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Effects of ZnO Nanoparticles and Biochar of Rice Straw and Cow Manure on Characteristics of Contaminated Soil and Sunflower Productivity, Oil Quality, and Heavy Metals Uptake

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Abstract: Contaminated soils can cause a potential risk into the health of the environment and soil as well as the quality and productivity of plants. The objectives of our study were to investigate the integrative advantageous effects of foliar ZnO nanoparticles (NPs) (60 mg Zn NPs L^{-1}), rice straw biochar (RSB; 8.0 t ha^{-1}), cow-manure biochar (CMB, 8.0 t ha^{-1}), and a combination thereof (50% of each) on sunflowers grown in agricultural land irrigated with polluted wastewater for the long term (≈50 years). The availability of heavy metals (HMs) in soil, HMs accumulation in whole biomass aboveground, growth, productivity, and quality characteristics of the sunflower were investigated. The combination treatment significantly minimized the availability of HMs in soil, and, consequently, substantially lessened the uptake of HMs by the sunflower, compared to treatments of ZnO NPs and control (i.e., untreated soil). The application of the combination treatment reduced the availability of Pb, Cr, Cu, and Cd in the soil by 78.6%, 115.3%, 153.3%, and 178.5% in comparison to untreated plots post-harvest, respectively. Compared to untreated plots, it also reduced the Pb, Cr, Cu, and Cd in plant biomass by 1.13, 5.19, 3.88, and 0.26 mg kg^{-1} DM, respectively. Furthermore, combination treatment followed by biochar as an individual application caused a significant improvement in sunflower productivity and quality in comparison to untreated soil. For instance, seed yield ha^{-1}, 100-seed weight, and number of seeds per head obtained from the combination treatment was greater than the results obtained from the untreated plots by 42.6%, 47.0%, and 50.4%, respectively. In summary, the combined treatment of NPs and both RSB and CMB is recommended as a result of their positive influence on sunflower oil quality and yield as well as on minimizing the negative influences of HMs.

Keywords: metals; growth; yields; oil quality; rice-straw biochar; cow-manure biochar; sunflower

1. Introduction

Terrestrial soil contamination by heavy metals (HMs) has become a serious environmental problem worldwide as a result of anthropogenic activities [1–9]. Moreover, HMs and metalloids can negatively influence the ecological integrity and soil quality, and decrease the usability of agricultural soils, which, consequently, results in food insecurity. HMs and metalloids can also cause irretrievable harm to ecological systems, animals, and human health [3,7,8]. Therefore, the remediation [10] or immobilization [3] of toxic HMs in contaminated agricultural lands is considered a serious, imperative, and imperious issue. Soil contamination with toxic metalloids and HMs such as arsenic (As), lead (Pb), cadmium (Cd), chromium (Cr), nickel (Ni), copper (Cu), and zinc (Zn) has meaningfully increased in recent decades due to the sewage wastes, agricultural pesticides, chemical fertilizers, and industrial waste application [2,3,8,11]. The dispersion of toxic HMs in agricultural lands are irrigated with wastewater, and, in plant biomass or edible parts, can pose a contamination for the food chain with hazardous consequences to both animals and humans [3,8,12,13].

However, water scarcity is considered a worldwide concern that can influence socio-economic activities and threaten natural resources sustainability [6]. Treated wastewater is a necessary nonconventional water resource that can be partially used in agricultural irrigation to allow crop survival during water shortages and agricultural expansion in Egypt [14]. The Bahr El-Baqar drain is considered one of the biggest drains in the Egyptian Nile Delta. It has been receiving different wastewater resources (i.e., mainly untreated or drainage return flow from agricultural areas, poorly treated domestic, and industrial wastewater) for approximately 50 years [14]. It receives the largest quantity of wastewater yearly (1.8 billion m^3) in the Egyptian Nile Delta region. The Bahr El-Baqar drain receives, daily, 4.52, 0.12, 0.06, and 0.18 million m^3 of agricultural diffuse, domestic diffuse, domestic, and industrial sources, respectively. Such discharge of municipal, agricultural, and industrial wastewaters in the Bahr El-Baqar drain can easily contaminate agricultural lands with toxic metals and metalloids. Thus, traditional or nontraditional soil amendments, foliar exogenous applications, and/or plant species must be used to remove or immobilize such metals and metalloids in contaminated soil.

Biochar is a carbonaceous material created from the pyrolytic conversion of agricultural biomass (i.e., plant or animal biomass or manure) and industrial residue with limited oxygen access [4,6,15–17]. Recently, biochar produced from different raw materials has been recommended for agriculture and horticulture use as an organic amendment for soil because of its specific physical and chemical characterization, and its capability of adsorbing HMs and metalloids in contaminated soil [3,4,18,19]. A biochar application to agricultural soils can improve soil characteristics such as pH, bulk density, stability of the organic matter, and nutrient retention via cation adsorption [3,6]. Moreover, its application can improve the aggregate stability, water availability, microbial abundance, and mycorrhizal activity in soils [6]. It contains high silicon that can also minimize the adverse drought stress effects [6]. Burning rice straw (RS) in open air typically causes a significant contribution to heavy haze formation. Therefore, biochar produced via thermal pyrolysis of RS with limited oxygen access has been proposed to provide a promising substitute solution for using RS as a residual return to agricultural lands. Typically, agricultural land suffers from a deficiency of Si and other nutrients because of cropping and harvesting processes. Thus, Si-rich biochar such as rice straw biochar (RSB) can directly import N, P, K, and Si into this soil [6,20]. Biochar made from poultry litter feedstock [21] and/or cow-manure biochar (CMB) [22–24] have superior quality and nutrient status compared with that made from plant biomass or crop residues [3,6]. Cow-manure biochar (CMB) can be used as a supplement to RSB for the integrative enhancement of this combination on soil and crop productivity.

Recently, the application of nanoparticles (NPs) as foliar and/or seed priming has received significant attention due to the increment in the nutrient accumulation by plants, which enhances the capability of agronomic nutrient biofortification [25–28]. Zinc oxide (ZnO) is an instance for the NP that can be useful in this respect due to the importance of Zn as micronutrients for plants and human's development [28,29]. Exogenous application of Zn as different forms is favored over its addition as an amendment for the soil due to its lesser bioavailability in the latter form [25,30]. The role of ZnO NPs, as an exogenous application, combined with the application of RSB or CMB has not been deeply investigated in terms of toxic metals and/or metalloids accumulating by oil crops. Agricultural lands irrigated with wastewater should also be cultivated with specific crops to prevent the entry of HMs and metalloids to the other environmental compartments. Previous studies reported that ZnO and zerovalent iron NPs caused an increase in heavy metal (i.e., Cd) accumulation by *Boehmeria nivea* [31] and *Leucaena leucocephala* [32], respectively. However, other works reported that NPs enhanced both growth characteristics and yields and lessened heavy metal accumulation in plants in comparison to a control treatment [26,27,33]. Similarly, Si-NPs lessened the toxicity of metal elements (i.e., Cr) in pea seedlings [34]. Foliar application of Fe_3O_4-NPs improved the wheat growth and its productivity and decreased the HMs uptake [35]. From the above, it is clear that the previous investigations have designated that NPs have different influences on heavy metal uptake due to the type and procedure of the application as well as the plant and heavy metal species involved.

Sunflower (*Helianthus annuus* L.) contributes 8% of the total oilseed production. The globe sunflower cultivated area and seed production were 23.1 M ha and 31.5 Mt during 2010, 25.3 M ha and 42.6 Mt during 2014, and 26.7 M ha and 52.0 Mt during 2018, respectively [36]. Sunflower seeds contain 45.5% oil and 23.8% protein [28]. The tolerance of sunflower into nutrient-poor soils, and its high seed and biomass yields make this crop a desirable feedstock for food, feed, and bioenergy production [5,25,37]. Seed oil with a high oleic acid percent are advantageous for food uses, whereas those with high linoleic acid percent are beneficial for biofuel production. Moreover, the ratio between oleic and linoleic acids is a very important characteristic for oil quality [5,38].

Therefore, the aim of our study was to investigate the effects of ZnO NPs, RSB, CMB, and/or their combination (50% for each treatment) on accumulation of HMs in whole plant biomass aboveground and on the growth, yield, and quality of sunflowers grown in soil irrigated over long periods with polluted wastewater. In addition, the effects of the different treatments on soil characteristics were studied.

2. Materials and Methods

2.1. Treatments, Design, and Plant Material of the Experiments

Two field experiments were performed in Bahr El-Baqar, East of the Nile Delta, Egypt during summer seasons in 2017 and 2018 with an objective to study the effects of plant organic amendment (8.0 t ha^{-1} rice straw biochar; RSB), animal organic amendment (8.0 t ha^{-1} cow manure biochar, CMB), inorganic NPs foliar application (60 mg Zn NPs L^{-1}), and combinations (50% of each) on available trace elements in soil post-harvest of sunflowers (*Helianthus annuus* L., cv Sakha 53) grown in soil irrigated with wastewater. The plant uptake of trace elements (Cd, Cr, Pb, Zn, Fe, and Cu), oil quality (oil percent, oil yield kg ha^{-1}, oleic acid, linoleic acid, and oleic/linoleic ratio), physiological, and productivity characteristics (total chlorophyll, proline content, plant leaf area, yield, and yield components) were also measured. The soil in the investigated area was contaminated via long-term irrigation with wastewater (i.e., for approximately 50 years). Before sowing, the biochar of animal and plant were applied into the surface and then ploughed into soil to a depth of 5–15 cm. ZnO NPs was added as foliar application at 25 and 45 days after sowing (DAS) with the rate of 60 mg Zn NPs L^{-1}.

Biochar was made by fast pyrolysis through 500–550 °C for 20 min [6], from RS and cow-manure (CM). The analysis of CMB and RSB was pH 8.9 and 8.3, electrical conductivity (EC) 2.92 and 0.14 dS m^{-1}, water holding capacity of 42.29% and 35.01%, carbon values at 409.3 and 465.9 g kg^{-1}, nitrogen values at 14.32 and 9.81 g kg^{-1}, phosphorus values at 11.42 and 1.94 and g kg^{-1}, specific surface area of 24.14 and 22.44 m^2 g^{-1}, and potassium values of 18.34 and 20.52 g kg^{-1}, respectively. The purity, specific surface area, particle size, and density of the ZnO NPs were 99.9%, 55 m^2 g^{-1}, 18 nm, and 5.6 g cm^{-3}, respectively.

The experimental design was by completely block design, and the number of replications was four. The investigated area was divided into plots with a size of 25.0 m^2 (5 m × 5 m) for each plot. Sunflower seeds (cv. Sakha 53) were sown on 2 June 2017 and 4 June 2018 (10 kg ha^{-1}), and were sufficient for guaranteeing healthy germination. Seeds of the sunflower were sown in rows with a 0.6 m distance. In addition, they were sown in hills with two or three seeds per hill, and the distance between the two hills was 20 cm. Seedlings were thinned at 18 DAS, and one plant was left per hill. The preceding crop cultivated at each site was *Beta vulgaris* L. in both seasons.

Prior to sowing of the sunflower, calcium superphosphate (15.5% P_2O_5) was applied at the rate of 40 kg P_2O_5 ha^{-1} as a soil amendment. Prior to the first and second irrigations, ammonium nitrate (33.5% N) was added at the recommended rate of 80 kg ha^{-1}. The total nitrogen amount was applied in two equal doses. Lastly, potassium fertilizer was added at the recommended rate of 54 kg K_2O ha^{-1} directly before the first irrigation.

2.2. Water and Soil analysis

The samples from water were collected during both growing seasons and placed into plastic bottles. They were immediately acidified with nitric acid (1 mL HNO_3 L^{-1} water) for analysis of different elements using ICP-Optical Emission Spectrometry (iCAP 6200, Thermo Fisher Scientific Inc., Cambridge, UK) as described by APHA [39]. Electrical conductivity (EC) and pH were measured using a Thermo Scientific Orion Versa Star™ advanced electrochemistry benchtop meter. The total suspended solids (TSS) as well as ammonium (NH_4), nitrate (NO_3), phosphate (PO_4), sulfate (SO_4), chloride (Cl), and molybdate (MoO_4) were measured using a YSI 9300 photometer. The analysis of the water, as the mean of six sampling dates, was 0.007, 0.235, 0.016, 0.114, 0.001, 0.07, 5.2, 111.4, 16.5, 185.4, 29.3, and 134.3 mg L^{-1} for Cd, Pb, Cu, Mn, Zn, Fe, MoO_4, SO_4, PO_4, NO_3, NH_4, and Cl, respectively.

The soil was clay loam with a sand value of 19.3%, a silt value of 34.3%, and a clay value of 46.4%, with pH 7.19, EC 1.02 dS m^{-1}, available N at 26.49 mg kg^{-1}, available P at 6.89 mg kg^{-1}, and available K at 45.17 mg kg^{-1} (Table 1). Before sowing, the content of Cr, Pb, Cd, Ni, Cu, and Zn in the experimental area were 14.34, 3.05, 39.45, 43.81, 40.91, and 54.38 mg kg^{-1}, respectively.

Table 1. Physicochemical characteristics of experimental soil and biochar.

	Soil (Season 1)	Soil (Season 2)	Rice Straw Biochar	Cow Manure Biochar
pH	7.16	7.22	8.31	8.95
EC (dS m^{-1})	1.00	1.04	0.15	2.92
Total N (g kg^{-1})	0.201	0.203	9.81	14.32
Total P (g kg^{-1})	-	-	2.05	11.42
Total K (g kg^{-1})	-	-	20.26	18.34
Total carbon (g kg^{-1})	-	-	465.97	409.32
Total magnesium (g kg^{-1})	-	-	3.75	-
Total Si (g kg^{-1})	-	-	6.341	-
Total Fe (g kg^{-1})	0.071	0.077	-	-
Available N (mg kg–^{1})	26.44	26.54	122.09	242.94
Available P (mg kg^{-1})	6.80	6.97	-	-
Available K (mg kg^{-1})	45.16	45.19	-	-
Organic matter (%)	2.29	2.37	25.97	29.78
Specific surface area m^2 g^{-1}	-	-	24.14	30.11
Water holding capacity (%)	-	-	35.01	42.29
Trace elements (mg kg^{-1})				
As	0.04	0.04	nd	nd
Pb	14.30	14.38	nd	0.09
Cd	3.01	3.09	nd	0.01
Cr	39.46	39.44	0.02	0.08
Ni	40.90	40.92	0.02	0.04
Cu	43.70	43.92	11.78	26.43
Zn	54.07	54.69	39.86	53.29

2.3. Measurements

2.3.1. Soil Analysis

Top soil samples (0–20 cm) were collected prior to sowing and post-harvest for analysis of pH (H_2O; 1:2.5) and EC using the same meter mentioned above in the water analysis section.

Before starting the experiments, the total content of Cd, Zn, Cu, Cr, Ni, and Pb in the soil were analyzed as follows. To begin, 100 mg of the soil was digested in 6 mL of a mixture of HCl and HNO3 (3:1, v/v) in a Teflon tube (7 mL) for 130 min at 185 °C. The resultant solution was filtered, transferred to a 100 mL flask, and used for the metal's measurement. The total content of HMs was measured with ICP-MS (Agilent 7500c, Agilent Technologies, CA, USA).

After harvest, subsamples of soil (250 mg from 0–20 cm depth) were taken and then well mixed to provide a single representative sample for each replication. The collected soil samples were dried in open air and ground. The soil was passed through a 2-mm sieve. The availability of HMs was extracted following Jones [40], and using the ammonium bicarbonate–diethylene triamine penta acetic acid (AB-DTPA) method. The contents of the different HMs were measured by ICP-MS (Agilent 7500c, Agilent Technologies, CA, USA).

2.3.2. Growth and Physiological Characteristics

All physiological characteristics were measured and analyzed at the flowering stage [41]. The proline content was measured in the fully expanded leaf (1.0 g) as explained by Bates et al. [42] and Seleiman et al. [6]. The absorbance was read at 520 nm using a spectrophotometer (UV-160A, Shimadzu, Japan). Lastly, proline content was measured from a calibration curve and presented as μmol proline g^{-1} fresh weight (FW).

The total chlorophyll was analyzed using a SPAD meter (Model: SPAD-502, Minolta Sensing Ltd, Osaka, Japan). The topmost fully expanded sunflower leaves were used for measuring total chlorophyll. We measured the total chlorophyll content from 10 different plants within each replicate.

Moreover, six plants were randomly harvested from each replication at the flowering stage to measure the leaves area per plant using Portable Leaf Area Meter (LI-3000C, LI-COR Inc., Lincoln, NE, USA). Furthermore, the sunflower plant height from the soil surface to the plant top were recorded. Additionally, the diameter of the sunflower stem at 30 cm from the soil surface was measured.

2.3.3. Yield and Yield Components

On September 14, 2017 and September 12, 2018, sunflower plants with an area of 2 m^2 were manually harvested for measuring yield and related characteristics. Head diameter (cm), head weight (g), and number of seeds per head were recorded from five sunflower plants, which were chosen randomly and, subsequently, averaged. Seed index (100-seed weight, g) was measured by counting 100 seeds from the collected heads by the random method. Seed yield of sunflowers (kg ha^{-1}) was measured as follows. The heads of collected plants from the inner ridges (two m^2) in each plot were kept for two weeks after harvest until being completely air dried. Then, seeds were separated from heads to measure seed yield ha^{-1}.

2.3.4. Plant Uptake for Trace Elements and Seed Quality at Harvest

To analyze the toxic metals, the oven-dried biomass plant samples were ground. A subsample of 0.3 g was weighed from each replication and inserted in a Teflon tube with HNO_3^- for digesting by microwave heating. The digested sunflower samples were filtered, and then analyzed via ICP-Optical Emission Spectrometry (iCAP 6200, Thermo Fisher Scientific Inc., Cambridge, UK) as explained by Seleiman et al. [1].

The sunflower seeds were oven dried for 4 h at 40 °C, and, afterward, were ground using a Waring Blender (Waring Product Division, New Hartford, CT, USA). The percentage of sunflower oil seeds was analyzed by using the petroleum ether extraction technique with a Soxhlet meter [43]. The oil extract of different samples was evaporated via distillation by using a rotary evaporator at 35 °C until the solvent was completely removed. Lastly, the crude extract of oil was weighed to get the seed oil percent.

The oil yield (kg ha^{-1}) was calculated as follows.

$$\text{Oil yield}\left(\text{kg ha}^{-1}\right) = \textit{Oil seed}\ \% \times \textit{seed yield}\left(\textit{kg ha}^{-1}\right). \quad (1)$$

For analyzing the fatty acids such as oleic and linoleic, a 2-g aliquot of seed oil was moved to a screw-capped vial containing 0.3 mL methanol:sodium methylate (28.5:1.5 *w/w*) and incubated at 90 °C for 2 h to allow the methylation of the fatty acids. The composition of oleic and linoleic acids in the oil was analyzed as explained by Rotunno et al. [44] and Seleiman et al. [6]. The oleic/linoleic ratio was calculated as follows.

$$leic/linoleic\ ratio = \frac{\text{Oleic content}}{\text{Linoleic content}} \quad (2)$$

2.4. Statistical Analysis

Results obtained from the effects of investigated treatments (Zn NP, RSB, CMB, and their combination) on soil analysis after the experiment, sunflower oil quality, plant elemental analysis, and productivity characteristics were subjected to analysis of variance (ANOVA) using PASW statistics 21.0 (IBM Inc., Chicago, IL, USA). Combined statistical analysis over the two growing seasons for some investigated measurements was used. Treatment means were compared using Tukey's multiple range test at a significant difference of $p \leq 0.05$. Least significant difference was also calculated. Simple correlation coefficient among different measurements such as metals in soil postharvest, metals in sunflower, yield, and quality traits was done.

3. Results

3.1. Integrative Effects of NPs, CMB, and RSB on Contaminated Soil Characteristics

Application of RSB, CMB, and a combination into soil enhanced organic soil carbon levels (Figure 1). However, these applications did not cause a significant increase in the soil pH and EC when compared to the untreated soil. On the other hand, the application of a combination treatment (i.e., RSB + CMB + ZnO NPs) after that application of CMB and RSB caused the lowest availability of HMs (Cr, Cd, Cu, and Pb) and the highest availability of Zn and Fe in the soil after sunflower harvest. This was compared to ZnO NPs treatment and untreated soil (Figure 1). Compared to the untreated plots post-harvest, the combination of different treatments reduced the availability of Pb, Cr, Cu, Cd, and Ni in the soil by 78.6%, 115.3%, 153.3%, 178.5%, and 193.7%, respectively.

3.2. Integrative effects of NPs, CMB, and RSB on HMs Accumulation in Biomass of Sunflowers Grown in Contaminated Soil

The application of both organic amendments (i.e., CMB and RSB) and inorganic NPs (Zn NPs) in the current investigation significantly lessened the contents of Cd, Cu, Cr, and Pb in the whole sunflower biomass, and significantly enhanced the Zn and Fe when compared with the plants grown in the control (Figure 2). The lowest Cd, Cr, Cu, and Pb contents in the whole plant biomass were found when a combination treatment was added. This was followed by the individual CMB, RSB, and/or Zn NPs application being compared with the data obtained from sunflowers grown in the untreated plots (Figure 2). Compared to the control treatment, the combination treatment (i.e., CMB + RSB + Zn NPs) reduced Cd, Cr, Cu, and Pb in plant biomass by 0.26, 5.19, 3.88, and 1.13 mg kg^{-1} DM, respectively. However, the highest Zn content (25.1 mg kg^{-1} DM) in the plant biomass was obtained when the soil was incorporated with a combination treatment, which was followed by CMB and Zn NPs compared with RSB and control treatments. The highest Fe content (75.4 mg kg^{-1} DM) in the plant biomass was obtained when the soil was treated with a combination treatment that was followed by CMB and RSB when compared to Zn NPs and control treatments (Figure 2). The highest content of trace elements in the sunflower biomass was Fe followed by Zn, Cu, Cr, and Pb while the lowest element was Cd (Figure 2).

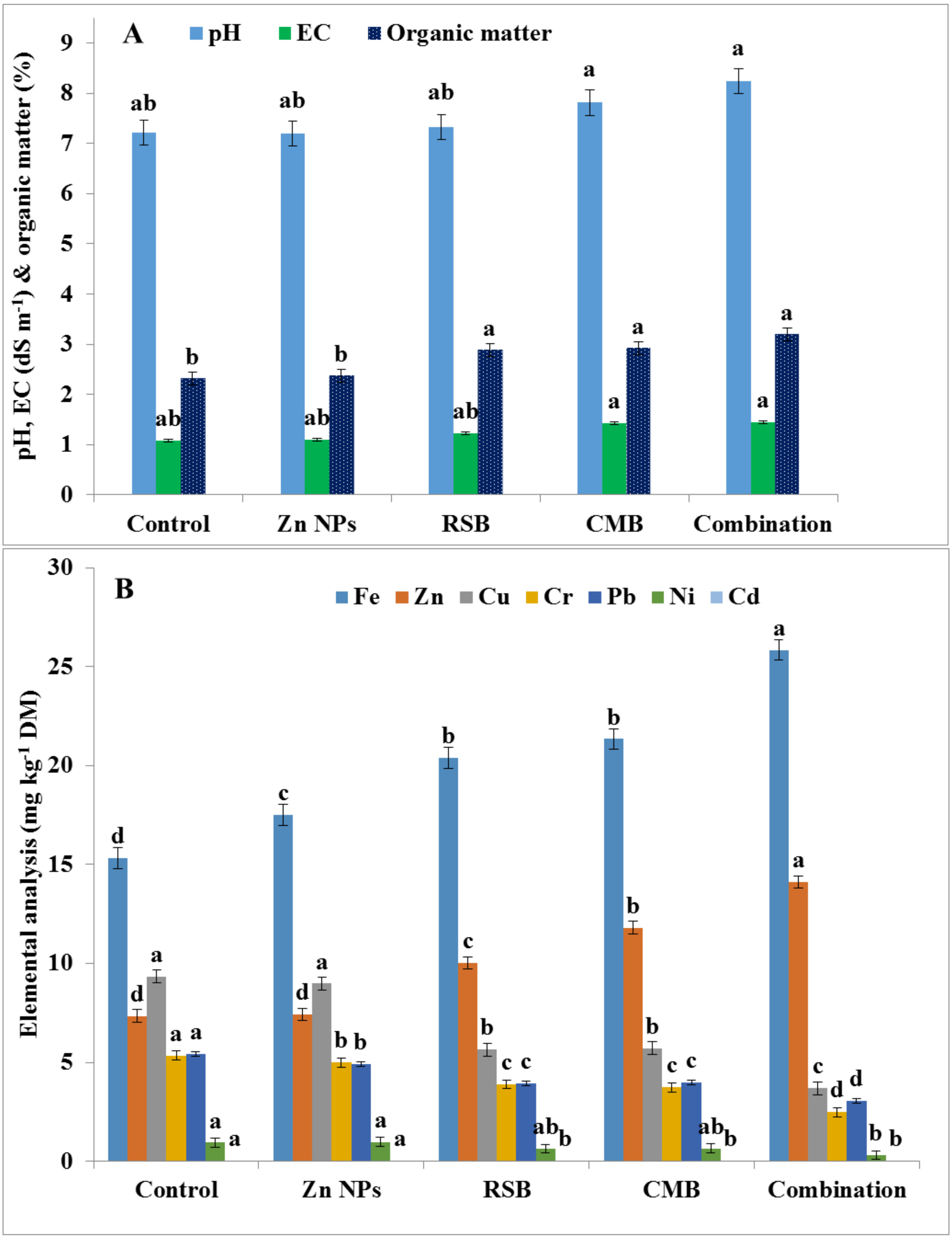

Figure 1. Effect of zinc nanoparticles and biochar of rice-straw and cow-manure on soil pH, EC, organic matter (**A**), and available heavy metals (**B**) after harvesting sunflowers grown in soil irrigated with wastewater for long-term (Data are the combined statistical analysis over the two seasons). Zn NPs = Zinc nano-particles, RSB = Rice straw biochar, CMB = Cow manure biochar, DM = dry matter, Error bars = Standard error of means (SEM). Means with different superscripts $^{a–e}$ for the same color of columns are significantly different at probability (p) ≤ 0.05.

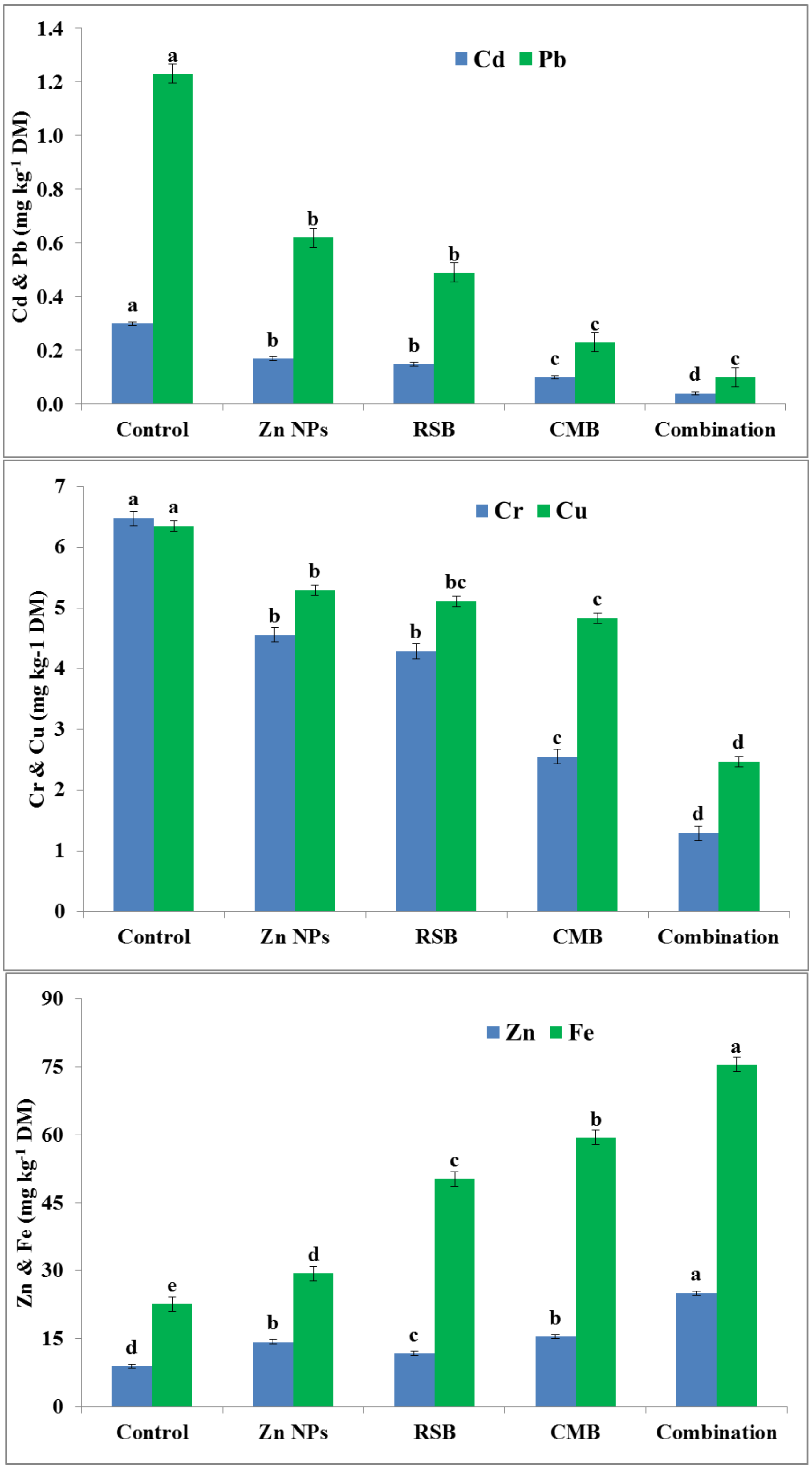

Figure 2. Effect of zinc nanoparticles and biochar of rice-straw and cow-manure on heavy metals accumulation in biomass of sunflowers grown in soil irrigated with wastewater over a long-term period (Data are the combined statistical analysis over the two seasons). Zn NPs = Zinc nano-particles, RSB = Rice straw biochar, CMB = Cow manure biochar, DM = dry matter, Error bars = Standard error of means (SEM). Means with different superscripts $^{a\text{–}e}$ for the same color of columns are significantly different at probability (p) ≤ 0.05.

3.3. Integrative Effects of NPs, CMB, and RSB on Growth, Physiological, And Yield Properties Of Sunflowers Grown In Contaminated Soil

The application of NPs (i.e., Zn NPs), CMB, RSB, and their combination enhanced growth, physiological, and yield characteristics of sunflowers grown in contaminated soil compared with untreated soil (Table 2 and Figures 3 and 4). The combination treatment (Zn NPs + RSB + CMB) resulted in the highest plants, widest stem, widest head diameters, greatest number of seeds per head, and seed yield ha^{-1}. This was followed by a single application of CMB, RSB, and Zn NPs when compared to the untreated soil. The seed yield ha^{-1}, 100-seed weight, number of seeds per head, and head diameter obtained from the combination treatment was greater than the results obtained from the untreated soil by 42.6%, 47.0%, 50.4%, and 52.4%, respectively (Table 2). Compared to the untreated soil, the application of a single CMB and RSB increased the seed yield ha^{-1} by 27.5% and 21.8%, 100-seed weight by 41.3% and 25.6%, number of seeds per head by 40.0% and 26.6%, and head diameter by 33.1% and 26.9%, respectively (Table 2). The foliar application with Zn NPs increased the seed yield ha^{-1}, 100-seed weight, number of seeds per head, and head diameter by 19.2%, 6.7%, 9.2%, and 5.7% when compared to the results obtained from the untreated soil, respectively.

The total chlorophyll content was increased gradually from 25 to 45 DAS, and was then decreased (Figure 3). The highest sunflower chlorophyll content at all sampling dates was obtained when the combination treatment was applied, compared to untreated soil. This was followed by applications of CMB, RSB, and Zn NPs (Figure 3). Compared to the untreated soil, the application of a combination treatment (i.e., CMB + RSB + Zn NPs) increased the total chlorophyll content by 26.6%, 29.9%, 27.4%, and 35.6% at 25, 45, 65, and 85 DAS, respectively (Figure 3).

Effects of NPs, RSB, CMB, and their combination on proline content and total leaf area of sunflowers grown in long-term contaminated soil are illustrated in Figure 4. The greatest leaf area per plant and proline content of sunflower grown in polluted soil was obtained from plots given the combination treatment. This was followed by CMB, RSB, and Zn-NPs compared to the untreated soil (Figure 4). The proline content obtained from sunflowers grown with a combination treatment, and single application of CMB, RSB, and Zn NPs was greater by 29.6%, 30.9%, 16.1%, and 17.6% than sunflowers grown in untreated soil, respectively (Figure 4).

Table 2. Effects of zinc nano-particles, plant-, and animal-biochars on growth, and yield and its components of sunflower grown in soil irrigated with wastewater over the long-term.

Treatment \ Traits	Stem Diameter (cm)	Plant Height (cm)	Head Diameter (cm)	Number of Seeds Per Head	100-Seed Weight (g)	Seed Yield (kg ha $^{-1}$)
Season 2017						
Control	2.09 ^{d}	180.1 ^{e}	17.7 ^{c}	953.3 ^{e}	5.07 ^{c}	2075.7 ^{e}
Zn NPs	2.17 ^{d}	193.2 ^{d}	18.5 ^{c}	1040.3 ^{d}	5.40 ^{c}	2481.4 ^{d}
RSB	2.36 ^{c}	216.9 ^{c}	22.3 ^{b}	1213.9 ^{c}	6.39 ^{b}	2531.0 ^{c}
CMB	2.45 ^{b}	220.5 ^{b}	23.1 ^{b}	1336.1 ^{b}	7.15 ^{a}	2652.8 ^{b}
Combination	2.70 ^{a}	241.9 ^{a}	28.0 ^{a}	1441.0 ^{a}	7.44 ^{a}	2953.0 ^{a}
$LSD_{0.05}$	0.08	2.2	0.9	35.2	0.34	39.8
Significant	*	**	**	**	**	**
Season 2018						
Control	2.13 ^{d}	182.5 ^{e}	17.3 ^{c}	958.3 ^{e}	5.09 ^{c}	2093.3 ^{e}
Zn NPs	2.19 ^{d}	198.2 ^{d}	18.5 ^{c}	1046.3 ^{d}	5.44 ^{c}	2506.6 ^{d}
RSB	2.34 ^{c}	214.5 ^{c}	22.1 ^{b}	1205.7 ^{c}	6.37 ^{b}	2545.0 ^{c}
CMB	2.43 ^{b}	224.5 ^{b}	23.5 ^{b}	1340.5 ^{b}	7.21 ^{a}	2664.4 ^{b}
Combination	2.80 ^{a}	239.7 ^{a}	28.4 ^{a}	1435.0 ^{a}	7.50 ^{a}	2991.2 ^{a}
$LSD_{0.05}$	0.07	2.7	1.5	39.4	0.36	32.5
Significant	*	**	**	**	**	**

Zn NPs = Zinc nano-particles, RSB = Rice straw biochar, CMB = Cow manure biochar, $LSD_{0.05}$ = least significant differences at 5% level. Means with different superscripts $^{a–e}$ within each column are significantly different at probability (p) ≥ 0.05 (not significant), $p \leq 0.05$ (*), $p \leq 0.01$ (**), Tukey's test was applied to compare means.

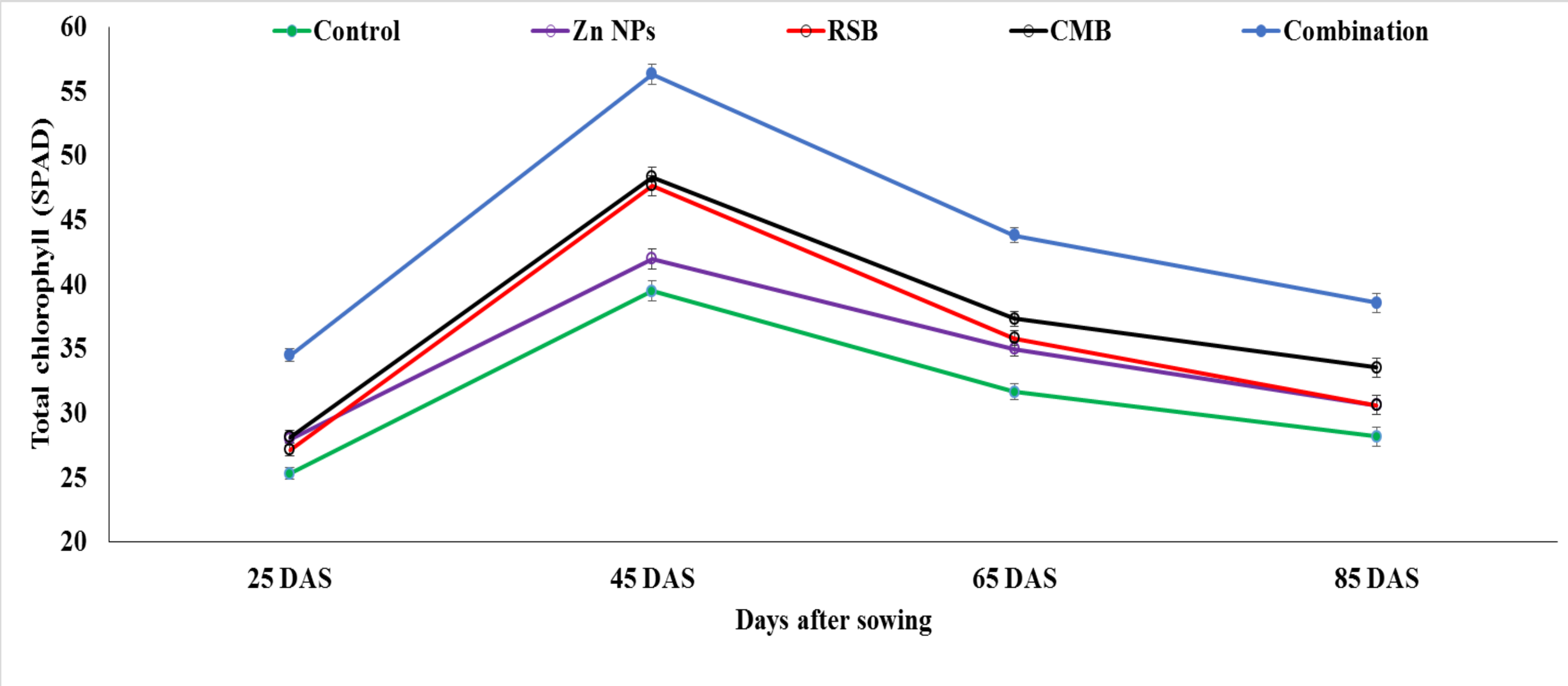

Figure 3. Effect of zinc nanoparticles, and biochar of rice-straw and cow-manure on total chlorophyll content (SPAD) of sunflowers grown in soil irrigated with wastewater for long-term (Data are the combined statistical analysis over the two seasons). Zn NPs = Zinc nano-particles, RSB = Rice straw biochar, CMB = Cow manure biochar, Bars = Standard error of means (SEM), DAS = Days after sowing.

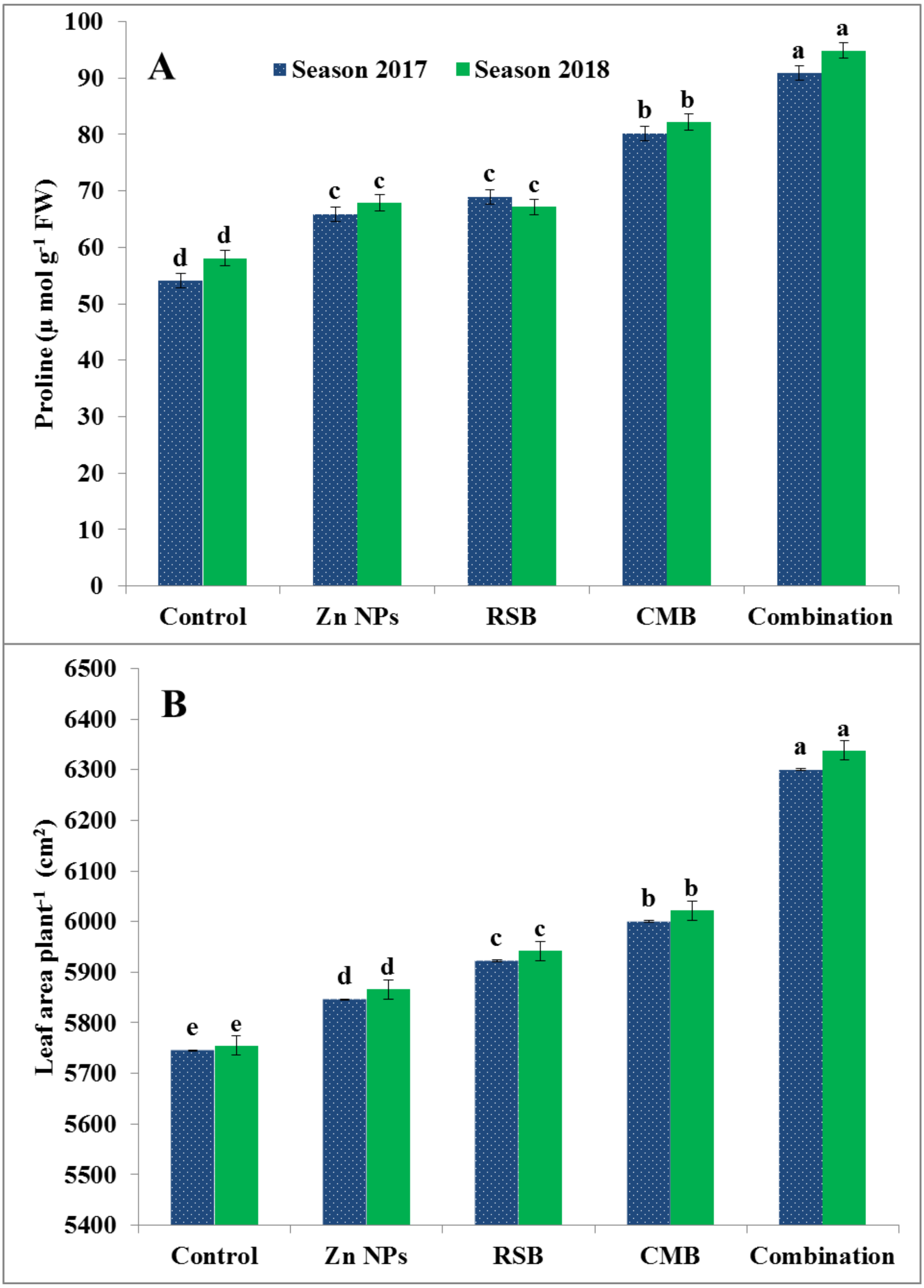

Figure 4. Effect of zinc nanoparticles, and biochar of rice-straw and cow-manure on proline content (**A**) and total leaf area (**B**) of sunflowers grown in soil irrigated with wastewater for long-term. Zn NPs = Zinc nano-particles, RSB = Rice straw biochar, CMB = Cow manure biochar, FW = fresh weight. SEM = Standard error of means, Means with different superscripts $^{a–e}$ are significantly different at $p \leq 0.05$. Tukey's test was applied to compare means.

3.4. Integrative Effects of NPs, CMB, and RSB on Oil Quality Characteristics of Sunflowers Grown in Contaminated Soil

The application of different soil amendments (i.e., CMB and RSB) and exogenous Zn NPs application increased the sunflower oil percentage and yield, oleic acid, and oleic/linoleic acids ratio compared to these factors in sunflowers grown in untreated soil (Table 3). The oil percentage was greater by 25.1% and 13.3% in seeds of sunflower grown on soil treated with a combination and CMB treatments. This was compared with those found in sunflowers grown in control treatment (Table 3). Compared with untreated soil, the oil yield increased by 537, 305, 202, and 214 kg ha^{-1} with a combination treatment and when CMB, RSB, and Zn NPs was applied into the soil, respectively. The application of a combination treatment (i.e., CMB + RSB + Zn NPs) increased the oleic acid by 12.4.0% and oleic/linoleic ratio by 316.7%. It reduced the linoleic acid by 252.5% when compared to the results obtained from the plants grown in the untreated plots (Table 3).

Table 3. Effect of zinc nano-particles, plant-biochars, and animal-biochars on oil percentage and its quality of sunflowers grown in soil irrigated with wastewater for the long-term.

Traits Treatments	Oil (%)	Oil (kg ha^{-1})	Oleic Acid (%)	Linoleic Acid (%)	Oleic/Linoleic Ratio
Season 2017					
Control	32.81 ^{d}	681.0 ^{d}	81.15 ^{c}	8.61 ^{a}	9.43 ^{d}
Zn NPs	35.56 ^{c}	882.4 ^{c}	82.37 ^{c}	7.94 ^{a}	10.37 ^{c}
RSB	35.42 ^{c}	896.5 ^{c}	86.18 ^{b}	4.43 ^{b}	19.45 ^{b}
CMB	37.18 ^{b}	986.3 ^{b}	86.09 ^{b}	4.32 ^{b}	19.93 ^{b}
Combination	41.10 ^{a}	1213.7 ^{a}	91.20 ^{a}	2.40 ^{c}	38.00 ^{a}
$LSD_{0.05}$	0.92	45.3	1.32	0.93	0.72
Significant	**	**	**	**	**
Season 2018					
Control	32.91 ^{d}	688.9 ^{d}	81.23 ^{c}	8.59 ^{a}	9.46 ^{d}
Zn NPs	35.54 ^{c}	890.8 ^{c}	82.41 ^{c}	7.86 ^{a}	10.48 ^{c}
RSB	35.38 ^{c}	900.4 ^{c}	86.20 ^{b}	4.49 ^{b}	19.20 ^{b}
CMB	37.26 ^{b}	992.8 ^{b}	86.05 ^{b}	4.30 ^{b}	20.01 ^{b}
Combination	41.12 ^{a}	1230.0 ^{a}	91.28 ^{a}	2.48 ^{c}	36.81 ^{a}
$LSD_{0.05}$	0.89	38.2	1.34	0.90	0.83
Significant	**	**	**	**	**

Zn NPs = Zinc nano-particles, RSB = Rice straw biochar, CMB = Cow manure biochar, $LSD_{0.05}$ = least significant differences at 5% level. Means with different superscripts $^{a\text{-}d}$ within each column are significantly different at probability (p) ≥ 0.05 (not significant), $p \leq 0.01$ (**), Tukey's test was applied to compare means.

3.5. Simple Correlation Coefficient Aming Different Traits over All Treatments

The results of a simple correlation coefficient among most investigated traits, such as heavy metals in soil post-harvest and metals uptake in sunflower, growth, yield, and quality traits, are presented in Table 4. Seed yield ha^{-1} and oleic acid in sunflower oil were significantly and positively correlated with Zn availability in soil and sunflower plants post-harvest, proline, leaf area per plant, and oil percentage. Reversely, they were negatively and significantly correlated with the Cu, Cr, and Cd in soil and sunflower plants post-harvest as well as with linoleic acid (Table 4). Conversely, correlation coefficient was non-significant between oleic acid with Zn and Cu in soil post-harvest or with an oil percentage.

Table 4. Simple correlation coefficient (r) between available heavy metals in soil at harvest, heavy metals accumulation in sunflower, seed yield, growth, and quality traits (overall treatments) as an average of the two seasons.

	Available Heavy Metals in Soil Post-Harvest				**Heavy Metals Accumulation in Sunflower**				**Proline (9)**	**Leaf Area (10)**	**Seed Yield ha^{-1} (11)**	**Oil % (12)**	**Oleic Acid (13)**	**Linoleic Acid (14)**
	Zn (1)	**Cu (2)**	**Cr (3)**	**Cd (4)**	**Zn (5)**	**Cu (6)**	**Cr (7)**	**Cd (8)**						
1		−0.964 **	−0.980 **	−0.985 **	0.843	−0.897 *	-0.936 *	−0.883 *	0.950 *	0.950 *	0.890 *	0.915 *	0.965 **	−0.963 **
2			0.984 **	0.991 **	−0.760	0.860	0.889 *	0.880 *	−0.883 *	−0.907 *	−0.881 *	−0.857	−0.975 **	0.998 **
3				0.992 **	−0.864	0.936 *	0.933 *	0.913 *	−0.939 *	−0.968 **	−0.929 *	−0.932 *	−0.997 **	0.981 **
4					−0.818	0.894 *	0.939 *	0.919 *	−0.936 *	−0.939 *	−0.919 *	−0.906 *	−0.979 **	0.993 **
5						−0.979 **	−0.909 *	−0.869	0.939 *	0.960 **	0.920 *	0.982 **	0.874	−0.759
6							0.922 *	0.898 *	−0.944 *	−0.990 **	−0.947 *	−0.986 **	−0.949 *	0.855
7								0.980 **	−0.993 **	−0.944 *	−0.977 **	−0.968 **	−0.915 *	0.904 *
8									−0.954 *	−0.907 *	−0.991 **	−0.939 *	−0.898 *	0.900 *
9										0.967 **	0.964 **	0.983 **	0.925 *	−0.893 *
10											0.945 *	0.985 **	0.973 **	−0.903 *
11												0.970 **	0.924 *	−0.894 *
12													0.933 *	−0.861
13														−0.968 **
14														

*, ** Significant and highly significant at 5%, respectively.

4. Discussion

4.1. Irrigation Water Analysis

In the investigated area, the HMs concentration in the Bahr El-Baqar Drain water were under the maximum limited values for field crops irrigation. Considering the crop tolerance level, the salinity range for crop irrigation water is 0–3 dS m^{-1} [45] while it was 1.5 dS m^{-1} in the irrigation water used in our investigation. In our study, the content of Mn, Cu, Fe, Zn, Pb, and Cd in the water of irrigation were 0.114, 0.016, 0.07, 0.001, 0.235, and 0.007 mg L^{-1}; while the recommended maximum values for these elements were 5, 2, 0.2, 0.2, 0.5, and 0.01 mg L^{-1}, respectively [45]. The high value of molybdenum (5.2 mg L^{-1}) in the irrigation water might be a result of the industrial wastewater, where molybdenum is encompassed in numerous chemicals such as catalysts, corrosion inhibitors, and pigments [46].

4.2. Integrative Effects of NPs, Plant, and Animal Biochar on Soil Trace Elements, pH, EC, and Organic Matter Postharvest

The pH in the soil mixed with biochar or plots treated with NPs at harvest were comparable with those of the control treatment (Figure 1). Such results show that both biochars and/or NPs fertilizers had no further liming impact on the treated soil, which can be a critical issue in alkaline soils. Regarding the soil EC, biochar application derived from CM or RS resulted in a non-significant increase in the soil EC when compared to the untreated soil or plots treated with ZnO NPs (Figure 1). This was a result of the high ash content of animal and plant biochar. However, the ECs were obtained from our study due to the different treatments being less than the recommended threshold for the majority of crops including sunflowers, and less than the ECs of saline soils (≥2000 μS cm^{-1}) [47]. The increment of the soil EC in plots treated with biochar can be linked to the release of fused-ring aromatic structures from both biochars.

The application of a combination treatment, CMB, RSB, and ZnO NPs into the contaminated soil significantly reduced the availability of HMs in the soil post-harvest compared to the results obtained from the untreated soil or plots treated with ZnO NPs (Figure 1). The possible mechanisms of toxic metals' mobility and bioavailability in different soils, as a result of biochar application, include complexation, ion exchange, electrostatic attraction, and precipitation [4]. Biochar made from animal or crop residues can adsorb HMs and metalloids by forming a surface complexation [48]. The functional groups such as -OH, -COOH, -C=O-, and C=N in biochar provide binding sites for toxic metals to form complexes, which can increase the specific adsorption of toxic metals [49]. The functional groups in biochar have demonstrated an immobilization of 38%–42% from total sorbed Pb (II) in acid solutions compared with untreated ones [50]. The inorganic ions present in biochar, such as Si, S, and Cl, can complex metals such as Cd by reducing their mobility in the soil [49]. Moreover, the elements presented in biochar can precipitate with different HMs to form insoluble precipitates [22,23]. For example, the application of phosphorus-rich biochar into contaminated soil can lessen the availability and leaching of Cd and Pb when compared to phosphorus-low biochar [51]. Conversely, the soil treated with a combination treatment, followed by CMB and RSB, contained greater Fe and Zn post-harvest than the untreated soil (Figure 1). This could be due to the ability of biochar to increase the capacity of the soils for adsorbing plant nutrients [3,6,52].

The application of biochar into contaminated soil can mitigate the risks of HMs by incrementing the soil pH [4] and/or number of cation exchange sites on the biochar surfaces [3,53]. Consequently, this could increase the hydrolysis of toxic metals and enhance their adsorption via the soil and accelerate the transformation of the oxidizable as well as residual fractions of the HMs [54]. Conversely, the released mineral elements could form mineral phases on the biochar surfaces and adsorb the HMs and metalloids from the soil solution [55]. For example, the phosphorus was enhanced in the soil solution due to an increased application of biochar, which causes heavy metal retention because of stable phosphate mineral formation [22]. In addition, oxides of Si, Ca, and Mn in biochar can be partially reduced and postulated high-energy sorption sites for heavy metal cations in the soils [55].

Moreover, biochar can release dissolved organic carbon (OC). Consequently, its application can enhance soil organic matter (Figure 1), which could, therefore, lessen the toxic metal mobility in the soil solution as a result of the complexation between the toxic metals and oxygen-containing functional groups presented in the biochar [56]. According to the biochar production cost and economic value, biochar derived from RS or CM can be used in heavy metal contaminated soils because such feedstock is abundant and low cost.

4.3. Integrative Effects of NPs, Plant, and Animal Biochar on Heavy Metal Accumulation in the Biomass of Sunflowers Grown in Contaminated Soil

The application of a combination treatment (i.e., RSB, CMB, and ZnO NPs) followed by a single application of each treatment into soil irrigated for a long period with wastewater significantly lessened the content of the toxic metals such as Cd, Cr, Cu, and Pb in the plant biomass when compared to the untreated soil (Figure 2).This can be due to the decrease in the mobility and/or bioavailability of the toxic metals in the soils (Figure 1). Biochar has high cation-exchange capacity (CECs), which can release cations such as Ca (II) and Mg (II). Such cations can exchange with the heavy metal ions on the biochar surfaces [53]. Moreover, the application of NPs such as ZnO can minimize the negative influence of the toxic metals on the sunflower growth and productivity when compared with the untreated plants. Hussain et al. [25] found that the exogenous and soil application of ZnO NPs improved photosynthesis, growth, and yield characteristics of wheat grown in soil polluted with Cd. At the same time, Cd and Zn content in different wheat parts were reduced and increased, respectively. They also reported that Cd content in the wheat grains was reduced by 30%–77%, and 16%–78% with exogenous and soil amendment of ZnO NPs when compared to the control, respectively.

The current investigation revealed that the combination treatment (CMB + RSB + ZnO NPs) followed by a single application of CMB and/or RSB was an effective application in terms of lessening the uptake of toxic metals and metalloids by the sunflowers (Figure 2). Biochar application into the contaminated soil can minimize the toxic metal uptake by the plants by depressing the heavy metal availability through the adsorption process and pH-driven fixation reactions [24,57,58]. In addition, biochar can influence the heavy metal detoxification in the plants by modifying soil pH, toxic metals immobilization, and improvement of chemical, physical, and biological soil characteristics. Moreover, biochar, as a soil amendment, can enhance the negative charge. Consequently, this can cause a suitable rhizosphere between the cations and soil particles [57].

The application of biochar in the current investigation had a low effect on the Zn content in the plant biomass. However, it significantly reduced the content of other toxic metals such as Pb, Cd, Cu, and Cr (Figure 2). This could be because of the variation in the mobility of specific HMs. The plant biomass in our investigation contained higher Pb than Cd under different treatments (Figure 2). HMs can compete with each other for active exchange surfaces in multi-metal contaminated soils. Hence, one specific heavy metal can become more mobile than another. Moreover, the low content of toxic metals obtained from the plants grown in plots treated with biochar, when compared with the untreated plots, might be due to the precipitation of these toxic metals in the root tissue of plants [24]

4.4. Effect of Different Treatments on Growth, Yield, and Oil Quality Characteristics of Sunflowers

The effects of CMB, RSB, ZnO NP, and their combination on the growth, physiological, yield, and quality characteristics of sunflowers were positively significant at $p \leq 0.01$. In addition, those treatments significantly enhanced the sunflower tolerance against heavy metal stress. Plant growth characteristics (i.e., plant height and stem diameter), physiological characteristics (i.e., total chlorophyll, proline content, and leaf area plant^{-1}), yield, and related characteristics (i.e., head diameter, number of seeds per head, 100-seed weight, seed yield ha^{-1}) are considered the major visual observations under abiotic and biotic stresses. The obtained improvements in such characteristics might be attributed to the mixed effects of soil nutrients and moisture availability induced by both biochars. The high porosity of carbonaceous material biochar might increase the surface area of the treated soil. Consequently, there was increased surface binding of the nutrient cations and anions [20,59]. Application of biochars to soil can work as adsorbers to lessen the nitrogen from leaching, which can increase N-use efficiency [60]. Moreover, the porous structure of biochar can improve the absorbance of water [61]. However, the low values of growth and yield characteristics obtained from plants (Table 2 and Figures 3 and 4) could be linked with the high toxic metals availability in the soil postharvest (Figure 1, Table 4) and high toxic metals uptake in the sunflower plants (Figure 2, Table 4). Such causes can reduce the total chlorophyll and proline contents in the sunflower leaves (Figures 3 and 4).

Different studies have illustrated that HMs, in particular Cd and Pb, initiated stress in plants and lessened the plant growth and its biomass [1–3,26,62]. In the current study, biochar or ZnO NP application significantly improved the growth, yield, and quality of the sunflowers compared to the untreated plants. However, the combination application of CMB, RSB, and ZnO NPs could have dual effects in improving the sunflower growth and productivity. This could be due to the positive influence of biochar (i.e., CMB and RSB) in terms of reducing the soluble HMs such as Cd, Pb, and Cr in the soil (Figure 1). Consequently, the HMs decreased in the sunflower biomass (Figure 2). This could be the reason for the enhanced growth, physiology, and productivity of the plants grown in the soil treated with the combination treatment (Table 2, Figures 3 and 4). Biochar has the ability to immobilize HMs and metalloids in the soil due to metal speciation and soil pH [3,19]. The significant improvement in proline, total chlorophyll content, and leaf area per plant as a result of the combined CMB, RSB, and ZnO NPs treatment in the current study could be due to minimizing of the oxidative stress and enhancing of the enzyme activities in the plant [26,27]. ZnO NPs can be considered slow-release for Zn fertilization [53]. These NPs can avoid the sudden absorption of Zn by plants, as the high uptake of Zn can cause toxicity in plants. Therefore, foliar application of nutrients could be considered an efficient agronomic strategy for enhancing the nutrients in plants. The optimal content of Zn in the soil or plants can interfere with HMs and metalloids such as Cd. Thus, it can lessen the accumulation of HMs by plants because of the antagonistic effects for these metals on each other [63].

Recent investigation has reported that crop biochar contains biogenic silica and can rapidly release bioavailable silicon to enhance plant growth and its biomass as well as promote the biological silicon cycle in the soil [6,64]. Biochar as a soil amendment has the ability to store nitrogen by increasing NH_3^- and NH_4^+ retention. In addition, it can enhance the nitrogen bacteria, which can directly increment the soil productivity [65].

A combination treatment followed by an individual treatment of CMB resulted in the highest oil percent and yield ha^{-1} compared to RSB, ZnO NPs, and untreated plants (Table 3). Moreover, a combination treatment followed by both animal and plant biochar significantly increased the oleic acid and oleic/linoleic acid ratio when compared to the ZnO NPs or untreated plants (Table 3). This could be because of the beneficial integrative effects of the combination treatments in terms of reducing the stress physiology of HMs on the plant growth and productivity. The high quality of sunflower oil (i.e., 91.2% oleic acid and 2.4% linoleic acid, 41.1% oil percent) obtained from the plants grown with a combination treatment when compared to other treatments could be a beneficial product for human health. The high density of the oleic acid in oil is important since humans cannot synthesize such a fatty acid [6,66].

5. Conclusions

The combination treatment, which included CMB, RSB, and ZnO NPs, significantly improved the soil characteristics in terms of reducing toxic metals availability, lessened the uptake of toxic metals in the biomass, enhanced growth and physiological characteristics, increased yield, and improved quality of the sunflowers grown in soil irrigated with long-term wastewater when compared to each individual treatment. For instance, seed yield ha^{-1}, 100-seed weight, and number of seeds per head obtained from the combination treatment was greater than the results obtained from the untreated plots by 42.6%, 47.0%, and 50.4%, respectively. Furthermore, the application of the combination treatment reduced the availability of Pb, Cr, Cu, Cd, in the soil by 78.6%, 115.3%, 153.3%, and 178.5% in comparison to untreated plots post-harvest, respectively. Compared to untreated plots, it also reduced the Pb, Cr, Cu, and Cd in plant biomass by 1.13, 5.19, 3.88, and 0.26 mg kg^{-1} DM, respectively. In conclusion, the combined application of NPs and both animal and plant biochar is recommended due to the positive influence on sunflower yield and quality, and due to alleviating and minimizing the negative influence of HMs and metalloids in semi-arid regions. Further research is needed to investigate the residual effect of NPs and biochar over the long-term.

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