

Original Research Paper

# Environmental Risk Assessment of Coal-Ash-Amended Soil Based on Continuous Planting of Pakchoi

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**Abstract:** The agricultural application of coal ash which contains a variety of chemical nutrients may also cause heavy metal pollution of crops and soil. In this study, pakchoi was cultivated for four consecutive seasons in pots of brown soil amended with fly ash or bottom ash. With subsequent plantings, the total concentrations in the four fractions of Pb, Cr and Cu decreased, while the concentrations of Pb, Cr and Zn dissolved in acetic acid increased. The lowest fresh weight of pakchoi were seen when 15% fly ash was applied. The edible parts of pakchoi contained more heavy metals than the roots. Calculating the Nemerow Pollution Index (NPI) according to the Environmental Protection Standards, the risk of heavy metals in coal ash-amended soils was low. With subsequent plantings, the Risk Assessment Code (RAC) of Pb, Cr and Zn increased gradually and Zn eventually reached a medium level. The study confirmed that coal ash had phytotoxic effects on pakchoi and application of coal ash conferred a risk of soil pollution.

**Keywords:** Bottom Ash, Environmental Risk Assessment, Fly Ash, Pakchoi, Heavy Metal

## Introduction

The annual worldwide output of coal ash reached about 600 million tons in 2010 (Ahmaruzzaman, 2010). There are two main types of coal ash: Fly ash, comprising particles in the range of 1-100  $\mu\text{m}$ , which can be discharged with flue gas and collected by electrostatic precipitators, accounts for 75-80% of the total ash (Ahmaruzzaman, 2010; Shi *et al.*, 2003; Qunhu *et al.*, 2008) and bottom ash, with particles of 100-10,000  $\mu\text{m}$ , accounts for 13-20% of the total ash. Bottom ash usually remains at the bottom of the coal-fired boiler after combustion (Mukhtar *et al.*, 2003).

Coal ash has attracted much attention as a soil amendment because it is rich in trace elements. It was found that fly ash can improve the physicochemical properties of soil, such as pH, water-holding capacity and conductivity (El-Mogazi *et al.*, 1998; Phung *et al.*, 1979; Sarkar *et al.*, 2017; Siddiqui *et al.*, 2004). However, fly ash contains elements that cause metal toxicity in plants, such as Arsenic (As), Cadmium (Cd), Lead (Pb), Mercury (Hg) and Chromium (Cr) (Gupta *et al.*, 2002; Pandey and Singh,

2020). In addition, trace elements such as Copper (Cu), Zinc (Zn), As, Pb and soon were detected at trace levels in rice grains produced in fly-ash-treated soil, but they did not exceed the critical levels for plant growth (Patra *et al.*, 2012). Another research showed that the addition of fly ash reduced the bioavailability of heavy metals in acidic soils polluted by steel slag (Hao *et al.*, 2012). The risk associated with long-term application of fly ash to soil-plant systems is an important research topic and long-term experiments have examined remediation of contaminated soil by fly ash. For example, after an 8-year field experiment, the concentrations of Cd, Pb and Zn extracted from polluted soil restored by fly-ash-aided plant remediation were lower than those extracted from untreated soil (Lopareva-Pohu *et al.*, 2011a). However, few studies have evaluated crop biomass or the heavy-metal contents of plants or soil after continuous use of coal ash. In addition, few studies have examined differences in the agricultural use of bottom and fly ash.

The negative impact of coal ash on the environment is multifaceted, affecting land use, particle flow and

heavy-metal and radioactive-material pollution and soon (Jala and Goyal, 2006; Li and Jiang, 1998). When coal ash is applied to soil, the heavy metals are retained in the leaching solution during migration, which leads to soil pollution and adverse effects on plants and human health. Therefore, it is important to study whether coal ash is sufficiently safe to be applied to soil and to assess the risks associated with the presence of heavy metals in soil after coal ash application.

This study analyzed the heavy-metal content and pH of coal-ash-amended soil after four consecutive plantings of pakchoi. Differences in the agricultural effects of fly and bottom ash were analyzed using three evaluation methods, to evaluate the general contamination characteristics of metals in coal-ash-amended soil. Based on the results, the safety of coal ash for agricultural use is discussed.

## Materials and Methods

### Coal-Ash Treatments

The coal ash used in this experiment was provided by Yancon Group, a coal chemical enterprise in Shandong Province, China. The types of coal ash were divided into bottom ash (8-100 mesh) and fly ash (100-200 mesh), which have different physicochemical properties (Table 1). Bottom ash is collected at the bottom of an industrial boiler furnace because of its large particle size, while fly ash is present in flue gas dust and is collected in a bag filter. The test soil was collected at depths of 0-20 cm from farmland in Laixi District, Qingdao, Shandong Province (Table 1). The coal ash and field soil were air-dried. The soil was passed through a 2-mm sieve and mixed with fly ash in five proportions (by weight): Blankcontrol (CK), 0% ash-100% soil; BA5, 5% bottom ash-95% soil; BA15, 15% bottom ash-85% soil; FA5, 5% fly ash-95% soil; and FA15, 15% fly ash-85% soil.

### Pots Experiment

20-cm-diameter and 17-cm-high plastic pots that had no holes at the bottom were filled with 5 kg of a coal ash soil mixture. Each pot was sown with 10 pakchoi seeds (*Brassica chinensis* L.). All pots were irrigated with tap water instead of natural precipitation and were placed in a net room. After the true leaves appeared, two seedlings of similar size were left in each pot. Each treatment was replicated five times and three plants with similar growth were analyzed. After harvesting, the soil was air-dried and re-mixed and pakchoi were planted again. The plants were cultivated from July 1, 2016 to July 22, 2016 for the first time (t1), from August 26, 2016 to September 19, 2016 for the second time (t2), from September 27, 2016 to

November 23, 2016 for the third time (t3) and from April 17, 2017 to June 4, 2017 for the fourth time (t4).

### Collection of Soil and Plant Sample

The harvested plants were first washed with tap water and then with distilled water. The roots and shoots were separated and weighed. The plant samples were put in an oven at 105°C for 30 min and then dried to a constant weight (24 h) in an oven at 70°C. The plant samples were powdered and screened through a 50-mesh sieve. The first batch of pakchoi was not analyzed chemically because of its insufficient biomass. Coal ash-soil samples were collected five times: Once before planting and four times after harvesting and labeled T0, T1, T2, T3 and T4, respectively. The soil samples were naturally air-dried, ground and stored.

### Chemical Analysis of Plant and Soil Sample

The three-step extraction method proposed by the European Community Bureau of Reference (BCR) was used to extract four fractions of heavy metals in the coal ash-soil samples (Feng *et al.*, 2009; Zhang *et al.*, 2010): The acetic-acid-soluble, reducible, oxidizable and residual fractions. To digest the residue, it was placed in a crucible, dried for 2 h in an oven at 100°C, weighted after drying and then stored in a muffle oven at 600°C for 5 h. The treated residue was weighted to 0.2 g and put in a Polytetrafluoroethylene (PTFE) crucible and digested by triacid method ( $\text{HNO}_3$ : HF:  $\text{HClO}_4$  = 5:5:8). The concentrations of Pb, Cr, Cu and Zn in treatment solution were determined by ICP-OES. The recovery rates of standard samples of Pb, Cr, Cu and Zn were 97.52, 90.97, 94.20 and 95.63%, respectively. The total heavy-metal concentration was the sum concentration of the four fractions of the individual metals and the extractable content was the sum of the contents of the acetic-acid-soluble, reducible and oxidizable forms.

0.4 g samples were weighted and digested in the PTFE crucible with triacid digestion ( $\text{HNO}_3$ : $\text{HClO}_4$  = 4:1 and a few drop of HF). The concentrations of Pb, Cr, Cu and Zn in treatment solution were determined by ICP-OES. The standard recoveries of Pb, Cr, Cu and Zn in the plant samples were 94.50, 101.87, 91.72 and 88.77%, respectively.

The pH of the coal ash-soil mixtures was determined in 1:2.5 soil:distilled water suspension (Okalebo *et al.*, 2002).

### Risk Assessment Methodology

Single-factor index ( $P_i$ ), Nemerow Pollution Index (NPI) (Song *et al.*, 2017), Potential Ecological Risk Index (PERI) (Ke *et al.*, 2017) and Risk Assessment Code (RAC) (Sundaray *et al.*, 2011) were used to analyse the pollution risk of heavy-metals to soil environment. The detailed formulas were presented as followed and the risk classification was presented in the Table 2.

**Table 1:** Basic physicochemical properties of the tested soil and coal ash

Parameters	Bottom ash	Fly ash	Soil	Risk screening values (GB 15618-2018)			
Particle size (mesh)	8 to 100	100 to 200	-	-	-	-	-
Sand (%)	-	-	46.7	-	-	-	-
Silt (%)	-	-	42.4	-	-	-	-
Clay (%)	-	-	11.0	-	-	-	-
pH	12.4	12.6	6.08	≤5.5	5.5~6.5	6.5~7.5	>7.5
SOM (g kg <sup>-1</sup> )	-	-	8.91	-	-	-	-
AP (g kg <sup>-1</sup> )	-	-	7.49	-	-	-	-
AK (g kg <sup>-1</sup> )	-	-	6.63	-	-	-	-
Cu (mg kg <sup>-1</sup> )	64.7	106	44.0	50	50	100	100
Pb (mg kg <sup>-1</sup> )	149	167	69.9	70	90	120	170
Cr (mg kg <sup>-1</sup> )	95.3	64.8	46.5	150	150	200	250
Zn (mg kg <sup>-1</sup> )	71.5	55.9	98.0	200	200	250	300

**Note:** SOM, AP and AK represents organic matter, available phosphorus and available potassium of soils

**Table 2:** Classification of the evaluation index and the pollution levels

Evaluation index	Evaluation values	Pollution degree
NPI	$P_i \leq 1$	$NPI \leq 0.7$ No risk
	$1 < P_i \leq 2$	$0.7 < NPI \leq 1$ Low risk
	$2 \leq P_i \leq 3$	$1 < NPI \leq 2$ Medium risk
	$P_i > 3$	$2 < NPI \leq 3$ High risk
	$E_{fj}^i < 40$	$RI < 150$ Low risk
PERI	$40 \leq E_{fj}^i < 80$	$150 \leq RI < 300$ Moderate risk
	$80 \leq E_{fj}^i < 160$	$300 \leq RI < 600$ Considerable risk
	$160 \leq E_{fj}^i < 320$	$RI \geq 600$ High risk
RAC	$E_{fj}^i \geq 320$	Very high risk
	$RAC \leq 1$	No risk
	$1 < RAC \leq 10$	Low risk
	$10 < RAC \leq 30$	Moderate risk
	$30 < RAC \leq 50$	High risk
	$RAC > 50$	Very high risk

Single-factor index ( $P_i$ ) was used to assess the degree of risk of a given element in soil and calculated using the following Equation:

$$P_i = C_i / S_i \quad (1)$$

where,  $C_i$  is the total content of the heavy metal in coal-ash-amended soil (mg kg<sup>-1</sup>) and  $S_i$  is the content of the same metal in the Soil Environmental Quality Standards (Table 2), or the reference value in the Environmental Quality Evaluation Standards for Edible Agricultural Products (HJ/T332-2006, China).

The Nemerow Pollution Index (NPI) was calculated as follows:

$$NPI = \sqrt{\frac{\bar{P}_i^2 + P_{i\max}^2}{2}} \quad (2)$$

where,  $\bar{P}_i$  and  $P_{i\max}$  are the mean and maximum values of the single factor indices ( $P_i$ ) for a given heavy metal in coal-ash-amended soil, respectively. The risk classification were categorized into four levels (Table 2).

The Potential Ecological Risk Index (PERI) of a given metal ( $E_f^i$ ) in fly-ash-amended soil is defined as:

$$E_f^i = T_f^i \times C^i / C_0^i \quad (3)$$

The results were used to calculate the PERI of the sampling sites, as follows:

$$PERI = \sum_{i=1}^n E_f^i \quad (4)$$

where,  $C_i$  is the concentration of metal  $i$  in soil amended with coal ash;  $C_0$  is the concentration of this metal in soil without coal ash;  $T_f^i$  is the biological toxicity factor of an individual element, which was determined for Zn = 1 < Cr = 2 < Cu = Pb = 5. The risk classification is presented in Table 2.

The Risk Assessment Code (RAC) is used to assess the biological risk and mobility of the acetic-acid-soluble form of heavy metals. The formula is as follows:

$$RAC = C_e^i / C_t^i \quad (5)$$

where, the  $C_e^i$  is the concentration of the acetic-acid extractable fraction of heavy metal  $i$  and  $C_t^i$  is the total content of heavy metal  $i$  in the four fractions. A five

level risk classification has been categorized in terms of RAC (Table 2).

### Statistical Analysis

All experimental values are the means of three replicates per treatment with Standard Deviation (SD). Statistical analyses of different treatments in the same batch were performed by ANOVA analysis and Duncan's multiple range tests ( $P < 0.05$ ) by SPSS software (version 19.0). Correlations among the heavy-metal contents of the experimental soils, the heavy-metal contents and fresh weight of the experimental pakchoi and the pH value of experimental soils were calculated by the "cor" function in the package of R and the graph was constructed by the Performance Analytics" function and "corrplot" function.

## Results and Discussion

### Concentrations of Heavy Metals in Coal-Ash Amended Soil

Before planting pakchoi, the total concentrations of the four fractions of heavy metals in the CK was in the order  $Zn > Pb > Cr > Cu$  and the total concentrations of the four fractions of the heavy metals in the coal-ash-amended soil was also in the same order but the concentration of all elements increased significantly (Fig. 1). Except Cu, the order of the total concentrations of Zn, Pb, Cr was similar to the result reported by (Nayak *et al.*, 2015).

With subsequent plantings of pakchoi, the total Pb, Cr and Cu concentrations in the four fractions in the CK were relatively stable, while the total Pb and Cr concentrations in the coal-ash-amended soil decreased gradually. The total Cu concentrations were higher in fly-ash-amended soil than in bottom-ash-amended soil, likely because the Cu content of fly ash was higher than that of bottom ash and the Cu dissolved more readily in fly-ash-amended soil. Zn showed different changes. Except for BA5, the total Zn concentrations of the four fractions in the other treatments changed little with subsequent plantings and even increased slightly.

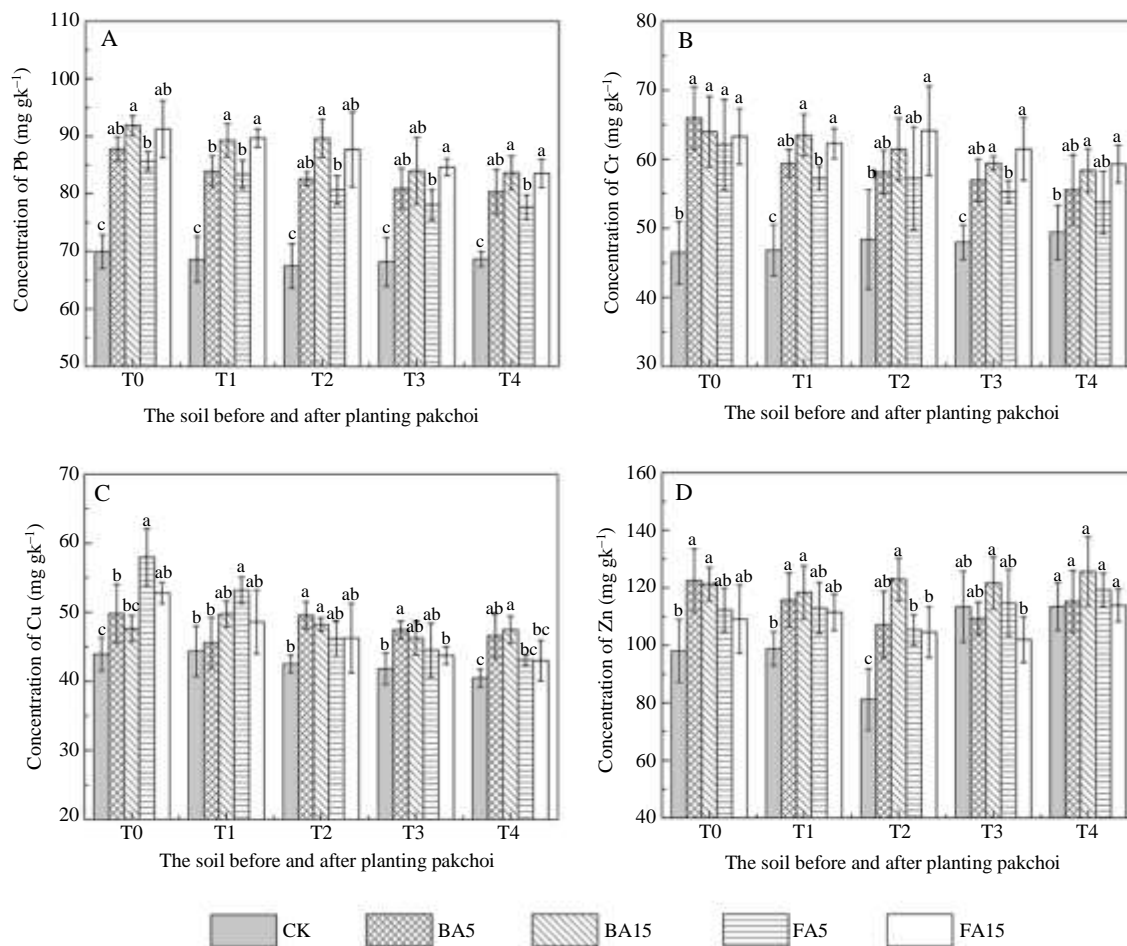
### Concentrations of Acetic-Acid-Extractable Heavy Metals in Coal-Ash-Amended Soil

The bioavailability or potential ecological risks cannot be characterized using only the total concentration of the heavy metal in the four fractions (Maiti and Jaiswal, 2008). The acetic-acid-extractable concentrations of the heavy metals did not exceed 15% of the total content (Fig. 1), but played a key role in crop uptake. Before planting pakchoi, the acetic-acid-extractable concentrations of heavy metals in CK were in the order  $Cu > Pb > Zn > Cr$  (Table 3). The order of total concentrations differed from that of the acetic-acid-extractable heavy metals. For example, the total Cu content was lowest, but the acetic acid-extractable Cu content was highest, indicating that different metals have different degrees of activation.

**Table 3:** The acetic-acid-extractable concentration of heavy metals in the soil under different coal-ash treatments and pakchoi plantings ( $mg\ kg^{-1}$ ) (Bai *et al.*, 2019)

Elements	Soil batches	CK	BA5	BA15	FA5	FA15
Pb	T1	1.52c	1.73e	2.15d	1.61e	1.82e
	T2	1.62ab	1.87d	2.23c	1.74d	1.90d
	T3	1.57bc	1.93c	2.37b	1.87c	1.98c
	T4	1.66a	2.05b	2.39b	1.96b	2.13b
	T5	1.65a	2.16a	2.57a	2.36a	2.45a
Cr	T1	0.52c	0.63d	0.80d	0.61d	0.82d
	T2	0.53c	0.86d	0.94d	0.74d	0.90d
	T3	0.56bc	0.93c	1.07c	0.87c	0.92c
	T4	0.60ab	1.15b	1.56b	0.96b	1.39b
	T5	0.65a	1.38a	1.79a	1.36a	1.52a
Cu	T1	5.88c	7.06a	7.49a	6.80a	7.56a
	T2	5.77bc	6.36b	7.07b	6.05b	6.97b
	T3	5.71c	5.68c	6.37c	5.33c	6.98b
	T4	6.06ab	5.63c	6.06d	5.05d	6.37c
	T5	6.19a	4.70d	5.71e	4.64e	5.98d
Zn	T1	0.89c	1.46e	1.66d	1.79d	1.97d
	T2	0.54d	1.81d	2.35c	2.07d	2.47c
	T3	0.74c	2.30c	2.57c	2.87c	2.63c
	T4	2.50b	4.44b	6.10b	8.82b	4.75b
	T5	8.16a	13.23a	11.9a	14.9a	14.4a

**Note:** T1, soil before planting the first batch of pakchoi; T2, soil before planting the second batch; T3, soil before planting the third batch; T4, soil before planting the fourth batch; T5, soil after planting the fifth batch. CK, 0% ash-100% soil; BA5, 5% bottom ash-95% soil; BA15, 15% bottom ash-85% soil; FA5, 5% fly ash-95% soil; and FA15, 15% fly ash-85% soil. The different letters indicate significant difference among treatment at  $P < 0.05$  (Duncan's multiple range test)



**Fig. 1:** Effects of different coal-ash treatments and pakchoi plantings on the heavy-metal content of soil; Note: T0, soil before planting the first batch of pakchoi; T1, soil before planting the second batch; T2, soil before planting the third batch; T3, soil before planting the fourth batch; T4, soil before planting the fifth batch. CK, 0% ash-100% soil; BA5, 5% bottom ash- 95% soil; BA15, 15% bottom ash-85% soil; FA5, 5% fly ash-95% soil; and FA15, 15% fly ash-85% soil. The different letters indicate significant difference among treatment at  $P < 0.05$  (Duncan's multiple range test). The same meanings are as follow

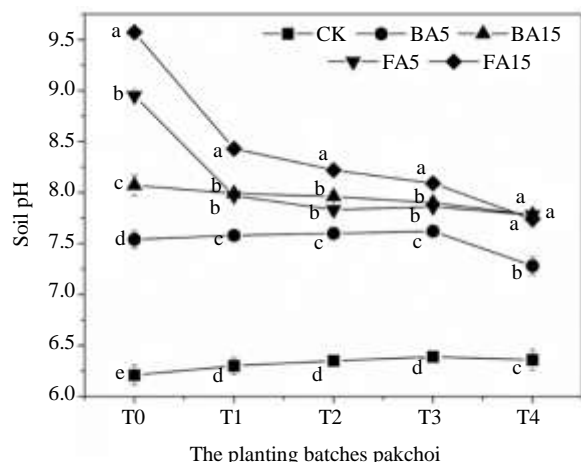
The acetic-acid-extractable concentrations of Pb, Cr and Zn in pakchoi increased with the plantings. In addition, in subsequent plantings, Pb and Cr gradually changed from the residual fraction to the potentially effective and aceticacid-extractable fractions in coal-ash-amended soil (Bai *et al.*, 2019). Therefore, the bioavailability of Pb and Cr improved continuously and the pakchoi absorbed and used more Pb and Cr, which could affect the quality of pakchoi and lead to potential food safety issues.

#### *PH of Coal-Ash-Amended Soil*

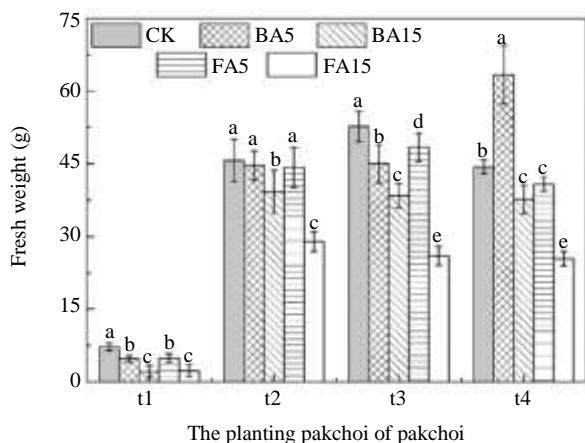
The bioavailability of Cu and Zn in soil is negatively correlated with soil pH and that of Pb is significantly lower than that of total Pb under alkaline conditions (Bhogal *et al.*, 1993; Bose and Bhattacharyya, 2008). The pH of dry ash is greater than 11.0, while that of wet ash

ranges from 7.7 to 8.7 (Pandey and Singh, 2020; Singh *et al.*, 2008; Wu *et al.*, 1995). As shown in Fig. 2, before planting pakchoi, the pH of the coal-ash-amended soil increased significantly, because alkaline matter in the coal ash reacted with acidic components in the soil (Matsi and Keramidas, 1999). The pH also increased with the coal-ash application rate. The influence of fly ash on soil pH was greater than that of bottom ash.

With subsequent plantings of pakchoi, the pH of the CK increased slightly, while that of the soil treated with coal-ash decreased after four pakchoi plantings. This may have been due to the neutralization of organic acids released from the pakchoi rhizosphere by alkaline substances in the soil due to coal-ash application. As most crops grow at neutral pH (6.5-7.0), coal ash should be treated before agricultural use or used to adjust the pH of acidified soil.



**Fig. 2:** Changes in soil pH with different coal ash treatments and pakchoi plantings



**Fig. 3:** Changes of fresh weight of pakchoi in different coal ash treatments and planting batches; Note: t1, the first batch of pakchoi; t2, the second batch of pakchoi; t3, the third batch of pakchoi; t4, the fourth batch of pakchoi. The same meanings are as follows

### Fresh Weight of Pakchoi Grown in the Coal-Ash-Amended Soil

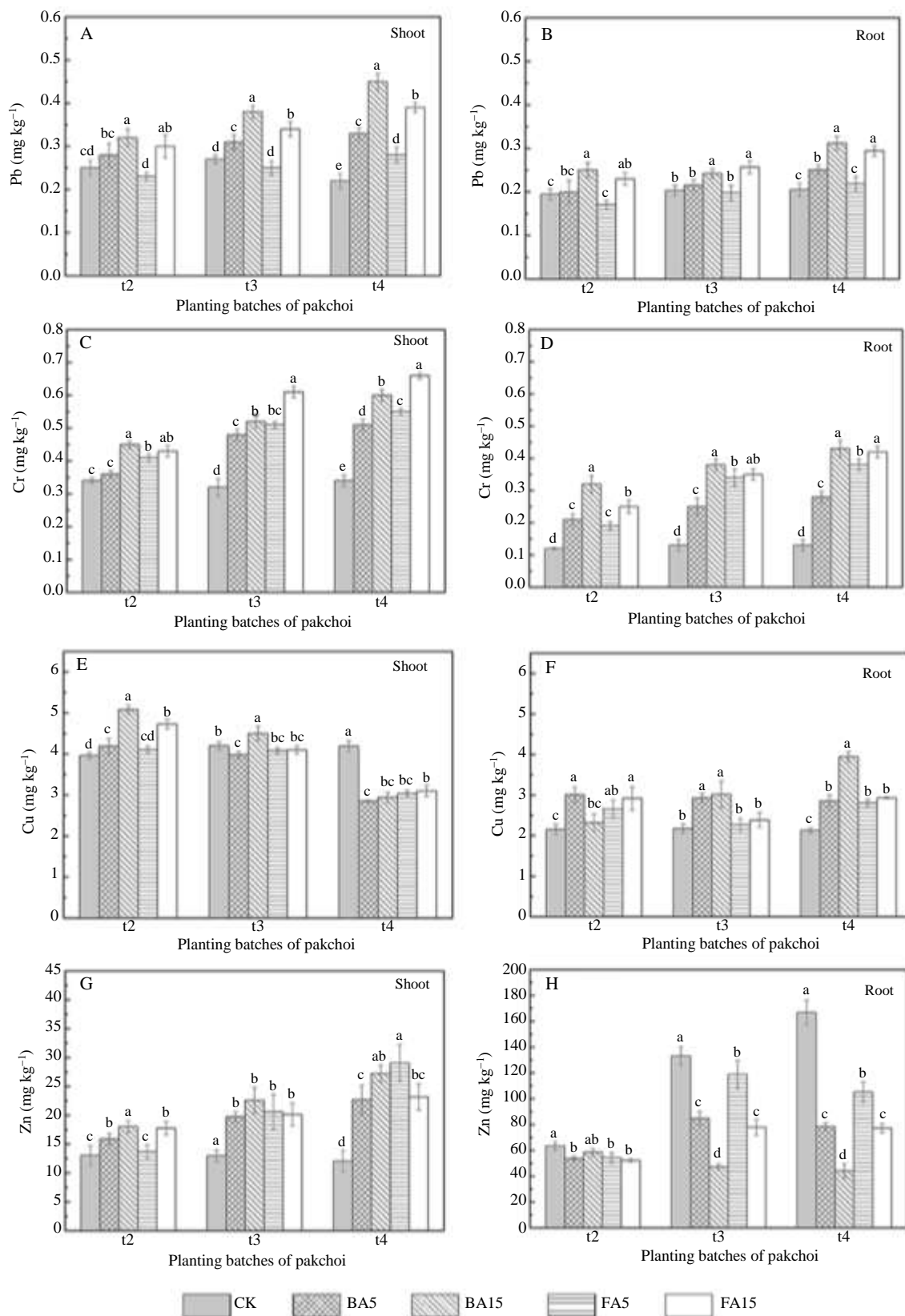
The fresh weights of pakchoi planted in BA15 and FA15 were lower than that of pakchoi planted in CK (Fig. 3), implying that the biomass of pakchoi was related to the amount of coal ash applied, which has been proved in rice, spinach, mung bean and other plants (Mitra *et al.*, 2005; Singh and Agrawal, 2010; Sinha *et al.*, 2007). It was because fly ash contains only traces of nitrogen and organic matter and a high application rate of fly ash dilutes the amounts present in soil, while increasing the heavy-metal contents (Nayak *et al.*, 2015). Application of coal ash also changes the physicochemical properties of soil and the

leached heavy metals and adverse growth environment inhibit the growth of crops (Gupta *et al.*, 2002; Pandey and Singh, 2020). When the pH of soil was higher with high coal-ash application (Fig. 2), pakchoi becomes stressed and grows poorly.

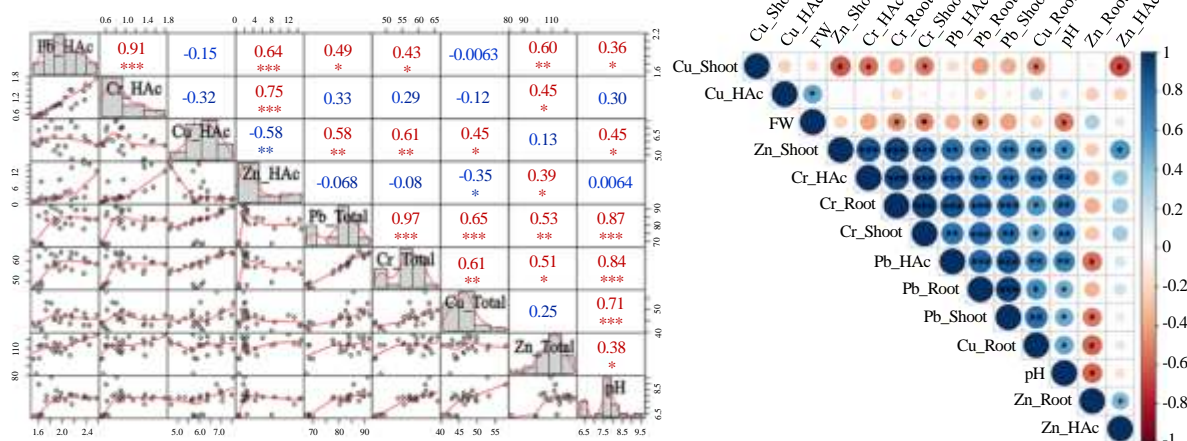
### Heavy-Metal Contents of Pakchoi

For the same coal-ash content, the total Pb content of the shoots and roots was greater in bottom-ash-amended soil than in fly-ash-amended soil (Fig. 4). With subsequent plantings, however, the total Pb content of pakchoi grown in the coal-ash-amended soil increased gradually, but not significantly, in the CK. It was also founded that the metal accumulation in ground organs and shoots of *Scirpus littoralis* increased with time (Bhattacharya *et al.*, 2006). The change in Cr in pakchoi was similar to that of Pb, but the Cr content of pakchoi grown in CK was the lowest. With subsequent plantings, the acetic-acid-soluble concentrations of Pb and Cr in coal-ash-amended soil increased gradually and the Pb and Cr contents of pakchoi also increased, indicating that the bioavailability of Pb and Cr in coal-ash-amended soil increased continuously. Considering the background levels of Pb and Cr in the CK, this increasing trend might lead to Pb and Cr pollution in the soil and toxic levels in pakchoi. Besides, Pb and Cr concentrations were higher in shoots than in roots, which was similar to the concentration in the mung bean but was opposite to the concentration in *Trifolium repens* (Lopareva-Pohu *et al.*, 2011b; Singh and Agrawal, 2010).

The total Cu content of pakchoi decreased with subsequent plantings. The Cu content was higher in shoots than in roots for all treatments, implying that in pakchoi Cu is transferred from the roots to the shoots. A cowpea (*Vigna unguiculata*) experiment had similar results and the Cr and Cu contents were higher in cowpea shoots than in roots (Chaudhary *et al.*, 2011). In our experiment, the Zn content was lower in pakchoi shoots than in roots, while the opposite was seen for cowpea, which might be attributed to differences in nutrient absorption by different crops. With subsequent plantings, the Zn content of pakchoi shoots increased in all ash treatments and was higher in the coal-ash-amended soil than in the CK for all plantings. Because of the low solubility of Zn compounds, the absorption of Zn by negatively charged colloidal soil particles increases and the availability of Zn decreases with increasing pH (Maiti and Jaiswal, 2008). The total Zn content was higher in pakchoi grown in the CK than in the coal-ash-amended soil (Fig. 4), indicating that the availability of Zn was lower in the coal-ash-amended soil.



**Fig. 4:** The metal contents of the roots and shoots of pakchoi according to the coal-ash treatment and pakchoi planting



**Fig. 5:** Pearson's correlation of the heavy-metal contents of the experimental soils and soil pH (A). Pearson's correlation of the heavy-metal contents in the roots and shoots of pakchoi and in the soil, pH and fresh weight of pakchoi (B); Note: Pb\_Total, Pb\_HAc, Pb\_Shoot and Pb\_Root represented the total contents of Pb in the soils, the acetic-acid-extractable content of Pb in the soils, the Pb content in the shoots and the Pb content in the roots of pakchoi, respectively. The representation of other elements was similar. pH and FW represented the pH value of soils and fresh weight of pakchoi. The significance is indicated: \*  $P < 0.05$ ; \*\*  $P < 0.01$ ; \*\*\*  $P < 0.001$

### Correlation Among Heavy-Metal Content, Pakchoi Biomass and Soil pH

From the Fig. 5A, there was a significant positive correlation between total contents of Pb and Cr in the soils ( $r = 0.97$ ,  $P < 0.001$ ) and between acetic-acid-extractable contents of Pb and Cr ( $r = 0.91$ ,  $P < 0.001$ ), which indicated that they changed similarly between treatments. It was obvious that there were significantly positive correlations between the total content of Pb, Cr, Cu, or Zn and pH in the soils ( $P < 0.05$ ) (Fig. 5A), these phenomena also occurred in previous published researches (Chen *et al.*, 2011; Li *et al.*, 2009). The exchangeable heavy-metal content of soil is negatively correlated with pH, while the heavy-metal content of the carbonate-bound state is positively correlated with pH (Han *et al.*, 2005) and the relationship between the carbonate-bound state and pH is stronger. In our experiment, there were positive correlations of the acetic-acid-extractable concentrations of Pb or Cu in the soils with pH. Figure 1 and 2 show that the relationship between pH and the four heavy metals was consistent with the results of the correlation analysis. Therefore, pH is an important factor determining the concentrations of different heavy metals (Huang *et al.*, 2012).

As showed in Fig. 5B, the Pb and Cr contents of shoots were positively correlated with the contents of roots, and the acetic-acid-extractable Pb and Cr contents of soil were positively correlated with those of the roots and shoots, respectively. Therefore, the rates of migration of Pb and Cr in the soil-pakchoi system were similar; the acetic acid-extractable content of Pb and Cr in soil affect the content of pakchoi. While, the Cu and Zn contents of shoots were

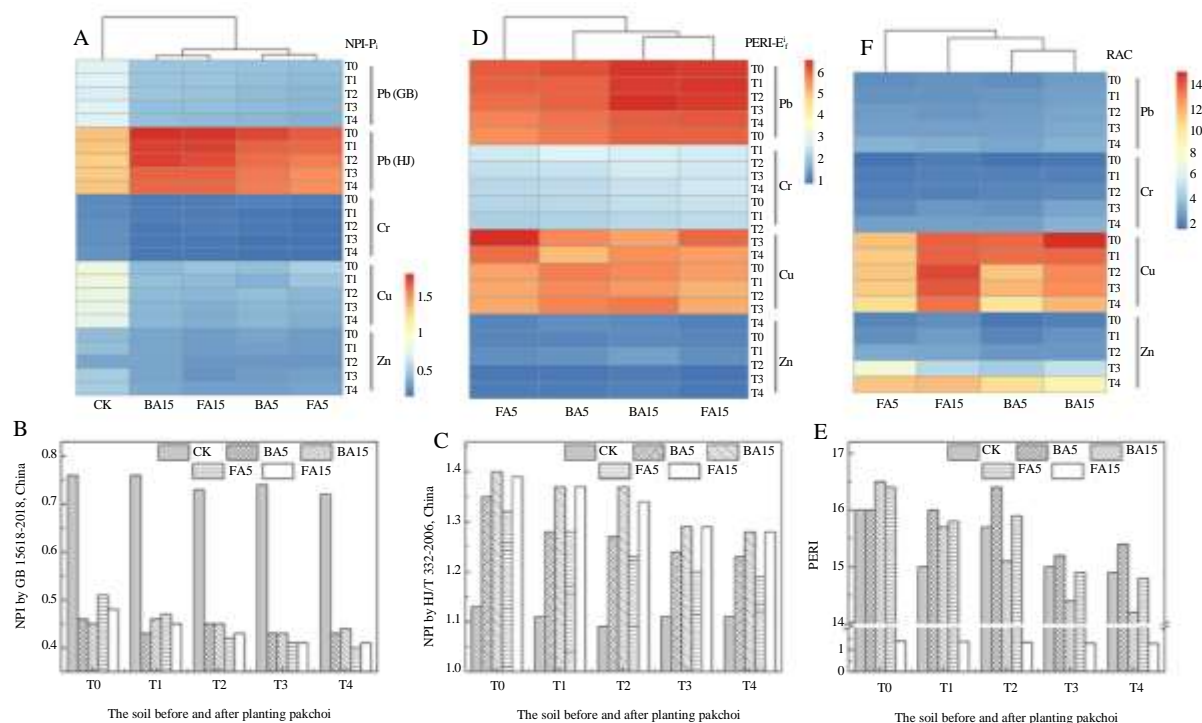
negatively correlated with the contents of roots and were positively correlated with the acetic-acid-extractable Cu and Zn contents of soil, with coefficients of 0.566 and 0.873, respectively (all  $P < 0.05$ ). The Pb, Cu or Zn contents in different organ of rice also showed obvious correlation (Zhou *et al.*, 2014). Besides, the Pb, Cr, Cu and Zn contents in the roots and roots all hold negative correlation with the fresh weight of pakchoi.

### Environmental Risk Assessment of Coal-Ash-Amended Soil

#### Single-Factor Index ( $P_i$ ) and the Nemerow Pollution Index (NPI)

Figure 6A shows that the average value of  $P_i$  calculated according to the environmental quality standards (China, 2018) declined in the order  $1 > \text{Cu} > \text{Pb} > \text{Zn} > \text{Cr}$ , which means that all four elements in the soil tested were in the safe range. However, the average value of  $P_i$  calculated according to the environmental protection vocation standards (China, 2006) declined in the order  $\text{Pb} > 1 > \text{Cu} > \text{Zn} > \text{Cr}$ . The  $P_i$  of Pb in CK was greater than 1, implying a low risk of Pb in the CK. The  $P_i$  of a specific metal was higher in CK than in coal-ash-amended soil. Soil pH increased with application of coal ash, which resulted in a limited change in the value of  $S_i$  in the environmental quality standards (China, 2018). In subsequent plantings, the  $P_i$  for Cu declined more significantly in fly-ash-amended soil than in bottom-ash-amended soil. The  $P_i$  for Zn was higher in bottom-ash-amended soil than in fly-ash-treated soil.





**Fig. 6:** Heatmap of Single-factor pollution index of heavy metals ( $NPI-P_i$ ) (A), potential ecological risk index of a given metal ( $PERI-E_f^i$ ) (D) and risk assessment code (RAC) (F) in coal-ash-amended soil; Nemerow pollution index (NPI) (B and C) and potential ecological risk index (PERI) (E) of the four metals in coal-ash-amended soil; Note: the GB 15618-2018, China (GB) and HJ/T 332-2006, China (HJ) provided the different  $S_i$  values of Pb to calculate the  $NPI-P_i$  and NPI, while the  $S_i$  values of Cr, Cu and Zn are the same as in the two standards

In China, the excess multiples of Pb, Cr, Cu and Zn in sewage irrigation in 1980-2010 were 7.5, 2.4, 4.1-8.2 and 5.3, respectively (Xin *et al.*, 2011). The As, Hg, Pb, Cd, Cr and Ni from atmospheric deposition account for 35-85% of that in farmland (Luo *et al.*, 2009). At the same time, the absorption of heavy metals by vegetables comes not only from the contaminated soil, but also from atmospheric deposition (Feng *et al.*, 2018). Therefore, the background value of agricultural soil should be considered before applying coal ash, to prevent superimposed pollution. The NPI calculated using the relatively strict environmental protection standard was greater than 1 and the risk was moderate (Fig. 6B and 6C).

#### Potential Ecological Risk Index (PERI)

The  $E_f^i$  of specific metals in all samples was in the order  $40 > Pb > Cu > Cr > Zn$  (Fig. 6D), indicating that Pb carries more potential risk than the other three elements. The  $E_f^i$  of Pb and Cr decreased in subsequent plantings. The PERI of the four metals was  $< 1$ , indicating low risk. The average PERI of the four metals decreased in the order  $BA5 > FA5$ ,  $BA15 > FA15$  (Fig. 6E). Therefore, fly ash is more environmentally friendly than bottom ash.

#### Risk Assessment Code (RAC)

Pb and Cr were low risk based on RAC and the RAC of Pb and Cr increased in subsequent plantings (Fig. 6F). The acetic-acid-extractable fractions of Pb and Cr increased and the residual fraction decreased, which increased the extractable content and bioavailability of Pb and Cr, indicating that both have strong releasing ability. The RAC of Pb and Cr in all treatments was in the order  $BA15 > FA15 > BA5 > FA5$ , indicating that the bottom ash releases more Pb and Cr than fly ash. Based on the RAC, the Cu in coal-ash-amended soil was classified as moderate risk. The researches have also showed that the organic acids secreted by the roots of crops could dissolve the carbonate and oxidized heavy metals, increasing the most effective heavy metals in the soluble and exchangeable fraction (Mench and Fargues, 1994; Mo *et al.*, 2002). With subsequent plantings, the RAC of Cu in BA5 decreased from 14.17 to 8.03% and the pollution risk decreased from medium to low. After the fourth planting of pakchoi, the level of Cu pollution was still moderate. Compared with the other three elements, Cu seems to be more easier to be dissolved out, which makes the RAC value larger and the potential risk stronger (Zhou *et al.*, 2013). The RAC of Zn

increased sharply, especially in FA15. Except BA15, the RAC of Zn increased from low to moderate risk.

Therefore, although there is huge output of coal ash at present and many researches focused on its effective utilization (Hao *et al.*, 2012; Patra *et al.*, 2012; Sarkar *et al.*, 2017). Coal ash, whether as fertilizer additive or soil improvement material, has the environmental pollution risk, according to our results. However, coal ash, as a kind of hydrophobic, water and fertilizer retention agent with good physical and chemical properties (Pandey and Singh, 2020), could be applied to non-agricultural fields such as landscaping but should be forbidden to use near farmland, so as to cause the agricultural pollution by surface runoff.

#### *Comparison of the Three Risk Assessments*

The results differed by evaluation method.  $P_i$  and NPI adopt relevant national standards as evaluation limits, where use of different standards will lead to different results. The  $P_i$  and NPI of the specific heavy metals calculated using the national soil environmental quality standards were in the clean level, while the  $P_i$  and NPI of Pb calculated using the environmental protection standard indicated low and moderate risks, respectively, due to the stricter limits of the protection standards. The PERI usually takes the soil background value in a certain area as the evaluation limit, while we took the content of the CK as the background value to represent the pollution level of the coal-ash-amended soil. In addition, that PERI could describe both ecological risk caused by single pollutant and overall risk or contamination from varied pollutants (Yuan *et al.*, 2015). The single-factor and composite indexes of specific heavy metals indicated that they are not a risk by PERI. However, the results only based on the total contents of heavy metals are not accurate. It is more practical to evaluate the heavy metal pollution combining with the heavy metal effective fraction which can more effectively reflect the bioavailability and heavy metal pollution (Chojnacka *et al.*, 2005; Li *et al.*, 2007).

The RAC uses the acetic-acid-extractable fraction as the effective part, calculates its ratio relative to the total and evaluates the risk of release of heavy metals into the soil (Zhang *et al.*, 2017). Using this method to evaluate heavy-metal pollution would yield different results for different heavy metals and plantings of pakchoi. With subsequent plantings, the RACs of Pb, Cr and Zn increased and Zn eventually reached a medium risk, while the RAC of Cu decreased. Therefore, the results from the two other risk assessment methods showed that the pollution assessment index of the four heavy metals decreased with subsequent pakchoi plantings, but the risk of metal availability increased gradually.

## Conclusion

Coal-ash application had an adverse effect on pakchoi growth and biomass yield, especially application of 15% coal ash. With subsequent plantings, the aceticacid- extractable concentrations of Pb and Cr increased. The Pb, Cr and Cu contents were higher in pakchoi grown in the coal-ash-amended soil than in the CK and the Pb and Cr contents gradually increased in subsequent plantings. The findings demonstrate that application of unmodified coal ash, including bottom and fly ash, will cause heavy-metal pollution in soil, improve the bioavailability of some metals and increase the heavymetal content of pakchoi. The pollution risk would increase with subsequent plantings.

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## Author's Contributions

**Wenxuan Sun, Liyong Bai and Huihui Ji:** Designed and performed the experiments, wrote original draftpreparation.

**Dongyun Yan, Wentao Huo, Zhen Huang and Kezhong Liu:** Revised the manuscript.

## Ethics

The authors declare their responsibility for any ethical issues that may arise after the publication of this manuscript.

## Conflict of Interest

The authors declare that they have no competing interests. The corresponding author affirms that all of the authors have read and approved the manuscript.

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