horticulturae

Article

Effects of Edaphic Fertilization and Foliar Application of Se and Zn Nanoparticles on Yield and Bioactive Compounds in *Malus domestica* L.

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Citation: Montaño-Herrera, A.; Santiago-Saenz, Y.O.; López-Palestina, C.U.; Cadenas-Pliego, G.; Pinedo-Guerrero, Z.H.; Hernández-Fuentes, A.D.; Pinedo-Espinoza, J.M. Effects of Edaphic Fertilization and Foliar Application of Se and Zn Nanoparticles on Yield and Bioactive Compounds in *Malus domestica* L. *Horticulturae* **2022**, *8*, 542. https://doi.org/10.3390/horticulturae8060542

Academic Editor: Robert Veberič

Received: 21 May 2022
Accepted: 14 June 2022
Published: 17 June 2022

Abstract: In this study, we evaluated the effects of edaphic fertilization with N, P, and K (150-50-80, 100-60-60, and without edaphic fertilization (SFE)) and foliar fertilization with nanoparticles (NPs) of Se and Zn (Se: 50 ppm, Zn: 250 ppm, and no nanoparticles (NP0)) on the yield and antioxidant compounds of apple fruits. We conducted this study in a 20-year-old commercial orchard. The experimental design was a randomized complete block design of nine treatments. The treatments with fertilization doses of 150-50-80 and 100-60-60, supplemented with Se and Zn NPs, generally increased the yield, sugar content, and ascorbic acid of the apple fruits. The SFE + NPZn treatment produced the highest increase (+193% compared with the control) in fruit yield. The SFE + NPSe and SFE + NPZn treatments led to higher contents of phenols and flavonoids, with maximum values of 7.6 mg GAE and 15.82 mg QE per gram of dry weight. These compounds presented a direct correlation with the antioxidant activity in the fruits. The foliar application of Se and Zn nanoparticles supplemented the soil fertilization with N, P, and K to improve the yield and bioactive-compound synthesis of the apple fruits.

Keywords: antioxidants; apple fruits; phenolic compounds; sugars; agricultural nanotechnology; plant nutrition

1. Introduction

Apple fruits (*Malus domestica* L.) are one of the most consumed fruits worldwide after citrus, grapes, and bananas [1]. Apple production for the year 2020 was 86,443,757 tons, and the primary producers in the world were China, the United States of America, and Turkey [1,2]. Apple fruits are important for the human diet because of their excellent taste, health benefits, biologically active substances—such as phenolic compounds, polysaccharides, and organic acids—and because of their high fiber content [3–5]. Generally, apples are consumed fresh, when the fruit is ripe, but they may also be found in processed foods, such as juices, ciders, wines, purees, jellies, marmalades, and others [5,6].

To satisfy the food's demands, both in terms of production and quality, it is necessary to seek alternatives to improve the yield and intrinsic quality of apple fruits. One of these alternatives is the addition of fertilizers that provide the necessary nutrients for plant growth [7]. Nitrogen (N), phosphorus (P), and potassium (K) are the most important macroelements that apple trees require and are generally applied to the soil [8]. The lack of these elements negatively affects the production and growth of the plants [9]. In general, apple trees can extract these mineral elements from the soil in amounts of 2.3 kg of N, 0.6 kg of P (as P_2O_5), and 3 kg of K (as K_2O), per ton of harvest. Different formulas or fertilization doses are established on the basis of the need to promote the balance between the vegetative growth, yield, and fruit quality [10]. Soto-Parra et al. [11] evaluated the impact of fertilization on the yield and quality of Golden Delicious apple fruit produced in northern Mexico and found that a fertilization dose of 138-45-40 increased the yield and fruit quality at harvest and postharvest. Foliar fertilization satisfies the nutritional requirements of crops that soil fertilization does not, whereby micronutrients improve the balance of nutrition in the plant and act in the fruit set and development, thereby improving the fruit yield and quality [12,13].

In recent years, researchers have used nanoparticles for the application of these microelements, which, due to their reduced size (<100 nm), present unique physicochemical characteristics in contrast to conventional fertilization [13,14]. The application of metallic nanoparticles in agriculture has been a complete success; their properties guarantee the effective delivery of the nutrients necessary for the plants and a faster physiological response, with a substantial reduction in conventional fertilization requirements [12]. The use of nanoparticles has been found to improve the resistance of plants to different types of abiotic and biotic stress, such as salt stress, low temperatures, and plant diseases, and to increase crop yields and antioxidant compound levels in the plants [15–17]. The application of nanoparticles of zinc, copper, iron, selenium, and boron increased the yields, bioactive-compound contents, and antioxidant capacities in some plants, such as the habanero pepper [13], jalapeño pepper [18], tomato [19], moringa [20], coffee [21], and strawberry [22], among others.

In fruit trees, nanoparticles increased the vegetative growth and improved the reproductive growth and flowering, thereby increasing the productivity and fruit quality [23]. Genaidy et al. [24] obtained a higher yield of olive fruits, with a high percentage of oil in the seed and low acidity, with foliar applications at 20 ppm of NP B_2O_3 plus 200 ppm of NP ZnO. Elsheery et al. [12] reported increased nutrient absorption after combined applications of ZnO and Si nanoparticles, which positively modified the growth, productivity, and quality of mango fruits. Davarpanah et al. [25] reported that, in pomegranate trees, combined applications of B and Zn NPs increased the yield and improved fruit quality. Ranjbar et al. [26] compared the effect of Ca NPs with conventional applications of calcium chlorine in apple trees, and the fertilizers with Ca NPs improved the postharvest quality attributes. The foliar application of Se NPs in Granada trees improved the maturity index and increased the fruit yield and antioxidant-compound contents, and decreased cracking in the fruits [27].

Research proves the effectiveness of Se and Zn NPs in crop yields and quality improvement; however, evaluations are lacking as to their effects in complementing edaphic fertilization with N, P, and K in apple trees. Therefore, in this study, we aimed to evaluate the effects of edaphic fertilization applications with N, P, and K and foliar applications with selenium and zinc nanoparticles on the yield, bioactive-compound contents, and antioxidant activity in apple fruits.

2. Materials and Methods

2.1. Reagents

We acquired the anhydrous sodium carbonate and aluminum trichloride from J.T. Baker S.A. de C.V. (Avantor Performance Materials, Center Valley, PA, USA). We purchased gallic acid; quercetin 2,2′-diphenyl-1-picrylhydrazyl (DPPH); 2,2′-azino-bis (3-

ethylbenzothiazoline-6-sulfonic acid) (ABTS); Trolox (6-hydroxy-2,5,8-tetramethylchroman-2-carboxylic acid); Folin–Ciocalteu reagent; anthrone; sulfuric acid; 3,5-dinitrosalicylic acid; potassium sodium tartrate; sodium hydroxide; trichloroacetic acid; and ethanol from Química Meyer (Química Suastes S.A. de C.V. Tlahuac, Ciudad de México, Mexico).

The Applied Chemistry Research Center (CIQA), Saltillo, Coahuila, Mexico, provided the Se and Zn nanoparticles. According to the supplier, the Se NPs were of a spherical morphology, with a size range of 2–20 nm, determined by transmission electron microscopy (TEM). González-García et al. [28] and Treviño-López et al. [29] provided complete characterizations. We synthesized the ZnO NPs according to the procedure reported by Garza-Alonso et al. [30], and they had a quasi-spherical shape and an average particle size of 16.49 nm, as determined by TEM.

The fertilization sources were urea (46-00-00), calcium triple superphosphate (00-46-00), and potassium chloride (00-00-60).

2.2. Experimental Site, Plant Material, and Treatments

We conducted this study during two production seasons (2020 and 2021) in a 20-year-old commercial apple orchard (*Malus domestica* L., Golden Delicious). The orchard is located in Cuaunepantla, a municipality of Acaxochitlan, Hidalgo, Mexico (20°09′37.6′′ N and 98°13′46.7′′ W), at 2260 m above sea level. The tree arrangement was a square system (5 × 5 m), and water was supplied by the rainy season.

For the establishment of the experiment, we selected three trees per treatment, with similar trunks and crown diameters, and we distributed them in a randomized complete block design, with nine fertilization treatments with edaphic fertilization with N, P, and K, the foliar application of nanoparticles (NP) of Se at 50 ppm and Zn at 250 ppm, and three repetitions per treatment: T1, control, without edaphic fertilization and without foliar application (SFE + NP0); T2, without edaphic fertilization + foliar application of Se NPs at 50 ppm (SFE + NPSe); T3, without edaphic fertilization + foliar application of Zn NPs at 250 ppm (SFE + NPZn); T4, edaphic 150-50-80 + without foliar application (150-50-80 + NP0); T5, edaphic 150-50-80 + foliar application of Se NPs at 50 ppm (150-50-80 + NPSe); T6, edaphic 150-50-80 + foliar application of Zn NPs at 250 ppm (150-50-80 + NPZn); T7, edaphic 100-60-60 + without foliar application (100-60-60 + NP0): T8, edaphic 100-60-60 + application of Se NPs at 50 ppm (100-60-60 + NPSe); and T9, edaphic 100-60-60 + foliar application of Zn NPs at 250 ppm (100-60-60 + NPZn).

We applied fertilizers to the soil in early January in both production seasons. We carried out foliar applications with nanoparticles at full bloom, at fruit set, and during fruit development. We applied five liters per tree until we had completely moistened the foliage. We harvested the apple fruits at physiological maturity in the month of July in both 2020 and 2021. We harvested apple fruits without visible mechanical damage and that were free of diseases and pests.

2.3. Fruit Yield, Number, and Weight

For the yield, we considered the total number of fruits and total weight (kg) per tree. We express the results as kilograms per tree (kg tree^{-1}).

2.4. Total, Reducing, and Nonreducing Sugars

We determined the total sugar content according to the method of Zahedi et al. [27]. We mixed a known amount of sample with 10 mL of distilled water, and we then sonicated it in an ultrasonic bath (Ultrasonic Cleaner, Mod. 32V118A, Freeport, IL, USA) for 15 min at 30 °C and a frequency of 40 kHz. We centrifuged the samples at 10,000× g for 10 min at 4 °C (Thermo Scientific Mod. ST 16R, Karlsruhe, Germany). We mixed the supernatant with 5 mL of anthrone, boiled it for 10 min, then allowed it to cool to room temperature, and we measured the absorbance in a spectrophotometer (Mod. 6715 UV/Visible, Jenway, Techne Inc., San Diego, CA, USA) at 625 nm. We express the results as milligrams of glucose equivalent per gram of dry weight (mg GE g^{-1} DW).

We determined the content of reducing sugars by the DNS method (3.5 dinitrosalicylic acid), according to Ávila et al. [31]. We mixed a known amount of sample with 0.5 mL of the DNS reagent. We boiled the tubes for 5 min, stopped the reaction with ice-cold water, added 5 mL of distilled water, allowed the tubes to cool to room temperature, and determined the absorbance in a spectrophotometer at 540 nm.

We obtained the contents of nonreducing sugars by the difference between total sugars and reducing sugars. We express the results in equivalent milligrams of glucose per gram of dry weight (mg EG g^{-1} DW).

2.5. Bioactive Compounds and Antioxidant Activity

We used freeze-dried apple fruits to evaluate the bioactive compounds and antioxidant activity. First, we froze them at −76 °C (Thermo Scientific 303 ultra-low temperature Freezer, Waltham, MA, USA) for seven days, and subsequently lyophilized them at 133×10^{-3} mBar, −40 °C (Labconco, Mod. 79480, Kansas City, MO, USA). We ground the fruits in a blade mill (RTSCH GM 200, Haan, Germany) at 9000 rpm for 1 min until we obtained a fine powder. We placed the lyophilized samples in hermetic black bags to protect them from light and stored them at 5 °C until use.

2.5.1. Total Phenolic Content, Flavonoids

We mixed the samples with 10 mL of ethanol, placed them in an ultrasonic bath (Ultrasonic Cleaner, Mod. 32V118A, Freeport, IL, USA) for 15 min, and centrifuged them at 10,000× *g* for 10 min (centrifuge Thermo Scientific, Mod. ST 16R, Waltham, MA, USA). We used the supernatant for the determination of the total phenolic content, flavonoids, and antioxidant activity through the ABTS and DPPH assays.

We determined the content of total phenols using the Folin–Ciocalteu reagent Singleton et al. [32]). We mixed 1 mL of the supernatant with the Folin–Ciocalteu reagent, and we added 1.5 mL of 2% sodium carbonate solution and left it to react in complete darkness for 1 h. Subsequently, we read the absorbances in a spectrophotometer (Genesys 150 UV/Visible, Daly City, CA, USA) at 725 nm. We express the results in milligrams of gallic acid equivalent per gram of dry weight (mg GAE g^{-1} DW).

We determined the flavonoids by the method described by Lahlou et al. [33], with some modifications. We mixed 0.5 mL of the supernatant with 2 mL of a 2% $AlCl_3$ solution, which we allowed to react for 20 min; subsequently, we measured the absorbance at 415 nm in a spectrophotometer, and we performed each treatment in triplicate. We express the results as milligrams of quercetin equivalent per gram of dry weight (mg QE g^{-1} DW).

2.5.2. Vitamin C Content in Apple Fruits

We quantified the ascorbic acid in apple fruits according to the method proposed by Dürüst et al. [34]. We mixed the samples with 10 mL of metaphosphoric acid solution at 3% (*v*/*v*) and sonicated them in an ultrasonic bath (Mod. 32V118A, Freeport, IL, USA) for 15 min at a frequency of 40 kHz. We centrifuged the samples at 10,000× *g* for 10 min. We added 2 mL of supernatant to 2 mL of buffer at pH 4 (glacial acetic acid:sodium acetate at 5% (*p/v*), 1:1), 3 mL of dichloroindophenol, and 15 mL of xylene, and vigorously mixed. We measured the absorbance on a spectrophotometer (model 6715 UV/Vis, Jenway, Techne Inc., Staffordshire, UK) at 520 nm. We express the results in milligrams of ascorbic acid equivalent per gram of dry weight (mg AA g^{-1} DW).

2.5.3. Determination of Antioxidant Activity

We determined the antioxidant capacity through the 2,2′-azino-bis (3-ethylbenzothiazoline-6-sulfonic acid) (ABTS) method, according to Re et al. [35]. First, we prepared the $ABTS^{\bullet+}$ radical by mixing ABTS at 7 mM and potassium persulfate at 2.45 mM, and we left the solution under constant stirring and in complete darkness for 16 h. Subsequently, we mixed 0.1 mL of the sample with the $ABTS^{\bullet+}$ solution and left it to stand for 6 min. Then, we measured the absorbance at 734 nm. To obtain the results, we prepared a Trolox standard curve at a concentration of 0–50 mg/L. We express the results in micromolar Trolox equivalents per gram of dry weight (μM TE g^{-1} DW).

We investigated the antioxidant activity by the DPPH method, according to Brand-Williams et al. [36]. We prepared an ethanolic solution at 6×10^{-5} M of DPPH, which we left stirring in complete darkness for 2 h. Subsequently, we mixed 0.5 mL of the sample with the DPPH reagent, which we allowed to react for 1 h at 4 °C; then, we measured the absorbance at 517 nm. We express the results in micromolar Trolox equivalents per gram of dry weight (μM TE g^{-1} DW).

2.6. Statistical Analysis

We used a randomized complete block design with three replications per treatment. We analyzed the data using the statistical program SAS system for Windows version 9.4. We compared the means using Tukey's multiple comparison test, at a significance level of $p < 0.05$.

3. Results and Discussion

3.1. Crop Yield

In Figure 1, we present the crop yields, numbers of fruits per tree, and apple fruit weights. With regard to the yield and the number of fruits per tree, we found the highest values in the SFE + NPZn, 150-50,80 + NPSe, 100-60-60 + NP0, and 100-60-60 + NPZn treatments, which outperformed the control (SFE + NP0) by a factor of up to two. The highest yield and the largest number of fruits per tree were 58.17 kg $tree^{-1}$ and 433 fruits, respectively, in the SFE + NPZn treatment. The 100-60-60 + NPSe and 150-50-80 + NPZn treatments did not present significant differences in the yield and the number of fruits with respect to the control. With regard to the weights of the fruits, the highest values were 145.45 g for the 150-50-80 + NPSe treatment, followed by the 100-60-60 + NPZn, SFE + NPZn, and 100-60-60 + NP0 treatments, which presented higher weights compared with the fruits of the control treatment. In general, we observed a greater response in the crop yield due to the effect of the application of the Zn NPs alone. The Se NPs complemented the soil fertilization dose of 150-50-80; this behavior is similar to that reported by Ghazi [37], who observed an increase in eggplant yield when they supplemented the conventional NPK formulation with a foliar spray of Se. According to the results, the foliar application of Zn and Se NPs influenced higher yields in apple production. Some studies have reported that the application of ZnO NPs had a positive effect on the yields of pomegranate [25], mango [12], olive [24], melon [38], strawberry [39], and grapes [40]. Zn is an essential element that acts as an enzyme activator for many metabolic processes. As an NP, it is absorbed more quickly by the leaves and acts to regulate the hormonal metabolism of plants, modifying the auxin levels through the synthesis of tryptophan; it thus promotes cell division and, hence, fruits of a larger size [12,38,41]. Similarly, Se NPs increase the fruit yield because they stimulate the formation of plant organs, as occurs in tomato and citrus fruits [22,42]. The reduction in the parameters in the 150-50-80 + NP0 and 150-50-80 + NPZn treatments may have been due to a reduction in the P in the fertilization dose. According to Soto-Parra et al. [11], when P and K are reduced in apple tree fertilization, the crop yield is generally reduced. Mineral nutrition with N, P, and K can be complemented with Zn and Se NPs for increased assimilation of nutrients that improve the yields of apple fruits.

3.2. Total, Reducing, and Nonreducing Sugars in Apple Fruits

Table 1 presents the contents of total sugars (TS), reducing sugars (RS), and nonreducing sugars (NRS). We observed higher concentrations in the contents of TS, RS, and NRS in the SFE + NPSe and SFE + NPZn treatments, which consisted of foliar applications with Se NPs at 50 ppm and Zn NPs at 250 ppm, respectively; these had beneficial effects, in that the foliar applications with Zn NPs presented significantly higher contents of TS (92%) and RS (35%) with respect to the control treatment (SFE + NP0). In other fruits, such as pomegranate [25], grapes [43], and orange [44], ZnO NP application also increased the sugars. The foliar application of Se NPs increased the sugars in strawberry, pomegranate, and mandarin [22,27,45] because Se increases the activity of the enzyme fructose 1,6-biphosphatase, which is related to the metabolism of carbohydrates [27]. The determination of the sugar contents in fruits is an important indicator to evaluate the quality and flavor of the fruit; sugar acts as the main substrate that provides structural material and energy for the plant's defense response, hormone-signaling molecules, and regulation of the plant immune system [25,45,46]. NPZn at 250 ppm and Se at 50 ppm are potential stimulants and can increase the total sugar content in apple fruits. The 100-60-60 + NP0 and 100-60-60 + NPSe treatments also presented higher sugar contents in the fruits compared with the control treatment, which may be due to the higher concentration of P in the fertilization dose. For the Golden Delicious variety, a higher fertilization dose of phosphorus increased the concentration of the total sugars in apple trees [11].

Table 1. Effects of edaphic fertilization and foliar application of Se and Zn nanoparticles on the contents of total, reducing, and nonreducing sugars in apple fruits. Data shown are the averages of the production years 2020 and 2021.

Treatments	Total Sugars (mg GE g^{-1} DW)	Reducing Sugars (mg GE g^{-1} DW)	Nonreducing Sugars (mg GE g^{-1} DW)
SFE + NP0	0.38 ± 0.03 ^{d,e}	0.292 ± 0.02 ^{c,d}	0.10 ± 0.01 ^{d}
SFE + NPSe	0.63 ± 0.01 ^{b}	0.329 ± 0.03 ^{b}	0.30 ± 0.03 ^{a}
SFE + NPZn	0.73 ± 0.01 ^{a}	0.393 ± 0.04 ^{a}	0.33 ± 0.01 ^{a}
150-50-80 + NP0	0.34 ± 0.01 ^{f}	0.304 ± 0.03 ^{b,c}	0.04 ± 0.02 ^{e}
150-50-80 + NPSe	0.38 ± 0.04 ^{e,f}	0.302 ± 0.02 ^{b,c}	0.08 ± 0.03 ^{d,e}
150-50-80 + NPZn	0.42 ± 0.04 ^{c,d}	0.268 ± 0.02 ^{d,e}	0.15 ± 0.02 ^{c}
100-60-60 + NP0	0.45 ± 0.03 ^{c}	0.293 ± 0.01 ^{c,d}	0.16 ± 0.03 ^{c}
100-60-60 + NPSe	0.46 ± 0.05 ^{c}	0.251 ± 0.01 ^{e}	0.21 ± 0.04 ^{b}
100-60-60 + NPZn	0.38 ± 0.03 ^{d,e,f}	0.291 ± 0.03 ^{c,d}	0.09 ± 0.02 ^{d}

SFE: without edaphic fertilization (00-00-00), NP: foliar fertilization of nanoparticles (NP0: nanoparticles at 0 ppm; NPSe: selenium nanoparticles at 50 ppm; NPZn: zinc nanoparticles at 250 ppm). DW: dry weight. Values are the mean ± standard deviation (n = 3). Different letters between columns indicate significant differences ($p \leq 0.05$).

We observed the lowest contents of TS and NRS in the fruits of the 150-50-80 + NP0, 150-50-80 + NPZn, and 100-60-60 + NPZn treatments. High doses of N can reduce the quality with regard to the contents of sugars in apples [47], which, in the treatments with Zn, may have been due to an antagonistic response among the nutrients. Zn acts negatively with P, where Zn precipitates as Zn phosphate when P is added to the fertilization doses [48].

3.3. Contents of Total Phenols, Flavonoids, and Ascorbic Acid

Table 2 presents the contents of total phenols and flavonoids. According to the results, the fruits of the SFE + NPZn treatment, which consisted only of the foliar application of Zn NPs, registered significantly higher contents of total phenols and flavonoids, followed by the 150-50-80 + NPSe treatment, whereas we found the lowest concentrations of total phenols and flavonoids in the fruits of the 150-50-80 + NP0, 100-60-60 + NP0, and control treatments, which did not include any NPs. This may have been due to the reduced size of the NPs, which can cross the epidermis of the plant leaf through the stomata and then move through the apoplast and symplast pathways, which is followed by transport to the mesophyll cells, where they are distributed to different parts of the plants through the xylem and phloem [49,50]. NPs within subcellular organelles can induce oxidative-stress-signaling cascades in cells; however, to counteract the increased levels of reactive oxygen species, organisms activate antioxidant defense mechanisms, including the synthesis of phenolic compounds [51,52]. In other studies, authors reported increases in the total phenols and flavonoids in fruit trees due to Zn and B NPs, such as pomegranate [25], and, in one study, the authors reported an increase in these compounds in melon with foliar applications with Zn NPs at 50 mg L^{-1} [38]. Se NPs at a concentration of 75 mg L^{-1} increased the phenols and flavonoids by up to 54.23 and 46.99%, respectively, in mandarin fruits [45]. Other researchers reported higher proportions of flavonoids than total phenols [53]. The increase in these phenolic compounds is important because they determine the quality of apple fruits, such as the color, flavor, and aroma [54]. In addition, they have positive biological effects on human health [25,27]. Se and Zn NPs have positive effects on the increase in the phenolic compounds in apple fruits.

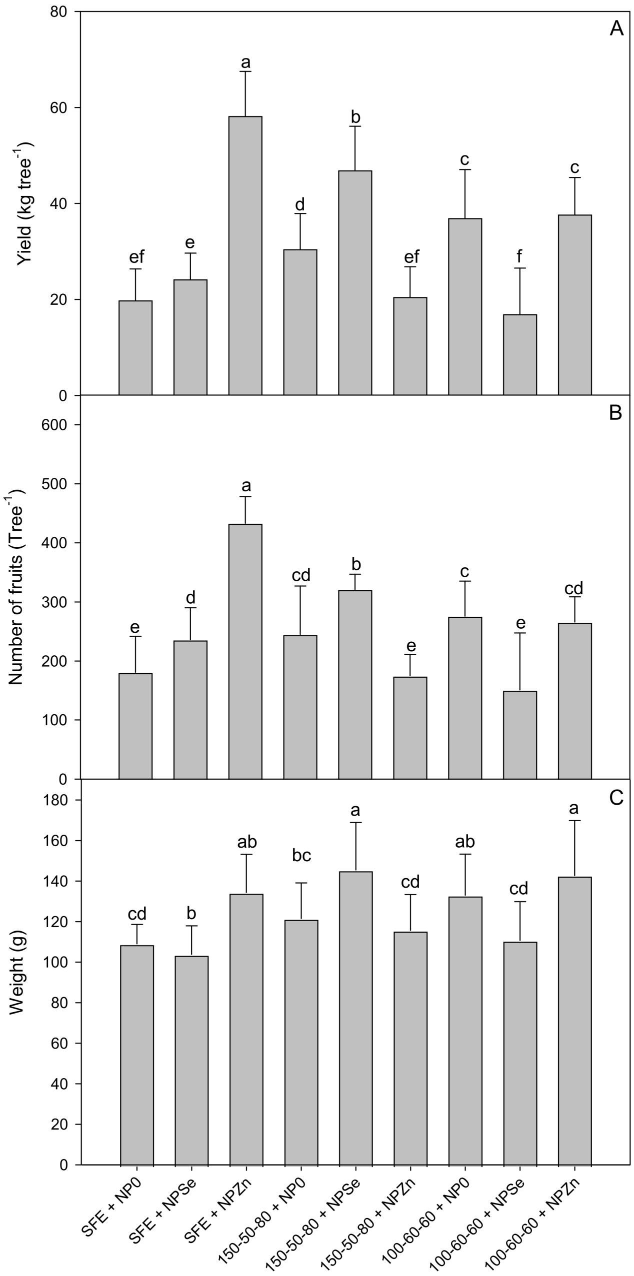

Figure 1. Effects of edaphic fertilization and foliar application of Se and Zn nanoparticles on (**A**) apple fruit yield, (**B**) number of fruits per tree, and (**C**) fruit weight. Data shown are averages for the years of production, 2020 and 2021. SFE: without edaphic fertilization (00-00-00), NP: foliar fertilization of nanoparticles (NP0: nanoparticles at 0 ppm; NPSe: selenium nanoparticles at 50 ppm; NPZn: zinc nanoparticles at 250 ppm). Bars are mean value ± standard error (n = 3). Means with a different letter indicate a statistically significant difference (Tukey, $p \leq 0.05$).

Table 2. Effects of edaphic fertilization and foliar application of Se and Zn nanoparticles on the contents of total phenols, flavonoids, and ascorbic acid and antioxidant activity (ABTS y DPPH) in apple fruits. Data shown are averages for the years of production, 2020 and 2021.

Treatments	Phenols (mg GAE g^{-1} DW)	Flavonoids (mg QE g^{-1} DW)	Ascorbic Acid (mg AA g^{-1} DW)	DPPH (μM TE g^{-1} DW)	ABTS (μM TE g^{-1} DW)
SFE + NP0	$4.79 \pm 0.26^{c,d}$	$8.02 \pm 1.71^{d,e}$	1.03 ± 0.09^{d}	$14.95 \pm 1.72^{d,e}$	21.77 ± 2.01^{d}
SFE + NPSe	$5.86 \pm 0.45^{b,c}$	$11.24 \pm 1.52^{c,d,e}$	$1.43 \pm 0.07^{b,c}$	18.50 ± 0.46^{b}	26.83 ± 0.12^{b}
SFE + NPZn	7.64 ± 0.73^{a}	15.82 ± 1.69^{a}	$1.51 \pm 0.05^{a,b}$	23.23 ± 0.47^{a}	34.05 ± 0.99^{a}
150-50-80 + NP0	4.35 ± 0.75^{d}	$8.72 \pm 1.60^{c,d,e}$	1.25 ± 0.10^{c}	13.86 ± 0.93^{e}	20.56 ± 1.75^{d}
150-50-80 + NPSe	6.62 ± 0.46^{b}	16.86 ± 1.84^{a}	$1.54 \pm 0.17^{a,b}$	17.65 ± 0.49^{b}	25.62 ± 0.14^{b}
150-50-80 + NPZn	$5.50 \pm 0.58^{b,c,d}$	$12.26 \pm 1.73^{b,c}$	$1.62 \pm 0.18^{a,b}$	$16.42 \pm 0.40^{b,c}$	25.72 ± 0.79^{b}
100-60-60 + NP0	4.34 ± 0.78^{d}	7.75 ± 1.72^{e}	1.36 ± 0.07^{c}	$14.68 \pm 1.68^{d,e}$	22.60 ± 2.13^{d}
100-60-60 + NPSe	$6.06 \pm 0.72^{b,c}$	$11.46 \pm 1.59^{c,d}$	$1.49 \pm 0.11^{a,b}$	$17.40 \pm 0.77^{b,c}$	$25.36 \pm 0.86^{b,c}$
100-60-60 + NPZn	$4.96 \pm 0.75^{c,d}$	$10.32 \pm 2.23^{c,d,e}$	1.78 ± 0.24^{a}	$15.27 \pm 0.26^{c,d}$	22.83 ± 0.31^{c}

SFE: without soil fertilization (00-00-00), NP: foliar fertilization of nanoparticles (NP0: nanoparticles at 0 ppm; NPSe: selenium nanoparticles at 50 ppm; NPZn: zinc nanoparticles at 250 ppm), DPPH: 2,2-diphenyl-1-picrylhydrazyl, ABTS: 2,2′azinobis(3-ethylbenzthiazolin-6-sulfonic acid), DW: dry weight. Values are mean ± standard deviation (n = 3). Different letters between columns indicate significant differences ($p \leq 0.05$).

With regard to the ascorbic acid content, we observed that the fruits of the treatments that included foliar applications with Zn and Se NPs presented higher contents of ascorbic acid (Table 3), followed by the fruits of the treatments with edaphic fertilizations (150-50-80 + NP0 and 100-60-60 + NP0), where we observed that the NPs positively influenced the increase in ascorbic acid, surpassing the fruits of the control treatment (SFE + NP0). According to Soto-Parra et al. [11], N and K have a preponderant influence on the content of organic acids in Golden Delicious apple fruits. Potassium contributed to the juice and vitamin C contents in fruits [55], and its application helped to increase the ascorbic acid in apples. According to the above, NPK soil fertilization contributes to the content of ascorbic acid to a considerable degree. Thus, the results in this study are consistent with those of Chang-Zheng et al. [54], who reported an increase in the ascorbic acid in apple fruits when the soil fertilization was combined with foliar applications of Zn NPs at 250 ppm. Moreover, the values found in this study are higher than those reported by other authors for Golden Delicious and other varieties of commercial apples [53].

Table 3. Pearson's correlation analysis between variables of antioxidant activity in apple fruits treated with edaphic fertilization and foliar application of Se and Zn nanoparticles. Data shown are averages for the years of production, 2020 and 2021.

Variables	TP	FL	DPPH	ABTS	AAS
FT	1.00	0.903 ($p = 8.65 \times 10^{-31}$)	0.906 ($p = 3.70 \times 10^{-31}$)	0.881 ($p = 2.10 \times 10^{-27}$)	0.261 (p = 0.0184)
FL		1.00	0.756 ($p = 3.23 \times 10^{-16}$)	0.749 ($p = 8.67 \times 10^{-17}$)	0.373 (p = 0.00060)
DPPH			1.00	0.973 ($p = 4.55 \times 10^{-52}$)	0.185 (p = 0.0991)
ABTS				1.00	0.261 (p = 0.0187)
AAS					1.00

TP: total phenols; FL: flavonoids; AAS: ascorbic acid. Values are mean ± standard deviation (n = 3).

Antioxidant Capacity

We determined the antioxidant capacity in the apple fruits in the different treatments through the DPPH and ABTS assays. As seen in Table 2, the apple fruits of the SFE + NPZn and SFE + NPSe treatments presented significantly higher values according to the DPPH and ABTS tests, with the lowest values corresponding to the 150-50-80 + NP0, 100-60-60 + NP0, and control treatments, which showed that the foliar application with the Se and Zn NPs increased antioxidant activity. Moreover, this behavior of the antioxidant activity is in agreement with the results of the total phenols and flavonoids, which are responsible for conferring this activity to apple fruits, according to the Pearson's correlation analysis (Table 3). In addition, ascorbic acid had less of an influence on the antioxidant activity of the fruits, which could have been due to a lower concentration of ascorbic acid in the apple fruits in relation to the concentrations of total phenols and flavonoids, which showed the highest correlations with the antioxidant activity (Table 3). This behavior is in agreement with that reported by Kschonsek et al. [56] for 15 different varieties of apple. The main phenolic compounds that influenced the antioxidant activity in these varieties were phenolic acids and quercetin glycosides. The antioxidant activity values that we found in this study are higher than those reported in the literature. Oszmiański et al. [57] reported the antioxidant activity values for 22 apple varieties; the highest value was 0.7214 µmol Trolox/g DW. This is much lower than what we found in this study and may be due to the age of the cultivars, as older cultivars produce more antioxidant compounds [56]), and to the application of NPs, which influenced the increase in more bioactive compounds.

4. Conclusions

Fertilization applications to the soil with doses of 150-50-80 and 100-60-60 and foliar applications with nanoparticles of Se and Zn improved the yield, number, and weight, and increased the contents of sugars and ascorbic acid in apple fruits. In this study, the foliar application of nanoparticles of Se at 50 ppm and Zn at 250 ppm increased the contents of total phenols and flavonoids, and these bioactive compounds mainly influenced the antioxidant activity of the fruits. We recommend the foliar application of Se and Zn NPs as a practice to complement the doses of edaphic fertilization with N, P, and K and to improve the production and nutraceutical quality of apple fruits.

Author Contributions: A.M.-H., J.M.P.-E., C.U.L.-P. and A.D.H.-F.: performed the experiment in the field and laboratory; A.M.-H.: redaction; C.U.L.-P. and Y.O.S.-S.: writing review, software. G.C.-P. and Z.H.P.-G. provided the Se and Zn nanoparticles and analysis tools. All authors have read and agreed to the published version of the manuscript.

Funding: This research received no external funding.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: All data generated or analyzed during this study are included in this published article.

Acknowledgments: We would like to thank the apple growers of Acaxochitlán, Hidalgo, Mexico, for allowing us to set up the experiment in their apple orchards. The main author also thanks the National Council for Science and Technology (CONACyT, Mexico) for scholarship No. 440998.

Conflicts of Interest: The authors declare no conflict of interest.

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