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Biochar and Polyhalite Fertilizers Improve Soil's Biochemical Characteristics and Sunflower (*Helianthus annuus* L.) Yield

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Abstract: Biochar (BC) applications have multiple impacts on crops' nutrient availability, growth and yield depending on the feedstock type and pyrolysis conditions. Pot and field experiments were conducted to examine the effects of biochars (BCs) prepared from three different feedstocks, *Acacia modesta* wood biochar (AWB), *Dalbergia sissoo* wood biochar (DWB) and poultry litter biochar (PLB), on soil's nutrient availability, uptake by wheat (*Triticum aestivum)* and sunflower (*Helianthus annuus*) crops and their yield attributes. All BCs were applied at the rate of 10t ha^{-1} in each treatment in both experiments, and pot and field trials were designed according to a two-factor factorial completely randomized design (CRD) and two-factor factorial randomized complete block design (RCBD), respectively. The concentration of soil NO_3-N, NH_4-N, Olsen P and extractable K increased by 98.5, 296, 228 and 47%, respectively, in the pot experiment with the application of PLB+polyhalite (PH) treatments. Similarly, in field experiments, NO_3-N, NH_4-N and Olsen P contents increased by 91, 268 and 156% under the PLB+PH treatment, respectively. However, in both experiments, soil's microbial biomass phosphorus (MBP) was significantly higher after AWB+PH treatment, and the increments were 127 and 109% while microbial biomass nitrogen (MBN) contents were 16 and 14% higher than the control under DWB+PH and AWB+PH treatments, respectively, in the field experiment. Similarly, combined PLB+PH increased the total organic carbon (TOC) of soil by 193%. Moreover, PLB+PH co-applications with PH significantly increased sunflower grain yields by up to 58% and the harvest index by 45%. Overall, no negative impact with respect to BCs was observed on the soil's nutrient content and plant growth. Hence, for immediate crop benefits and soil health, using nutrient biochar (PLB) alone or in combination with chemical fertilizers is recommended.

Keywords: biochar; polyhalite; soil fertility; nutrient uptake; crop yield

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1. Introduction

Land degradation is a globally emerging issue as it is associated with drylands, such as arid and semi-arid regions, and the conversion of these drylands into deserts is termed desertification [1]. It has been observed that about 2.6 billion people in over one hundred countries are affected by this dilemma, while the total area that falls within this range constitutes almost 33% of Earth's land surface [2]. In Pakistan, this situation is even worse because nearly 61% of the cultivated land was under severe threat of land degradation in 2006 [3]. In the most populated province, Punjab, about 1.58 million hectares (Mha) of sandy and loamy soils is known to comprise nutrient-deficient soils [4]. Growing nutrient-exhaustive crops, as well as inappropriate agricultural practices such as conventional tillage practices, and the imbalanced use of chemical fertilizers are considered key factors in land degradation [5].

Organic matter (OM) plays a vital role in soil fertility as it provides nutrients for soil [6] and enhances water-holding capacities [7] and soil aggregation [8], which consequently leads to better aeration for seed germination and the better growth of plant roots [9]. Via OM, the rate of granulation also increases [10]. Unfortunately, the average OM of Pakistani soils is less than 1% [11]. Besides OM, approximately 90% of Pakistani soils are deficient in phosphorus (P) [12] and 85–90% of soils are deficient in nitrogen (N) [13]. Low C inputs and the growth of nutrient-exhaustive crops are major reasons behind these deficiencies [14].

Biochar (BC) is a carbon-rich material that is produced by pyrolysis (a process in which the burning of biomass takes place in the absence of oxygen) of plant biomass, food waste and animal waste [15]. Biomass such as crop residues, wood chips, animal manure, composts and forestry by-products are some common raw materials in the production of BC [16]. The physical and chemical properties of BC mainly depend on the feedstock type, pyrolysis temperature and time [17,18]. The elemental composition of BC normally includes C, H, N and a few other nutrient elements in lower concentrations such as Ca, K, Mg and Na, which are also present in it. The carbon content of BC increases with the pyrolysis temperature from 300 °C to 800 °C [19]. However, BC produced via slow pyrolysis carries additional aliphatic compounds, more organic functional groups of COOH and C-OH nutrients [20] and labile carbon, which are useful for agricultural soils [21]; however, BC produced from fast pyrolysis holds fixed C [22] and extra aromatic compounds [23], which are suitable for soil C sequestration [24].

Polyhalite (PH) ($K_2Ca_2Mg(SO_4)_4{\cdot}2H_2O$) is a mineral fertilizer that is known as a polysulphate and carries four essential plant nutrients, including SO_3 at a concentration of 48%, K_2O at 14%, MgO at 6% and CaO at 17% [25]. Besides these nutrients, minor concentrations of some other elements have also been observed, such as Zn at 1.07 mg/kg, Mn at 2.43 mg/kg, Ni at 2.2 mg/kg and Ba at 4.31 mg/kg [26,27]. The market availability of this fertilizer is in both granular and powder form, which increases its suitability for a wide range of crops, including greenhouse vegetables as well as for open fields [28]. Furthermore, the salt index (SI) of PH fertilizers is 68.5 ± 10.8, which is lower than other K fertilizers such as the sulphate of potash (SOP), the muriate of potash (MOP) and the sulphate of potash magnesia (SOPM) [27]. The lower the SI, the higher the seed germination and plant growth as higher salt contents increase the osmotic potential of soil solutions [29], which affects seed and plant germination. In addition, the solubility of PH fertilizer ranges from 11.9 to 17.3 g/L at 25 °C, which is lower than other potassium fertilizers such as MOP 344 g/L and SOP g/L [30]. As PH has a low salt index, it can be applied alongside crop seeds; furthermore, the low solubility rate of this fertilizer does not affect its nutrient bioavailability [27,31]. In cases of leaching, studies suggest that K, Ca, Mg and SO_4S in PH are more freely available rather than the nutrients of SOP in clay and sandy soils [32]. Hence, nutrient availability for plants is not affected by the solubility of PH.

BC improves the soil's water-holding capacity because the structure of BC is very porous [33], allowing water to be retained in its small pores, which ultimately leads to the enhancement of the soil's water-holding capacity. The literature suggests that the application of BC could increase available water capacities by up to 22% [34]. Moreover, BC improves soil structure and increases the soil's carbon level [35]. Due to its properties of having a greater surface area and negative surface charge, these properties increase the ability of BC to adsorb more cations per unit of carbon relative to other organic amendments [36]. It has been observed that the application of rice husk BC improves the soil's aggregate stability from 8 to 36% [36]. The application of BC from medium (20 t ha^{-1}) to high (100 t ha^{-1}) range improved soil compaction by up to 22% [34]. BC significantly decreases soil bulk density while soil porosity increases on the other hand [37]. Additionally, BC applications improved N mineralization by enhancing the labile carbon pool in the soil, which increases the soil's microbial activity and N mineralization [38]. Wood BC application improves the nutrient uptake of crops and crop yields [39]. The abundance and absorption of plant nutrients such as P, K, Ca and Zn content in plant roots also increase in BC-amended soil [40,41]. BC applications minimize the runoff losses of nitrogen and phosphorus in water aquifers and also decrease the requirement of inorganic fertilizers [42]. Low levels of organic matter, nutrient availability and biological activity are the major concerns for alkaline soils in terms of crop productivity. BC effects on soil macronutrient availability have been reported in several studies, while few of them have addressed its interaction with micronutrients along with MBN and MBP under alkaline soil. Many studies documented the effect of a single BC type, but there is also a lack of research regarding the comparative effects of BCs on soil fertility parameters made from different feedstocks, such as poultry litter, *acacia modesta* and *Dalbergia sissoo*. Hence, we hypothesized that (i) combining the application of BCs and PH fertilizers will increase soil fertility status and crop yields; (ii) increments in crop growth and soil nutrient contents would be dependent on BC feedstock types; (iii) BC produced from nutrient rich feedstock, i.e., poultry litter (nutrient biochar) when applied in cultivated soil will increase sunflower yields and nutrient uptake in wheat crops.

2. Materials and Methods

2.1. Experimental Site

Pot and field experiments were conducted at the research vicinity of PMAS-Arid Agriculture University Rawalpindi, Pakistan (latitude: 33°18′6.786″; longitude: 73°12′40.5756″) during October 2021 and February 2022, respectively.

2.2. Biochar Preparation and Characterization

Three different feedstocks were used in the BC's preparation such as poultry litter, *acacia modesta* wood and *Dalbergia sissoo* wood. Initially, all three biomasses were air-dried and then heated for 4h at 400 °C in a muffle furnace (pyrolysis). The produced BCs were analyzed for some nutrient content including total organic carbon (TOC), nitrate nitrogen (NO_3-N), ammonium nitrogen (NH_4-N), Olsen P, potassium (K), microbial biomass nitrogen (MBN), microbial biomass phosphorus (MBP) and micronutrients (Table 1). For the pH and EC measurement of BCs, a calibrated pH meter and a conductivity meter were used in a suspension of 1:5 BC to water.

The ash content of all BCs was measured according to the following formula:

$$\text{Ash } (\%) = \frac{\text{D}}{\text{B}} \times 100$$

where D is the mass of residue while B is the mass of the sample after drying at 105 °C.

For TOC, BCs were heated in a muffle furnace for 5 h at 500 °C and calculated by the following formula.

$$\text{TOC } (\%) = \frac{100 - \%\text{Ash}}{1.724}$$

For the total NO_3-N estimation, BC samples were digested using a catalyst and H_2SO_4 mixture in the digester block where NO_3-N was measured using a Kjeldahl Distillation Analyzer. K and P using the ammonium heptamolybdate–ammonium vanadate method. The properties of BC varied with respect to each feedstock type (Table 1). In contrast, for micronutrient analysis, BC samples were digested by the solution of selenium powder, potassium sulfate (K_2SO_4) and sulfuric acid (H_2SO_4); then, this digested solution was filtered, and atomic absorption spectroscopy analysis was applied to examine its micronutrients (Zn, Cu, Mn and Fe). The basic properties of each biochar are provided in Table 1.

Table 1. The physical, chemical and biological properties of biochars and soils of both experiments.

Parameter	Pot Soil	Field Soil	AWB	DWB	PLB
Sand (%)	54.7 ± 3.17	51.26 ± 2.69	—	—	—
Silt (%)	23.3 ± 2.70	25.63 ± 1.92	—	—	—
Clay (%)	22 ± 2.8	23.11 ± 2.21	—	—	—
Moisture	32.2 ± 3.47	36.7 ± 3.61	—	—	—
pH	7.58 ± 0.15	7.70 ± 0.18	8.23 ± 0.55	8.51 ± 0.13	8.63 ± 0.29
EC (dS m^{-1})	0.31 ± 0.11	0.37 ± 0.13	0.71 ± 0.10	0.77 ± 0.12	0.68 ± 0.15
Ash content (%)	—	—	16.2 ± 1.51	17 ± 2.29	14.27 ± 1.73
TOC (%)	—	—	62.31 ± 4.59	55.78 ± 4.16	41.43 ± 4.13
NO_3-N (mg kg^{-1})	0.89 ± 0.09	0.94 ± 0.08	2.88 ± 0.12	2.11 ± 0.09	3.24 ± 0.17
NH_4-N (mg kg^{-1})	2.87 ± 1.17	2.62 ± 0.72	7.41 ± 1.48	8.82 ± 1.19	11.55 ± 1.79
Olsen P (mg kg^{-1})	0.87 ± 0.07	0.81 ± 0.1	3.34 ± 0.04	3.22 ± 1.12	3.41 ± 1.16
Ext. K (mg kg^{-1})	87.4 ± 4.12	84.72 ± 2.19	109.8 ± 2.72	103 ± 3.81	111.3 ± 4.26
MBN (mg kg^{-1})	8.33 ± 1.29	8.71 ± 2.19	12.55 ± 1.75	11.37 ± 2.41	13.81 ± 1.92
MBP (mg kg^{-1})	1.13 ± 0.08	1.08 ± 0.04	2.78 ± 0.05	2.64 ± 0.07	3.19 ± 0.07
Zn (mg kg^{-1})	2.12 ± 0.03	2.43 ± 1.14	3.7 ± 0.08	2.13 ± 0.09	5.10 ± 0.04
Cu (mg kg^{-1})	1.29 ± 0.02	2 ± 0.01	3.34 ± 0.03	4.14 ± 0.02	4.00 ± 0.05
Fe (mg kg^{-1})	2.31 ± 0.07	2.53 ± 0.09	4.14 ± 0.8	4.00 ± 1.21	4.20 ± 0.15
Mn (mg kg^{-1})	1.84 ± 0.1	2.19 ± 0.03	3.12 ± 0.07	2.09 ± 0.40	3.80 ± 0.80

AWB (*Acacia modesta* wood biochar), DWB (*Dalbergia sissoo* wood biochar), PLB (poultry litter biochar), EC (electrical conductivity), TOC (total organic carbon), NO_3-N (nitrate nitrogen), NH_4-N (ammonium nitrogen), P (phosphorus), K (potassium), MBN (microbial biomass nitrogen), MBP (microbial biomass phosphorus), Zn (zinc), Cu (copper), Fe (iron) and Mn (manganese). Data are the mean of 3 replications, and (±) denotes the standard error.

2.3. Pot Experiment

The pot study was conducted at the university research vicinity of Koont, where collected soil was transferred into plastic pots at a rate of 5kg per pot on a dry weight basis. Treatments of the experimental study are given in Table 2. Each BC was applied in the soil at a rate of 10 t ha^{-1} on a weight-to-weight basis. In the pot experiment, all treatments were replicated four times and laid out according to a completely randomized design (CRD). Soil sampling took place at the time of treatment application (0 day) and at the time of crop harvesting (45th day). All soil samples were collected in plastic bags and analyzed for NO_3-N, NH_4N, microbial biomass N (MBN), Olsen P, microbial biomass P (MBP), extractable K and micronutrients. The properties of the pot experiment site's soil are shown in Table 1. Wheat variety MARKAZ-19 was tested in the pot experiment. Four seeds were initially placed in each pot; after germination, seedlings were thinned out to keep three in each pot and allowed to grow for 45 days. After harvesting, plant residue was dried at 65 °C and chopped, ground and tested for micronutrients (Zn, Mn, Cu and Fe), total N, P and K.

Table 2. Treatments of pot and field experiments along with their abbreviations.

Pot Experiment Treatments	Field Experiment Treatments
Control (C)	Control (C)
Polyhalite (PH)	Polyhalite (PH)
Acacia wood biochar (AWB)	Acacia wood biochar + Polyhalite (AWB+PH)
Dalbergia wood biochar (DWB)	Dalbergia wood biochar + Polyhalite (DWB+PH)
Poultry litter biochar (PLB)	Poultry litter biochar + Polyhalite (PLB+PH)
Acacia wood biochar + Polyhalite (AWB+PH)	
Dalbergia wood biochar + Polyhalite (DWB+PH)	
Poultry litter biochar + Polyhalite (PLB+PH)	

2.4. Field Experiment

A field experiment was also conducted at Pir Mehr Ali Shah Arid Agriculture University research farm, Koont. The basic properties of the experimental site are given in Table 1. The best-performing treatments of pot experiments were tested in field experiments. Treatments of the field experiment are given in Table 2. Similarly to the pot experiment, in field experiments, BC was applied at a rate of 10 t ha^{-1}, and the effects of all these treatments were analyzed with respect to soil nutrient stocks and properties.

Sunflower was considered as a test crop in the field experiment and was grown throughout the maturity stage. At the maturity stage, crops were harvested, and soil samples were collected for analyses. Sequence analysis in the field experiment remained the same as per the pot experiment, while some extra yield analyses such as crop grain yield, biological yield and harvest index were calculated.

2.5. Analytical Methods

2.5.1. Soil Analysis

The soil's texture was calculated by a standard hydrometer where 1% solution of sodium hexametaphosphate was used for the pre-treatment of soil samples, and then a hydrometer was used to measure the soil's texture [43]. Soil pH and EC was calculated by the preparation of a soil–water suspension at rates of 1:1 and 1:2.5, respectively [44,45]. TOC was calculated by using the Walkley black test with the addition of 0.5 N ferrous sulphate solution as the titrant [45]. Soil NO_3-N was quantified by extracting soil samples using a 0.5 M K_2SO_4 solution, and the samples were analyzed on a spectrophotometer at a wavelength of 410 nm [46]. Soil NH_4-N was measured by a 2 M KCl extract solution, and samples were examined using a spectrophotometer [47]. Soil Olsen P was calculated by spectrophotometric analyses where the $NaHCO_3$ solution (0.5 M) was used as an extractant [48]. K concentrations were measured on a flame photometer, where a 1 N ammonium acetate solution was used to run the samples [49]. Micronutrients in the soil were determined by using the AB-DTPA extraction method [50]. Fumigation techniques were used to analyze soil microbial biomass P [51]. MBN was measured, where 100 mL of $NaHCO_3$ solution was used to extract three 5 g soil samples (0.5 N). The first sample of soil was used for fumigation treatments, the second sample was used for non-fumigation treatments, and the third sample was combined with phosphorus as KH_2PO_4 (according to soil weight, i.e., 25 g KH_2PO_4 for 1 g of soil) for phosphorus fixation [52]. The ammonium molybdite ascorbic acid method was used to adjust soil P, and MBN was calculated by using the following formula:

$$Microbial\ biomass\ P = E_P / K_{EP} / Recovery$$

where

$$\begin{gathered} EP = (\mathrm{PO_4} - \mathrm{P\ extracted\ from\ fumigated\ soil}) \\ -(\mathrm{PO_4} - \mathrm{P\ extracted\ from\ nonfumigated\ soil}) \\ K_{EP} = 0.40 \end{gathered}$$

Recovery was calculated by using the following formula.

$$\begin{gathered} 1 - [(PO_4 - \mathrm{P\ extracted\ from\ non} - \mathrm{fumigation\ and\ spiked\ soil}) - (PO_4 \\ -\mathrm{P\ extracted\ from\ non} - \mathrm{fumigated\ soil})] / 25 \end{gathered}$$

A Shimadzu-N chemiluminescence detector was used to measure the total N from the extracted solution [53,54], and microbial biomass N (MBN) was calculated by the following formula:

$$Microbial\ biomass\ N = E_N / K_{EN}$$

where

$$\begin{gathered} E_N = (\mathrm{total\ N\ extracted\ from\ fumigated\ soils}) \\ -(\mathrm{total\ N\ extracted\ from\ non} - \mathrm{fumigated\ soils}) \\ K_{EN} = 0.54 \end{gathered}$$

2.5.2. Plant Analysis

At harvest, randomly selected plants were used to determine the plant's height (both crops), number of leaves (wheat), spike diameter, stem diameter and 100 seed weight (sunflower). The fresh root–shoot was determined by an electrical balance. Plant samples were oven dried at 65 °C and pulverized in a grinding mill and placed in plastic bags for further analyses.

Plant material and the digestion mixture (Se powder, Li_2SO_4, H_2SO_4) were added to a digestion tube (100 g volume); then, these digestion tubes were placed in a block digester and heated at 360 °C for 2 h [46]. By using the colorimetric technique, the digested solution was used to calculate the plant's total N and P. For total N quantification, plant digest was mixed with 55 mL of NaOH (35%) and 50 mL of DI water, and after that, this solution was examined by a Kjeldahl Nitrogen Analyzer (BKN-983) [55]. The plant's total P was determined by taking 5 mL of digested material and 5 mL of color reagents (ammonium heptamolybdate–ammonium vanadate) in nitric acid. The sample's absorbance was calculated using a spectrophotometer at a wavelength of 410 nm [56]. The total K was calculated by the wet digestion method where the digestion mixture (2:1 nitric-perchloric acid) was added in plant materials on a block digester at 235 °C for 3 h; later, this plant digest material was placed in a flame photometer for K determination [57].

The harvest index of sunflower crops was calculated from the total air dry weight of plant samples and grain yield. The following formula was used for the calculation of the harvest index (HI):

$$HI = \frac{EY}{BY} \times 100$$

where HI is the harvest index, EY is the economic yield (grain yield) and BY is the biological yield [4].

2.6. Statistical Analysis

The pot experiment was designed according to a randomized complete block design (RCBD). while a completely randomized design (CRD) was used in the field for the experiment's setup. All presented data were analyzed statistically on Statistix 8.1 software. Tukey's and least significant difference (LSD) tests were used to analyze multiple comparisons among the treatments. The significance level among treatments was tested at a 5% probability level.

3. Results

3.1. Soil pH and EC

All biochar-based treatments on soil introduced variable effects. Each treatment had different results on both soil chemical parameters. Soil treated with PLB along with PH fertilizers significantly ($p < 0.05$) increased soil pH in both pot and field experiments (Table 3). In the pot experiment, there was no significant difference between C and PH alone, and the values were 7.55 and 7.58, respectively. The PLB+PH-amended treatment had significantly higher soil pH, i.e., 14% and 3%higher than the control in both experiments (Table 3), respectively. EC values varied from 0.39 to 0.84 and from 0.43 to 0.83 in pot and field experiments, respectively. Table 3 shows that soil treated with PLB+PH had significantly higher EC compared to other treatments.

3.2. Macronutrient Availability in Soil

The quantity of soil macronutrients (NO_3-N, NH_4-N, Olsen P and extractable K) varied according to BC types and application methods. Soil NO_3-N increased 98.59% and 91% over the control in pot and field experiments, respectively (Figures 1 and 2). In the pot experiment, T7 (PLB+PH) significantly increased soil NO_3-N 27% compared to the sole application of PLB (T4). Similarly, the soil NH_4-N content of pot and field experiments was 196% and 168% higher than the control, respectively.

Table 3. pH and EC content of soil under the effect of each treatment.

Treatments	Pot Experiment		Treatments	Field Experiment	
	pH	**EC**		**pH**	**EC**
C	7.55 ± 0.09 d	0.39 ± 0.02 d	C	7.68 ± 0.07 c	0.43 ± 0.04 c
PH	7.58 ± 0.15 d	0.57 ± 0.04 cd	PH	7.74 ± 0.11 b	0.69 ± 0.03 bc
AWB	7.63 ± 0.08 cd	0.66 ± 0.03 c	AWB+PH	7.86 ± 0.09 ab	0.71 ± 0.03 bc
DWB	7.71 ± 0.16 c	0.70 ± 0.03 bc	PLB+PH	7.88 ± 0.13 ab	0.76 ± 0.05 b
PLB	8.00 ± 0.21 abc	0.76 ± 0.05 b	DWB+PH	7.93 ± 0.10 a	0.83 ± 0.02 a
AWB+PH	8.14 ± 0.07 b	0.80 ± 0.02 ab			
DWB+PH	8.38 ± 0.09 ab	0.77 ± 0.06 ab			
PLB+PH	8.68 ± 0.11 a	0.84 ± 0.04 a			

pH and EC concentrations of pot and field experimental soil under each treatment. Values denote the mean with three replications. Treatment abbreviations can be found in Table 1. Small letters with values indicate significant differences among treatments at 5% probability levels, where significance was tested by a multiple comparison LSD test. (±) Standard error of the mean (n = 3).

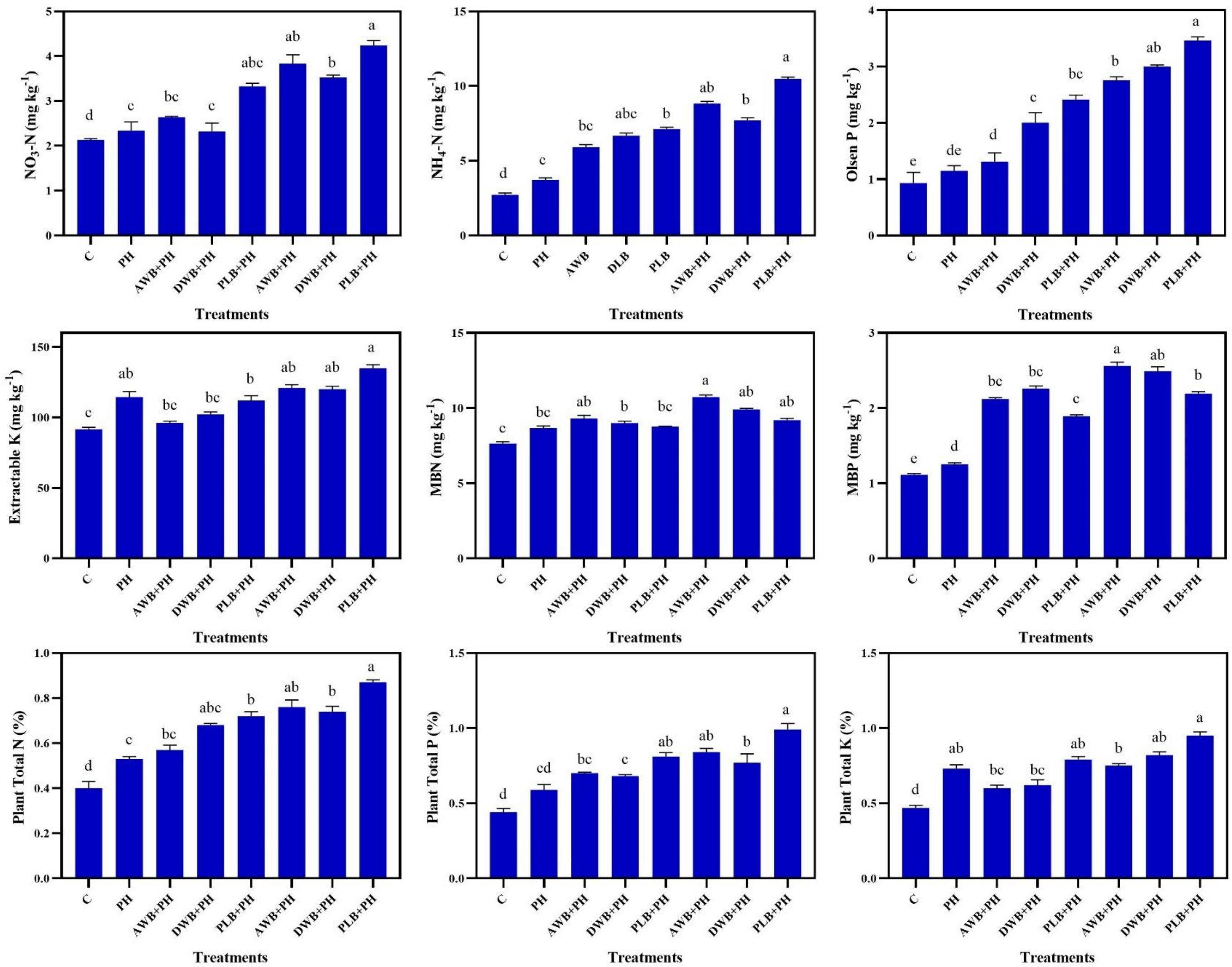

Figure 1. Macronutrient concentrations in soil and plants under each treatment. Values represent the mean with three replications. Treatment abbreviations can be found in Table 1. The small letters on bars indicate significant differences among treatments at 5% probability levels, where significance was tested by using the multiple comparison LSD test. Error bars indicate the standard error of the mean (n = 3).

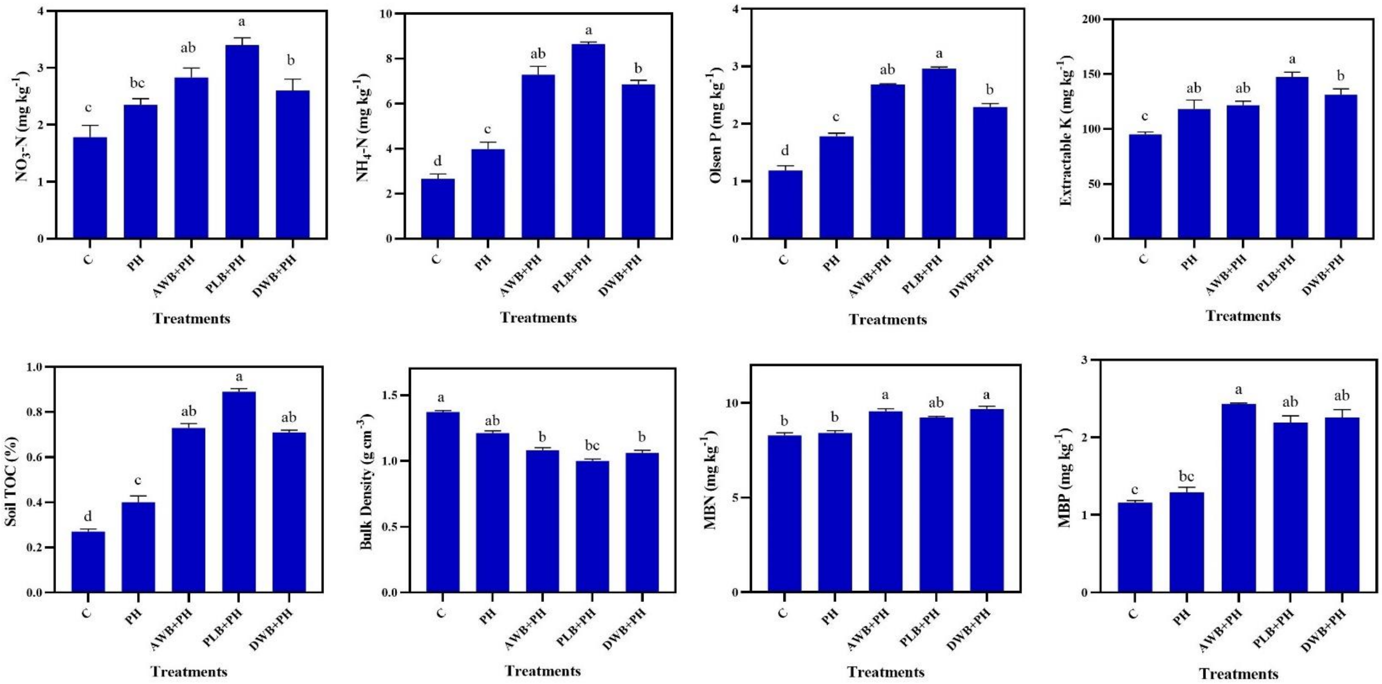

Figure 2. Effect of each treatment on soil nutrient content under field conditions. Small letters on bars indicate significant differences among treatments at 5% probability levels, where significance was tested by using the multiple comparison LSD test. Error bars show the standard error of the mean (n = 3). Treatment abbreviations can be found in Table 1.

Likewise, the soil Olsen P of the PLB+PH-amended treatment also increased by 228% in the pot experiment and 177% in the field experiment. Besides PLB+PH treatments, two other BC-based treatments, AWB+PH and DWB+PH, also increased soil Olsen P by 79% and 65% in the pot experiment while 29% and 70% percent increases were observed in the field experiment, respectively, as shown in Figure 1 and 2. Soil extractable K increased with an almost similar trend. Similarly to soil treated with PLB+PH, major impacts on the availability of soil K were observed rather than other amendments. In both experiments, PLB+PH application increased soil K content up to 47 and 51%, respectively (Figures 1 and 2). Moreover, AWB+PH and DWB+PH improved soil K contents by 32% and 38% in the pot experiment, while 37% and 47% increases were observed in the field experiment, respectively.

However, the combined application of wood-based BCs (AWB and DWB) with PH increased the soil's MBP up to 127 and 116%, respectively, in the pot experiment. Similarly, under field conditions, MBP increased by 109 and 89%, respectively, under similar treatments. In contrast, MBN's increments were 40 and 29% in the pot experiment under AWB+PH and DWB+PH treatments; however, in the field experiment, its increment was 16% under the DWB+PH treatment and 14.92% with respect to the AWB+PH amendment. The combined application of PLB with PH played a significant role in soil TOC increments where it was 193% higher than the control. However, the co-application of wood-based BCs with PH, i.e., AWB+PH and DWB+PH, increased the soil's TOC by 82.5 and 78%, respectively (Figures 1 and 2). Overall, the performance of PLB+PH was better compared to other biochar-based treatments.

3.3. Micronutrient Availability in Soil

Micronutrient availability in soil was affected by the application of BCs. PLB+PH significantly ($p < 0.05$) increased the availability of micronutrients (Zn, Mn, Cu and Fe) in pot and field experiments. In the pot experiment, the availability of Zn, Cu, Fe and Mn increased 169, 275, 97 and 186%, respectively, by the PLB+PH treatment, while in the field experiment, their availability increased by 132, 221, 56 and 132%, respectively, as shown in Table 4.

Table 4. Effect of each treatment on soil AB-DTPA extractable micronutrients under pot and field conditions.

Pot Experiment				
Treatments	**Zn (mg kg^{-1})**	**Cu (mg kg^{-1})**	**Fe (mg kg^{-1})**	**Mn (mg kg^{-1})**
C	0.82 ± 0.018 d	0.83 ± 0.015 c	1.78 ± 0.15 d	0.9 ± 0.021 d
PH	0.7875 ± 0.02 cd	1.24 ± 0.12 bc	2.15 ± 0.04 cd	1.4 ± 0.17 cd
AWB	0.965 ± 0.019 cd	1.2375 ± 0.09 bc	2.31 ± 0.09 c	2.15 ± 0.08 b
DWB	1.0425 ± 0.33 c	1.39 ± 0.11 b	2.72 ± 0.016 bc	2.3 ± 0.02 ab
PLB	1.15 ± 0.02 c	1.48 ± 0.02 ab	2.89 ± 0.10 abc	1.89 ± 0.07 c
AWB+PH	1.6775 ± 0.015 b	1.55 ± 0.03 b	3.09 ± 0.02 b	1.98 ± 0.16 bc
DWB+PH	2.035 ± 0.06 ab	1.72 ± 0.08 ab	3.26 ± 0.018 ab	2.26 ± 0.04 ab
PLB+PH	2.1125 ± 0.03 a	2.03 ± 0.015 a	3.12 ± 0.7 a	2.47 ± 0.09 a
Field Experiment				
Treatments	**Zn (mg kg^{-1})**	**Cu (mg kg^{-1})**	**Fe (mg kg^{-1})**	**Mn (mg kg^{-1})**
C	1.02 ± 0.06 c	0.98 ± 0.19 c	2.21 ± 0.02 b	1.11 ± 0.09 d
PH	1.08 ± 0.08 c	1.56 ± 0.02 bc	2.51 ± 0.19 ab	1.34 ± 0.05 cd
AWB+PH	1.42 ± 0.03 b	1.81 ± 0.10 b	3.49 ± 0.11 ab	2.06 ± 0.03 c
PLB+PH	2.37 ± 0.02 a	2.82 ± 0.08 a	3.8 ± 0.16 a	2.48 ± 0.07 a
DWB+PH	2.05 ± 0.041 ab	2.15 ± 0.06 ab	2.32 ± 0.09 ab	2.18 ± 0.13 b

Micronutrient (Zn, Cu, Fe and Mn) concentration of pot and field experimental soil under each treatment. Values denote the mean with 3 replications. Treatment abbreviations can be found in Table 1. Small letters with values indicate significant differences among treatments at the 5% probability level, where significance was tested by using the multiple comparison LSD test. (±) Standard error of the mean (n = 3).

3.4. Crop Growth and Nutrient Uptake

Plant growth and yield parameters are affected by the application of these BC-based treatments. According to the results after the amendment of treatments, it was observed that the wheat plant's height increased by 22% in PLB+PH-amended treatments in the pot experiment (Figure 1). In the field experiment, sunflower crop agronomic parameters also improved, i.e., plant height increased by 13%, stem diameter increased by 23%, head diameter increased by 26% and 100 seed weight increased by 17% in the PLB+PH-combined amendments; however, the other treatments also performed well compared to the control. Besides agronomic parameters, plant nutrient uptake also increased; for example, plant total N, P and K uptake increased by 97, 89 and 103% in the pot experiment, and they increased by 105, 168 and 115% in the field experiment, respectively (Figure 3).

3.5. Grain and Biological Yield

Sunflower grain yield varied according to BC types, but the co-application of PLB+PH significantly increased crop grain yields by 58%. In contrast, the other two treatments such as AWB+PH and DWB+PH increased grain yields by 25.55 and 11.27%, respectively, as shown in Figure 3. Similarly, the crop's biological yield was also the highest under the combination of PLB+PH, and that particular increment was 34%.

3.6. Harvest Index

BC-based treatments showed variable results in the crop's harvest index. The harvest index was significantly higher in PLB+PH-treated plots, while it was the lowest in the control. The overall harvest index of the PLB+PH-amended treatment had a 45% higher harvest index than the control (Figure 3).

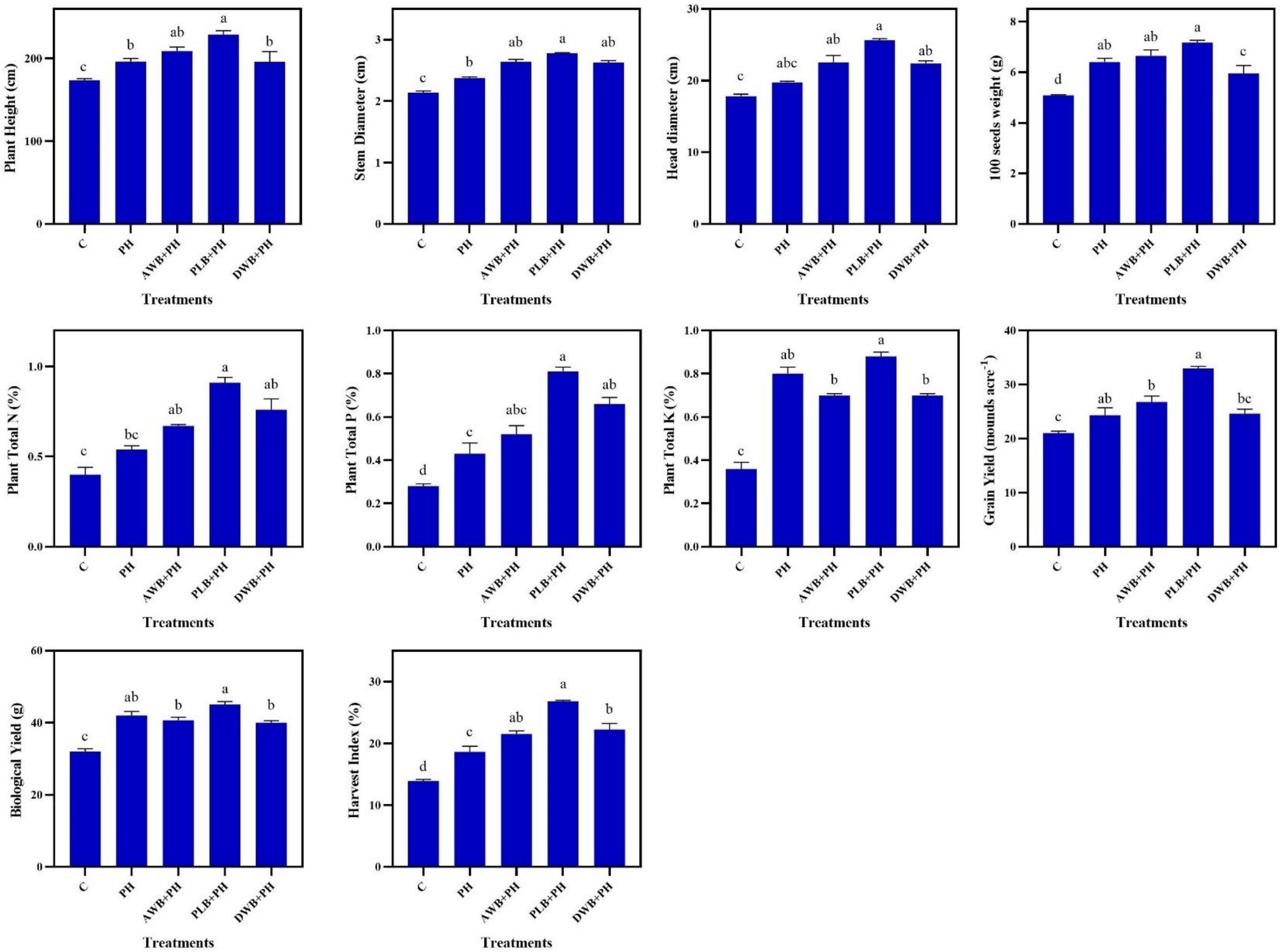

Figure 3. Effect of each treatment on plant nutrient stock and crop yield attributes under field conditions. Small letters on bars indicate significant differences among treatments at 5% probability levels, where significance was tested by using the multiple comparison LSD test. Error bars show the standard error of the mean (n = 3). Treatment abbreviations can be found in Table 1.

4. Discussion

The results of this study proved a substantial improvement in soil and plant parameters by the addition of BCs. BCs contain variable concentrations of plant nutrients, such as N, P, K, Mg, Ca, S and a few micronutrients. The feedstock's type and pyrolysis temperature are key factors in the availability of all these nutrients. All BCs (PLB, AWB and DWB) used in this study were prepared under similar pyrolytic conditions, but the variation in their effectiveness is because of their feedstock type. Moreover, the amount of cellulose and lignin affected BC's formation specifically, such as cellulose increasing the production of tar while lignin promoted char [58]. The availability of plant nutrients was affected by feedstock type: for example, the plant's total N was high in PLB treatments and limited in AWB and DWB (wood-based BC). The main reason behind the limited availability of N is due to heterocyclic structural formations in wood-based BCs [59], while animal-waste-derived BC contains hydrolyzed organic N, which can easily break down into amino acid [60]. Although the elemental composition of BC does not directly correlate with the concentration of nutrients that is actually present, the feedstock type has an impact on nutrient availability [61]. For example, PLB was high in P and K contents, and the availability of both these nutrients was higher in pot and field treatments that received PLB. Similarly, micronutrient concentrations were also higher in PLB, and their availability relative to the plant and soil was richer in PLB-treated field and pot treatments. Micronutrients are present in BC in abundant quantities, because it has been observed that BCs made from different biomasses are good sources of micronutrients, such as Mn, Zn, Cu, Co and Mo [62].

The amount of nutrients from BC that are available in the soil is also influenced by pyrolysis temperatures [63]. The volatilization of nitrogen increases with pyrolysis temperatures, and it usually starts at 400 °C, while about half of the nitrogen is lost at 700 °C [64]. Therefore, to avoid nutrient loss via volatilization, BC preparation was carried out at 350 °C (low temperature). Moreover, BC comprises crystallized phosphorus-associated minerals at low temperatures, which increases the availability of P; contrarily, at high temperatures, the availability of P is reduced [65]. BC increased the P availability for soil by increasing anion exchange capacities [66]. Moreover, at low pH levels, phosphate forms precipitates with Fe^{3+} and Al^{3+}, while it forms precipitates with Ca^{2+} and Mg^{2+} at high pH levels [67]. BC may boost the availability of P relative to plants by decreasing the production of phosphate precipitates [68]. Similar results were observed in our study where PLB+PH-combined treatment significantly increased the soil P content over all other amendments for both pot and field experiments, while the Labile form of K was also present in BC, which increased this nutrient's availability in the soil. Previous studies show that BC prepared from various biomasses (dung, plant residues and public waste) at high temperatures, i.e., >500, has limited available plant N, P and K nutrients due to mineral crystallization compared to BC prepared at <500 °C [69]. Another important perspective of BC is that it protects soil nutrients from leaching losses due to its higher surface area, CEC, negative charge and functional groups [70]. The specific surface area of AWB is 376 m^2/g [71], which is much higher than PLB; therefore, it holds more N, P and micronutrients and releases them slowly into the soil. Moreover, BC's specific surface area offers additional exchange sites for nutrient absorption [72]. Therefore, the reactive surface groups of BC (ketones, hydroxyl and carboxylic groups) decrease nutrient leaching into the soil's surface [73]. Moreover, BC has oxonium functional groups on its surfaces, which provide higher anion exchange capacities and can retain NO_3-N and phosphate [74]. The negative surface charge of BC retained NH_4^+ and K^+ via sorption [75]. BC produced at low pyrolysis temperatures carries more functional groups, such as carboxylic and hydroxyl groups, which act as binding sites and hold nutrients [20]. The results of the present study proved that different feedstock-based BCs increase soil nutrient concentrations due to additional exchange sites and their retention [59,76]. Similar results were concluded by Oladele et al. (2019), as increased BC applications significantly increased soil organic carbon (SOC), CEC and higher exchange cations, while BC applications at a low rate did not have any significant impact on SOC and CEC [77]. Similarly, the effectiveness and benefits of BC increase as time passes because freshly made BCs become hydrophobic with the passage of time; additionally, its interaction with water and oxygen in the soil helps develop more reactive sites [78], and these phenomena increase the adsorption and retention of nutrients in soil solutions [79]. Besides the physical properties of soil, BC also plays a crucial role in soil microbial contents. The results of the present study proved that wood-based BCs increased soil MBN and MBP. For example, AWB+PH treatments increased soil MBN and MBP by 40 and 127%, respectively, in the pot experiment, while under field conditions, soil MBN was richer in the DWB+PH treatment (16% higher than the control), and MBP was at its maximum under AWB+PH-based treatments. Similar results were examined by Zhang et al. [80], where they concluded that BC applications at 9 t ha^{-1} increased soil MBP from 118% to 246%. Additionally, Liu et al. [81] also stated that the co-application of BCs and compost can increase soil MBC up to 376 mg C kg^{-1}. The study of Guo et al. [82] proved that BC applications at 20 t ha^{-1} can increase soil MBN from 45.02% to 72.23% compared to the control under wheat fields.

The mechanism behind higher microbial biomass (MB) with BC addition is due to physical protection, which is provided to the microbial community by BC [83]. BC increased the nutrient supply to microbes, which helps in the decomposition of soil organic matter and also increases the sorption and retention of organic C [84]. Moreover, MB depends on pyrolysis temperatures; as the temperature rises to 600 °C, the MB becomes limited as the amount of labile carbon also starts decreasing at such high temperatures [85]. Therefore, we produced BCs at low temperatures, i.e., 400 °C for the maximum MB. Thus, higher BC applications (prepared at low temperatures) led to an increase in microbial biomass by supplying more labile C fractions and pyrolyzed feedstock [86]. Due to the availability of nutrients and their uptake by both crops (wheat and sunflower), the BC-amended soil had higher plant agronomic attributes compared to the control. Additionally, BC directly supplies plant-available nutrients to the soil after application.

BC applications increase plants' nutrient uptake because nutrients are directly supplied to the soil as labile organic compounds, and nutrient accumulation increases in plant tissues as BC decomposes with the passage of time [61]. In return, the addition of BC improved crop performance and yield. As the literature suggests, BC plays a crucial role in the soil's nutrient use efficiency [87], our study also proved the potential of BC with PH in both experiments. According to our results, BC applications boosted the availability of NO_3-N, NH_4-N, MBN, MBP, Olsen P, extractable K and micronutrients in both wheat and sunflower crops, which resulted in better crop growth and yields. Moreover, the results of our study indicated that nutrients BC or PLB had higher levels of available N, P and K for plants and soil, whereas AWB and DWB BC co-applications with PH contained higher levels of MBN and MBP, which indicates that the BC type plays an important role in improving nutrient supplies and plant growth. Therefore, according to these results, it can be stated that BC has the potential to maximize agricultural production by improving the soil's fertility status. From these pot and field trials, we can propose that BC applications with PH improved many aspects of the soil–plant system and would be a better option to cope with land degradation and food security.

5. Conclusions

Both our studies proved the significance of BC on soil nutrient stock and their availability to plants. Although the potential of BC varied according to feedstock types, PLB (nutrient BC) in combination with PH showed significant results on soil NO_3-N, NH_4-N, Olsen P, extractable K and micronutrients (Zn, Cu, Fe and Mn). Moreover, sunflower yield parameters such as biological yield and grain yield enhanced by 58% and 34%, respectively, under the same treatment. On the other hand, the co-application of AWB with PH resulted in a higher MBP (109%) and MBN (14.92%) in the field experiment compared to the control. Soil TOC also increased under BC applications; however, the co-application of PLB and PH had more significant effects (193% higher than control) contrary to AWB+PH and DWB+PH treatments. Thus, the results of our study indicated that BC's combined application with PH performed significantly better than the control under both experiments. Therefore, it can be concluded that the combined application of nutrient BC (PLB) with PH would be the most suitable measure in intensively managed soils in order to achieve high grain yields with improved soil fertility statuses.

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