EFFECTS OF TiO_2 NANOPARTICLES ON MAIZE (*ZEA MAYS* L.) GROWTH, CHLOROPHYLL CONTENT AND NUTRIENT UPTAKE

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(Received 5th Aug 2018; accepted 28th Sep 2018)

Abstract. Nanotechnology, as the source of new industrial materials, has been widely used in recent years and has appeared in almost every field. Nowadays, nanoparticles are used in many areas like textiles, cosmetics, pharmaceuticals, automotive and defense (military) industries. The usage of nanoparticles has increased in recent years, but their effects on the environment are not exactly known. In this study, TiO_2 nanoparticle (TiO_2-NP) was applied at increasing concentrations (0, 5, 10 and 20 mg L^{-1}) to maize (*Zea mays* L.) plant grown in hydroponic culture at 16 h light/8 h dark, 25/20 °C temperature, 60% humidity and 10 Klux light intensity for 20 days. Application of TiO_2-NP on biomass production, nitrogen (N), phosphorus (P), potassium (K), zinc (Zn), iron (Fe), manganese (Mn), copper (Cu) and chlorophyll contents were investigated. The results showed that the plants' shoot and root biomass and leaf chlorophyll contents were significantly reduced with increasing TiO_2-NP applications. On the other hand, TiO_2-NP applications positively affected macro- (N, P, K) and micronutrients' (Zn, Mn, Cu) concentration except for Fe. Compared to the control treatment, the concentration of Zn, Mn, Cu, N and P significantly increased with the application of TiO_2 nanoparticles. Consequently, TiO_2-NPs treatments have increased nutrient uptake of maize excluding iron while decreased the dry biomass of maize at high doses.
Keywords: *chlorophyll, nanoparticle, maize, phytotoxicity, TiO_2 nanoparticles*

Abbreviations: TEM: Transmission Electron Microscopy; SEM: scanning electron microscopy; DW: dry weight; ICP-MS: inductively coupled plasma mass spectrometry; SPAD: soil-plant analysis development

Introduction

Nanotechnology, one of the most popular scientific disciplines, has been widely used in different branches of science and technology in recent years (Siddiqui et al., 2015; Reddy et al., 2016; Cox et al., 2017). Although today nanotechnology has a billion-dollar industry around the world, ongoing comprehensive research shows that this technology is still in the discovery stage and that technology is expected to grow even further (Reddy et al., 2016; Cox et al., 2017).

Nanoparticles, rare in nature and being used in nanotechnology are widely used in cosmetics, agriculture, industry, technology, transportation, pharmaceutics, and energy due to their different properties (Kavaz, 2011; Rafique et al., 2014; Rastogi et al., 2017). The nano is a word from the Greek and it means very small, tiny. The size of these particles are less than 100 nm and they have unique chemical and physical properties (Du et al., 2011; Doğaroğlu and Köleli, 2017a; Rastogi et al., 2017). These properties of nanoparticles depend on their size, shape, morphology and properties of surface area.

Nanoparticles (NPs) are widely produced to supply increasing industrial demands. Enormous and unlimited use of NPs in recent years has led researchers to investigate this issue, regarding the problems that may arise in practice, and the environmental impact of these problems (Gottschalk et al., 2015; Tolaymat et al., 2015; Reddy et al., 2016).

http://www.aloki.hu ● ISSN 1589 1623 (Print) ● ISSN 1785 0037 (Online)
DOI: http://dx.doi.org/10.15666/aeer/1605_68736883

Metallic nanoparticles such as TiO_2, ZnO, CuO etc., are the most common nanoparticles used in agriculture and industry. TiO_2-NP is the oxide of the metal titanium (Ti) and belongs to the family of transition metal oxides (Samadi et al., 2014; Lyu et al., 2017). Titanium dioxide is the most-produced nanoparticle (88.000 metric tons/year) after silicon dioxide (SiO_2) in the world (Medina-Velo et al., 2017) and it is used quite wide range areas such as cosmetics, pharmaceuticals, paints, coatings, antibacterial products, textiles (Da Costa and Sharma, 2015; Cox et al., 2017). Because of its intensive usages, its entry into the environment, concentration of soil and water is increasing day by day. There is no data directly published about the toxic concentration of TiO_2 and other metallic nanoparticles in soil and water (Da Costa and Sharma, 2015). But the knowledge about the toxic effect of TiO_2-NPs on the environment is limited and not well known. However, the researches done to evaluate the effects of TiO_2-NPs on the plant are not much. Several studies reported TiO_2 impact on plant development and physiology (Lyu et al., 2017). According to some reports, TiO_2-NPs are beneficial to some organisms and have positive effects on plant growth, chlorophyll synthesis and photosynthesis (Lyu et al., 2017). For instance, in spinach, TiO_2-NPs increased chlorophyll synthesis, photosynthesis and plant dry weight (Zheng et al., 2005; Hong et al., 2005). On the other hand, some investigations have reported that TiO_2-NP has an adverse impact on seed germination and plant growth and may lead to phytotoxicity (Samadi et al., 2014; Ruttkay-Nedecky et al., 2017).

Maize is a cereal plant that has been the most-cultivated crops in the world after wheat and rice. According to the Food and Agriculture Organization (FAO), the world maize harvested area was 1.8 billion hectares with an approximately billion tones production in 2016 (FAO, 2018). For these reasons, maize was used in the current experiment to investigate the effects of TiO_2-NP on growth and development of maize and the possible participation of TiO_2-NP in the food chain.

The toxic effects of nanoparticles such as TiO_2, ZnO, CuO, etc. on the plant were tested in petri-dishes (Lee et al., 2010; Castiglione et al., 2011; Doğaroğlu and Köleli, 2017a, b) or in the agar medium (Lee et al., 2008; Nair and Chung, 2014). These experiments could give very limited information. However, a hydroponic experiment gave more information about the uptake, accumulation of NPs in a different part of plants (shoot and root) and also the impact of these NPs on plants (such as chlorophyll content, plant growth, etc.) in a short time (Pošćić et al., 2016). After seedlings, plants would need essential mineral nutrients in growing media for healthy growth. Because of that reason, hydroponics systems with nutrient supply would be useful for phytotoxicity testing (Song et al., 2013). Because of these advantages, a hydroponic experiment was conducted under controlled climate chamber condition. The effect of TiO_2-NPs on growth, chlorophyll content, and mineral nutrient uptake of maize was investigated.

Materials and methods

The TiO_2 (<100 nm) nanoparticles, used for the hydroponic experiment, were synthesized by Dr Birol Karakaya in Gebze MAM institute.

The identification of TiO_2 nanoparticle as one of the primary nanomaterials by the Organization for Economic Co-operation and Development (OECD) is the most important criterion in selecting the nanoparticles to be used in this study (OECD, 2013). Maize, a widely grown plant, was used as plant material in this study. KERMESS (FAO 600-630) hybrid maize seeds were obtained from the KWS Seed Company.

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The synthesized and characterization of nanomaterials

Titanium dioxide (~30-60 nm) nanoparticles were synthesized by Dr. Birol Karakaya through using a combination of Sol-Gel and hydrothermal synthesis with small changes in traditional methods at a research centre (BME-Kocaeli/Turkey) (Doğaroğlu and Köleli, 2017a). In this study, Variable Pressure Field Emission Scanning Electron Microscope (VP FE-SEM) (Carl Zeiss Supra 55) was used to characterize TiO_2-NPs coated with platinum-palladium. Titanium dioxide nanoparticles coated with platinum-palladium were imaged in SEM and elemental analysis was performed with EDX.

Hydroponic experiment

The maize seeds were germinated in a mixture of peat and perlite (1:1 w/w). When seedlings were getting 2-3 leaves and hairy rooted, they were transferred into the 4.5 L polyethylene pots supplied with the Hoagland nutrient solution medium (Hoagland and Arnon, 1950). The composition of the nutrient solution was as follows; the macronutrients (1 mM KH_2PO_4, 3 mM KNO_3, 0.25 mM $MgSO_4.7H_2O$, 2 mM $Ca(NO_3)_2.4H_2O$ and $2.5x10^{-2}$ mM KCI) and micronutrients (1 μM $MnSO_4.H_2O$, 1 μM $ZnSO_4.H_2O$, 0.25 μM $CuSO_4.H_2O$, 0.25 μM $(NH_4)_6Mo_7O_{24}$, and 0.125 μM H_3BO_3), pH was 5.2. Freshly prepared 0.1 mM Fe EDTA solution was added to each pot for the supply of the iron requirement of the maize plants. The nutrient solution was continuously aerated with a pump (KNF vacuum pump No.22.AN.18). Five maize plants were transferred to the pots and TiO_2-NP was applied with increasing dose 0, 0.5, 10, 20 mg L^{-1} to the nutrient culture. The nutrient solution was changed every 2-3 days. The plants were grown under controlled conditions (16/8 h light/dark period, 25/20 °C, 60% humidity and 10 Klux light intensity) for 20 days. The experiment design was a randomized block method with tree replication.

The effects of TiO_2-NP application on leaf chlorophyll contents were determined by the Konica Minolta SPAD-502 (Konica-Minolta, Japan, 0.06 cm^{-2} measurement area and its accuracy is 1.0 SPAD units) chlorophyll meter. The SPAD-502 calculates the chlorophyll content as soil Plant Analysis Development value (SPAD value). After the chlorophyll measurements, the plants were harvested as shoots and roots part and then washed with distilled water. After that, all samples were dried at 65°C in an oven until reaching a constant weight. The dry weights of plant samples were taken, and then ground in the mixer mill (Retsch MM301) for plant analysis. Plant samples were digested with HNO_3 and H_2O_2 in microwave oven (MarsXpres CEM). Total K, P, Zn, Fe, Cu, and Mn concentrations of the samples were determined by Inductively Coupled Plasma Mass Spectrometry (ICP-MS) (Agilent 7500ce Model). All results were given based on dry plant matter at 65 °C. The nitrogen concentrations of shoots were analyzed according to Bremner and Mulvaney (1982). Certified reference materials (SRM 1573A, SRM 1547) were also analyzed in order to check the accuracy of the extraction technique used in this study.

Statistical analysis

The variance analysis of the results was statistically analyzed by using the IBM SPSS-20 statistical analysis package program. The difference between the averages was grouped by applying the Least Significant Difference (LSD) test.

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DOI: http://dx.doi.org/10.15666/aeer/1605_68736883

Results and discussion

The characterization of TiO_2-NP

The SEM image of synthesized TiO_2-NPs is shown in *Figure 1* and the average size of nanoparticles was found about 30-50 nm^{-1}. The SEM image showed that the TiO_2-NPs tend to agglomerate and this might be based on its hydrophobic surface properties (Nia et al., 2015; Doğaroğlu and Köleli, 2017a). In addition, SEM-EDX showed that Ti, O and C were identified using SEM-EDX (*Fig. 1*).

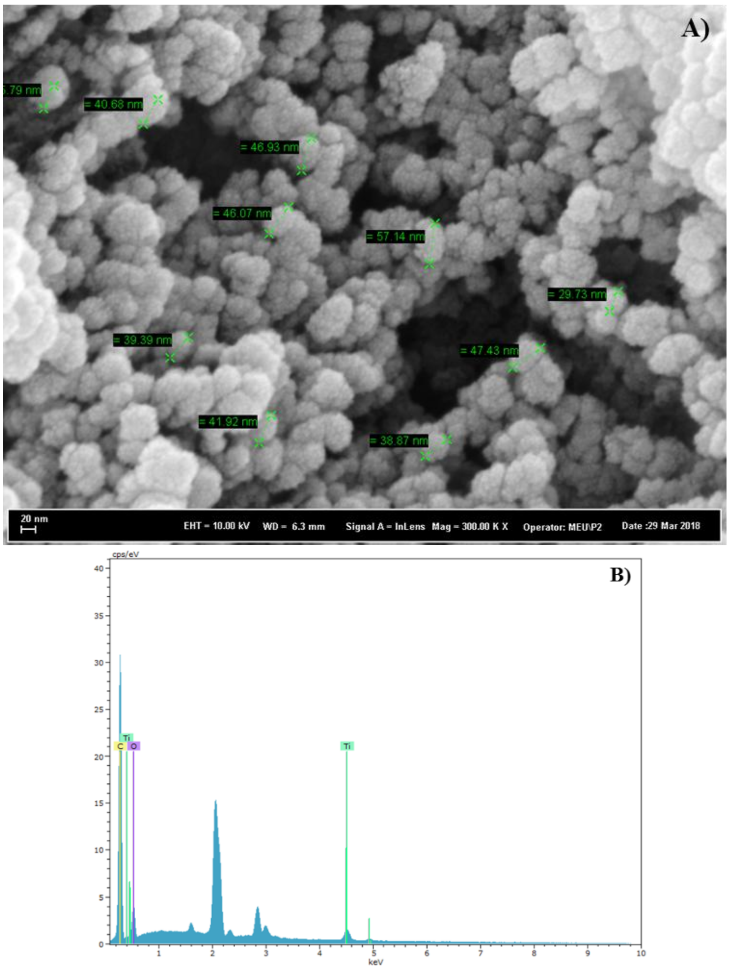

Figure 1. *SEM image and EDX spectrum of synthesized the TiO_2-NPs. Scanning Electron microscopic image of TiO_2-NPs (A) and elemental analysis of the TiO_2-NPs (B)*

Hydroponic experiment

The effects of increasing doses (0, 5, 10 and 20 mg L^{-1}) of TiO_2-NP treatment on maize plants were investigated in hydroponic culture experiment.

Morphological observations and chlorophyll content

Chlorophyll does not only give plants green color, it is also vital for plants. It produces energy and carbohydrates for physiological processes, plant growth, and development (Tan et al., 2017). If chlorophyll damage with any phytotoxicity, plant

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growth also reduces. Generally, the phytotoxicity of nanoparticle negatively affects the physiology and growth of a plant. Physiologically, the chlorophyll content leads to a decrease and this cause decrease in biomass production. The phytotoxic effects of NP-TiO_2 are related to the size, concentration, surface properties of the particles and their effects on germination and chlorophyll content, biomass production and other parameters (Samadi et al., 2014; Doğaroğlu and Köleli, 2017a; Yaqoob et al., 2018). Very slight chlorosis at 5 and 10 mg TiO_2 L^{-1} doses, and moderate chlorosis at 20 mg TiO_2 L^{-1} dose on the leaves of maize were observed (*Fig. 2*). The roots of plants had no significant visual symptoms.

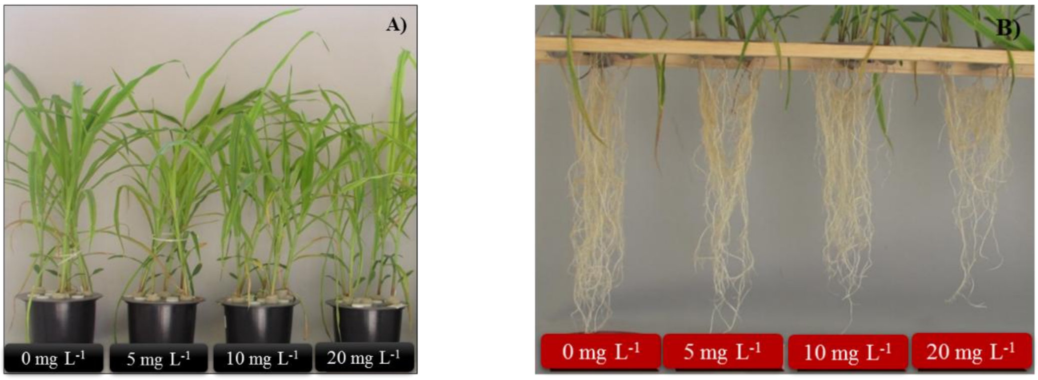

Figure 2. *TiO_2-NP application effects on shoot (A) and root (B) growth of maize*

Increasing TiO_2-NP applications has significantly reduced the chlorophyll contents of old and young leaves (*Fig. 3*). While the highest chlorophyll contents (SPAD Unit) were measured in old and young leaves of the control plants (24.2 and 30.4 respectively) and the lowest chlorophyll content (14.2 SPAD Unit) was measured on old leaves at 20 mg TiO_2 L^{-1} dose ($p \leq 0.01$). Doğaroğlu and Köleli (2017a) had the similar results. They have reported the chlorophyll contents of barley decreased at 20 mg kg^{-1} ZnO-NP and TiO_2-NP treatments. On the contrary to our result, many studies reported that TiO_2-NPs treatments increased photosynthetic activity and chlorophyll content of plants such as spinach (Hong et al., 2005), cucumber (Servin et al., 2012, 2013), Arabidopsis (Lenaghan et al., 2013), rapeseed (Li et al., 2015).

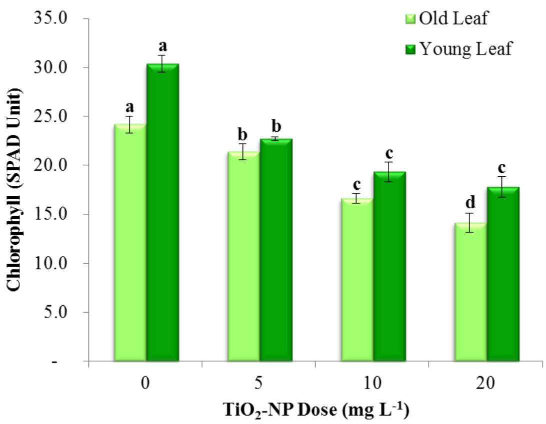

Figure 3. *TiO_2-NP application effects on chlorophyll contents of maize. Letter(s) on each bar show significant level ($p < 0.01$)*

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Dry weight (DW)

The dry weights (DWs) of the shoot and root decreased with the increasing TiO_2-NP application compared to the control treatment plant (*Fig. 4*). Controlled plant was has produced the highest shoot (2.13 g) and root (0.192 g) DWs. The lowest shoot (1.50 g) DW was obtained at 20 mg L^{-1} TiO_2-NP application dose. The root DW decreased up to 10 mg L^{-1} TiO_2 doses; however, DW production increased at 20 mg L^{-1} TiO_2 doses. Because of chlorophyll inhibition, the phytotoxicity of TiO_2-NPs application may be reduced with shoot and root DWs of the plant. In addition, these decreases may depend on the TiO_2-NPs size and surface properties with the application of increasing doses of TiO_2-NPs.

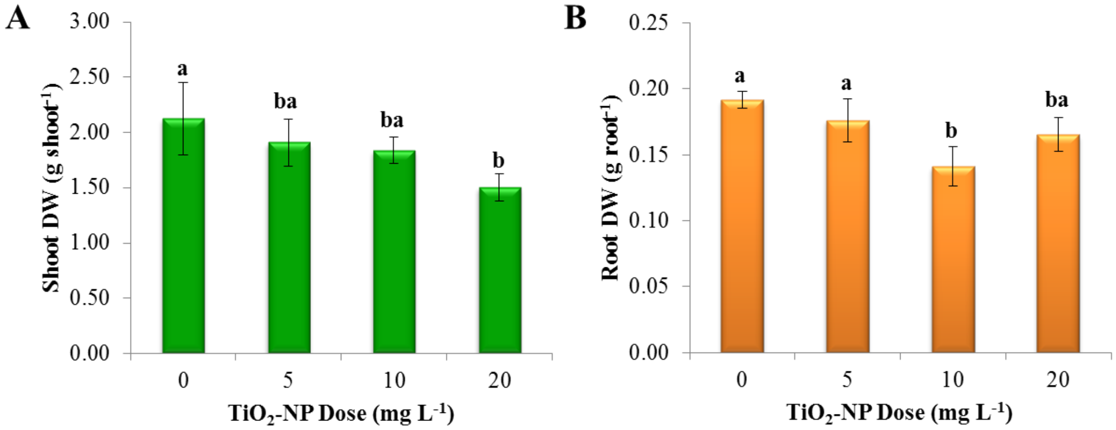

Figure 4. *TiO_2 application effects on shoot (A) and root (B) DWs of maize. Letter(s) on each bar show significant level ($p < 0.05$)*

Asli and Neuman (2009), that the plant leaf growth was inhibited by 300 mg TiO_2 L^{-1} treatment in maize, reported similar finding. Du et al. (2011) reported that the application of TiO_2 and ZnO nanoparticles (10 g TiO_2-NPs and 5 g ZnO-NPs mixed with 110 kg soil separately) reduced wheat growth and enzyme in field conditions. Feizi et al. (2012) investigated the effect of increasing doses of TiO_2-NPs (0, 5, 20, 40, 60 and 80 mg L^{-1}) on the fennel seed germination and early growth. On the contrary, they reported that the total germination percentage increased at 60 mg L^{-1} TiO_2 application after 14 days of seed incubation. The germination of *Zea mays* L. and *Vicia narbonensis* L. seeds were delayed by TiO_2-NPs applied at concentrations ranging from 0.2% to 4.0% for the first 24 hours (Castiglione et al., 2011). Kumar and Udayasoorian (2014) investigated the effect of three different types of nanoparticles (ZnO, TiO_2, and Al_2O_3) on growth parameters (germination percentage, vigor index, shoot and root length) of maize. They found that the highest toxic effect on growth parameters of the 2000 mg L^{-1} dose of the all three nanoparticles suspensions in the order of ZnO>TiO_2 > Al_2O_3.

Mineral nutrient concentrations

Unfortunately, many scientists have not analyzed or reported the nutrient concentration of plant after nanoparticle exposure. In fact, the relationship of toxicity (such as heavy metal, NPs, salt etc.) and plant nutrient uptake can be synergistic, antagonistic or neutral. Because of this reason, when the phytotoxic effect of

http://www.aloki.hu ● ISSN 1589 1623 (Print) ● ISSN 1785 0037 (Online)
DOI: http://dx.doi.org/10.15666/aeer/1605_68736883

nanoparticles is investigated, the mineral nutrient concentration should also be also measured. In this study, the effects of increasing TiO_2-NP doses on macro (N, P and K) and micro (Cu, Fe, Mn and Zn) nutrient element concentrations of the shoot were investigated (*Table 1*) and root (*Table 2*).

Table 1. *The effects of increasing TiO_2-NP application on mineral nutrient concentrations (N, P, K, Zn, Fe, Mn, Cu) in shoots*

Cultivar	TiO_2-NP (mg L^{-1})	N	P	K	Zn	Fe	Mn	Cu
		(%)			(mg kg^{-1})			
Maize	0	2.88 b[§]	0.50 b	7.40	36.8 b	64.3 a	62.0 c	6.49
	5	3.02 b	0.60 a	7.41	44.5 a	56.8 b	75.0 b	6.04
	10	3.24 a	0.62 a	7.52	43.0 a	54.3 bc	77.6 b	6.19
	20	3.20 a	0.64 a	7.69	44.4 a	51.5 c	84.2 a	6.34
Dose	F	17.4^{**}	15.0^{**}	$3.20^{n.s.}$	5.46^{*}	15.1^{**}	25.6^{**}	$2.24^{n.s.}$

$^{*}p \leq 0.05$, $^{**}p \leq 0.01$. n.s.: not significant. [§]Means followed by the same letters in a column do not differ significantly by the LSD test ($p < 0.05$)

The shoot nutrient (N, P, K, Zn, Cu, Mn) concentrations were increased with TiO_2-NP applications except for Fe (*Table 1*). The highest N (3.24%), P (0.64%), K (7.69%), Zn (44.5 mg kg^{-1}) and Mn (84.2 mg kg^{-1}) were recorded at the shoot of TiO_2 treatment plants compared to control plant. However, the highest Fe (64.3 mg kg^{-1}) and Cu (6.49 mg kg^{-1}) concentrations were obtained from control plant. While TiO_2-NP applications were positively affecting N, P, K, Zn and Mn uptake, negatively affecting Fe and Cu uptake to the shoot of the plant. All results were significantly important ($p < 0.05$) except for K and Cu concentrations result.

The highest Fe (4618 mg kg^{-1}) concentration was obtained in the roots of maize plant ($p \leq 0.01$) (*Table 2*). However, the highest concentrations of P (1.23%), K (4.80%), Zn (119 mg kg^{-1}), Mn (71.2 mg kg^{-1}), and Cu (48.2 mg kg^{-1}) were obtained at 20 mg L^{-1} TiO_2-NP dose in plant roots. All results were significantly important ($p < 0.01$) except for the Mn concentration result.

Table 2. *The effects of increased TiO_2-NP application on mineral nutrient concentrations (P, K, Zn, Fe, Mn, Cu) in roots*

Cultivar	TiO_2-NP (mg L^{-1})	P	K	Zn	Fe	Mn	Cu
		(%)		(mg kg^{-1})			
Maize	0	1.04 b[§]	3.85 c	93.9 c	4618 a	56.2	39.5 c
	5	0.97 b	4.48 b	109 b	3797 b	62.5	36.4 d
	10	1.05 b	4.34 b	110 b	3350 c	65.7	45.5 b
	20	1.23 a	4.80 a	119 a	1501 d	71.2	48.2 a
Dose	F	23.3^{**}	53.2^{**}	68.5^{**}	493^{**}	$3.88^{n.s.}$	77.5^{**}

$^{**}p \leq s0.01$. n.s.: not significant. [§]Means followed by the same letters in a column do not differ significantly by the LSD test ($p < 0.05$)

Tan et al. (2017) reported that increasing amount of three different TiO_2-NPs particles (unmodified, hydrophobic, and hydrophilic TiO_2-NPs) affected plant growth

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and mineral nutrition concentration of basil plants. Compared with the control, hydrophobic and hydrophilic TiO_2-NPs significantly reduced seed germination (41% and 59%, respectively); while unmodified and hydrophobic TiO_2-NPs significantly decreased shoot biomass (31% and 37%, respectively). On the other hand, they reported that the unmodified particles increased Cu (104%) and Fe (90%); hydrophilic particles increased Fe (90%); while hydrophobic increased Mn (339%) but reduced Ca (71%), Cu (58%), and P (40%) at 500 mg kg^{-1} soil treatment. Servin et al. (2013) reported that TiO_2-NPs (27 ± 4 nm) treatment (250, 500, and 750 mg kg^{-1}) to the soil were enhanced K and P concentration of cucumber fruit.

Pošćić et al. (2016), studied the application of increasing doses (0, 500 and 1000 mg kg^{-1}) of cerium oxide ($nCeO_2$) and titanium dioxide ($nTiO_2$) nanoparticles effects on the nutrient concentration of barley (*Hordeum vulgare* L). They were obtained significantly increased Ca and significantly decreased sulfur (S) in both $nTiO_2$ treatments. Potassium concentration was decreased at 1000 mg kg^{-1} $nTiO_2$. Manganese and Zn concentrations were increased at 500 mg $nTiO_2$ kg^{-1} treatment.

All these results indicated that there was a relation between TiO_2-NPs and mineral nutrient uptake. On the other hand, NPs size, concentrations, application medium (soil, hydroponic, agar, etc.) are also related to the plant nutrient uptake and toxic effects of NPs on plant physiology and growth.

Concluding remarks

The TiO_2-NP application decreased chlorophyll and plant growth, while interestingly, it enhanced some of the mineral nutrient uptakes such as N, P, and K. This study showed possible toxic effect of TiO_2-NPs on maize growth and physiology. Still, some uptake and toxic effect mechanism of NPs in maize plant is unknown. In the future study, it will be necessary to investigate the effects of phytotoxicity mechanisms, the size distribution of nanoparticles in plant and possible effects of uptake and translocation of nanoparticles by plants.

However, the potential impacts of nanoparticles on agricultural and environmental systems, their transport and mobility in the ecosystem, accumulation and toxicity on plants and the risk of entry of these particles into the food chain need to be investigated in the future especially plants grown in natural environments or in the field.

Acknowledgements. The author acknowledges the financial support of the project by Eskisehir Osmangazi University Scientific Research Fund (BAP, Project No: 201423049). The author would like to thank Dr. Nurdilek Gülmezoğlu and Dr. Nurcan Köleli for their valuable advice, comments, and Dr. Birol Karakaya for preparing the TiO_2-NPs.

Conflict of Interest. The authors have declared no conflict of interest.

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