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Can Hydroxyapatite and Boron Oxide Nano-fertilizers Substitute Calcium Superphosphate and Boric Acid for Broccoli (*Brassica oleracea var. italica*) Grown on A Heavy Clay Soil?

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NANO-fertilizers are effective substitutes for the traditional ones. However, to what extent can nano hydroxyapatite (NHA) and nano-boron oxide (NBO) be suitable substitutes for calcium superphosphate(CSP) and boric acid (BA)? The answer required conducting a field experiment on broccoli (*Brassica oleraceavar. italica*) cultivated on a heavy claysoil for two successive seasons of 2016/2017 and 2017/2018.The nano form of NHA surpassed CSP by 14.2 to 17.8 % for leaf area and 13.6 to 15.8% for total head yield. Foliar spray with NBO increased leaf area, head yield and vitamin C content in heads as compared with BA. P and B contents in broccoli shoots receiving the nano forms surpassed those of the conventional fertilizers. Combined application of the two nano-fertilizers surpassed the combined application of the two conventional fertilizers by 16.0 %. Values for yield and yield components were significantly positively correlated with P and B contents in plant shoots and heads.

Keywords: Broccoli,Nano-hydroxyapatite, Nano-boron oxide, Calcium superphosphate, Boric acid, Head yield, Vitamin C.

Introduction

Broccoli is one of the most widely cultivated plants of family *Brassicaceae* which has been used extensively for human consumption due to its high nutritional values (Branca et al., 2018 and Gao et al., 2018). The edible part of broccoli (*Brassica oleraceavar.italica*) is the flowering buds or heads. These heads are rich in phenolic compounds, minerals, antioxidants, vitamins C and E (Podsędek, 2007 and Mølmann et al., 2015), as well as the anti-carcinogenic bioactive phytochemicals (Herr & Büchler, 2010 and dos Reis et al., 2015). The quantity and quality of broccoli heads may be affected significantly by the nutritional status of the grown plants (Singh et al., 2017a and Pankaj et al., 2018). Accordingly, managing nutrient inputs can probably improve the quantity and quality of broccoli heads yield.

Phosphorus (P) is an essential plant nutrient influencing the production of food and bioenergy (Rowe et al., 2016), yet, its supply is often limited from the environment (Elser, 2012). Thus, mineral P-fertilizers are widely used to satisfy P requirements (Ortas and Islam, 2018) and to attain higher yield and better crop quality (Bernardes et al., 2015). The over-use of P-fertilizers may cause soil eutrophication (Dodds and Smith, 2016). Although, rock phosphate (RP) is an insoluble P amendment (Yadav et al., 2015) and mainly composed of hydroxyapatite or appetite (Ganesh et al., 2017). However, this amendment when applied in the form of nanoparticles may satisfy P nutrient while reduces the risks of water eutrophication with this nutrient (Liu and Lal, 2014). Generally, P is termed as a phloem mobile nutrient (Chien et al., 2018) and therefore, its deficiency symptoms appears on old leaves (Bianco et al., 2015) in the form of necrotic spots (Solanki et al., 2015).

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Boron (B) is another essential nutrient for plant growth (Batabyal et al., 2015). Its application can provide further improvements in the vegetative and reproductive growth of the plants (Singhet al., 2015), whereas, its deficiency may lead to significant physiological and morphological disorders e.g. reductions in plant height,total leaf area and maximum leaf width (Choi et al.,2016) besides,thehead shape becomes irrigular, smaller in size and bitter in taste (Thapa et al.,2016). On the other hand, it is considered as a relatively phloem immobile nutrient (Mora et al., 2016) and its deficiency symptoms appear mainly on the younger growing parts of plants (Miwa and Fujiwara, 2010). Thus, foliar applications with boron can effectively correct B-deficiency (Ratan and Kavita, 2017) and exhibit more marketable products of broccoli yield (Thapa et al., 2016), especially when applied in the form of boron nanoparticles (Davarpanah et al., 2016).

Food security is the main challenge for many developing countries (Haile et al., 2017) that suffer from continuous increases in food prices (Tadasseet al., 2016). This might be attributed to the high input costs including the synthetic fertilizers (Blackwellet al., 2015, Mew, 2016). Alternatively, nanotechnology may offer economically cheap fertilizers (Smalley, 2005). The mode of action of the nanoparticles on plant growth may be attributed mainly to their small diameters that do not exceed the pore size of plant cell walls (Navarroet al., 2008). These nano-fertilizers are also coated with thin nano-materials that increase their surface tension and hence facilitate various metabolic processes within the plants (Weil and Brady, 2016, Singhet al., 2017b). This might, in turn, improve the utilization efficiency of nutrients (around 70 %) by plants as compared with the traditional fertilizers (El-Ramady et al., 2018, Raliyaet al., 2018). A lot of recent researchers assured the importance of using nano-materials for fertilization of broccoli e.g., Kuppusamy et al.(2015), Martínez-Ballesta et al.(2016),Kapur et al.(2017), El-Henawyet al.(2018). Some studies confirmed the superiority of the nano-N fertilizers over the common urea fertilizer (Davarpanahet al., 2017 and Abdel-Salam, 2018a), nano-ZnO over ZnSO4 (Rameshraddy et al., 2017)orZn. DTPA (Morsy et al., 2017), nano-Ca over calcium chloride (Davarpanah et al., 2018).However, according to the best of our knowledge, a few or no study has been carried out to compare between the effect of boron nano-fertilizers and that of boric acid on a vegetable crop, especially broccoli. In this concern, the uptake of uncharged boric acid takes place through aqua-pores (Ampah-Korsah et al., 2016), which are membrane channels (Li et al., 2014) and this might indicate optimum absorption and utilization of B by plants. Thus, the comparison between nano-B-fertilizer and boric acid may indicate to what extent nano-particles can satisfy plant requirements of boron. Although the nano-particles of hydroxyapatite can enrich treated soils of Egypt with both P and Ca, yet, these soils are also rich in Ca-salts (Belal et al., 2019 and El-Ramady et al., 2019) and, therefore, this nano-fertilizer might not be of substantial effect on Ca uptake by plants. On the other hand, the available content of P in the Egyptian alluvial soils is thought to be low (Mohamed et al., 2019). Thus, the implications of amending soils with nano-hydroxyapatite on the grown plants may be attributed mainly to the consequence of enriching these soils with nano-P-particles rather than its content of nano-Ca-particles.

The current study aims at evaluating the extent to which the nano-hydroxyapatite and boron oxides fertilizers can substitute for calcium superphosphate and boric acid in broccoli production under heavy clay soil conditions. The individual and combined effects of these nano-fertilizers on growth, yield and quality traits of broccoli plant were highlighted.

Materials and Methods

Materials of study

Surface soil samples (0-30 cm) were collected from the Experimental Farm of the Faculty of Agriculture, Benha University, Qaluobia Governorate. Soil samples were air dried, sieved to pass through a 20-mm sieve and then analyzed for their particle size distribution as well as the chemical characteristics as outlined by Klute (1986) and Sparks et al. (1996).

Seeds of broccoli (*Brassica oleraceavar. italica* cv. Waltham 29) were obtained from Modesto Seed Co. Inc., California, USA. Nano particles (i.e., nano- hydroxyapatite, 118 g P kg^{-1}) and nano-boron-oxide (B_2O_3, 99.5%) were obtained from the Nanotechnology & Advanced Material Central Laboratory (NAMCL), Agricultural Research Center (ARC), Egypt. High resolution transmission electron microscope (HR-TEM, Tecnai G20, FEI, the Netherland) was used to image the crystal structure revelation of these nano particles at 2 different modes. The first one is the bright field at electron accelerating voltage 200 kV using lanthanum hexaboride (LaB6) electron source gun and the diffraction pattern imaging, whereas the second is Eagle CCD camera with (4k×4k) image resolution was used to acquire and collect transmitted electron images. Afterwards, TEM Imaging & Analysis (TIA) software was used for spectrum acquisition and analysis of EDX peaks (Fig 1).

The field study

A field experiment was carried out at the Experimental Farm of the Faculty of Agriculture, Benha University for two successive seasons (i.e., 2016/2017 and 2017/2018). To maximize the broccoli yield and to improve its quality, two different forms of P-fertilizers (i.e., nano-hydroxyapatite and calcium superphosphate) combined with foliar application of boron sources (i.e., nano-size boron oxide and/or boric acid) were considered in this study. This study was designed into a split plot design,with three replicates,including twelve treatments. The forms of the applied phosphorus fertilizers were arranged within the main plots, whereas the forms of the applied boron were arranged within the sub-plots (Table 2). Each plot (11.2 m^2) included 4 ridges. At the first week of October (during both seasons of study), all plots were transplanted

TABLE 1. Particle size distribution and chemical characteristics of the surface soil (0-30 cm) samples.

Parameter	Value	Parameter	First season 2016/2017	Second season 2017/2018
Particle size distribution		EC*, dS m^{-1}	2.16	1.94
Coarse sand	13.08	pH	7.9	7.6
Fine sand	11.32	OM, g kg^{-1}	1.41	1.36
Silt	24.60	**Available nutrients, mg kg^{-1}**		
Clay	51.0	N	22.5	29.53
Texture*	Heavy clay	P	9.10	8.32
$CaCO_3$, g kg^{-1}	1.53	K	120.0	131.26
Total P, mg kg^{-1}	40.23	B	0.352	0.281
Total B, mg kg^{-1}	5.24			

*Texture is estimated according to the International Soil Texture Triangle (Moeys 2016), EC of paste extract, The extracts include KCl, $NaHCO_3$, NH_4Ac, hot water for measuring N, P, K and B, respectively.

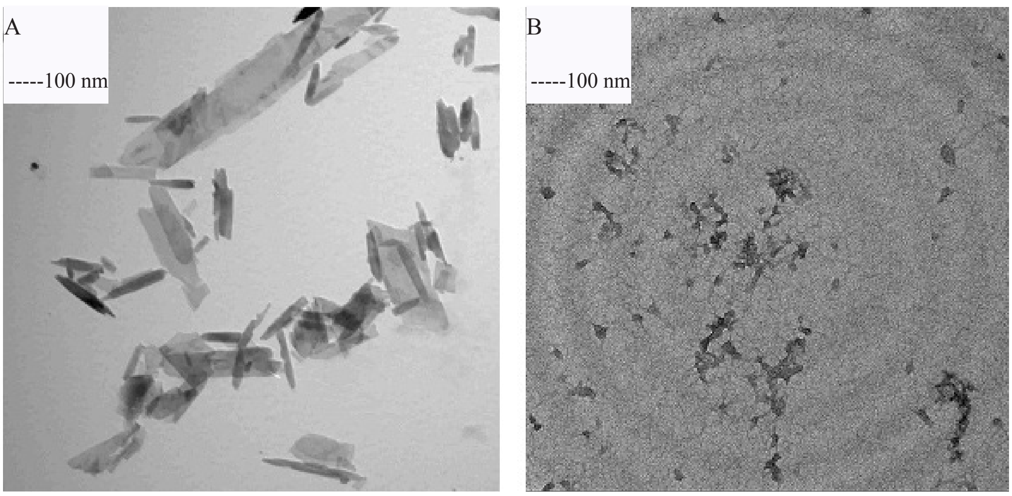

Fig.1. HR-TEM images of nano hydroxyapatite (A) and nano-B-oxide (B)

with broccoli seedlings at 30 cm apart from each other on one side of ridges (80 cm wide and 3.5 m long) in presence of water. All plants received the recommended doses of N (216 kg N ha^{-1}) as ammonium nitrate (33.5% N) and K (96 kg K ha^{-1}) as potassium sulphate (40% K) fertilizers. Other agricultural practices were followed as recommended by the Egyptian Ministry of Agriculture. Thirty days after transplanting, broccoli plants were sprayed twice with boron in 15 daystime-interval.

Data collection

Measurements of plant growth parameters

Sixty days after transplanting, five plants were sampled randomly from each plot to estimate the following plant growth parameters: plant height, number of leaves per plant, leaf area per plant and plant foliage fresh weight). Concerning the leaf area, it was measured at the 5^{th}true full expanded leaf from plant top by using laser leaf area meter.

Head yield and its quality

Plant harvest took place 85 days after transplanting. The total yield of broccoli heads (megagram per hectare, Mg ha^{-1}) was measured for each treatment as well as the head diameter was also recorded.

Chemical characteristics of broccoli plants and the quality traits

The chemical characteristics of broccoli were determined according to the standard methods described by AOAC (2000). Leaf chlorophyll a and b contents were determined photometrically after being extracted with ethanol. Total soluble solids (TSS) were estimated by a hand refractometer, while ascorbic acid content (vitamin C) was determined by titration against 2, 6-di-chlorophenolindophenol dye. Samples of broccoli shoot and head were randomly collected from each plot, oven dried at 70 ºC for 48 h, weighed, ground, and then digested in a mixture of sulphuric and perchloric acids (2:1 ratio) as mentioned by Chapman and Pratt (1961). Nitrogen, P, K and B were determined in the digested solutionsof plant samples according to AOAC (2000). Nitrogen was determined by micro-Kjeldahl, while P was measured by spectrophotometer (Jenway 6705 UV/Vis, UK) using ammonium molybdate and ascorbic acid reagents. Potassium was measured using flame photometer (Jenway PFP-7, UK) and B was measured using Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES, Ultima 2 JY Plasma, USA).

Statistical analysis

The obtained data in both seasons of study were subjected to the analysis of variance as a factorial experiment in split plot design. Duncan method was used to differentiate the significance among means according to Snedecor and Cochran (1991). Data were presented graphically using Sigma Plot 10.0.

Results

Growth parameters as affected by phosphorus and boron sources

Figures 2-4 reveal that the investigated growth parameters increased significantly due to the application of P-fertilizers (nano hydroxyapatite or calcium superphosphate). These growth parameters include plant height, shoot fresh weight, chlorophyll a and b, number of leaves per plant and leaf area. In this concern, significant increases in shoot fresh weight, chlorophyll b content and the average leaf area appeared during the first season only for the nano-hydroxyapatite as compared to those addressed with calcium superphosphate. However, such previous variations seemed to be insignificant in the second growing season. On the other hand, no significant differences were detected for the effect of source of P-fertilizer on plant height, number of leaves per plant and chlorophyll a.

TABLE 2. Details regarding treatments of phosphorus and boron

Phosphorus treatments		Boron treatments	
P0	0 kg P ha^{-1}	B0	0 mg B L^{-1}
P1	63 kg P ha^{-1} in the form of calcium super phosphate	B1	25 mg B L^{-1}nano-boron oxide
P2	63 kg P ha^{-1} in the form of nano-hydroxyapatite	B2	50 mg B L^{-1}nano-boron oxide
		B3	50 mg B L^{-1} boric acids (170 g B kg^{-1})

Foliar application of boron (in the form of boric acid or B-nanoparticle) also improved significantly the investigated growth parameters. In this concern, the growth parameters estimated for plants that received nano-boron oxide at a rate of 50 mg B L^{-1}were generally higher than thosesprayed with boric acid during the first season only, however, such variations seemed to be insignificant during the second growing season. The effect of nano-boron oxide was also superior to the effect of the boric acid on broccoli leaf area during both seasons of study. On the other hand, the number of plant leaves was not significantly affected by the source of B-fertilizers.

A significant reduction occurred in the investigated growth parameters owing to the foliar application of a half dose of nano-boron oxide(25 mg B L^{-1}) when comparedto the full dose of boron (50 mg B L^{-1})amended either in the form of boric acid or nano-boron oxide. The interaction effect between the foliar application of nano-boron oxide and the soil application of nano hydroxyapatite (P2 B2) recorded the highest significant increases on the following growth parameters: plant height, number of leaves per plant, leaf area and plant fresh weight as well as the chlorophyll a and b contents during the two studied seasons. Such increases exceeded those recorded for plants that received calcium superphosphate and boric acid (P1 B3 traditional application).

Application of calcium superphosphate together with nano-boron oxide (P1 B2) came in the second order recording significant superiority over the P1 B3 in both leaf area and plant height of broccoli during the two studied seasons. Moreover, this treatment recorded significant increases in plant fresh weight, chlorophyll a and b contents in leaves as compared to the traditional mineral treatment during the first season only. Foliar application of a half dose of nano B-oxide together with either calcium superphosphate (P1 B1) or nano-hydroxyapatite (P2 B1) came in the third order recording comparable effects to P1 B3 on the following growth parameters: plant height, number of leaves per plant, plant fresh weight, and both chlorophyll a and b contents in leaves during the two seasons of study, while, the positive effect on leaf area was only significant during the first growing season. On the other hand, the control (P0 B0) treatment recorded the least significant effect on broccoli growth parameters (i.e., plant height, number of leaves per plant and plant fresh weight) during both seasons of study.

Yield and quality of broccoli heads as affected by phosphorus and boron sources

Phosphorus application in the form of nano-hydroxyapatite or calcium superphosphate increased significantly the total yield of broccoli heads during the two seasons of study (Fig. 5, 6). Such improvementsalso includedbroccoli quality traits (i.e.head diameter, content of vitamin C and total soluble solids TSS). Furthermore, the outcome head yield increased significantly owing to the soil application of nano-hydroxyapatite comparing with calcium superphosphate (first season only). Though, the head diameters and vitamin C content in broccoli heads increased significantly in the first season due to the application of nano hydroxyapatite comparing with calcium superphosphate. Yet such effects seemed to be insignificant in the second growing season. On the other hand, TSS in broccoli heads did not vary significantly between the two sources of P-fertilizers during the two successive seasons.

Spraying broccoli plants with nano-boron also improved significantly the head yield (first season only), head diameter (second season only),TSS (first season only) and vitamin C in broccoli heads when compared to the corresponding ones attained for the application of boric acid. Decreasing the dose of nano-B application to the half (from 50 to 25 mg L^{-1}) generally resulted in significant reductions in yield and quality traits of broccoli heads as compared with those sprayed with full dose of either nano-B particles or boric acid.

Combination between the nano-hydroxyapatite and nano-B-oxide (P2 B2) seemed to be more effective in increasing the head yield of broccoli and its quality traits than the dual application of calcium superphosphate and boric acid (P1 B3). The corresponding increases in broccoli head yields, recorded in the first and second seasons,were estimated by 18.47 and 13.86%, respectively, as compared to the traditional treatmentthat received the full dose of P and B chemical fertilizers (P1B3). The treatment P2 B3 came in the second order after P2 B2 recording significant increases inboth total head yield in the first season only and head diameter in both seasons as compared to the traditional treatment. The treatments P1 B1 and P2 B1 recorded comparable effects to P1 B3 on the total head yield of broccoli as well as head quality (head diameter, vitamin C and total soluble solids) in both seasons.

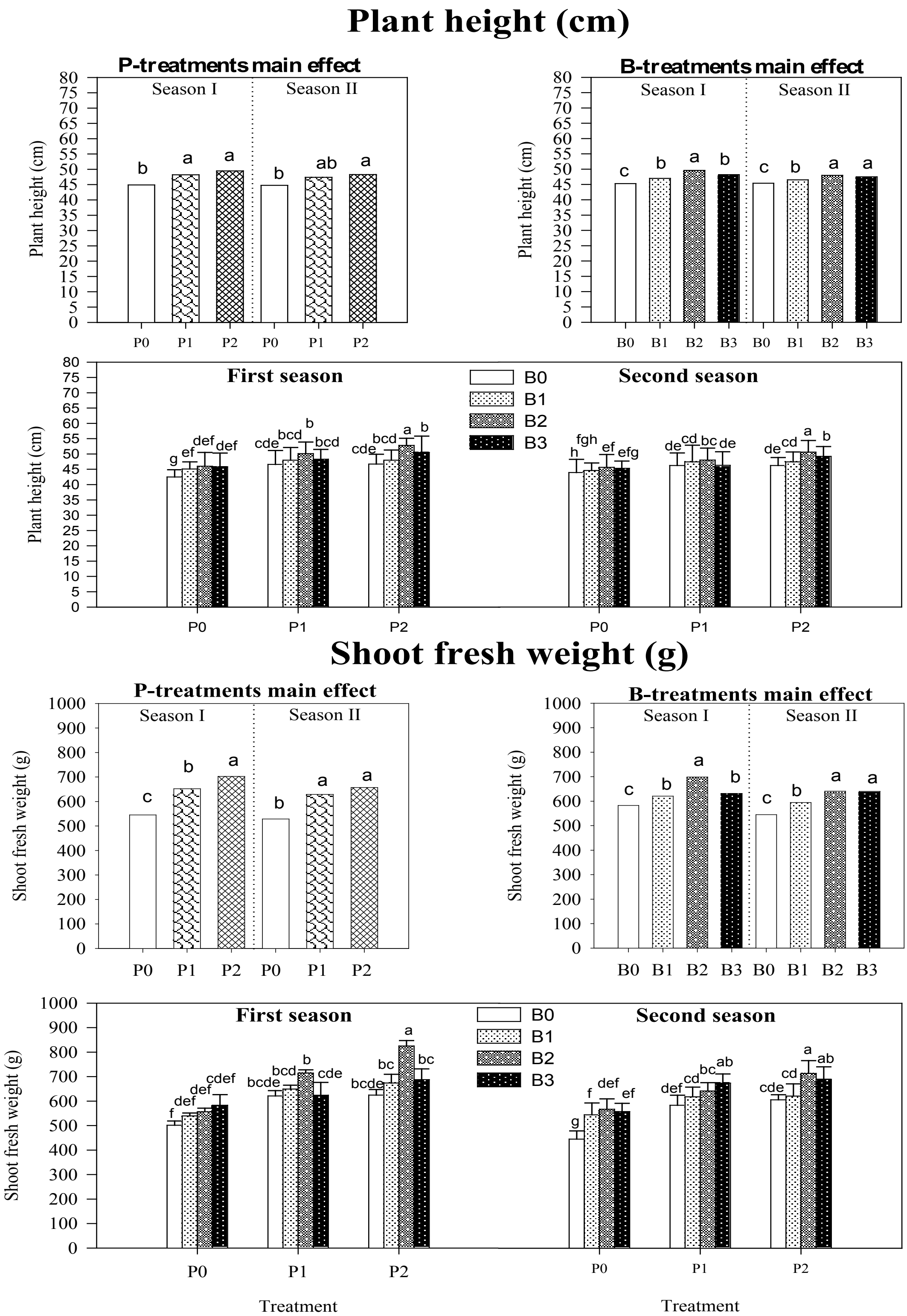

Fig. 2. Plant height (cm) and fresh weight (g) of broccoli plants (means ±SD) as affected by P and B nano-fertilizers either individually or in combinations. (P0, P1, P2 corresponding to zero kg P ha^{-1}, 63 kg P ha^{-1} in the form of calcium superphosphate and 63 kg P ha^{-1} in the form of nano-hydroxylapetite, respectively. B0, B1, B2, B3 corresponding to 0 mg B L^{-1}, 25 mg B L^{-1} nano-boron, 50 mg B L^{-1}nano-boron and 50 mg B L^{-1} boric acids (170 g B kg^{-1}), respectively.

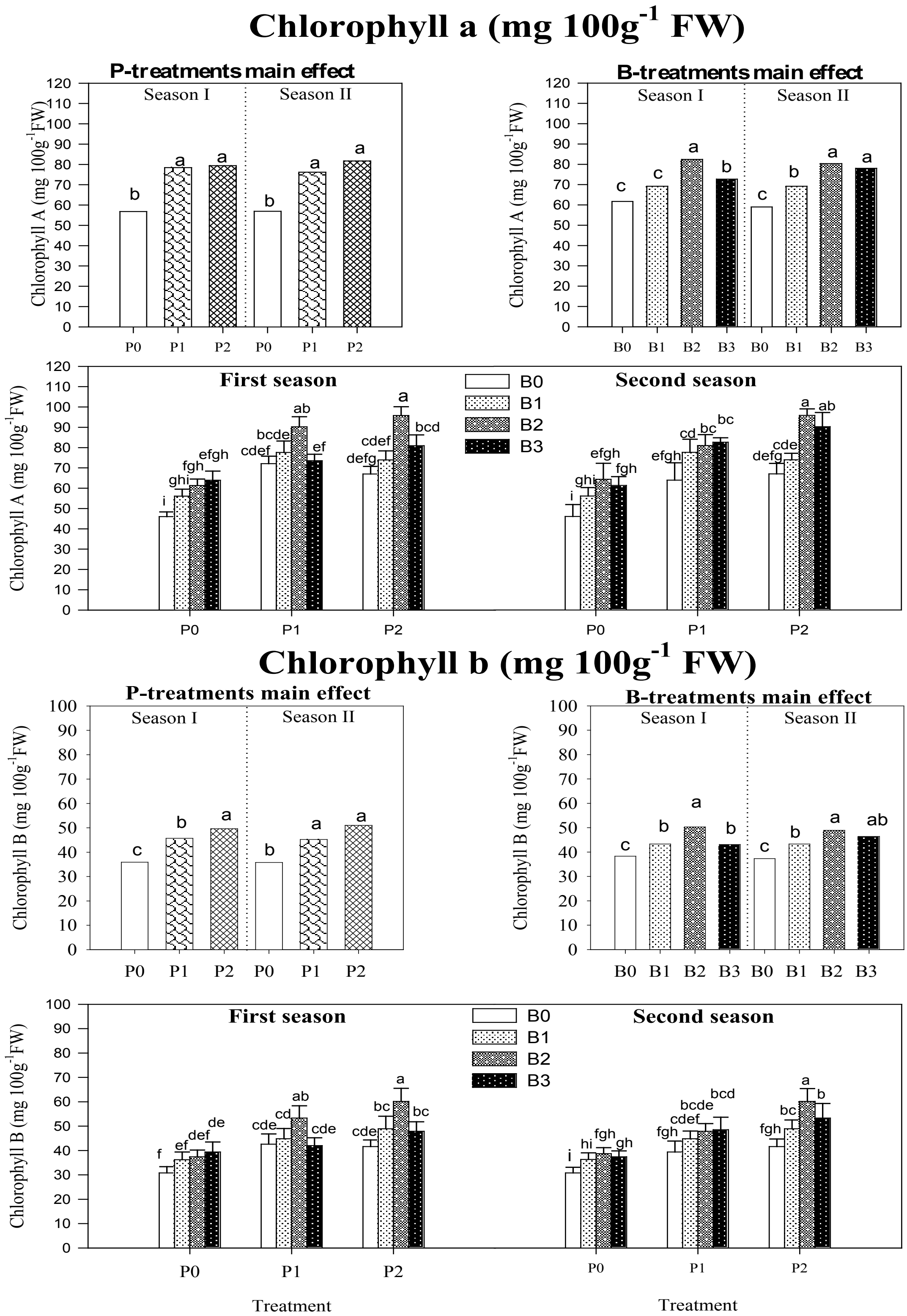

Fig. 3. Chlorophyll a and b contents in broccoli plants (means ±SD) as affected by P and B nano-fertilizers either individually or in combinations. See footnote Fig. 2.

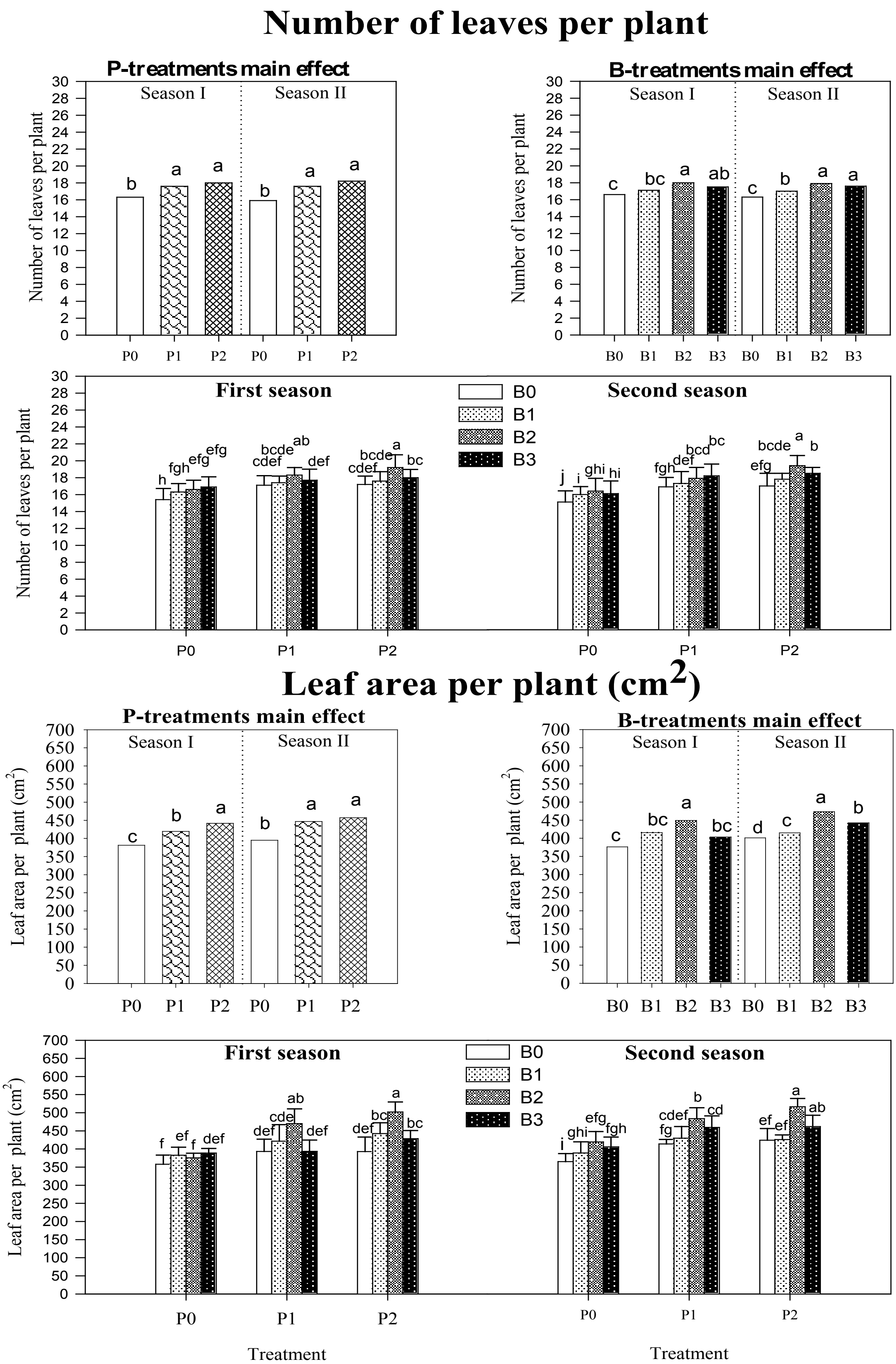

Fig. 4. Number of leaves per plant and the leaf area (means ±SD) as affected by P and B nano-fertilizers either individually or in combinations. See footnote Fig. 2.

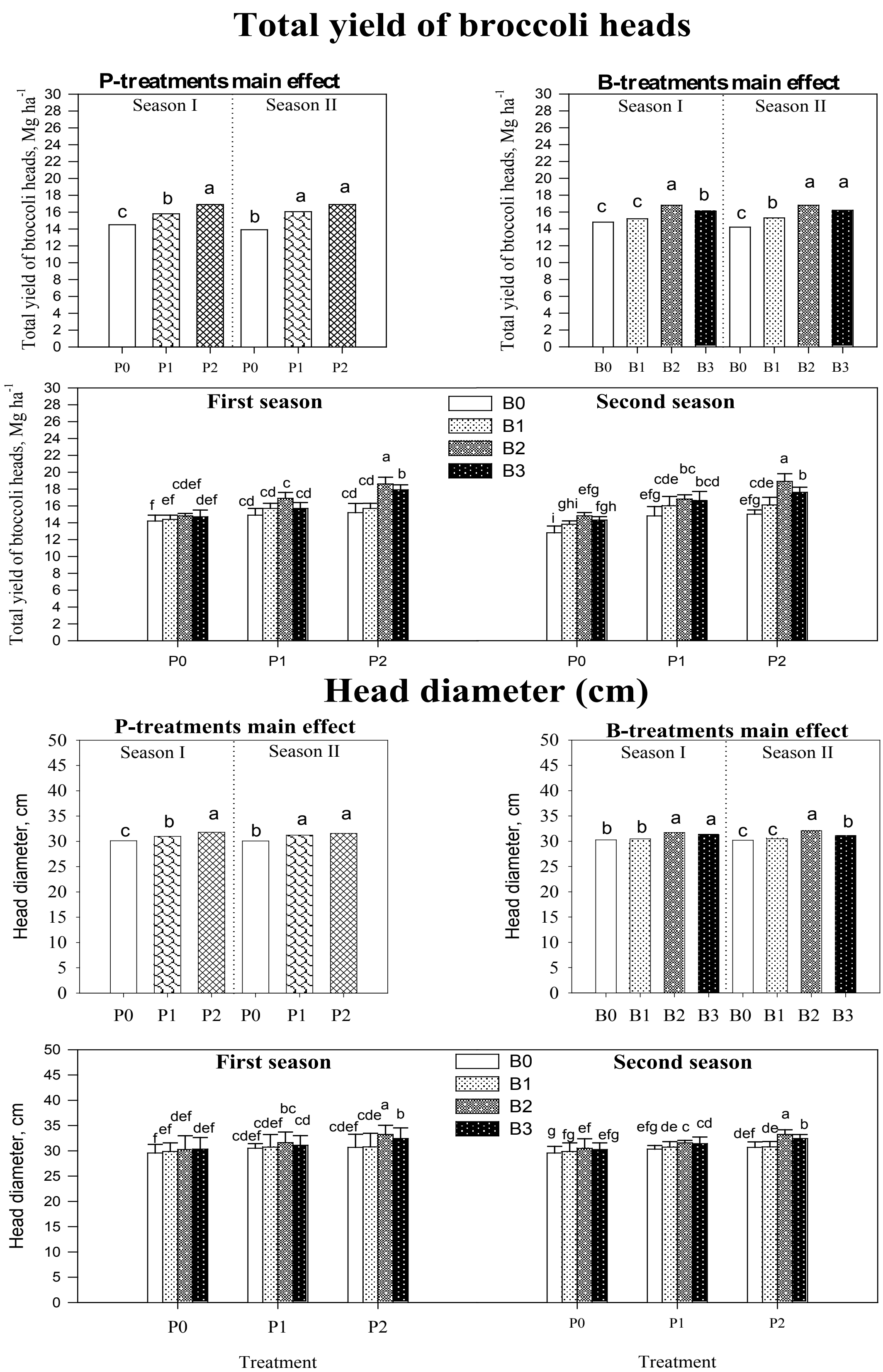

Fig. 5. Total yield of broccoli heads and the head diameters (means ±SD) as affected by P and B nano-fertilizers either individually or in combinations. See footnote Fig.2.

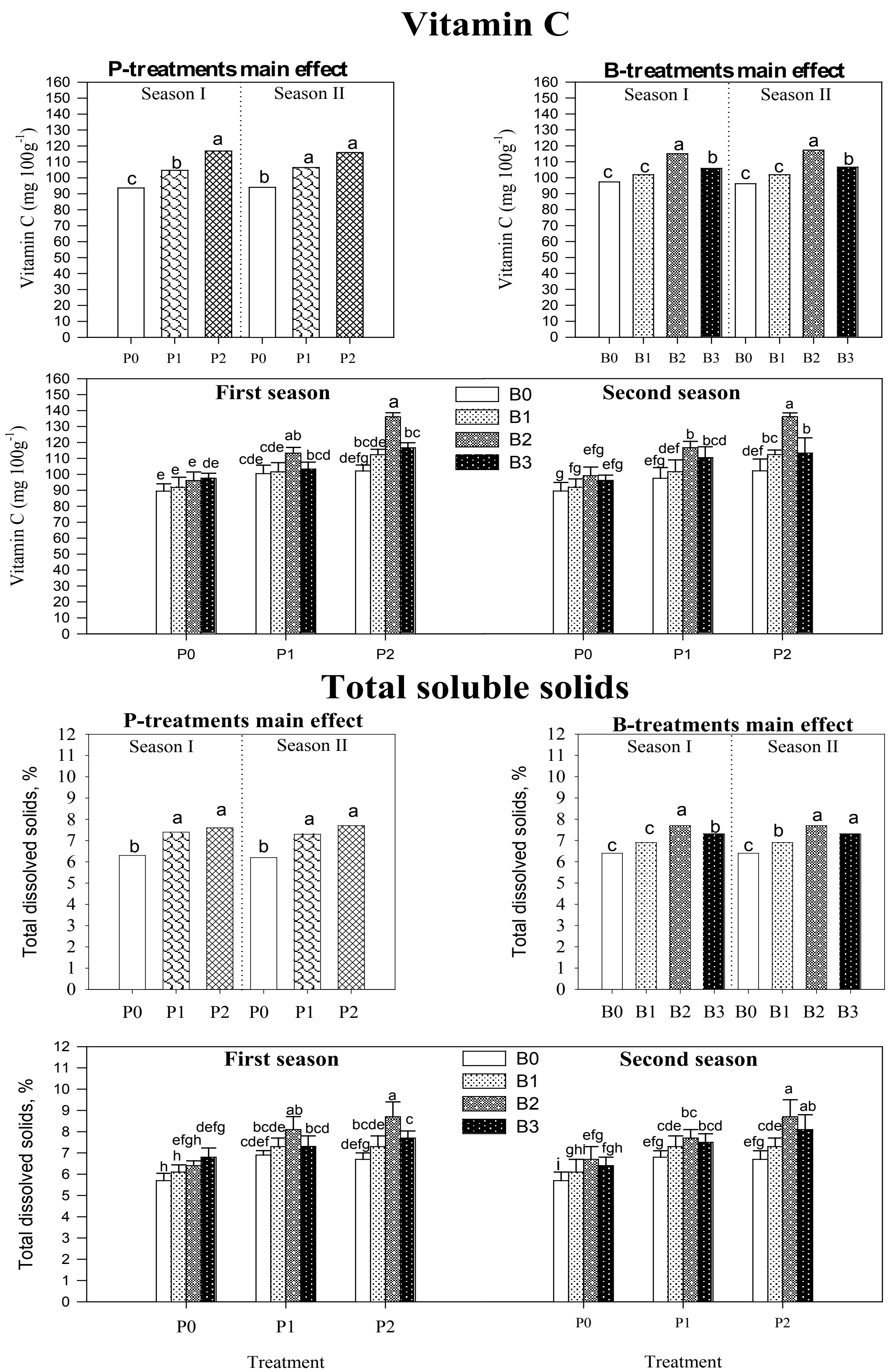

Fig. 6. Vitamin C and total soluble solids in broccoli heads (means ±SD) as affected by P and B nano-fertilizers either individually or in combinations. See footnote Fig 2.

Nitrogen, phosphorus, potassium and boron contents as affected by phosphorus and boron sources

Table 3 reveals that the individual application of nano-hydroxyapatite or nano-B oxides raised significantly the concentrations of P and B within shoots of broccoli plants when comparedwith the control treatment (P0 B0). Such increases were even significantly higher than the corresponding ones fertilized with either calcium superphosphate or boric acid. The effect of nano-B-oxide was also significant in increasing B content in heads of broccoli plants when compared to the effect of boric acid during the secondseasons only. On the other hand, P content within broccoli heads did not vary significantly between the nano-hydroxyapatite and calcium superphosphate treatmentduring the two seasons of study.

The combination between these two nano-fertilizers resulted in significant higher increases in concentrations of the investigated nutrients within heads and shoots of broccoli plants exceeding those attained for the individual application of each of these fertilizers. On the other hand, no significant effect could be deduced for the application of the individualnano-fertilizers on N or K contents within either shoots or heads of broccoli plants as compared to the traditional chemical fertilizers (i.e., calcium superphosphate or boric acid). Decreasing the rate of foliar application of nano-B-oxide from 50 to 25 mg B L^{-1}led to significant reductions in concentrations of the studied macro- and micro- nutrients in shoots and heads of broccoliwhen compared to the full dose of nano-B-oxides or even boric acid (H_3BO_3).

Results also reveal that concentrations of P, K and B increased significantly in shoots and heads of broccoli owing to the dual application of nano-hydroxyapatite and nano-B-oxides (P2 B2) as compared to the traditional treatment (P1 B3). However, in case of nitrogen, the significant increases occurred only in the second growing season. The treatment P1 B2 also improved nutritive contents within shoots and heads of broccoli. Coming in the second orderafter P2 B2, its significant effect was detected on N content in both shoots and heads of broccoli during the first season only. It is worthy to mention that this treatment recorded no significant variations in either P or K concentrations in shoots (during the second season only) as well as P, K or B concentrations(during the two seasons of study) as compared to the reference treatment (P1 B3).

Concentrations of P and B in broccoli shoots and heads and their relations to both the different growth parameters and yield components

Concentrations of P and B in broccoli heads were correlated significantly with the corresponding ones in broccoli shoots (Table 4). Likewise, the investigated growth parameters (i.e., plant height, number of leaves per plant, leaf area and fresh weight) as well as chlorophyll a and b were correlated significantly with the nutritive contents of the leaves. Moreover, the yield of broccoli heads and their quality traits (diameter of head, TSS and vitamin C)were significantly correlated with the nutritive contents of the heads. Finally, the yield and the quality of heads significantly correlated with each of the investigated growth parameters. It is worthy to mention that, P contents within the parts of broccoli plant were significantly correlated with B content in both shoots and heads.

Discussion

Amending soils with phosphate fertilizers or spraying plants with boron increased significantly the concentration of N, P and K within shoots and heads of broccoli. This, in turn, improved the different growth parameters and yield quantity and quality of this vegetable crop. The positive effect of P-fertilizers on head yield of broccoli was also observed by Islamet al.(2010). Likewise, Hussainet al.(2012) noticed remarkable increases in the head yield of broccoli due to the application of B-fertilizers. Such increases might be attributed to the significant roles of these nutrients in plants. Phosphorus has a crucial role as an integral component of metabolic, genetic, structural and regulatory molecules (White and Hammond, 2008). It is also involved in the energy transfer within plants (Armstrong, 1999) and plays important roles in the development of plant roots (Niuet al., 2013) and shoots (Abdel-Salam, 2018b). Hence, P-fertilizers probably increase the plant nutrient uptake like boron (Mühlbachováet al., 2017) and magnesium (Mg). In this concern, Mg is the central ion in the structure of chlorophyll a and b (Gerendás and Führs, 2013). Thus, there is no wonder to find out that chlorophyll a and b contents increased significantly in broccoli leaves owing to the application of P-fertilizers in form of calcium superphosphate or the nanoparticles of -hydroxyapatite.

TABLE 3. The nutritional status of broccoli shoots and heads as affected by application of P and B either individually or in combinations

Boron source and Rate (A)	Shoots								Heads (flowering buds)							
	First season				Second season				First season				Second season			
	P0	P1	P2	Mean	P0	P1	P2	Mean	P0	P1	P2	Mean	P0	P1	P2	Mean
	N (g kg^{-1})								N (g kg^{-1})							
B0	32.3^{e}	36.5^{bc}	35.3^{bcd}	34.7^{C}	30.2^{h}	34.1^{efg}	34.5^{ef}	32.9^{C}	36.8^{ef}	39.5^{bc}	35.2^{fg}	37.2^{B}	33.9^{g}	36.8^{def}	37.1^{de}	35.9^{C}
B1	33.3^{de}	37.2^{ab}	36.0^{bc}	35.5^{BC}	31. 7^{gh}	36.0^{cde}	35.8^{de}	34.5^{B}	38.5^{cd}	41.1^{b}	34.6^{g}	38.1^{AB}	35.0^{fg}	38.4^{cd}	38.6^{cd}	37.3^{B}
B2	34.4^{cde}	39.4^{a}	39.4^{a}	37.7^{A}	34.8^{ef}	38.4^{bc}	41.3^{a}	38.2^{A}	39.9^{bc}	38.5^{cd}	38.4^{cde}	38.9^{A}	36.8^{def}	39.8^{bc}	43.1^{a}	39.9^{A}
B3	34.8^{cd}	36.5^{bc}	37.0^{b}	36.1^{B}	33.0^{fg}	38.1^{bcd}	39.7^{ab}	36.9^{A}	37.6^{de}	36.7^{ef}	42.9^{a}	39.1^{A}	36.4^{ef}	39.6^{bc}	41.3^{b}	39.1^{A}
Mean	33.7^{B}	37.4^{A}	36.9^{A}		32.4^{B}	36.7^{A}	37.8^{A}		38.2^{A}	39.0^{A}	37. 8^{A}		35.5^{b}	38.7^{a}	40.02^{a}	
	P (g kg^{-1})								P (g kg^{-1})							
B0	2.5^{f}	3.2^{c}	3.07^{d}	2.9^{B}	2.5^{e}	3.3^{cd}	3.3^{d}	3.0^{A}	2.4^{e}	3.32^{cd}	3.13^{d}	3.1^{C}	2.47^{g}	3.1^{def}	3.3^{de}	3.0^{C}
B1	2.6^{f}	2.9^{e}	3.2^{cd}	2.9^{B}	2.5^{e}	3.4^{cd}	3.4^{c}	3.1^{A}	2.5^{e}	3.6^{bcd}	3.6^{bcd}	3.2^{BC}	2.8^{efg}	3.5^{cd}	3.6^{bcd}	3.3^{B}
B2	2.6^{f}	2.9^{e}	3.7^{a}	3.1^{A}	2.6^{e}	3.6^{b}	4.1^{a}	3.4^{A}	2.6^{e}	4.1^{ab}	4.2^{a}	3.6^{A}	2.9^{efg}	3.9^{bc}	4.7 ^{a}	3.9^{A}
B3	2.5^{f}	3.2^{cd}	3.4^{b}	3.1^{A}	2.5^{e}	3.6^{b}	3.6^{b}	3.2^{A}	2.5^{e}	3.7^{abc}	3.9^{ab}	3.4^{AB}	2.7^{fg}	3.8^{bc}	4.1^{b}	3.5^{B}
Mean	2.5^{C}	3.1^{B}	3.3^{A}		2.5^{C}	3.5^{B}	3.6^{A}		2.5^{B}	3.7^{A}	3.7^{A}		2.71^{B}	3.61^{A}	3.93^{A}	
	K (g kg^{-1})								K (g kg^{-1})							
B0	23.6^{e}	25.2^{cd}	24.9^{cd}	24.6^{B}	24.4^{f}	25.23^{e}	25.6^{de}	25.1^{C}	19.0^{ef}	20.1^{bc}	18.4^{fg}	19.2^{C}	17^{g}	19.0^{def}	19.0^{def}	18.3^{C}
B1	24.3^{de}	25.4^{bcd}	26.1^{bc}	25.3^{B}	25.0^{ef}	26.3^{cd}	26.6^{c}	26.0^{B}	19.9^{cd}	20.7^{ab}	17.9^{g}	19.5^{BC}	18.3^{f}	19.9^{cd}	19.4^{cde}	19.2^{BC}
B2	24.4^{de}	26.5^{b}	280^{a}	26.3^{A}	25.0^{ef}	26.6^{c}	28.4^{a}	26.7^{A}	20.2^{bc}	19.6^{cde}	19.3^{de}	19.7^{AB}	19.0^{ef}	20.2^{bc}	21.3^{a}	20.2^{A}
B3	24.6^{de}	24.9^{cd}	26.1^{bc}	25.2^{B}	25.0^{ef}	26.3^{cd}	27.6^{b}	26.3^{B}	19.6^{cde}	18.9^{ef}	21.3^{a}	19.9^{A}	18.7^{ef}	20.2^{bc}	20.8^{ab}	19.9^{AB}
Mean	24.2^{C}	25.5^{B}	26.3^{A}		24.9^{B}	26.1^{AB}	27.1^{A}		19.7^{A}	19.8^{A}	19.2^{A}		18.2^{B}	19.8^{A}	20.1^{A}	
	B (mg kg^{-1})								B (mg kg^{-1})							
B0	25.7^{j}	24.4^{k}	24.6^{jk}	24.9^{D}	27.9^{hi}	24.6^{i}	25.9^{i}	26.1^{D}	4.9^{gh}	4.2^{h}	4.3^{h}	4.5^{C}	5.1^{e}	5.6^{de}	5.4^{de}	5.4^{C}
B1	33.5^{g}	37.9^{e}	50.5^{b}	40.7^{B}	33.7^{ef}	39.1^{d}	53.6^{b}	42.1^{B}	5.4^{fg}	6.5^{cde}	7.2^{bc}	6.4^{B}	5.5^{de}	6.2^{bcde}	7.3^{abc}	6.3^{B}
B2	31.5^{h}	43.9^{d}	62.5^{a}	46.0^{A}	31.8^{fg}	44.3^{c}	58.4^{a}	44.9^{A}	6.0^{def}	7.0^{bc}	8.5^{a}	7.2^{A}	6.1^{cde}	7.0^{bcd}	8.8^{a}	7.3^{A}
B3	30.1^{i}	35.5^{f}	46.1^{c}	37.3^{C}	30.2^{gh}	35.8^{de}	47.3^{c}	37.8^{C}	5.8^{efg}	6.8^{bcd}	7.6^{ab}	6.7^{AB}	5.9^{cde}	6.8^{bcd}	7.8^{ab}	6.8^{AB}
Mean	30.2^{C}	35.4^{B}	45.9^{A}		30.9^{C}	35.9^{B}	46.3^{A}		5.5^{B}	6.1^{AB}	6.9^{A}		5.6^{C}	6.4^{B}	7.3^{A}	

See footnote Fig.2.

TABLE 4. Concentrations of P and B- in broccoli and their relations to both the different growth parameters and the yield quantity and quality

		Growth parameters						Yield and head quality				P and B contents		
		Plant height	**No. of leaves**	**Leaf area**	**Plant fresh wt**	**Chlorophyll a**	**Chlorophyll b**	**Total yield**	**head diameter**	**Total soluble solids**	**Vitamin C**	**P-shoot**	**B-shoot**	**P-head**
Growth parameter	No. of leaves	0.944 ***												
	Leaf area	0.818 ***	0.873 ***											
	Plant fresh wt	0.955 ***	0.946 ***	0.842 ***										
	Chlorophyll a	0.949 ***	0.976 ***	0.892 ***	0.946 ***									
	Chlorophyll b	0.939 ***	0.974 ***	0.919 ***	0.948 ***	0.972 ***								
	Total yield	0.933 ***	0.954 ***	0.884 ***	0.914 ***	0.943 ***	0.944 ***							
Yield and yield component	Head diameter	0.918 ***	0.911 ***	0.894 ***	0.878 ***	0.900 ***	0.903 ***	0.953 ***						
	TSS	0.961 ***	0.982 ***	0.910 ***	0.945 ***	0.989 ***	0.979 ***	0.961 ***	0.934 ***					
	Vitamin C	0.914 ***	0.930 ***	0.917 ***	0.900 ***	0.902 ***	0.955 ***	0.944 ***	0.961 ***	0.940 ***				
P and B content	P-shoot	0.760 ***	0.860 ***	0.800 ***	0.752 ***	0.816 ***	0.827 ***	0.837 ***	0.818 ***	0.824 ***	0.834 ***			
	B-shoot	0.800 ***	0.780 ***	0.793 ***	0.754 ***	0.765 ***	0.854 ***	0.822 ***	0.790 ***	0.812 ***	0.871 **	0.631 **		
	P-head	0.908 ***	0.860 ***	0.890 ***	0.752 ***	0.953 **	0.942 **	0.924 ***	0.894 ***	0.954 ***	0.904 ***	0.888 ***	0.772 ***	
	B-head	0.817 ***	0.807 ***	0.820 ***	0.746 ***	0.796 ***	0.837 ***	0.857 ***	0.826 ***	0.847 ***	0.857 ***	0.653 **	0.928 ***	0.797 **

Note: ***Significant at $p<0.001$, **Significant $p < 0.01$ and *Significant $p < 0.05$

Boron also plays important roles in cross linking the pectic networks (Blevins and Lukaszewski, 1998, Miwa and Fujiwara, 2010). Thus, it improves the structural and functional integrity of plant cell walls and membranes (Ozturk et al., 2010, Martínez-Cuencaet al., 2015). Furthermore, B involves in many vital processes with plants i.e. the division of cells and their elongation, metabolism of nitrogen and carbohydrate, the transport of sugars, the bound enzymes for cytoskeletal proteins and plasmalemma (Shireen et al., 2018). The positive effect of spraying plants with B may be attributed to the concurrent increases that occurred in ion influxes across the membrane(Naqib and Jahan, 2017) such as phosphate (Shireen et al., 2018), nitrogen and potassium (Ullah et al., 2012). Moreover, boron uptake by plants may favorably enhance the uptake of calcium by plants (Tariq and Mott, 2007), which is considered the associated cation in calcium superphosphate fertilizer and this might, in turn, increase indirectly the uptake of P by plants.

On the other hand, amending soil with nano hydroxyapetite or spraying nano-B-particles on plants either solely or in combinations seemed to be of more efficient effect on increasing the total yield of broccoli heads than the application of soluble super phosphate fertilizer and boric acid. Such nano fertilizers probably improved the growth parameters and yield quantity and quality of broccoli, however, most of these increases seemed to be insignificant. The mode of action of these nano-fertilizers might be attributed to the concurrent increases that occurred in P and B within shoots and heads of broccoli plants as compared with those amended with the traditional P or B fertilizers. This result seems confusing especially when the doses of application of either P or B fertilizers, in the form of insoluble nanoparticles or their soluble fertilizers, were equal. Probably, the nano-B- fertilizers entered leaf stomata via gas uptake (Abdel-Aziz et al., 2016), yet, this fertilizer released B slowly for the metabolic processes (Duhan et al., 2017, Iavicoli et al., 2017). This might in turn signal nutrient deficiency (García et al., 2015) expressing boric acid channels (Kato et al., 2009) to increase the uptake of boron by plant roots. Afterwards, B was transferred passively long distances along the water streams (Tanaka and Fujiwara, 2008) to the areal parts of the plants and then to the heads. Accordingly, plants sprayed bynano-boron-oxides seemed to have relatively higher contents of B than those received boric acid.

In case of P-fertilizers, the release of P from nano-hydroxyapatite seemed to be controlled and steadily (White and Hammond, 2008, Nair et al., 2010) and can reach plant roots via mass flow (Montalvo et al., 2015). Although, this process seemed to be slow (White and Hammond, 2008), consequently,minimizing P leaching from soils (Liu and Lal, 2014, Cui et al., 2018). However, it also maystimulate P deficiency in plants. Accordingly, plants involve high- and low-affinity P-transporters (Heuer et al., 2017) and then P was loaded in the xylem and transferred efficiently to the aerial parts of the plants (Zhang et al., 2016). Moreover, nano-hydroxyapatite may increase the soil microbial diversity and this may alter the microbial community composition (Cui et al., 2018). On the other hand, the calcium superphosphate fertilizer was rapidly retained in soil forming less bioavailable forms (McLaughlin et al., 2011). Accordingly, plants that received nano-hydroxyapetite fertilizer exhibited relatively higher contents of P than those received the calcium superphosphate fertilizer.

It is worth to mention that the mass flow and diffusion processes are the important factors controlling the movement of phosphorus and boron in the soil solution, respectively. Thus, the uptake of available P and probably available B via plant roots in addition to the nutrients that released from the nanofertilizers might account for such increases in concentrations of nutrients within the investigated plant parts (except for P in heads of broccoli), and this consequently increased the outcome yield and quality traits of broccoli heads.

The head diameter according to Kałużewicz et al. (2010) and Peñaloza and Toloza (2018) and vitamin C according to Karitonas (2001) are considered within quality factors in the marketing of broccoli. The first parameter (i.e. the head diameter) increased significantly only in the first season of this study due to the application of nano hydroxyapatite as compared to calcium superphosphate, yet, such an effect seemed to be insignificant in the second growing season. The second one (vitamin C) improved significantly in heads of broccoli owing to the application of the investigated nano-fertilizers rather than the synthetic ones. Decreasing the rate of the foliar applied nano boron to half its dose resulted in significant reductions in the investigated growth parameters and yield quality as compared to the application of the full dose of the nano boron oxides. However, its effect seemed to be comparable with the foliar application of boric acid.

The complicated relationships between soil, nano-materials and plants are still representing the major areas of interest within the field of environmental nanotechnology. This means that some nano-materials have the ability to decontaminate soils polluted with heavy metals (Zhu et al., 2019). Others may promote plant growth and improve nutrient uptake from the rhizosphere (Tohren and Strevett, 2019). However, the excessive use of nano-materials may create a problem of nano-pollutants, which is increasingly recognized as a serious, worldwide public health concern (Loureiro et al., 2018 and Jośko, 2019). Accordingly, further studies should consider the accumulation of nano-fertilizers within the edible parts of vegetables.

Conclusion

Soil application of nano-hydroxyapatite as a source of phosphorus or spraying plants with nano-B-oxide increased significantly plant growth parameters and the head yield (quantity and quality) of broccoli comparing with the reference treatment (calcium superphosphate and boric acid). Moreover, these nano fertilizers improved significantly the uptake of P and B by plants, consequently their contents increased in shoots. Interactions between these two nano-fertilizers recorded further significant increases in the outcome yield and yield quality parameters of broccoli. Thus, nano hydroxyapatite and nano-boron oxide at rates of 63 kg P ha^{-1} + 50 mg B L^{-1} are highly recommended to substitute the traditional calcium superphosphate and boric acid for the broccoli production under heavy clay soil conditions. Further investigations are needed concerning the behavior of such nano-fertilizers in soils and their interactions and toxicity on soil agro-ecosystem.

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Conflicts of Interest

"The authors declaredthat no conflict of interest."

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هل يمكن للأسمدة النانو من الهيدروكسي أباتيت وأكسيد البورون أن تحل محل سوبر فوسفات الكالسيوم وحمض البوريك لنبات البروكلى (*Brassica oleracea var. italica*) النامى فى أرض طينية ثقيلة ؟

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الأسمدة النانو هي بدائل فعالة للأسمدة التقليدية. ومع ذلك، إلى أي مدى يمكن أن يكون الهيدروكسي أباتيت نانو (NHA) وأكسيد البورون نانو (NBO) بدائل مناسبة لسوبر فوسفات الكالسيوم (CSP) وحمض البوريك (BA)؟ وللأجابة عن ذلك تم إجراء تجربة حقلية على البروكلي (*Brassica oleracea var. italica*) المنزرع بنجاح فى تربة طينية ثقيلة لمدة موسمين متعاقبين ٢٠١٧/٢٠١٦ و ٢٠١٨/٢٠١٧. الصورة النانو منالهيدروكسى أباتيتNHA تجاوزت سوبر فوسفات الكالسيوم CSP بنسبة من ١٤,٢ إلى ١٧,٨ ٪ للمساحة الورقية و من ١٣,٦ إلى ١٥,٨ ٪ للمحصول الكلى من الرؤوس. الرش الورقي من أكسيد البورون نانوNBO أدى إلى زيادة مساحة الورقة، ومحصول الرؤوس الكلى والمحتوى من فيتامين C في الرؤوس بالمقارنة مع حمض البوريك. محتوى الفوسفور والبورون فى عرش نبات البروكلى الذى استقبل الصورة النانو من السماد تفوق على المحتوى فى حالة الأسمدة التقليدية. أدت الإضافة المجمعة من الأسمدة النانومعا إلى تجاوز الإضافة المجمعة من الأسمدة التقليدية بنسبة ١٦,٠٪ ارتبطت قيم المحصول ومكوناته بشكل إيجابي مع المحتوي من الفوسفورP والبورون B في العرش والرؤوس لنباتات البروكلى.

الكلمات الدالة: البروكلى ، هيدروكسى أباتيت نانو، أكسيد بورون نانو ، سوبر فوسفات الكالسيوم ، حمض البوريك ، محصول الرؤوس ، فيتامين سى.