$ and ZnO were uniformly dispersed in the UF matrix, without any signals of particle segregation or agglomeration. The UF morphology in the UFZO composite was changed by the nucleation of the original polymer needles around ZnO particles. In UFZS, the Zn soluble source was embedded in the polymer matrix, acting as an electrostatic dispersing agent for the polymer nucleation (Giroto et al., 2021).

3.2. Greenhouse experiments

3.2.1. Maize shoots and roots biomass

Images of the shoot area of the maize plants are shown in Fig. 4, where distinct differences in the response of the maize plants to each fertilizer treatment can be seen. All treatments performed better than the control in all measured traits and were similar in effectiveness to AN + ZS ($p < 0.05$) it is considered a super positive treatment for having both nutrient N and Zn prompt available for the plants (Table 1). The treatment Ur (without additional Zn) showed a visible nutrient deficiency (Fig. 4d) by discolored leaves and stunted growth. Zinc deficiency may inhibit plant growth by reducing the plant Zn content itself and altering the balance of other nutrients assimilated, such as Fe, P, and Cu, affecting plant metabolism (Escudero-Almanza et al., 2012). Shoot chlorosis was observed only in the Ur and UF treatments, which was also reflected in the results on biomass production. Plants of the negative control also showed nitrogen deficiency symptoms, besides chlorosis, which were very pronounced since there was no nutrient application in this treatment (data not shown).

Plants that were subjected to nitrogen application produced greater shoot biomass than the negative control treatments which were fertilized with other nutrients unless N and Zn (Table 1). Maize plants treated with AN + ZS, UF + ZS, UFZO, and UFZS showed no significant differences in biomass production, indicating the UF treatments achieved comparable performance to the positive reference (AN + ZS). Moreover, the results suggest ZnO embedded in the UF matrix was as efficient as the soluble source $ZnSO_4$. Ur + ZS and UF + ZS also displayed statistically similar biomass contents to pure UF and both UFZO and UFZS composites. In contrast, maize plants subjected to only Ur had the lowest biomass production ($p < 0.05$). Due to lower N absorption limited by the absence of Zn, the N released by pure urea may have been more susceptible to losses, such as NH_3 volatilization. This aspect may have affected growth even more and gave a difference in responses between Ur and UF, as the UF polymer releases N more slowly (Giroto and Ribeiro, 2018; Yamamoto et al., 2016; Zhang et al., 2020; Giroto et al., 2021). It is essential to highlight that maize grown in the presence of UF, even without Zn, had a superior performance than maize grown in pure urea.

Equivalent biomass was produced in the presence of the composites and AN + ZS. It is important to reinforce that the AN + ZS treatment has two N forms readily available (NH_4^+ and NO_3^-) that are directly assimilated by plants, in contrast to urea, which first needs to be hydrolyzed by urease to form ammonium and, subsequently, nitrate. The comparable response to the composites as to AN + ZS could mean an increased exudation of compounds from the maize roots to support the activity of substrate and roots-associated microorganisms since the sand substrate had a shallow organic matter content and a very low urease activity. The results suggest that UF + ZS, UFZO, and UFZS composites can replace highly soluble N sources like the commercial AN + ZS.

The total projected shoot area acquired before the harvest was estimated from images captured in the automatic shoot phenotyping platform ScreenHous3 (Fig. 2e). In line with the biomass production, UF + ZS (33.5 cm^2), UFZO (33.5 cm^2), and UFZS (30.8 cm^2) had the largest shoot area and did not differ from the AN + ZS treatment (31.5 cm^2) (Table 1). The treatment Ur + ZS had a shoot area value (26.5 cm^2) close to UF (23.6 cm^2), while the Ur treatment resulted in an overall inferior shoot area (13.4 cm^2).

3.2.2. N and Zn uptake in shoots and roots by the maize plants

Regarding shoot N uptake, maize fertilized with Ur showed the lowest N content, significantly different from maize fertilized with AN + ZS, Ur + ZS, or UF + ZS, but similar to UF, UFZO, and UFZS (Table 1). As other results

Fig. 3. SEM images of (a, ai) urea, (b, bi) UF polymer, (c, ci) UFZS and (d, di) UFZO. Regions highlighted in yellow were enlarged in Figure (i). EDX images of the elementary distribution have been added for the UF polymer (bi) and composites (ci and di).

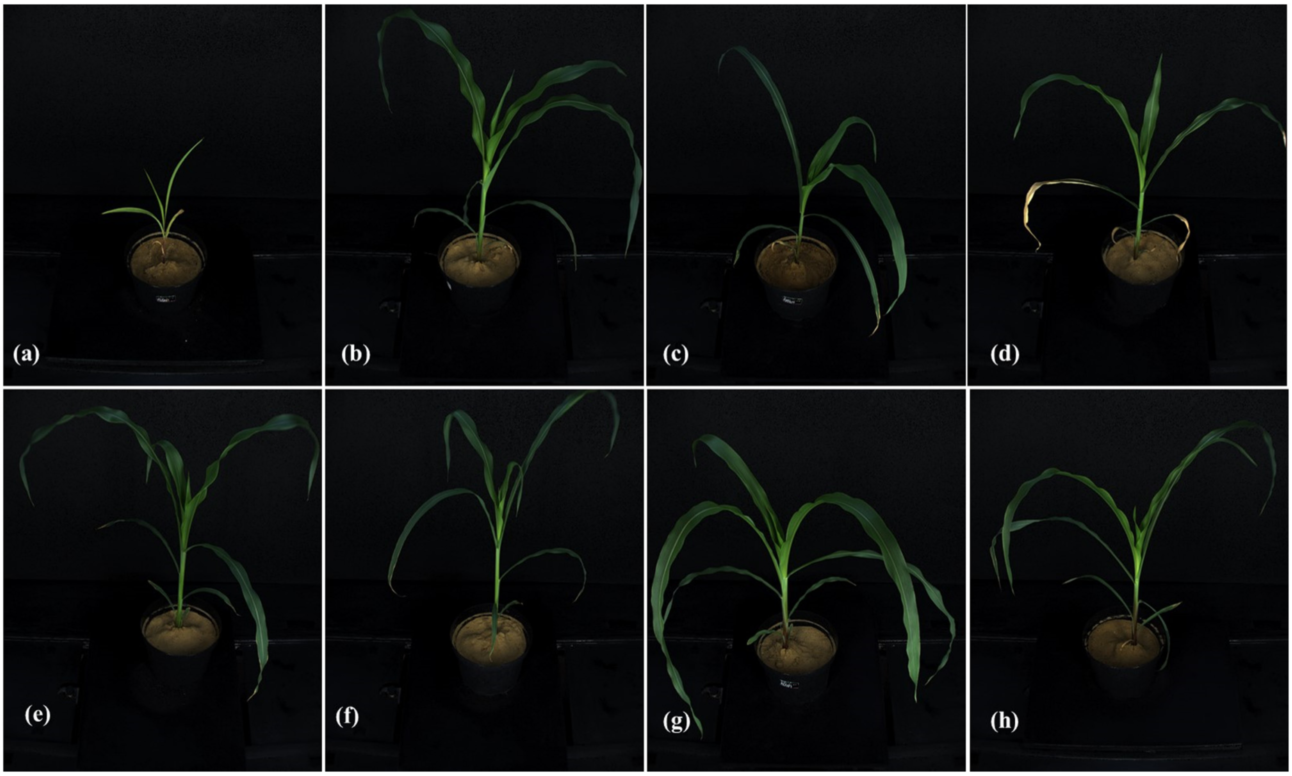


Fig. 4. Effects of different N and Zn sources supply on maize growth. Images were acquired after six weeks of growth and before harvest. Treatments were (a) control; (b) AN + ZS; (c) Ur + ZS; (d) Ur; (e) UF + ZS; (f) UF; (g) UFZO; and (h) UFZS.

pointed out, the absence of zinc strongly influenced the urea fertilizer efficiency, limiting plant development and nutrition (Cakmak et al., 1994; Mattiello et al., 2017). A synergistic effect of Zn in the soil N cycle has been discovered since this metal serves as a cofactor for some enzymes involved in N metabolism (Glass and Orphan, 2012). Moreover, the enhancement of biomass yield as a result of Zn application could also have a positive effect on plant N uptake (Montoya et al., 2021), thus reducing potential N losses. Almendros et al. (2019) also observed this synergistic effect in the yield of a rain-fed barley crop, applying Zn with a mixture of synthetic chelating compounds and urea as the N source. As reported by Montoya et al. (2021) fertilization with Zn sulfate combined with N in the form of urea or ammonium nitrate, respectively, can positively affect the yield in a maize plant.

Considering that N uptake from the UF treatments was not significantly different from AN + ZS, the slow-release of N from the polymer matrix proved to be an efficient alternative to the commercial ammonium nitrate (AN) source. The results indicate that UF-based sources can supply N to plants in a short period even following their controlled release, as also suggested in our previous study (Giroto et al., 2021). Regarding the release test in water (full immersion of the composites) after 6 days both UFZS and UFZO composites still kept 30 % of urea non-solubilized (Giroto et al., 2021). Although urea provides high availability of N-NH_4^+ 14 days after incubation in soil, the available N for plant absorption considerably declined after 28 days. In contrast, UFZS and UFZO composites were able to keep NH_4^+ availability almost constant, with no NH_3 losses after 42 days of incubation, reaching the same value found for urea (Giroto et al., 2021). Since they deliver N in a slower manner, the composites are less harmful to the environment and more efficient in the longer term due to reduced N losses. As expected, the N released from these fertilizers within 6 weeks was sufficient to meet the nutritional N demand of maize, such as in the conventional N sources ammonium nitrate (AN) and urea employed in this study as controls. The Zn uptake by shoots featured more differences between the treatments. Maize fertilized with AN + ZS and Ur + ZS had the highest Zn uptake, followed by the plants fertilized with UF + ZS and UFZO. Despite the different water solubility behaviors of ZnO and $ZnSO_4$ (McBeath and McLaughlin, 2014), little difference was observed in Zn bioavailability between these two sources when present in the composites.

Roots showed the same tendency as shoots, with maize growing in the control and treatments without Zn application having the lowest root biomass (Table 1). UFZO and AN + ZS showed the highest values regarding the N content in roots, while UF was the lowest. The Zn accumulated in maize roots was higher when the plants were fertilized with UF + ZS, AN + ZS, and UFZO, suggesting similar assimilation of Zn from the oxide and $ZnSO_4$. Our results agree with those observed by Korndörfer et al. (1995) since the authors did not verify differences in maize production when the Zn source applied was Zn oxide compared to those with Zn sulfate. The only difference observed was in the treatments without Zn, in which the plants had lower N uptake. This conclusion was also verified

Table 1
Influence of N fertilizer and Zn source applied on the shoot and root biomass, N and Zn recovery efficiency (RE), and total projected shoot area of maize plants growing in sand supplied with: ammonium nitrate + zinc sulfate (AN + ZS), Urea, and UF polymer (with or without Zn supply), composites UFZO and UFZSO, and no fertilization (Control). The values shown are the mean per trait.

Treatments	Shoot Biomass	Shoot area	Shoot N RE	Shoot Zn RE	Root Biomass	Root N RE	Root Zn RE
	g	cm^2	%	%	g	%	%
Control	0.28d	2.80d	–	–	0.24b	–	–
AN + ZS	6.37a	31.5a	14.41a	1.40a	1.18a	2.23a	1.70a
Ur + ZS	4.73b	26.5b	15.52a	0.96acd	0.80a	1.37b	0.68b
Ur	1.88c	13.4c	9.73b	0.26b	0.56ab	1.09b	0.45b
UF + ZS	5.77ab	33.5a	13.95a	0.82 cd	1.08a	1.16b	0.95ab
UF	4.16b	23.6b	10.79ab	0.36bcd	0.73ab	0.72c	0.56b
UFZO	5.53ab	33.5a	12.91ab	0.78d	1.11a	2.84a	1.14ab
UFZS	5.13ab	30.8ab	10.58ab	0.47d	0.99a	0.86b	0.72b

$n = 15$. Different letters indicate significant differences at $p < 0.05$.

by the appearance of chlorosis in the treatments without Zn (Santos et al., 2018), as also shown in our presented study.

3.2.3. Roots morphology in response to Zn—N co-fertilization

The fertilized treatments displayed a greater root length, root surface area, and root diameter than the control, except for pure Ur, which featured the lowest root length (Table 2). This fact reflects the poor development of maize fertilized only with urea, which was also observed in biomass and nutrient uptake data (Table 1). Total root length and surface area from the control (AN + ZS) were inferior to UFZO and UFZS fertilizer treatments. The lower root dimensions in the presence of AN + ZS might be because of the high salt content of this source since the salt content of ammonium nitrate is equal to 105 % while for urea is 75.4 % (Malavolta et al., 1981). Ammonium nitrate (AN), as a salt, dissolves and may raise the electrolyte concentration of the fertilized soil solution in proximity to the roots. This high electrolyte concentration close to the seeds or roots can reduce or inhibit water absorption due to the increased osmotic pressure of the solution (Taiz et al., 2014). These factors may have reduced plant root growth in the AN + ZS, Ur treatment. On the other hand, the readily available nutrient source AN + ZS promoted the aboveground and root biomass production (Table 1) significantly similar to the UFZn composite, even though its total root length and root surface area were smaller compared to UF and the composites (Table 2), stressing the advantage of the Zn-N-composite fertilizers again concerning plant development. When nutrients are readily available anyway, roots do not need to grow in length to acquire further nutrients from the surrounding substrate. Reach an equilibrium between the nutrients released and plant needs is the key to achieving an adequate plant growth because both the absence of N and Zn and excess of N can compromise the growth of roots, either by a deficiency of these nutrients or by the phytotoxins caused by the salt index of the fertilizers as verified in Table 2 (Schröder et al., 2000; de Souza et al., 2007; Vargas et al., 2015). In this context, the UF + ZS presented the best results from all root measurements, followed by the UFZS and UFZO composites. As discussed above, we hypothesized that maize root morphology is altered in the presence of this polymeric structure, with increasing length and surface area as a strategy to improve soil nutrient uptake, possibly also increasing root exudation of compounds that are essential for N release from the composite structure.

The smaller root diameters observed in the control and urea treatments (Table 2) can be attributed to the lower development of the maize root system due to the inherent nutrient limitations in these treatments. The average root lengths according to diameter class ($0 < d \leq 1$) and ($1 < d \leq 2$) of maize fertilized with different sources are shown in Fig. 5. In general, the relative diameter class length (rDCL) of the roots with ($1 < d \leq 2$) was 70 %, while rDCL of the roots ($0 < d \leq 1$) was approximately 30 %. These fine root rDCL was underestimated because the employed sampling method was insufficient to collect thinner roots (Robles-Aguilar et al., 2020). Consequently, a considerable portion of the tertiary roots was not separated from the sandy substrate, hence not contributing to the measured results. Thus,

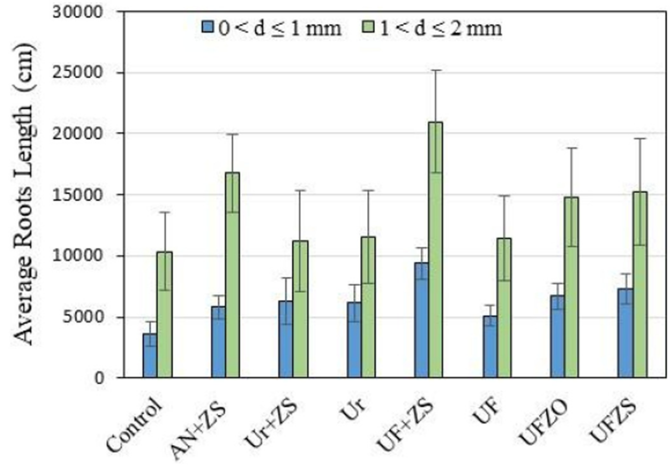


Fig. 5. Average roots length of maize in the diameter class ($0 < d \leq 1$) and ($1 < d \leq 2$) according to the different sources: control (with no fertilizer); ammonium nitrate and zinc sulfate (AN + ZS); urea with zinc sulfate (Ur + ZS), pure urea (Ur), UF polymer with zinc sulfate (UF + ZS), pure UF polymer (UF) and composites UFZO and UFZS.

the average length of fine roots was certainly greater than that measured in the current work. Nonetheless, these results are consistent with the results of the root parameters presented in Table 2.

3.2.4. Residual N and Zn in sand

A crucial aspect of controlled release fertilizers is their ability to maintain the excess fertilization still available in the soil to be used by subsequent cultures. Table 3 presents the concentrations of mineral N (NH_4^+ and NO_3^-) and Zn availability in the sand after the experimental maize cultivation. Regarding mineral N, the sand fertilized with AN + ZS showed the highest remaining NH_4^+ and NO_3^- contents. On the other hand, the sand fertilized with Ur + ZS or Ur presented the lowest residual NH_4^+ contents. Sand fertilized with UF-based polymers showed intermediate NH_4^+ concentrations, with UF showing similar levels to sand fertilized with AN + ZS. However, both the sand fertilized with urea and that fertilized with UF showed identical concentrations of residual NO_3^-. These results suggest that the used sand presents a low capacity for nitrification of N-NH_4^+ coming from the hydrolysis of urea or UF because of its low autochthonous microbial activity (Dendooven et al., 1994).

In addition, the nitrification process can be limited when there is intense N loss by ammonia volatilization (Giroto et al., 2017; Guimarães et al., 2016). High ammonia (NH_3) concentration in the soil, in general, can reduce the activity of the bacterium of the genus *Nitrobacter* responsible for nitrification from NO_2^- to NO_3^- (Dendooven et al., 1994). The higher

Table 2
Total root length, root surface area, and average root diameter of maize supplied with: ammonium nitrate + zinc sulfate (AN + ZS), urea, and UF polymer (with or without Zn supply), composites UFZO and UFZSO, and no fertilization (Control). The values shown are the mean per trait.

Treatment	Total root length	Root surface area	Average root diameter
	cm	cm^2	mm
Control	2605.1 e	244.8 e	1.3 d
AN + ZS	5161.2 c	640.2 b	2.2 b
Ur + ZS	6967.9 b	750.2 b	2.5 b
Ur	190.7 f	551.6 d	1.6 c
UF + ZS	10,794.5 a	953.9 a	3.0 a
UF	7440.6 b	634.5 b	2.3 b
UFZO	8562.4 b	870.5 a	2.8 b
UFZS	9797.6 ab	802.8 a	2.7 b

n = 15. Different letters indicate significant differences at $p < 0.05$.

Table 3
The concentration of mineral N as NH_4^+ and NO_3^- and available Zn in the sand substrate was measured after six weeks of maize growth supplied with: ammonium nitrate + zinc sulfate (AN + ZS), urea, and UF polymer (with or without Zn supply), composites UFZO and UFZSO, and no fertilization (Control). The values shown are the mean per trait.

Treatments	N-NH_4^+	N-NO_3^-	Zn
		mg kg^{-1}	
Control	0.00 d	1.59 b	0.85 cd
AN + ZS	32.24 a	60.61 a	1.18 c
Ur + ZS	0.82 d	1.57 b	1.08 c
Ur	0.77 d	1.55 b	0.61 d
UF + ZS	12.97 c	1.57 b	1.08 c
UF	26.82 ab	1.69 b	0.57 d
UFZO	16.99 bc	1.90 b	4.22 a
UFZS	12.46 c	1.79 b	2.38 b

n = 15. Different letters indicate significant differences at $p < 0.05$.

concentration of NH_4^+ in the sand fertilized with UF can be attributed to the controlled release of urea and, possibly, the lower loss of N by the volatilization of NH_3. Sandy soils with low cation exchange capacity and acidity buffering are more prone to ammonia volatilization, as reported by Guimarães et al. (2016), whereas N-NH_3 losses were up to 70 % in sandy soils fertilized with urea (Guimarães et al., 2016). Our results suggest that the controlled release of N by UF provided a higher availability of N-NH_4^+ in the sand after six weeks of maize cultivation compared to pure urea. Recent works have shown that urea polymerized with paraformaldehyde (UF polymers) can increase the agronomic efficiency of urea (Giroto and Ribeiro, 2018; Pereira et al., 2017; Yamamoto et al., 2016). In addition to reducing N losses, the controlled release of urea in UF polymers can prolong the availability of N in the soil, as demonstrated in this work.

After six weeks of maize cultivation, zinc fertilization from the composites (UFZO and UFZS) provided a higher micronutrient concentration in the soil. Despite not providing an increase in biomass production and Zn uptake (Table 1), the application strategy of the ZnO and $ZnSO_4$ sources incorporated into the UF matrix provided higher residual Zn concentration in the sand compared to the $ZnSO_4$ source applied directly to the sand. According to various authors, Zn fertilizers could have a residual effect of several years (Gonzalez et al., 2019). Therefore, we assume that this Zn treatment left sufficient Zn available to grow later crops without any further micronutrient Zn additions.

The strategy of co-granulation of the soluble source $ZnSO_4$ into the UF matrix controls Zn's release to the soil, while the co-granulation of low solubility sources such as ZnO intensifies the release of this micronutrient (Giroto et al., 2021).

4. Conclusions

Our results showed the advantage of the N—Zn co-application in the composite granule structure, which was efficient even in very harsh substrate conditions. As summarized in Fig. 6 nitrogen and zinc must be used simultaneously because these two nutrients behave synergistically. Their co-application following Zn dispersion in the UF matrix is encouraged, allowing for its simultaneous application without any extra labor as necessary by separate nutrient applications. ZnO dispersed in the UF matrix resulted in similar plant biomass production compared to the treatment with ammonium nitrate (AN) with the addition of zinc sulfate (ZS), which implies avoiding the negative effects of counterions in high concentrations. Concerning maize development, we found that root morphology is altered in the fertilizer nanocomposite with increased root length and surface area,

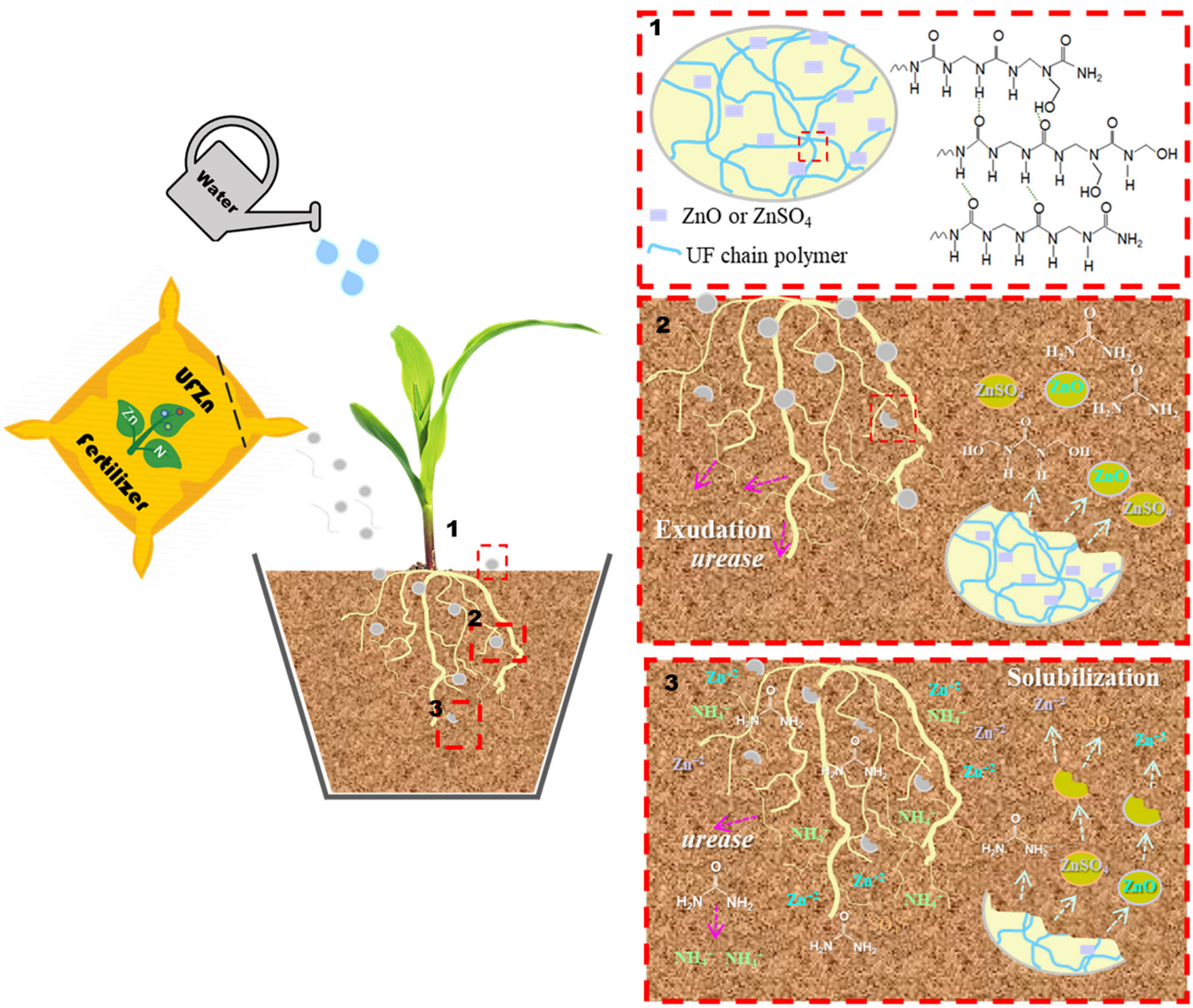


Fig. 6. A schematic diagram describing the release of nitrogen and zinc: Once the fertilizer is applied to the soil (1), the UF polymers are solubilized y the water and its chain is broken into molecules of urea, and the particles of zinc sulfate and zinc oxide are released into the soil. The urease enzymes released from the maize roots start to convert urea to ammonium (2) releasing the Nitrogen into the soil at the same time the particle of zinc sulfate and oxide are solubilized releasing Zn into the soil (3).

improving nutrient uptake. Root exudation of compounds essential for N release from the composite structure has risen potentially in the presence of the urea:urea-formaldehyde matrix loaded with Zn.

Our results open perspectives for designing an integrated system for an easy application of N and Zn in an optimized manner. The procedures herein used are easily scalable, aiming to the scale level needed for fertilizer production. Future agronomic experiments under real field and different soil conditions are needed, to further indicate the application conditions and to provide more economic advantages of the presented N-Zn-fertilizer formulations over common fertilizer practices.

Credit authorship contribution statement

Amanda S. Giroto, **Stella F. do Valle**, **Nicolai D. Jablonowski**, **Caue Ribeiro**, and **Luiz H. C. Mattoso** designed research; **Amanda S. Giroto**, **Benedict Ohrem**, **Nathalie Wuyts,** and, **Stella F. do Valle** conducted the experiment; **Gelton G. F. Guimarães** performed the statistical analyses; **Amanda S. Giroto**., **Stella F. do Valle**, **Gelton G. F. Guimarães**, **Nicolai D. Jablonowski**, **Caue Ribeiro** and **Luiz H. C. Mattoso,** wrote the paper. All authors reviewed the manuscript.

Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: Amanda Soares Giroto reports financial support was provided by State of Sao Paulo Research Foundation. Amanda Soares Giroto reports a relationship with State of Sao Paulo Research Foundation that includes: funding grants.

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Appendix A. Supplementary data

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