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Comparative effects of biochar-nanosheets and conventional organic-amendments on health risks abatement of potentially toxic elements via consumption of wheat grown on industrially contaminated-soil

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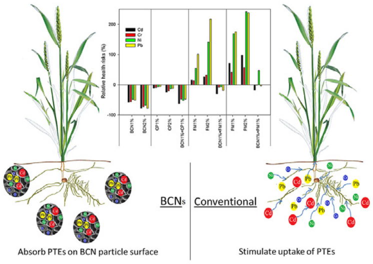
HIGHLIGHTS

- Impacts of BCNs addition on immobilization and health risks of PTEs were studied.
- BCNs have strong ability to efficiently adsorb PTEs in soil system.
- BCNs restrict the entry of PTEs into food-chain through impacts on bioavailability.
- BCNs eliminate potential hazards to human life by reducing the uptake of PTEs.

GRAPHICAL ABSTRACT



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ABSTRACT

Potentially toxic elements (PTEs) discharge to the soil environment through increased anthropogenic activities is a global threat. These PTEs can have harmful and chronic-persistent health effects on exposed populations through food consumption grown on contaminated soils. Efforts to investigate the transformation mechanism and accumulation behavior of PTEs in soil-plant system and their adverse health-effects have focused extensively in previous studies. However, limited studies address biochar nanosheets (BCNs) as a potential soil amendment to reduced humans health risks through dietary intake of food-crop grown on PTE-contaminated soil. Here, we showed how BCNs cutback health hazards of PTEs through impacts on bioavailability and phytoaccumulation of PTEs, and their daily intake via consumption of wheat. When BCNs amendment was compared with both conventional organic amendments (COAs) and control, it significantly ($P \leq 0.05$) reduced bioavailability and uptake of PTEs by wheat plants. Based on risk assessment results, the hazard indices (HIs) for PTEs in all treatments were <1, however, BCNs addition significantly ($P \leq 0.05$) reduced risk level, when compared to control. Furthermore, the cancer risks for Cd, Cr and Ni over a lifetime of exposure were higher in all treatments than the tolerable limit (1.00E-4 to 1.00E-6), however BCNs addition significantly suppressed cancer risk

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compared to control. Conclusively, our results suggest that BCNs can be used as soil amendment to reduce potential risks of PTEs through consumption of food grown in PTE-contaminated soils.

1. Introduction

Soil is one of the world's most important natural resource and fundamental component of the life-support system in terrestrial environment (Wyke et al., 2014; Yousaf et al., 2016b). Its health can be deteriorated by natural and anthropogenic activities, which include loss of organic matter and nutrients through water and wind erosion, salinization-desertification processes, soil aggregate destruction, mining and processing metal ore, and presence of extensive environmental contaminants due to rapid urbanization and industrialization (Khan et al., 2014; Peña-Fernández et al., 2014; Tiwari et al., 2011; Weldegebriel et al., 2012; Yousaf et al., 2016c). Typically, environmental pollutants of concern in soil system are inorganic elements (PTEs and artificial radionuclides), pesticides (herbicide, insecticide, fungicide etc.) and organic compounds (PAHs, PCBs, dioxins etc) (Amin et al., 2013; Hu et al., 2013; Yousaf et al., 2016b). According to the Environmental Protection Ministry of China, almost a fifth of China's soil (16.1% of total soil in China and 19.4% of its arable land) is contaminated about which 82.8% is polluted with inorganic chemicals e.g., PTEs (BBC News, 2014; Ministry of Environmental Protection of the People's Republic of China, 2014).

Soil contamination by PTEs is of great concern in the debates about food safety-security (FSS) in all over the world, due to their abundance, rapid bioaccumulation and long biological half-life, which may result remarkable human exposure and development of life-threatening health effects (Mohamed et al., 2015; Rinklebe et al., 2016; Weldegebriel et al., 2012; Yousaf et al., 2016b; Zhang et al., 2016a). The degree of immediate or chronic toxicity to these exposures can be influenced by various factors e.g., exposure pathway, absorption, distribution, metabolism, and excretion (ADME), and biotransformation in body (Augustsson et al., 2015; Liu et al., 2013). Recent investigations have suggested that diet incorporates the main exposure pathway to PTEs in humans, which alone can overshoot permissible safe-levels of these PTEs. Thus, peoples are more likely to be exposed to PTEs through dietary intake of wheat due to its higher phytoextraction potential (Liu et al., 2013; Yousaf et al., 2016b). Long-term and continual intake of PTEs through dietary route has adverse physiological and clinical health impacts (Augustsson et al., 2015; Liu et al., 2013; Zheng et al., 2007). Several studies have indicated that immoderate dose of PTEs (Cr, Cu, Zn etc.) have propensity to aggravate non-carcinogenic health hazards including acute and chronic toxicities (Choudhury et al., 2000; Farmer et al., 2011; Liu et al., 2013; Ni et al., 2011). Furthermore, it has been shown that low amount of some PTEs (As, Cd, Ni, Pb etc.) could cause severe human health risks by developing carcinogenicity from lifetime of exposure in humans (Itoh et al., 2014; Lin et al., 2013).

In order to protect the environment and human health, it is obligatory to rehabilitate, reintegrate and reclaim soils degraded by PTE-contamination. Various modern remediation strategies have progressively focused recently to mitigate/eliminate the increasing level of PTEs. One of the cost-effective and environmental friendly remediation approach is *in-situ* application of organic amendments such as biochar (BC), compost and manures, to reduce the bioavailability and uptake of these PTEs (Mohamed et al., 2015; Rinklebe et al., 2016; Yousaf et al., 2017; Zhang et al., 2016a,b). However, among these organic materials used for remediation, biochar (BC) has obtained noteworthy attention due to its tendency and impressive capability to *in-situ* stabilize PTEs (Khan et al., 2014; Zhang et al., 2016b). Recently, the potential influence of BC on soil-agronomic characteristics (pH, EC, CEC, organic carbon, soil fertility by facilitate nutrient retention, and crop productivity), mobility and phytoavailability, and transformation of PTEs in soil-plant system has been increasingly studied for sustainable agriculture (Eyles et al., 2015; Paneque et al., 2016; Yousaf et al., 2016d). Furthermore, most investigations presented that the application of BC to soil markedly decrease the uptake and accumulation of PTEs in food crops. BCNs are well appropriate to absorb/bind PTEs by capturing in soil matrix-solution due to high surface area and presence of extensive function groups on its surface (Gul et al., 2015; Upamali et al., 2015). To our knowledge, no previous study has contextualized to illustrate the ability of BCNs to eliminate phytoaccumulation of PTEs by food crops with respect to diminished health hazards.

In view of the importance of health risk mitigation, present study was conducted with following objectives: (1) to investigate the impact of BCNs addition on soil properties and wheat crop yield; (2) to assess the efficacy of BCNs as soil ameliorant on bioavailability and phyto-translocation of PTEs in soil-plant system and (3) to estimate the dietary exposure via consumption of wheat, and potential health risks (noncarcinogenic and carcinogenic risks) of PTEs influenced by BCNs.

2. Methods and materials

2.1. Preparation of BCN

The biochar nanosheets (BCNs) were synthesized from pinewood saw-dust (45.1% C, 6.6% H, 46.3% O, 0.17% N, 1.83% trace elements) as a feed-stock via thermochemical decomposition (pyrolysis) using an Isotemp muffle furnace (550 series, Fisher Scientific, Pittsburgh, PA). The complete process and pyrolysis conditions used for the production of BNCs are described elsewhere (Genovese et al., 2015; Yousaf et al., 2016a). In brief, the wood saw-dust was ground, passed through 200 mesh size sieve and soaked in 2 M HNO_3 (1:10 ratio of pinewood saw-dust: HNO_3 solution) at 80 °C for 4 h. After the dilute acid pre-treatment step, the pre-treated pinewood saw-dust was recovered by filtration using 0.22 μm pore size nitrocellulose MF-millipore membrane, dried overnight (at 65 °C) and pyrolyzed at 500 °C under continuous flow of argon (50 sccm) with temperature rising rate of 10 °C/min for 60 min retention time (Genovese et al., 2015; Yousaf et al., 2016a). The SEM and TEM image, FTIR spectra, N_2 adsorption-desorption isotherm and pore-size distribution for BCN sample are shown in Fig. S1 & S2. Furthermore, detailed physico-chemical properties of BCN are presented in Table 1.

2.2. Collection and preparation of soil and conventional organic amendments (COAs)

Rhizospheric soil sample (0–20 cm) was collected from a multi-industrial area of the city (Hefei, Anhui, China) that has been cultivated with various crops over the past few decades. The collected soil sample was dried in air-shade condition, ground,

Table 1
Physico-chemical characteristics of soil, BCNs, CP, FM and PM used in this study.

Characteristic	Unit	Soil	Organic amendments			
			BCNs	CP	FM	PM
Texture	–	Loam[a]	–	–	–	–
Sand	%	45.01 ± 2.98	–	–	–	–
Silt	%	37.76 ± 2.18	–	–	–	–
Clay	%	17.23 ± 0.94	–	–	–	–
SP[c]	%	28.67 ± 3.62	–	–	–	–
CEC[d]	$cmol_c\ kg^{-1}$	7.82 ± 1.62	–	–	–	–
OC[e]	%	0.41 ± 0.08	63.03 ± 1.35	61.34 ± 2.85	54.02 ± 2.29	50.25 ± 3.86
N	%	0.016 ± 0.007	1.52 ± 0.22	2.32 ± 0.39	2.24 ± 0.33	4.46 ± 0.81
C/N	–	26.43	41.56	26.45	24.11	11.27
pH[b]	–	6.91 ± 0.25	10.83 ± 0.15	7.94 ± 0.24	7.69 ± 0.23	7.1 ± 0.18
EC_e[f]	$dS\ m^{-1}$	3.64 ± 0.48	0.84 ± 0.21	6.82 ± 0.42	7.85 ± 1.25	7.56 ± 0.29
PTE concentrations !	Total	Available	Total metal			
	$(mg\ kg^{-1})$		$(mg\ kg^{-1})$			
Cd	1.47 ± 0.36	0.53 ± 0.17	0.88 ± 0.08	3.21 ± 0.32	4.57 ± 0.92	4.78 ± 0.41
Cr	102.35 ± 11.78	14.48 ± 2.17	2.95 ± 0.57	6.74 ± 0.85	8.55 ± 0.98	9.84 ± 1.16
Ni	67.75 ± 8.39	8.24 ± 1.14	2.16 ± 0.35	4.15 ± 1.16	4.24 ± 0.54	6.54 ± 1.24
Pb	56.32 ± 6.73	9.61 ± 1.46	0.94 ± 0.13	1.33 ± 0.95	2.13 ± 0.22	3.54 ± 0.23

[a] USDA soil classification system.
[b] pH of soil saturated paste; BCN: biochar nanosheet; CP: compost; FM: farm manure; PM: poultry manure.
[c] Saturation percentage.
[d] Cation exchange capacity.
[e] Soil organic carbon contents.
[f] Electrical conductivity of soil saturated paste extract; ! maximum permissible limits of Cd, Cr, Ni and Pb are as 0.3, 50, 50 and 100 $mgkg^{-1}$, respectively; ($n = 3$).

passed through 10 mesh size sieve (2 mm) and stored at below 4 °C to restrict the further bio-chemical changes prior to analysis. Comprehensive information about the soil characteristics (texture, saturation percentage, cation exchange capacity, pH, moisture content, organic carbon and electrical conductivity) are summarized in Table 1. However, various conventional organic materials (compost, farm manure and poultry manure) were obtained from a local nursery, air-dried at 65 °C overnight and passed through 2 mm sieve. The physico-chemical characteristics of conventional organic amendments are given in Table 1.

2.3. *Experimental design*

A pot experiment was conducted under greenhouse conditions to evaluate the comparative effects of biochar nanosheets (BCNs) and conventional organic amendments (COAs) (e.g., compost (CP), farm manure (FM) and poultry manure (PM)) on the bioavailability of PTEs, soil-plant physico-chemical characteristics, daily intake exposure and human health risks (non-carcinogenic & cancer risks) via consumption of wheat grown in PTE-contaminated soil. A total of 36 rigid polyvinyl chloride (RPVC) pots were filled with the 5 kg soil (25 cm height and 15 cm diameter) and the pots were perforated to drain excess water. The experiment was conducted in greenhouse under controlled condition and soil amendments were prepared with 1% (BCN, CP, FM and PM), 2% (BCN, CP, FM and PM), and 1% BCN combined with 1% CP, FM and PM doses of BCN, CP, FM and PM on organic-carbon (OC) basis. The treatments were applied as: (1) control (without any amendment); (2) BCN@1% (BCN: 79.35 g pot^{-1}); (3) BCN@2% (BCN: 158.69 g pot^{-1}); (4) CP@1% (CP: 81.52 g pot^{-1}); (5) CP@2% (CP: 163.03 g pot^{-1}); (6) BCN@1% + CP@1% (BCN: 79.35 g pot^{-1} + CP: 81.52 g pot^{-1}); (7) FM@1% (FM: 92.56 g pot^{-1}); (8) FM@2% (FM: 185.11 g pot^{-1}); (9) BCN@1% + FM@1% (BCN: 79.35 g pot^{-1} + FM: 92.56 g pot^{-1}); (10) PM@1% (PM: 99.50 g pot^{-1}); (11) PM@2% (PM: 199.01 g pot^{-1}); and (12) BCN@1% + FM@1% (BCN: 79.35 g pot^{-1} + PM: 92.56 g pot^{-1}), with three replications of each using a completely randomized design. The recommended dose of chemical fertilizers (½ of N with full dosage of P and K as the basal dose: 0.22 g N pot^{-1}, 0.36 g P pot^{-1} and 0.17 g K pot^{-1}, respectively) was applied to soil and mixed-well. Remaining ½ of nitrogen (N) was applied in two splits (¼ of nitrogen at first irrigation (0.11 g N pot^{-1}) and ¼ of nitrogen at milking stage (0.11 g N pot^{-1})) (Yousaf et al., 2016a, 2016d). Wheat seeds were imbibed with H_2O_2 solution (30%) for 15 min to sterilize and enhance germination followed by rinsed with deionized water (Khan et al., 2014). These seeds were then incubated at 28 °C in glass-distilled water overnight under the supply of air (using an ultra-silent high out energy efficient aquarium air pump: RS electrical, Northants, NN17 9RS, UK). After the pretreatment, 10–15 seeds were placed in each pot and irrigated with deionized water. Subsequently, sprouts were diminished to the four uniform plants per pot as the final stand when seedlings have 3–4 true leaves. The pots were randomized on alternate weeks to make sure the uniform distribution of light and to reduce positional errors. At the starting of reproductive period, photosynthesis rate, transpiration rate, stomatal conductance and flag leaf area were measured as physiological characteristics.

2.4. *Post-experiment preparation of plant and soil samples*

At the termination of experiment, plants were harvested at 3 cm above from the soil surface and agronomic parameters (plant height, number of tillers, grain and shoot weight) were also measured. The collected samples (soil and plant samples) were packed in polyethylene bags, sealed with tape and carried to the laboratory. The soil samples were air-dried in shed (under shade) for 2–3 days, hand-grounded with agate mortar and pestle, and sieved to $<$ 2 mm. One-fourth soil sample of each was oven-dried at 105 °C for 24 h, ground in wiley mill (Thomas Scientific, Swedesboro, NJ, USA) and sieved through a 200 mesh (75 μm). Furthermore, the shoot and grain samples of wheat were washed with tap water to remove dust particles and then carefully rinsed with deionized water. The clean samples were allowed to air-dry at room temperature before the oven drying in a hot air cabinet dryer at 65 °C till the constant weight. After being powdered by a clean wiley mill (Thomas Scientific, Swedesboro, NJ, USA), all the samples were stored at room temperature prior to chemical analysis.

2.5. Plant and soil analysis

To determine the soil texture (sand, silt and clay), hydrometer method developed by Agricultural Chemistry Committee of China (ACCC, 1983) was used (Agricultural Chemistry Committee of China, 1983). However, gravimetric method was used to determine soil moisture content (SMC) and saturation percentage (SP) using a hot-air cabinet dryer at 105 °C ("Soil Mechanics Level 1, Module 3, USDA Textural Soil Classification," 1987). The ammonium acetate (NH_4OAc) method (Chapman, 1965) was used for the determination of soil CEC as the amount of exchangeable cations (per dry weight) that a soil is capable to hold. Total soil organic carbon content (OC) was measured using modified Walkly-Black method (Matus et al., 2009), involved wet oxidation of organic matter by potassium dichromate ($K_2Cr_2O_7$). To measure soil pH, an electrometric procedure (Method 9045D) was used described by Environment protection Agency (US EPA, 2015). Electrical conductivity (EC) of the soil saturated paste extract was measured using Fisher Scientific™ accumet™ AP65 Portable Conductivity Meter (Thermo Fisher Scientific. Waltham, MA, USA).

To analyze the total concentration of Cd, Cr, Ni and Pb, 0.5 g dried-powdered plant samples including shoot and grain, were digested in closed-vessels (pressurized) microwave heating system (QLABPro Close Vessel Microwave Digestion System, Questron Technologies Corporation. Mississauga, Ontario, Canada) using a mixture of 30% H_2O_2 and concentrated HNO_3. While, 0.5 g of prepared soil samples were digested with aqua-regia on a hot-plate (at 220 °C) and allowed to evaporate nearly to dry state (Khan et al., 2014; Yousaf et al., 2016b). Each sample was then diluted to 50 ml with deionized water followed by filtration through 0.22 μm pore size nitrocellulose MF-millipore membrane. Furthermore, the air-dried soil samples were extracted with 0.05 M Ethylenediamine-tetraacetic acid (EDTA) extraction solution (solution: soil = 20:1) to determine the bioavailable concentration of PTEs (Khan et al., 2014). The PTEs concentrations in plant and soil samples were measured by inductively coupled plasma mass spectrometry (ICP-MS).

2.6. Dietary exposure and health risk assessment

Health risk appraisal and/or health risk assessment is a key process to evaluate the probability and kind of deleterious impact in humans, who may be exposed to contaminants in the present-day or future. There are several PTE-exposure pathways to humans e.g., ingestion and dermal contact through soil, oral and dermal intake of water, inhalation through air, and diet through the food chain. However, dietary intake via food consumption is one of the most significant and extensive exposure route of PTEs in humans which alone can exceed the toxicological safe limits (Liu et al., 2013; Peña-Fernández et al., 2014; Yousaf et al., 2016b, 2016c). The risk assessment models developed by US-EPA are well known to calculate the chronic non-carcinogenic hazards and incremental lifetime cancer risks for humans (US EPA, 1989). Here, we used these models to predict/estimate daily intake exposure, chronic non-carcinogenic and lifetime carcinogenic risks of PTEs for human associated with food chain via wheat consumption and detailed descriptions of models (Eqs. S1-S5) are given in supplementary information.

2.7. Quality control and data analysis

In order to assure the precision of data, certified standard material (GBW07406 (soil), GBW07604 GSV-3 (plant), from the National Center of Standard Materials of China) was included in every batch of samples analyzed. The recovery rates (94.5–103.7%) for all the selected PTEs in the standard reference materials including soil and plants were within the range of the certified limitations. The recovery was ranged between 91.3 and 103.5% when digested solutions with known concentrations of PTEs were used. The acceptable precision was within ±5 wt% for all the selected PTEs. Each sample was analyzed thrice and accuracy of ICP-MS was verified by testing two standards, after every fifteen (15) samples. The calibration curves for all PTEs were linear and within the range ($R^2 > 0.99$) showing that the analytical method for PTE determination was accurate and consistent. Additionally, the descriptive data was statistically analyzed by using PASW Statistics 18 software (SPSS Inc., Chicago, IL, USA) and Sigmaplot 11.0 (Systat Software Inc., San Jose, California, USA) was employed for all the graph plotting.

3. Results and discussions

3.1. Influence of BCNs on soil OC, CEC, pH and EC

Addition of BCNs and COAs to soil markedly influenced post-experiment soil characteristics including OC, CEC, pH and EC and their comparisons with the control are presented in Fig. 1. The highest value of soil OC (2.28 times) was observed with the application of BCN when applied at a 2% OC basis (BCN2%), followed by mixed treatments of BCN with COAs (BCN1%+CP1%, BCN1%+FM1% and BCN1%+PM1%), individual treatments of COAs at 2% (CP2%, FM2% and FM2%), BCN1%, and individual treatments of COAs at 1% (CP1%, FM1% and FM1%), respectively. The efficiency of the treatments in enhancing soil OC contents was following the decreasing order: BCNs < CP < FM < PM < control. Moreover, soil OC contents significantly ($P \leq 0.05$) enlarged from 0.76 ± 0.24% to 1.21 ± 0.37%, 0.68 ± 0.22% to 0.89 ± 0.28%, 0.71 ± 0.19% to 0.85 ± 0.25% and 0.68 ± 0.19% to 0.81 ± 0.09% with increase in application rates from 1 to 2% (OC basis) of BCNs, CP, FM and PM compared with the control (0.53 ± 0.18%), respectively. Furthermore, combined applications of BCNs together with COAs (in a ratio of 1:1) enhanced soil OC contents compared with the control as well as with individual application of COAs (CP, FM and PM) at a 1% OC basis.

Likewise, remarkable increase ($P \leq 0.05$) in the CEC was noticed in the soils amended with BCNs and COAs compared with the control, exception with CP, FM and PM at a 1% OC basis by 10.05 ± 1.72, 9.15 ± 0.67 and 8.86 ± 1.04 $cmol_c\ kg^{-1}$, respectively.

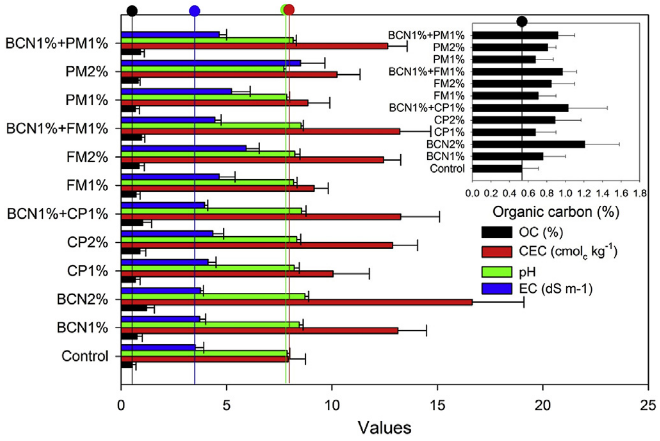

Fig. 1. Organic carbon content, cation exchange capacity, pH and electrical conductivity of post experiment soil influenced by BCNs and COAs (CP, FM & PM). Various color lines indicate the values of control. Error bars represent the standard deviation (n = 3). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

The highest value of CEC (13.13 ± 1.35 $\text{cmol}_c\ \text{kg}^{-1}$) was noted when BCNs was applied at a 2% OC basis compared with the control (7.92 ± 0.82 $\text{cmol}_c\ \text{kg}^{-1}$). Similarly, the application of BCNs individually (BCN1% and BCN2% as 8.45 ± 0.18 and 8.72 ± 0.17, respectively) and combined with COAs (BCN1%+CP1% and BCN1%+FM1% as 8.56 ± 0.21 and 8.53 ± 0.12, respectively) markedly ($P \leq 0.05$) increased pH values except of BCN%1 + PM1% and individual application of COAs (1% and 2% OC basis). The maximum value of pH (8.72 ± 0.17) was noted after addition of 2% BCN compared with the control (7.87 ± 0.13). Unlike other soil chemical properties, no remarkable difference was observed in EC of soils amended with BCNs (BCN1% and BCNs2%: 3.73 ± 0.28 and 3.76 ± 0.15 dS m^{-1}, respectively) compared with the control (3.51 ± 0.41 dS m^{-1}). However, both PM and FM markedly increase EC having a maximum value of 8.51 ± 1.15 dS m^{-1} with addition of PM2% followed by FM2% (5.93 ± 0.62).

Present results are in the harmony with the investigations of Zhang et al. (2016a), which described that the addition of biomass-derived biochars significantly enhanced the soil chemical properties (OC, pH and EC by 1.67–2.34, 1.01 to 1.07 and 0 to 1.62 times). In addition, Mohamed et al. (2015) showed that the soils amended with 0.5 and 1.5% BC remarkably increased OC, CEC, pH and EC by 9.25 and 18.84 mg kg^{-1}, 10.36 and 15.58 $\text{cmol}_c\ \text{kg}^{-1}$, 0.66 and 1.82 times, and 1.32 and 2.36 dS m^{-1}, respectively, in soil planted with cabbage. Higher OC contents in BCN amended soil may be attributed to the more stability of BCNs due to its complex aromatic structure having strong C—C double bonds (Naisse et al., 2013; Singh et al., 2012). Moreover, the additional contribution to the higher OC contents with BCN addition may be associated with the remarkably lower decomposition rate of BCNs compared with the COAs having the same OC contents marking the beginning (Yousaf et al., 2016a). Additionally, previous studies explained that thermochemical decomposition of organic material in the absence of oxygen (pyrolysis) had a prominent role in improving stability and enhancing number of surface functional groups, which could be responsible to greater pH value, and higher surface area and CEC in soil (Uchimiya et al., 2011; Yousaf et al., 2016d). During pyrolysis, the basic cations (calcium (Ca^{+2}), magnesium (Mg^{+2}), potassium (K^{+1}) and sodium (Na^{+1})) perhaps converted into certain ionic salt of an alkali metal (oxides, hydroxides and carbonates) (Houben et al., 2013; Tang et al., 2013). The dissolution of these ionic salts of an alkali metal (alkaline substances) in soil solution made the BCNs as a liming material to raise soil pH. Furthermore, Fellet et al. (2014) described that the relative concentration of positively-charged ions and negatively-charged ions in BCNs may influence the total EC and pH of the soil.

3.2. Influence of BCNs on agro-physiological characteristics

Plant growth, yield and physiological traits were markedly improved by addition of BCNs and COAs (Fig. 2). All applied treatments (BCNs, COAs and their mixtures) significantly ($P \leq 0.05$) increased number of tillers, whenever maximum rise (5.75 ± 0.56 tillers plant^{-1}) was observed in BCN1%+CP1% amended treatment followed by BCN2%, CP2% and BCN1%+FM1% with average values of 5.28 ± 0.34, 5.14 ± 0.85 and 5.13 ± 0.57 tillers plant^{-1}, respectively, compared with the control (2.90 ± 0.55 tillers plant^{-1}). Likewise, grain yield increased remarkably ($P \leq 0.05$) with all treatments having highest value of 14.57 ± 1.15 g pot^{-1} in BCN1%+CP1% amended treatment which was 1.48 times higher than that of control. Where the BCNs were applied alone at the rate of BCN1% and BCN2%, the average grain yields were increased by 1.40 and 1.43 times compared with the control (9.84 ± 1.07 g pot^{-1}), respectively. Moreover, when BCNs was applied as mixed treatment together with COAs, the grain yield remarkably increased compared with the individual application of COAs. In the same way, all the treatments remarkably ($P \leq 0.05$) enhanced shoot weight of wheat plants, the maximum increases in shoot weight was observed in treatment amended with BCN1%+CP1% (44.85 ± 3.29 g pot^{-1}) followed by BCN2%, CP2%, BCN1%+FM1% and BCN1% (44.27 ± 2.52, 43.24 ± 2.87, 41.82 ± 2.36 and 41.69 ± 3.43 g pot^{-1}, respectively). Similarly, plant height markedly ($P \leq 0.05$) increased in all treatments with highest values of 110.75 ± 2.85 and 109.52 ± 4.91 cm for CP2% and BCN1%+CP1% compared with the control (97.45 ± 5.15 cm), respectively. Furthermore, plant height was enlarged from 107.34 ± 4.21 to 110.75 ± 2.85 cm, and 103.64 ± 5.81 to 107.25 ± 5.34 cm with increase in application rates from 1 to 2% (OC basis) of CP and PM, respectively. However, the plants height was reduced from 107.86 ± 2.54 to 106.55 ± 3.16 cm, and 106.35 ± 3.46 to 105.98 ± 4.85 cm with increase in application rates from 1 to 2% (OC basis) of BCNs and FM, respectively.

In the case of leaf area, remarkable increase ($P \leq 0.05$) was noted after addition of BCNs and COAs in soil compared with the control. The highest leaf area (51.47 ± 1.75 cm^2) was noted in BCN1%+CP1% amended treatment followed by BCN2% and CP2%. Furthermore, leaf area was increased from 44.15 ± 2.14 to 50.95 ± 2.65 cm^2 with rise in application rates from 1 to 2% (OC basis) of BCNs, respectively. Likewise, the stomatal conductance, photosynthetic rate and transpiration rate of the flag leaves of wheat plant all increased markedly in the amended treatments (BCNs and COAs) compared with the control. The maximum increment of 0.21 ± 0.02, 9.6 ± 0.03 and 0.49 ± 0.06 $\mu\text{M m}^{-2}\ \text{S}^{-1}$ was noted in stomatal conductance, photosynthetic rate and transpiration rate, when BCNs was applied as mixed treatment with CP as BCN1%+CP1%. Furthermore, stomatal conductance, photosynthetic rate and transpiration rate were enlarged from 0.17 ± 0.03 to 0.21 ± 0.03, 0.16 ± 0.02 to 0.19 ± 0.04, 0.13 ± 0.02 to 0.15 ± 0.03 and 0.13 ± 0.02 to 0.16 ± 0.03 $\mu\text{M m}^{-2}\ \text{S}^{-1}$, from 8.4 ± 0.08 to 9.2 ± 0.09, 8.3 ± 0.05 to 9.4 ± 0.06, 7.4 ± 0.04 to 7.6 ± 0.02 and 7.2 ± 0.05 to 7.8 ± 0.06 $\mu\text{M m}^{-2}\ \text{S}^{-1}$, and from 0.47 ± 0.04 to 0.47 ± 0.05, 0.41 ± 0.02 to 0.48 ± 0.07, 0.37 ± 0.04 to 0.41 ± 0.06 and 0.34 ± 0.04 to 0.39 ± 0.02 $\mu\text{M m}^{-2}\ \text{S}^{-1}$, with increase in application rates from 1 to 2% (OC basis) of BCNs, CP, FM and PM, respectively. Additionally, when BCNs was applied as mixed treatment along with COAs (CP, FM and PM), all the physiological traits including leaf area, stomatal conductance, photosynthetic rate and transpiration rate markedly improved compared with the individual addition of COAs (CP, FM and PM).

Jointly, these findings described that addition of BCNs to soil was effectual to improve agro-physiological characteristics in an efficient manner. These results were consistent with previous studies, which showed significant increment in growth and yield related traits of maize, wheat, rice, sunflower, ryegrass, apple and tomato with the application of various biochars (Eyles et al., 2015; Khan et al., 2014; Paneque et al., 2016; Yu et al., 2016). In this study, the improved plant growth and grain yield following the application of BCN was comparable to finding of Akhtar et al. (2015), who showed remarkable increase in wheat growth and physiology after the addition of BC. Improved agro-physiological permanents with the addition of BCN to soil may be attributed to various soil physicochemical characteristics (soil pH, CEC, OC etc.). Wang and coworkers reported similar trend in rice and wheat cropping system, where the application of BC markedly improved grain yield and biomass (Wang et al., 2012).

3.3. Influence of BCNs on bioavailability of PTEs

The total and available contents of PTEs (Cd, Cr, Ni and Pb) in soil used for this experiment and their maximum permissible limits set by State Environmental Protection Administration, China are given in Table 1. The efficacy of applied treatments on the bioavailability

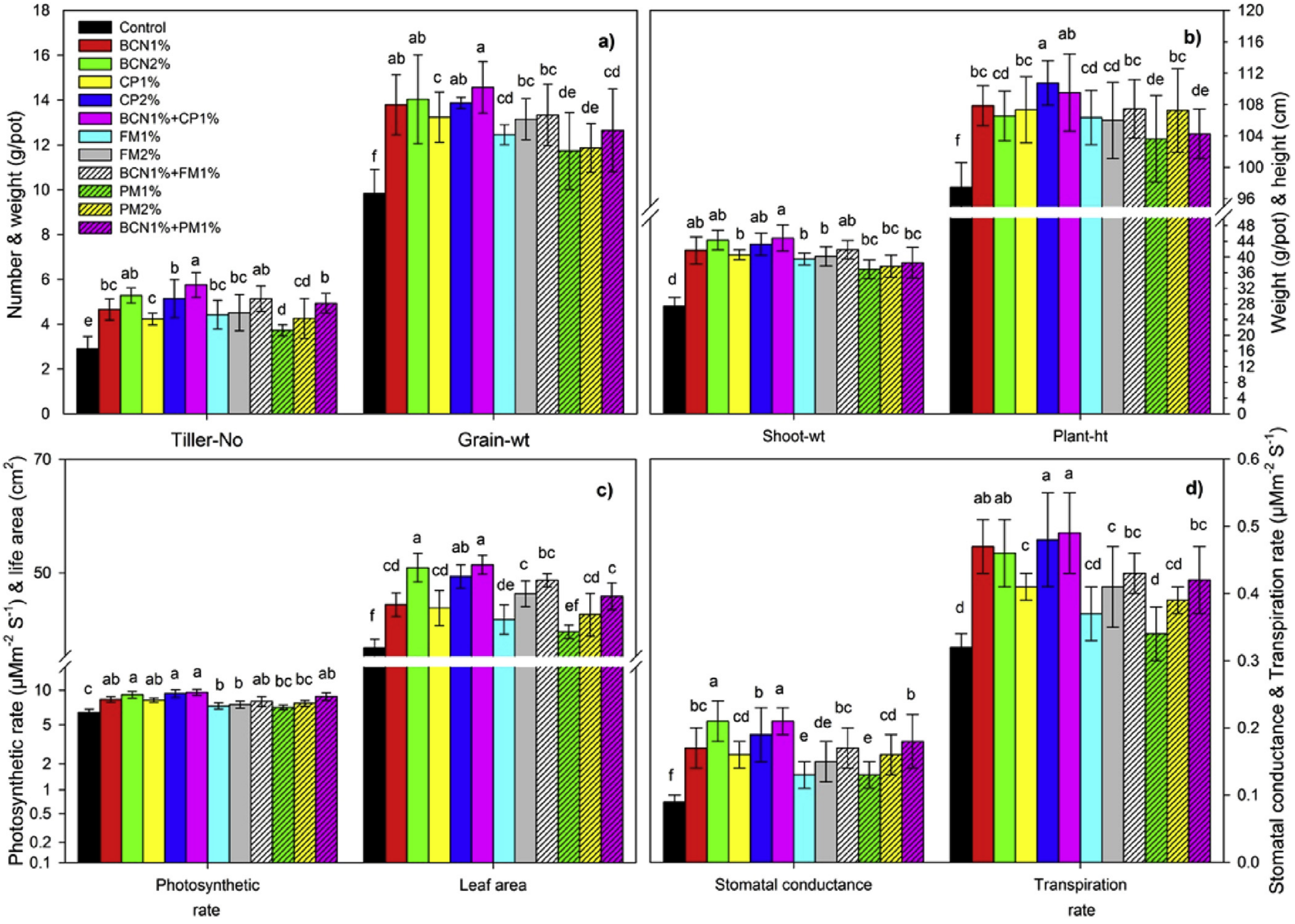

Fig. 2. Effect of BCNs and COAs (CP, FM & PM) on wheat growth and physiological characteristics: a) number of tiller and grain weight per pot; b) shoot weight per pot (excluding grain weight) and plant height (cm); c) photosynthetic rate and flag leaf area; d) stomatal conductance and transpiration rate. Error bars represent the standard deviation (n = 3).

of PTEs in the soils at the termination of the experiment and their relative differences (increase or decrease) over control are presented in Fig. 3. The extraction solution of EDTA can be used to represent reactive pool (bioavailable form) of PTEs in soils (Zhang et al., 2016b). Integration of BCN with soil was effectual in mitigating the mobility and bioavailability of PTEs, furthermore higher

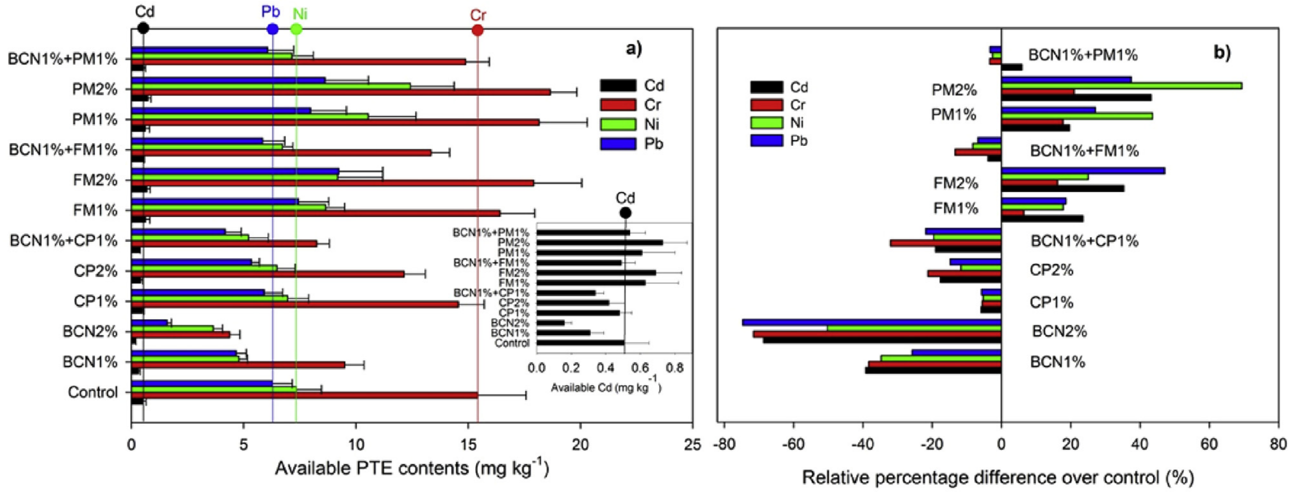

Fig. 3. Bioavailability of potentially toxic elements: (a) available PTE contents (Cd, Cr, Ni and Pb) influenced by BCNs and COAs (CP, FM & PM). Various color lines represent the available (Cd, Cr, Ni and Pb) contents of control soil; (b) relative percent difference (increase or decrease) of available PTE contents over control. Error bars represent the standard deviation (n = 3). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

application rate was more effective (Fig. 3a). Bioavailable concentrations of Cd, Cr, Ni and Pb were declined from 0.31 ± 0.08 to 0.16 ± 0.04 mg kg^{-1}, 9.51 ± 0.85 to 4.38 ± 0.45 mg kg^{-1}, 4.79 ± 0.38 to 3.65 ± 0.41 mg kg^{-1}, and 4.66 ± 0.45 to 1.59 ± 0.19 mg kg^{-1}, with increase in application rates from 1 to 2% of BCN, respectively, compared with the control (0.51 ± 0.14, 15.42 ± 2.15, 7.34 ± 1.12 and 6.28 ± 0.88 for Cd, Cr, Ni and Pb, respectively). Mixed treatments of BCN along with COA (BCN1%+CP1%, BCN1%+FM1% and BCN1%+PM1%) markedly reduced Cd (0.34 ± 0.05, 0.49 ± 0.08 and 0.54 ± 0.09 mg kg^{-1}), Cr (8.25 ± 0.56, 13.35 ± 0.82 and 14.89 ± 1.04 mg kg^{-1}), Ni (5.21 ± 0.88, 6.73 ± 0.46 and 7.15 ± 0.95 mg kg^{-1}), and Pb (4.18 ± 0.71, 5.85 ± 0.98 and 6.07 ± 1.16 mg kg^{-1}) compared with the individual COAs (CP, FM and PM) amended treatments, respectively.

Overall, our results indicated that BCN amended treatments markedly decreased bioavailability of PTEs with the exception BCN1%+PM1%, where available Cd concentration was slightly higher (5.88%) than that of control (Fig. 3b). The remarkable effectiveness of BCN in mitigating the mobility and bioavailability of PTEs in amended treatments may be attributed to higher values of soil OC, pH and CEC (Fig. 1). These results are in the agreement with previous findings of Khan et al. (2014), Mohamed et al. (2015) and Zhang et al. (2016a), which described that EDTA extractable (bioavailable) PTE concentrations were remarkably reduced in biochar amended soils compared with the control. In addition, the mitigation of PTE extractability increased because of the increase in application rate of BCN. Nevertheless, our findings represented that the impact of BCNs on the bioavailable concentration of PTEs varied, depending on the types and total contents of PTE, and physiochemical characteristics of BCN (Zhang et al., 2016a,b).

Decreased PTE mobility and phytoavailability are strongly associated with changes in CEC and OC in BCN amended soil (Zheng et al., 2012). Greater OC contents having very high CEC makes BCN a perfect and an effective material for PTE absorption in soil system (Yousaf et al., 2016a). Previously, it has been described that the higher the CEC of BC amended soil, the higher the PTE adsorption due to dense and large number of exchange sites on the surface of biochar (Harvey et al., 2011). In addition, rise in soil pH has been reported as a most prompted parameter for PTE sorption process (Zheng et al., 2012). Kołodyńska et al. (2012) explained that the bioavailability of PTEs in soil strongly depends on ionization and speciation processes, which are linked to pH-induced variations in the adsorbent surface charge. Furthermore, the surface functional groups produced during pyrolysis also played a significant role in PTE adsorption by making organometallic complexes (Uchimiya et al., 2011).

3.4. *Influence of BCNs on accumulation of PTEs in soil-plant system*

Uptake and phytoaccumulation of PTEs (Cd, Cr, Ni and Pb) by wheat plant markedly ($P \leq 0.01$) reduced with BCN addition compared with the control (Fig. 4). The accumulation of PTEs in above ground plant tissues depends mainly on the available concentration of PTEs, the lower the availability, the lower the phytoaccumulation, and vice versa. The efficiency of BCNs in mitigating PTE adsorption in soil system improved with the higher application rate. The accumulation of PTEs decreased from 3.51 ± 0.16 to 1.64 ± 0.48 (Cd: mg kg^{-1}), 23.35 ± 1.45 to 11.24 ± 0.95 (Cr: mg kg^{-1}), 13.71 ± 0.85 to 6.85 ± 0.77 (Ni: mg kg^{-1}) and 5.35 ± 0.76 to 2.19 ± 0.38 (Pb: mg kg^{-1}), and 0.49 ± 0.15 to 0.25 ± 0.16 (Cd: mg kg^{-1}), 1.53 ± 0.46 to 0.95 ± 0.25 (Cr: mg kg^{-1}), 1.24 ± 0.22 to 0.77 ± 0.18 (Ni: mg kg^{-1}) and 0.45 ± 0.15 to 0.20 ± 0.08 (Pb: mg kg^{-1}) in wheat shoot and grain with increase in application rate of BCN from 1 to 2%, respectively.

The mixed treatment of BCN with CP (BCN1%+CP1%) markedly diminished accumulation of Cd (by 32.63 and 62.61% in shoot and grain, respectively), Cr (by 37.57 and 47.70% in shoot and grain, respectively), Ni (39.83 and 52.28% in shoot and grain, respectively) and Pb (38.88 and 47.82% in shoot and grain, respectively) compared with the control (Cd, Cr, Ni and Pb as 6.16 ± 0.92 and 1.15 ± 0.15 mg kg^{-1}, 38.64 ± 4.14 and 3.48 ± 0.85 mg kg^{-1}, 21.49 ± 2.18 and 2.41 ± 0.48 mg kg^{-1}, and 8.59 ± 1.45 and 0.92 ± 0.11 mg kg^{-1} for shoot and grain, respectively). Although, the phytoaccumulation of PTEs in the mixed treatments of BCN with FM and PM (BCN1%+FM1% and BCN1%+PM1%) were non-significant, however these slightly reduced accumulation of PTEs in both shoot and grain except for Ni in grain with BCN1%+PM1% amended treatment. The soil-to-shoot transfer and shoot-to-grain translocation of PTEs were also markedly influenced by BCN addition (Fig. S3).

Our results are consistent with previous findings, which explained that the BC addition decreased transfer of PTEs in soil-to-plant system and diminished their accumulation in plant tissues (Mohamed et al., 2015; Yousaf et al., 2016d). Similarly, Khan et al. (2014) reported remarkable decrease in the accumulation of PTEs in rice tissues with the addition of sewage sludge biochar (SSBC). The reduction in phytoaccumulation of PTEs in plant tissues could be attributed to the lower mobility and availability of PTEs in BCN amended soils due to higher adsorption of PTEs onto BCN particles. In addition, uptake and acquisition of PTEs by plant tissues in BCN amended soils perhaps strongly influenced by various physicochemical mechanisms, which control the solubility/mobility, phytoavailability and transfer of PTEs in soil-plant system (Zhang et al., 2016a,b). The most influential variables for the immobilization of PTEs in BNC amended soils are the surface area and CEC, which can affect absorption and accumulation of PTEs in different tissues of wheat plant.

According to present results, the diminished concentrations of PTEs in plant tissues influenced by BCNs could be associated with large number of exchange sites and higher surface area (Houben et al., 2013; Mohamed et al., 2015). It has been mentioned previously that the availability of PTEs in BCN amended soil decreases at high pH value. Uchimiya et al. (2011) described that increasing pH contributed to oxygen containing surface functional groups. Furthermore, BCN contain large number of negatively charged surface functional groups, which can play central role in adsorption of PTEs in soil and as a consequent decreased phytoavaialabity and uptake of PTEs by plants (Mohamed et al., 2015). Zhang et al. (2016a) discussed that the “dilution effect” because of increased biomass also contribute to reduce phytoaccumulation of PTEs in plant tissues in BC amended soils. Several other factors including dissolved organic carbon (DOC) and changes in microbial community-level physiological parameters could also affect availability and phytoaccumulation of PTEs by wheat plant in BCN amended soils (Steinbeiss et al., 2009; Xu and Chen, 2013).

3.5. *Daily intake of PTEs and their health risks influenced by BCNs*

In order to estimate the mitigating impact of BCNs on PTE exposure through wheat consumption and their associated health risks to humans, EDI_{wheat}, HQ_{wheat} and CR_{wheat} were calculated using the methodology described by US-EPA (US EPA, 1989). Estimated daily intake, hazard quotient indices and cancer risks are given in Table S1, Table 2, respectively. The estimation of daily intake exposure of PTEs was done by using the average amount of wheat that consumed on a daily basis (Liu et al., 2013; Yousaf et al., 2016b). Both individual application of BCN and its mixed treatment with CP (BCN1%+CP1%), significantly ($P \leq 0.01$) diminished average daily intake of PTEs compared with the control. The results clearly show that the EDI_{wheat} values for Cd, Cr, Ni and Pb were markedly

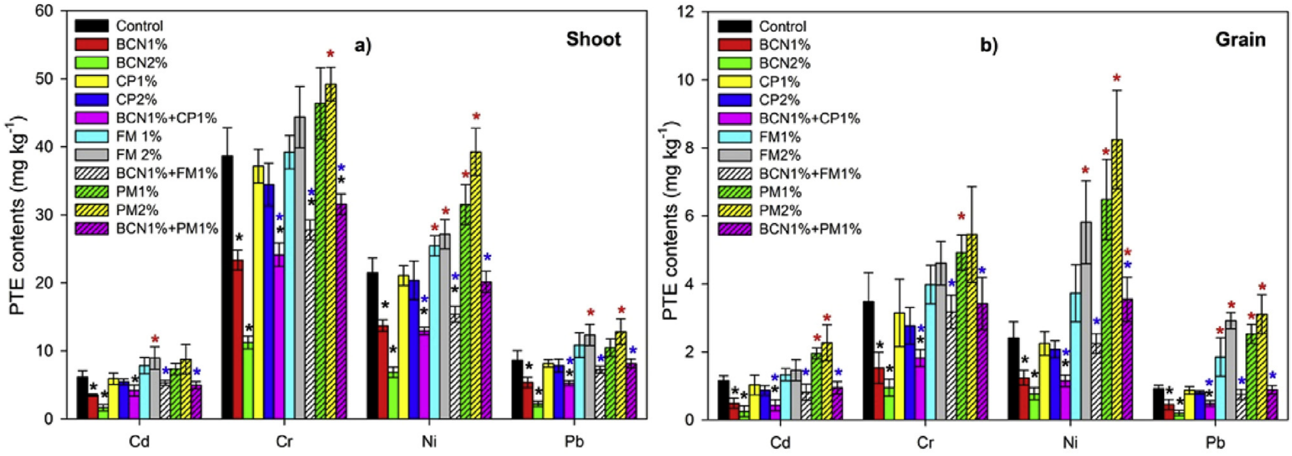

Fig. 4. Phytoaccumulation of PTEs in wheat plant: a) concentration of Cd, Cr, Ni and Pb in the shoots of wheat grown in control and amended soil (BCNs and COAs); b) concentration of Cd, Cr, Ni and Pb in the grains of wheat grown in control and amended soil (BCNs and COAs). Black asterisks represent the significant decrease in levels of PTEs over control; blue asterisks represent the significant decrease in PTEs accumulation in wheat plant tissues (shoot and grain) with BCNs addition compared with COAs; red asterisks represent the significant increase in the levels of PTEs in plant parts compared with the control. Error bars represent the standard deviation (n = 3). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Table 2
Predicted hazard quotient (HQ_{wheat}) and cancer risks (CR_{wheat}) of PTEs associated with wheat consumption influenced by BCNs and COAs (CP, FM & PM).

Treatments	Cd	Cr	Ni	Pb	HI[a]
	Hazard quotient (HQ_{wheat}) for non-carcinogenic risks				
Control	9.24E-03	3.99E-02	4.84E-03	7.39E-03	6.14E-02
BCN1%	3.94E-03	1.76E-02	2.49E-03	3.62E-03	2.76E-02
BCN2%	2.01E-03	1.09E-02	1.55E-03	1.61E-03	1.61E-02
CP1%	8.28E-03	3.62E-02	4.52E-03	6.99E-03	5.59E-02
CP2%	6.99E-03	3.18E-02	4.18E-03	6.51E-03	4.95E-02
BCN1%+CP1%	3.45E-03	2.09E-02	2.31E-03	3.86E-03	3.05E-02
FM1%	1.07E-02	4.57E-02	7.49E-03	1.49E-02	7.87E-02
FM2%	1.17E-02	5.29E-02	1.17E-02	2.35E-02	9.98E-02
BCN1%+FM1%	6.51E-03	3.65E-02	4.52E-03	6.03E-03	5.36E-02
PM1%	1.57E-02	5.65E-02	1.30E-02	2.03E-02	1.06E-01
PM2%	1.82E-02	6.26E-02	1.66E-02	2.50E-02	1.22E-01
BCN1%+PM1%	7.63E-03	3.93E-02	7.13E-03	7.15E-03	6.12E-02
	Cancer risks (CR_{wheat})				TCR_{wheat}[b]
Control	2.97E-03	3.00E-04	3.78E-04	1.35E-06	3.65E-03
BCN1%	1.27E-03	1.32E-04	1.94E-04	6.59E-07	1.59E-03
BCN2%	6.46E-04	8.18E-05	1.21E-04	2.93E-07	8.48E-04
CP1%	2.66E-03	2.71E-04	3.53E-04	1.27E-06	3.28E-03
CP2%	2.25E-03	2.38E-04	3.26E-04	1.19E-06	2.81E-03
BCN1%+CP1%	1.11E-03	1.57E-04	1.80E-04	7.02E-07	1.45E-03
FM1%	3.43E-03	3.43E-04	5.84E-04	2.71E-06	4.36E-03
FM2%	3.77E-03	3.97E-04	9.10E-04	4.27E-06	5.08E-03
BCN1%+FM1%	2.09E-03	2.74E-04	3.53E-04	1.10E-06	2.72E-03
PM1%	5.06E-03	4.24E-04	1.02E-03	3.70E-06	6.50E-03
PM2%	5.86E-03	4.69E-04	1.29E-03	4.55E-06	7.63E-03
BCN1%+PM1%	2.45E-03	2.94E-04	5.56E-04	1.30E-06	3.31E-03

[a] Combined non-carcinogenic risk/hazards index.
[b] Total cancer risk.

($P \leq 0.01$) decreased with BCN addition to soil from 2.05E-04 to 1.05E-04, 6.41E-04 to 3.98E-04, 5.19E-04 to 3.23E-04 and 1.89E-04 to 8.38E-05 mg kg^{-1} day^{-1} with increase in application rate from 1 to 2%, respectively. Moreover, all mixed treatments of BCN together with COAs including BCN1%+CP1%, BCN1%+FM1% and PM BCN1%+CP1% significantly reduced EDI_{wheat} values of PTEs compared with the individual treatment of COAs (CP, FM and PM) (Table S1).

Based on the estimated daily intake of PTEs through dietary intake of wheat grown in PTE-contaminated soil, the BCN addition significantly minimized non-carcinogenic risk (HQ_{wheat}) of PTEs compared with the control (Table 2). In the present study, the non-carcinogenic risks of Cd, Cr, Ni and Pb were 9.24E-03, 3.99E-02, 4.84E-03 and 7.39E-03 for wheat grown on PTE-contaminated soil (control), respectively, and which were markedly ($P \leq 0.01$) minimized from 3.94E-03 to 2.01E-03, 1.76E-02 to 1.09E-02, 2.49E-03 to 1.55E-03 and 3.62E-03 to 1.62E-02 in BCN amended treatments with increasing rate from 1 to 2%, respectively. Furthermore, the combine risk (HI_{wheat}) of PTEs with the addition of BCN was also significantly ($P \leq 0.01$) reduced compared with the control as well as with the COAs. Overall, the results indicated that the non-carcinogenic risks to humans were maximum for Cr followed by Pb, Cd and Ni.

Similarly, the values of CR_{wheat} and TCR_{wheat} associated with PTE exposure were markedly ($P \leq 0.01$) diminished with the addition of BCNs compared with the control (Table 2). The potential risk of developing carcinogenicity over a lifetime of exposure was maximum for Cd followed by Ni, Cr and Pb (Fig. 5). Although lifetime carcinogenic risks of PTEs were higher in all treatments except for Pb, than toxicological safe limits (1.00E-04 to 1.00E-06) set by US-EPA. However, addition of BCN was potentially effective in mitigating lifetime carcinogenic risks of PTEs compared with the control (Fig. S4). Furthermore, all mixed treatments of BCN together with COAs including BCN1%+CP1%, BCN1%+FM1% and BCN1%+PM1% significantly reduced CR_{wheat} and TCR_{wheat} values of PTEs compared with the individual treatments of COAs (CP, FM and PM). However, individual application of COAs including FM and PM to soil, remarkably intensified human exposure to PTEs. This increased health risks through dietary exposure could be attributed to the high bioavailability and uptake if PTEs in plants in COAs amended soil (Yousaf et al., 2017). In other hand, our results are in the agreement with finding of Khan et al. (2014), who reported that the addition of SS-biochar to soil remarkably reduced PTE exposure and mitigate their associated health risks.

The present findings support the use of BCNs as a soil ameliorant to alleviate expected health risks of PTEs. The results demonstrated herein specify that the BCNs addition to PTE-contaminated soil has valuable after-effect concerning food-safety-security (FSS) and mitigate health hazards of PTEs associated with dietary intake via consumption of wheat grown in contaminated soils. However, highly efficient, environment-friendly and cost-effective way to produce BCNs is necessary to realize the application benefits.

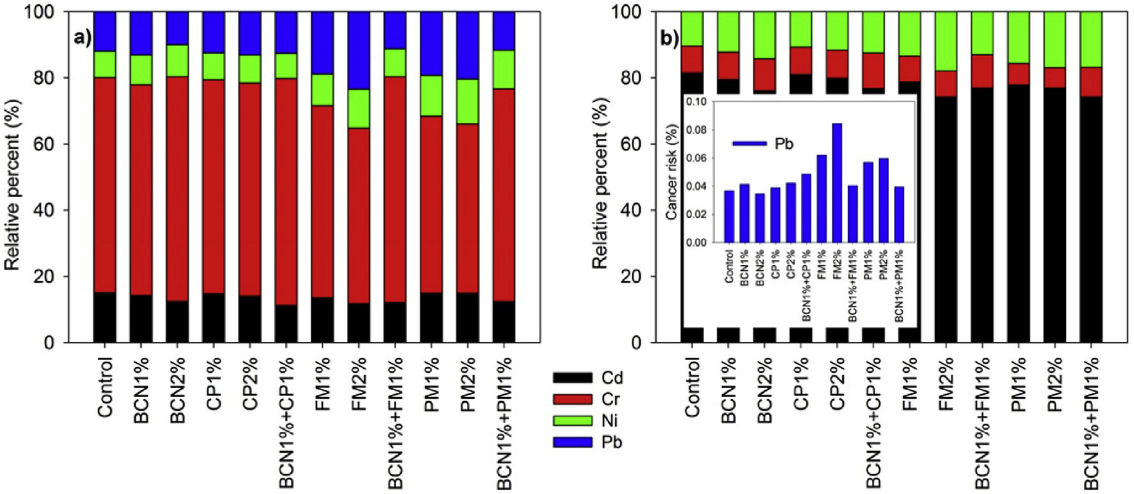

Fig. 5. Health risks: a) relative non-carcinogenic risks (%) of PTEs (Cd, Cr, Ni and Pb) influenced by BCNs compared with the control; b) relative cancer risks (%) of PTEs (Cd, Cr, Ni and Pb) influenced by BCNs compared with the control.

4. Conclusion

Taking into account the chronic health risks of PTEs, the highly efficient BCNs were used as soil amendment to suppress increasing level of environmental and human health risks through impacts on bioavailability of PTEs and their accumulation in wheat crop. Current study clearly demonstrated that BCNs addition to soil remarkably enhanced adsorption of PTEs and reduced uptake by wheat plant due to their low solubility and mobility in soil matrix/soil solution system. Hence, this low phytoextraction of PTEs from BCNs amended soil led down in daily intake exposure and ultimate decrease in health risks (non-carcinogenic and carcinogenic risks). However, field studies are needed to heighten our understanding about potential of BCNs and certain other biomass-derived materials (biochars) to mitigate PTEs exposure and health risks in contaminate soils. Conclusively, dietary diversification/modification as alternative mitigation strategies should be adopted if health hazards of PTEs to be minimized.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at https://doi.org/10.1016/j.chemosphere.2017.10.137.

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