

Chemical Speciation, Leaching Behavior, and Environmental Risk Assessment of Trace Elements in the Bottom Ash from Biomass Power Plant

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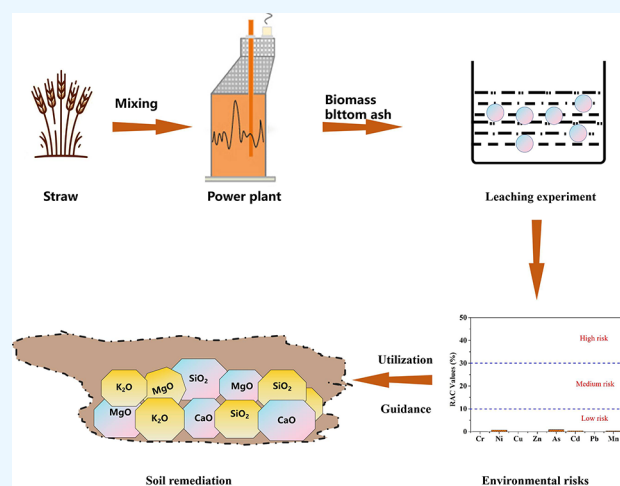
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ABSTRACT: Biomass combustion for power generation stands as a pivotal method in energy utilization, offering a promising approach for renewable energy utilization. However, the substantial volume of slag produced by biomass burning plants poses environmental challenges, impeding sustainable energy practices. This article systematically studies the characteristics of ash generated from typical biomass direct combustion power plant ash and analyzes the chemical composition, trace element content characteristics, leaching characteristics, and chemical forms of biomass bottom ash. Furthermore, it assesses the environmental ecology and bioavailability of trace elements in bottom ash using the ecological risk assessment method and RAC method. The results demonstrate that the biomass bottom ash contains plant nutrients, such as K, Ca, Mg, and P, while the content of harmful trace elements is lower than the relevant Chinese standards. In dissolution experiments, the leaching rate of nearly all elements remains exceptionally low, primarily due to the distribution of trace elements within the lattice structure of stable minerals. Trace elements predominantly exist in the residual phase, Cu and Zn primarily found in organic compounds and sulfide bound states, while other elements mostly exist in the form of iron manganese oxide bound states. Ecological risk assessment indicates a significant risk level for Cd, contrasting with the slight risk associated with other elements. RAC results indicated no ecological risk of all of the trace elements. Consequently, the utilization of bottom ash in agricultural and forestry soils is deemed to be viable. These findings serve as a crucial foundation for biomass bottom ash resource utilization and underpin the sustainable utilization of biomass energy.



1. INTRODUCTION

Due to the limitations of fossil fuels and the adverse effects on the environment during their use, energy and its sustainable utilization have become a hot topic of concern worldwide.¹ Biomass, as a plentiful and renewable clean energy source, is garnering significant attention and is poised to play an increasingly pivotal role in global energy provision.² The combustion of fossil fuels contributes to the release of greenhouse gases, precipitating worldwide climate changes.³ In contrast, the total amount of carbon dioxide produced by biomass combustion is equal to the content of that absorbed during growth process.^{4,5} Therefore, biomass energy is internationally recognized as a renewable energy source with characteristics of zero emission of carbon dioxide, helping to achieve the goals of “carbon neutrality” and “carbon peaking.”^{1,6}

Biomass energy stands as the fourth largest consumer of energy globally and is projected to constitute 33% to 50% of

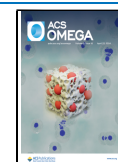
the world's primary energy consumption by 2050, with approximately 95% to 97% generated via direct biomass combustion.⁶ Biomass power plants are the most direct way to convert biomass through incineration, predominantly using waste biomass, particularly agricultural or forestry residues, to supply power. Ash, constituting an average yield of 6.8% of dry biomass during combustion,⁷ contributes to an estimated annual worldwide production of around 480 million tons. China alone produces approximately 600 million tons of annual biomass available for energy production,⁷ which is huge and increasing year by year. At present, the main treatment or

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utilization methods of biomass ash are landfill and use as soil remediation (improvement) agents and adsorbents,^{4,8,9} infrastructure materials,^{10,11} and composite materials.¹² And applying biomass ash to agricultural and forestry soils is generally regarded as the best approach.^{13,14} Some developed countries, such as Germany, Japan, and Denmark, demonstrate resource utilization rate of biomass ash is between 70% and 90%,¹¹ while the utilization rate of ash resources in China still needs to be improved.

After biomass combustion, nonvolatile components like inorganic minerals and trace elements are retained as solid ash residues. Biomasses are broadly categorized into woody and herbaceous types.¹⁵ The physical and chemical composition of the resultant ash residue closely correlates with biomass sources, types, seasonal, geographical variances, and combustion conditions.¹⁶ Generally, due to shorter growth cycles, herbaceous biomasses tend to contain lower levels of trace elements compared to woody biomasses, leading to higher trace element content in the ash of woody biomasses.¹⁷ To address fuel supply and operational issues such as preventing corrosion and ash accumulation, Chinese biomass power plants use fuel mixed with wheat straw, corn straw, and forestry waste. Residues from bark, waste wood, among others, with higher trace element contents than straws,¹⁸ result in higher trace element content in biomass ash and limit its agricultural and forestry applications due to potential environmental impacts. Biomass ash residue can be classified into fly ash and bottom ash based on collection methods. The majority of power plants employ grate-firing methods, with bottom ash comprising roughly 85% of the total ash residue generated in China.¹⁶ The bottom ash primarily comprises Si, Ca, Mg, Al, K, P, along with various trace/ultra-trace elements (Mn, Cu, As, Cr, Pb, and Cd).^{13,19} Assessing the trace element content and environmental risk evaluation posed by trace elements in bottom ash are essential for its resource utilization as an industrial solid waste.

Many studies that have been carried out primarily focus on individual biomass ash fraction characteristics in laboratory settings, with minimal emphasis on practical power plants by domestic and abroad researchers.²⁰ The existing knowledge and results are insufficient to provide a reliable basis for ash utilization. Prior to the resourceful treatment of biomass ash residue, it is essential to analyze the content of harmful trace elements and their leaching toxicity,²¹ preventing secondary pollution during use.²² Given the variability in biomass fuel sources globally and the combustion methods of biomass power plants in China, coupled with the lack of research on their environmental impacts, it is imperative to evaluate the chemical composition of biomass bottom ash and the leaching toxicity of trace elements and conduct ecological risk assessments for its application.

In this study, based on the characteristics of biomass fuel and typical combustion technologies used in domestic biomass power plants, trace elements from an actual biomass combustion power plant were taken as the research object. The main aims of this study are to (1) determine the chemical composition and trace element content characteristics of bottom ash; (2) analyze the leaching characteristics and chemical speciation of trace element in bottom ash; and (3) assess the ecological risk assessment and biological activity of trace elements. The results can provide a scientific basis for achieving high added value and large-scale utilization of biomass combustion ash and also provide reliable experimental

analysis data for the evaluation of the characteristics of ash in power plants of China.

2. MATERIALS AND METHODS

2.1. Samples. Biomass ash samples were collected from a typical power plant located in Huainan city, Anhui province. The plant adopts direct combustion power generation technology with an annual power generation capacity of 2.1×10^8 kwh/a. The fuel of the biomass power plant is mixture of wheat straw, corn straw, and forestry waste in the ratio of 4:4:2, with the consumption of approximately 260,000 tons a year. The bottom ash production of the power plant is an annual of 4.5×10^3 tons. The fuel and equipment of the biomass power plant remain constant, so the physicochemical properties of the bottom ash are relatively stable. In the burning process, the bottom ash accumulates in the bottom layer of the boiler hopper. The biomass samples were collected from the fuel of the biomass power plant, and the slag samples were taken from the boiler and stored in sealed bags to prevent weathering or deterioration. These samples were expeditiously transported to the laboratory. The samples were dried at 105 °C for 3 h, ground, and filtered through a 100-mesh sieve for analysis. All chemicals used in this study were of analytical grade to ensure accuracy.

2.2. Chemical and Mineralogical Detection. The crystal structure and composition were determined by using X-ray powder diffraction (XRD). Chemical composition was detected by an X-ray fluorescence analyzer (XRF). The samples were digested by a microwave digester with a mixed acid of hydrochloric acid (HCl), nitric acid (HNO₃), hydrofluoric acid (HF) with a volume ratio of 3:2:1 for analysis. The main element content was analyzed by an inductively coupled plasma emission spectrometer (ICP-OES, Perkin. Elmer's OPTIMA 2000DV), and the trace element content was determined using an inductively coupled plasma mass spectrometer (ICP-MS, Agilent's 7700x) after filtering with 0.45 μm pressure filter.

The fractionation of trace elements was accomplished by a five-step sequential extraction procedure, following the methodology proposed by Tessier et al.²³ This extraction protocol categorized trace elements into five distinct forms of occurrence, as detailed in Table 1. To ensure the reliability of the test results, parallel samples, a blank experiment, standard addition, and recovery analyses were conducted. The measured recovery percentage ranged between 85% and 115%, ensuring accuracy and precision of the results.

Table 1. Sequential Extraction Procedure for Metal Fractionation Analysis

sequences	fractionations	extractants	extractant conditions
I	exchangeable fraction (F1)	8 mL 1.0 mol·L ⁻¹ MgCl ₂ (pH = 7.0)	25 °C oscillation for 1 h
II	carbonate fraction (F2)	8 mL 1 mol·L ⁻¹ CH ₃ COONa (pH = 5.0)	25 °C oscillation for 8 h
III	Fe/Mn oxide fraction (F3)	20 mL 0.04 mol·L ⁻¹ NH ₂ OH·HCl	96 °C oscillation for 4 h
IV	organic matter fraction (F4)	3 mL 0.02 mol·L ⁻¹ HNO ₃ + 5 mL 30% (v/v) H ₂ O ₂ (pH = 2.0)	85 °C oscillation for 2 h
V	residual fraction (F5)	HCl + HNO ₃ + HClO ₄	oscillation in 100 °C water bath at 250 r·min ⁻¹ for 2 h

2.3. Leaching Experiment. To evaluate the dissolution characteristics and potential environmental impacts of trace elements, static immersion tests were conducted. Initially, the crushed biomass bottom ash samples were sieved through a 100-mesh sieve. Subsequently, these samples were placed in conical flasks with a liquid:solid ratio of 5:1 (L/kg), and the flasks were maintained at room temperature. The samples were stirred every 24 h to ensure proper soaking of the slag for specific time intervals. Then, the concentration of trace elements in the solution was analyzed. The static leaching duration encompassed specific intervals, including day 1, day 4, day 7, day 10, day 14, day 18, day 24, and day 30, enabling a comprehensive assessment of leaching behavior over time.

2.4. Evaluation Method. **2.4.1. Potential Ecological Risk Index.** The potential ecological risk index, as proposed by Hakanson,²⁴ is widely used to evaluate the potential risk of trace metals on the ecosystem, ecological risk assessment according to its characteristics and environmental behaviors in soil or sediment.²⁵ It combines the concentration and toxicity levels of trace elements as well as the sensitivity of the ecological environment to these trace elements. This assessment was estimated using the following equations:

$$C_f^i = C_0^i / C_n^i \quad (1)$$

$$E_r^i = T_r^i C_f^i \quad (2)$$

$$RI = \sum E_r^i \quad (3)$$

Where the C_f^i is the contamination factor for trace element i , C_0^i is the concentrations measured for element i , C_n^i is the reference standard for element i , which was the reference background value of Huainan city.²⁶ The values of C_n^i are 0.06, 30.7, 32.0, 23.5, 91.5, 525.2, 10.5, and 58.4 mg/kg for elements Cd, Cu, Ni, Pb, Cr, Mn, As, and Zn, respectively. E_r^i is the ecological risk factor of element i . T_r^i is the toxicity coefficient of element i (i.e., As = 10, Cd = 30, Cr = 2, Cu = 5, Ni = 5, Mn = 1, Pb = 5, and Zn = 1).²⁷ RI is the sum of all trace element risk factors.

Based on the E_r^i values, the ecological risk degree of individual trace elements could be divided into five levels: low level ($E_r^i < 40$), moderate level ($40 < E_r^i < 80$), considerable level ($80 < E_r^i < 160$), very high level ($160 < E_r^i < 320$), and dangerous level ($E_r^i > 320$).²⁸ Additionally, four groups of values correspond to low level ($RI < 150$), moderate level ($150 < RI < 300$), considerable level ($300 < RI < 600$), and very high level ($RI > 600$).²⁸

2.4.2. Risk Assessment Code. The risk assessment code (RAC) method was used to evaluate the mobility and availability based on the different occurrence fractions of trace elements from sequential extraction. The formula was calculated as follows:

$$RAC = \frac{F_1 + F_2}{C_t} \times 100\% \quad (4)$$

where F_1 is the fraction of exchangeable, F_2 is the fraction of carbonate bound, and C_t is total concentration of trace element in five fractions. The classification of environment risk was divided into five classes according to their RAC values: no risk ($RAC < 1\%$), low risk ($1\% < RAC \leq 10\%$), medium risk (10%

$< RAC \leq 30\%$), high risk ($30\% < RAC \leq 50\%$), and very high risk ($RAC > 50\%$).²⁷

3. RESULTS AND DISCUSSION

3.1. Mineralogical Composition of Slag. XRD analysis was conducted on the collected biomass bottom ash samples, and the results are shown in Figure 1. According to XRD phase

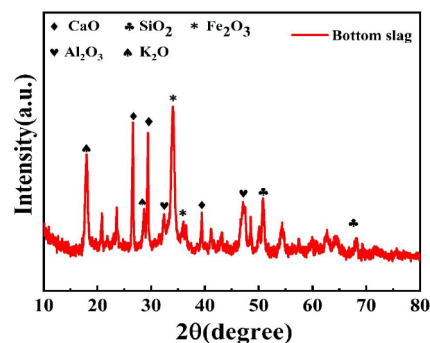


Figure 1. Result of XRD analysis.

analysis, the bottom ash contained SiO_2 , Fe_2O_3 , CaO , Al_2O_3 , MgO , etc. Both biomass ash and fuel showcased similar elemental compositions, predominantly containing substantial nutrients like Si, Al, Ca, and K.²⁹ Si emerges as the primary element contributing to ash formation in rice husks and straw, with straw showing a higher K content. Meanwhile, woody biomass, such as bark, tends to contain higher levels of Si and Ca, thus contributing to their increased presence in the ash. The Al content in biomass fuels remains moderate; however, elevated Al content in ash may stem from impurities such as sand, stone, or soil introduced during fuel transportation and processing. Ca and Mg, prevalent in woody biomass, exhibit limited volatility and are therefore prone to entering the bottom ash. The results also indicate that significant chemical reactions occurred among the main inorganic components during the combustion process.

The results of the XRF analysis are summarized in Table 2. The bottom ash contains Fe_2O_3 , CaO , SiO_2 , K_2O , and Al_2O_3 , which is consistent with the chemical composition of XRD. Biomass power plant ash predominantly comprises alkaline compounds along with various nutrients and trace elements, such as K, Si, Ca, and Mg. Applying biomass power plant ash to soil can not only alleviate soil acidification but also enrich the soil with essential nutrients, achieving resource utilization of biomass bottom ash and avoiding interruption of element cycling.^{9,12,22,30} The bottom ash contains various trace nutrients absorbed by biomass growth, making it suitable as an auxiliary material for the production of composite fertilizers and worthy of further development and application.^{4,21}

3.2. Content Characteristics of Trace Elements. The content of trace elements is an indicator that limits the utilization of the biomass bottom ash. The content of trace elements in biomass bottom ash, as listed in Table 3, demonstrates varying concentrations, arranged in descending order: with a decreasing order of Mn (562.149 mg/kg) > Zn (158.381 mg/kg) > Ni (56.243 mg/kg) > Cu (38.846 mg/kg) > As (12.351 mg/kg) > Cr (5.817 mg/kg) > Pb (2.473 mg/kg) > Cd (0.526 mg/kg). The content of Mn in the bottom ash is the highest, while the content of Cd is the lowest. With the exception of Pb, the distribution trend of content in ash is

Table 2. Results of XRF Spectrum Analysis

chemical composition	SiO ₂	Fe ₂ O ₃	CaO	K ₂ O	Al ₂ O ₃	TiO ₂	MgO	ZrO ₂	P ₂ O ₅	Na ₂ O
percentage (%)	21.61	30.23	22.38	10.26	4.52	4.16	1.38	1.67	1.34	2.45

Table 3. Contents of Trace Elements (mg/kg) and Their Enrichment Factors (EF) in Bottom Ash and Biomass Fuel^a

elements	biomass ash	biomass fuel	EF	risk screening values	risk control values
Zn	158.38	146.24	1.08	300	-
Cu	38.85	18.24	2.13	100	-
Pb	2.47	18.55	0.13	170	-
Cd	0.53	0.56	0.94	0.6	4
Ni	56.24	76.23	0.74	190	-
Cr	5.82	2.59	2.25	250	1300
As	12.35	4.74	2.60	25	100
Mn	562.15	246.60	2.28	-	-

basically consistent with that in the fuel. Although the enrichment factors of trace elements in bottom ash are different, they all have varying degrees of enrichment compared to biomass raw materials. Cr and Mn are more easily enriched in slag, indicating that these elements are related to coarse particles. This finding is consistent with the prior research of Xu et al.²⁹

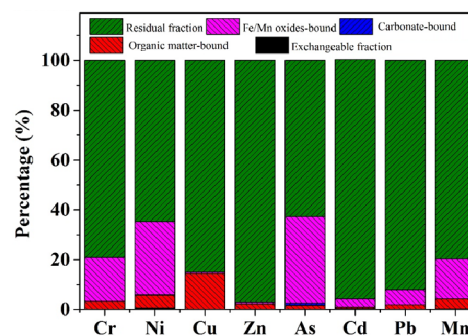
^aRisk screening values and risk control values according to soil environmental quality. Risk control standard for soil contamination of agricultural land (GB 15618-2018) (pH > 7.5).

Comparing the concentrations of these elements in the bottom ash with the established limit values for heavy metals in agricultural land soil, as specified in the "Soil Environmental Quality Standard for Soil Pollution Risk Control of Agricultural Land (Trial)" (GB15618-2018), none of the elements' contents surpass the prescribed screening and risk control values. However, the concentration of Cd is closest to the risk screening value; therefore, when biomass slag is used in soil, it is necessary to evaluate the potential environmental risks.

3.3. Fractionation of Trace Elements in Biomass Slag.

According to the research of Tessier et al.²³ the chemical speciation of trace elements can be divided into five forms: exchangeable fraction, carbonate fraction, Fe/Mn oxide fraction, organic matter fraction, and residual fraction. Different forms exhibit different biological toxicity and environmental behaviors.³¹ Exchangeable and carbonate bound states have weaker binding with soil, making them more susceptible to being released and migrated. Trace elements bound to iron and manganese oxides are more easily released under reducing conditions, while organic bound states are more prone to decomposition and gradual release in oxidizing environments. In contrast, elements in the residual state are relatively stable, exhibiting a limited migration and utilization by organisms.

The percentages of trace elements in different fractions are listed in Figure 2. It can be observed that the trace elements in the bottom ash samples mainly exist in the residual state, typically within the lattice of silicates and primary and secondary minerals. In natural conditions, this state shows stability over an extended period, posing low environmental risks as it is not readily absorbed by plants. Additionally, except for the residual state, Cu and Zn predominantly exist in the form of organic matter bound, posing minimal environmental

**Figure 2.** Percentage of trace elements in different fractions.

pollution risks. While other elements primarily exist in the form of Fe/Mn oxide bound, usually found in the outer capsule of minerals and fine dispersed particles,²⁷ and the active iron manganese oxide has a large specific surface area, formed through anion adsorption or coprecipitation, demonstrating reduced precipitation tendencies and lower environmental risks in comparison to other elements.³² In contrast, Ni exhibits a higher proportion of exchangeable state than other trace elements, making it relatively more prone to precipitate and be absorbed by plants.³³

3.4. Leaching Characteristics of Trace Elements. The leaching test is widely used for studying the precipitation of harmful trace elements from solid waste; based on the simulation results of the interaction between ash and water, which can explain the release rate and mechanism of harmful elements and predict the potential environmental effects of slag under natural conditions.³⁴ And the leaching characteristics of trace elements can provide a basis for its resource utilization and harmless treatment.²⁹ As shown in Figure 3, the effects of leaching solution pH and soaking time on the leaching concentration of trace elements through the static soaking experiment can be found.

During the leaching test, the Cr concentration in the leaching solution reached its maximum value on the first day, then decreased and gradually stabilized at around 30 μg/L after the fifth day. The decrease in leaching concentration may be related to the adsorption of Cr in the ash and solution. The concentration of Ni in the leaching solution remains relatively stable, ranging between 3 and 5 μg/L. During the leaching process, the leaching concentration of Cu is stable and at an extremely low level, between 1 and 2 μg/L, within a safe concentration range. The leaching concentration of Zn gradually increased with the prolongation of leaching time from 1st to 13th days, but showed a significant decrease on 17th days, followed by a notable decrease on the 17th day, possibly due to interactions between bottom ash and Zn in the leaching solution. As exhibits strong regularity during the leaching process, and its leaching concentration significantly increases with the prolongation of leaching time on the 1st to 13th day of leaching. After 13th day, its leaching concentration remained stable at 25–30 μg/L. The concentration of Cd in the leaching solution remains relatively stable and at an extremely low concentration level (<1 μg/L). Similarly, Pb concentrations remained stable (1–2 μg/L) within a safe

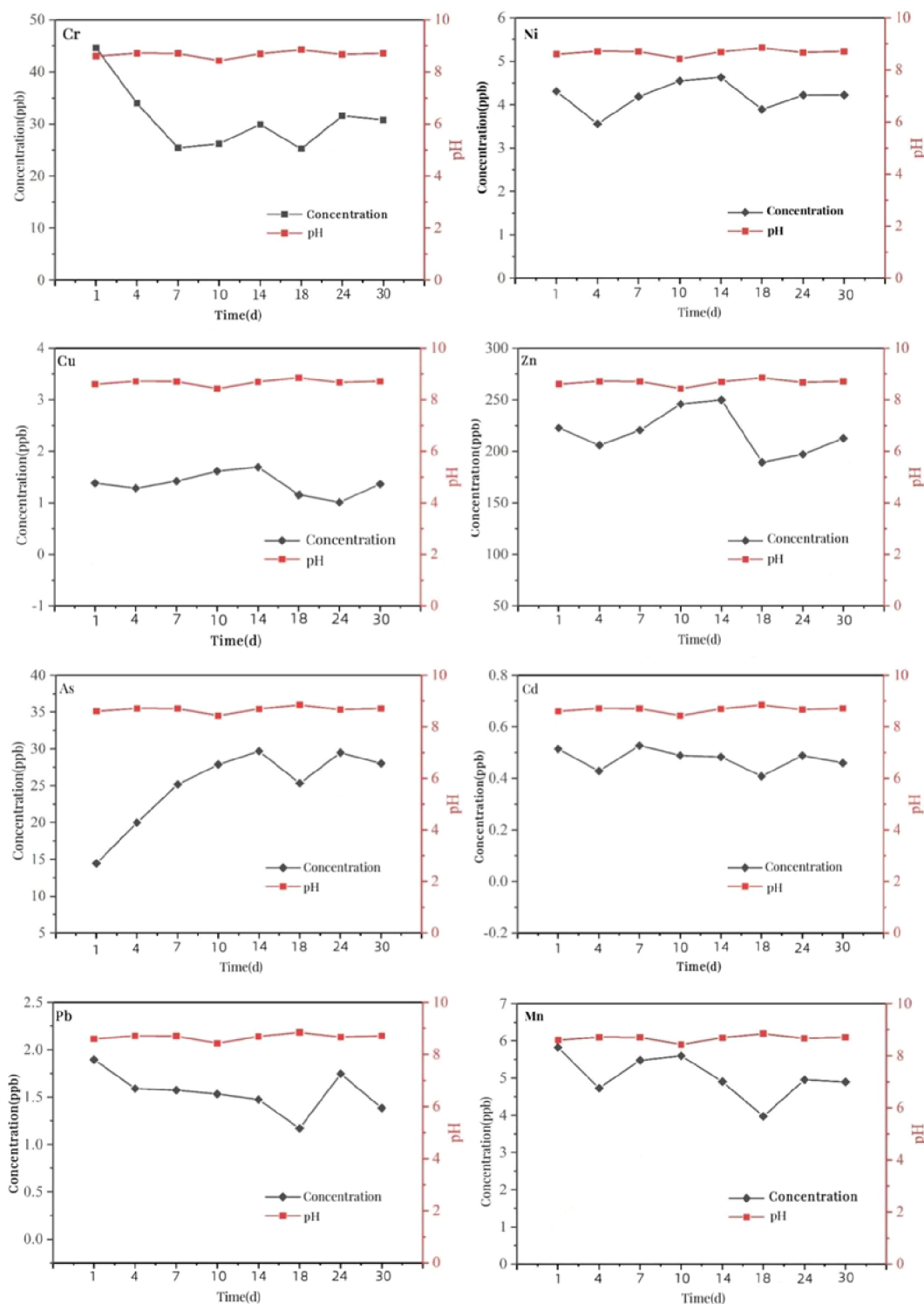


Figure 3. Leaching concentration and pH change curve of trace elements in the biomass bottom ash leaching solution.

range, causing minimal environmental impact. The concentration of Mn in the leaching solution is at a relatively low level, between 4 and 6 $\mu\text{g/L}$, within a safe concentration range.

The leaching characteristics of trace elements are related not only to the content of each element in the bottom ash but also to their specific states of occurrence. Some studies have shown that the majority of trace elements in ash are distributed in the lattice structure of insoluble minerals (such as aluminosilicates) in ash, resulting in lower leaching rates.^{13,35} Conversely,

some elements exhibit higher leaching ability because they exist in soluble salts (like carbonates), bind to organic matter, or are adsorbed on the surface of stable compounds (such as quartz and lime).^{29,34,36} Moreover, the leaching characteristics of trace elements are influenced by their elemental compositions, mineral makeups, and morphological features. Different leaching conditions can also modify the leaching amounts of trace elements to a certain extent.¹³ In this study, the solid–liquid contact area and time are more sufficient than

those for the natural leaching process, and the leaching amount should be higher than that for the latter. The results did not exhibit adverse environmental effects, suggesting that natural leaching processes may not pose a significant risk of environmental pollution.

3.5. Ecological Risk Assessment of Trace Element.

The potential ecological risk index is usually considered an indicator that can quantitatively reflect the overall potential ecological risk caused by various pollution sources among soils. On the basis that the utilization of biomass bottom ash in agricultural and forestry soils is usually considered as the best approach,³⁷ the potential ecological risk index was used to evaluate the potential ecological risk on the slag based on the methodology proposed by Hakanson.²⁴ The values of E_r^i for trace elements are presented in Figure 4 and summarized in Table 4.

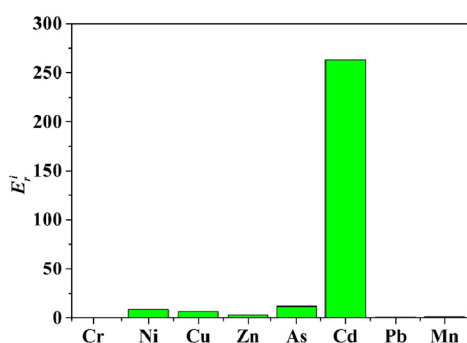


Figure 4. Potential ecological risk assessment results for the trace elements in the bottom ash.

Table 4. Evaluation Results of Potential Ecological Risks

item	potential ecological risk factor		potential ecological risk index	
	Eri	risk level	RI	risk level
Cr	0.13	Low	294.31	moderate
Ni	8.79	Low		
Cu	6.33	Low		
Zn	2.71	Low		
As	11.76	Low		
Cd	263.00	Very high		
Pb	0.53	Low		
Mn	1.07	Low		

Regarding the ecological risk of individual heavy metal elements, the potential ecological risk coefficients of the eight trace elements in the sample are as follows in descending order: Cd (263.00) > As (11.76) > Ni (8.79) > Cu (6.33) > Zn (2.71) > Mn (1.07) > Pb (0.53) > Cr (0.13). The ecological risk assessment indicates that Cd is very high level ($160 \leq E_r^i < 320$), whereas the ecological risk level of other elements are considered low level ($E_r^i < 30$). The content of Cd (0.53 mg/kg) is lower than that of the other elements, but the potential ecological risk level is relatively high. The main reason is that Cd has a higher value of toxicity coefficient (T_r^i).

According to the calculation results of the comprehensive potential ecological risk index RI (Table 4), the value of RI is 294.31, categorizing it as a moderate level ($150 < RI < 300$). Cd predominantly contributes to this index, accounting for 89.36% of the total, while the contribution of other elements

remains relatively low. Studies indicate that the primary source of Cd stems from human activities, specifically the extensive use of pesticides and fertilizers in agricultural practices, contributing to its increasing presence in the environment.^{27,38} Cd is easily absorbed and accumulated by organisms and enriched in ash. Consequently, when utilizing bottom ash in agricultural and forestry applications,²⁸ careful attention should be paid to the ecological risks posed by Cd.

The RAC values, calculated based on the F1 and F2 fractions, were employed to assess the bioavailability and mobility of trace elements. The findings, illustrated in Figure 5,

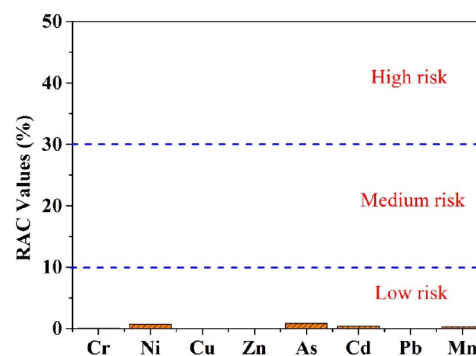


Figure 5. RAC results for the trace elements in ash samples.

depict the average RAC values of seven trace elements in the ash samples, following the order of effectiveness and environmental risk: As (0.87%) > Ni (0.74%) > Cd (0.36%) > Mn (0.28%) > Cr (0.06%) > Pb (0.01%) > Cu (0.004%) > Zn (0.003%), which represents the order of effectiveness and environmental risk of trace elements to a certain extent. And all the elements fall within the no-risk range. The conclusion is consistent with the research by Xu et al.²⁹ Furthermore, the results also demonstrated that the chemical fractions of trace elements have an influence on the assessment of the results of bioavailability and mobility. The RAC values indicate that the possibility of harmful elements in slag being prone to precipitation and migration is relatively low, and there is relatively little environmental risk during the treatment and utilization process.

4. CONCLUSION

Biomass is a rich and renewable clean energy source. In recent years, the rapid expansion of biomass power plants has led to increased environmental pressure due to the rising volume of ash generated. This study focuses on the bottom ash of a typical biomass direct combustion power plant as a research object. The chemical composition analysis results revealed that the bottom ash contains nutrients that promote plant growth and has the potential feasibility to be used as a fertilizer. The results of XRF analysis are shown that the main chemical components of the bottom ash are SiO_2 , Fe_2O_3 , CaO , K_2O , Al_2O_3 , TiO_2 , MgO , etc. All the trace elements have different concentrations, and their enrichment factors vary compared to the biomass raw fuel. The chemical speciation of trace elements mainly exists in the residual state. Leaching characteristics indicated low rates for all elements due to their presence in the lattice structure of insoluble minerals, suggesting no adverse environmental effects. The result of potential ecological risk showed that the risk level of Cd is very high, while that of other elements was in low risk level, and

special attention should be paid to the ecological risks caused by Cd. Furthermore, the indexes of RAC indicated that all of the trace elements pose no ecological risk. Therefore, the bottom ash can be applied as soil conditioner materials of compound fertilizer on agricultural and forestry soils.

■ ASSOCIATED CONTENT

Data Availability Statement

The raw/processed data required to reproduce these findings cannot be shared at this time due to technical or time limitations, and data will be available on request.

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Author Contributions

M.Y. contributed to writing—original draft and writing—review and editing. M.X. contributed to supervision, visualization, and methodology. Y.H. contributed to conceptualization, experiment, supervision, and writing—review and editing. S.X. contributed to project administration and data curation. J.Z. contributed to methodology.

Notes

The authors declare no competing financial interest.

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■ REFERENCES

- (1) Munawar, M. A.; Khoja, A. H.; Naqvi, S. R.; Mehran, M. T.; Hassan, M.; Liaquat, R.; Dawood, U. F. Challenges and opportunities in biomass ash management and its utilization in novel applications. *Renewable Sustainable Energy Rev.* **2021**, *150*, 111451.
- (2) Yao, X.; Zhao, Z.; Chen, S.; Zhou, H.; Xu, K. Migration and transformation behaviours of ash residues from a typical fixed-bed gasification station for biomass syngas production in China. *Energy* **2020**, *201*, 117646.
- (3) Eskander, S. M.; Fankhauser, S. Reduction in greenhouse gas emissions from national climate legislation. *Nat. Clim. Change* **2020**, *10* (8), 750–756.
- (4) Ondrasek, G.; Kranjčec, F.; Filipović, L.; Filipović, V.; Kovačić, M. B.; Badovinac, I. J.; Peter, R.; Petravić, M.; Macan, J.; Rengel, Z. Biomass bottom ash & dolomite similarly ameliorate an acidic low-nutrient soil, improve phytonutrition and growth, but increase Cd accumulation in radish. *Sci. Total Environ.* **2021**, *753*, 141902.
- (5) Costa, M.; Piazzullo, D.; Di Battista, D.; De Vita, A. Sustainability assessment of the whole biomass-to-energy chain of a combined heat and power plant based on biomass gasification: biomass supply chain management and life cycle assessment. *J. Environ. Manage.* **2022**, *317*, 115434.
- (6) Guo, J.-X.; Zhu, K. Operation management of hybrid biomass power plant considering environmental constraints. *Sustainable Prod. Consumption* **2022**, *29*, 1–13.
- (7) Vassilev, S. V.; Baxter, D.; Andersen, L. K.; Vassileva, C. G. An overview of the composition and application of biomass ash. Part 1. Phase—mineral and chemical composition and classification. *Fuel* **2013**, *105*, 40–76.
- (8) Zhang, Z.; Han, Z.; Sheng, C. Feasibility evaluation of biomass fly ashes from power station using as fertilizer. *Trans. Chin. Soc. Agric. Eng.* **2016**, *34* (7), 200–205.
- (9) Hasan, H.; Dang, L.; Khabbaz, H.; Fatahi, B.; Terzaghi, S. Remediation of Expansive Soils Using Agricultural Waste Bagasse Ash. *Proc. Eng.* **2016**, *143*, 1368–1375.
- (10) Qi, T.; Gao, X.; Feng, G.; Bai, J.; Wang, Z.; Chen, Q.; Wang, H.; Du, X. Effect of biomass power plant ash on fresh properties of cemented coal gangue backfill. *Constr. Build. Mater.* **2022**, *340*, 127853.
- (11) Cabrera, M.; Galvin, A. P.; Agrela, F.; Carvajal, M. D.; Ayuso, J. Characterisation and technical feasibility of using biomass bottom ash for civil infrastructures. *Constr. Build. Mater.* **2014**, *58*, 234–244.
- (12) Shi, Y.; Cong, X.; Yu-Ping, Q. Analysis and prospect of resource utilization of ash and slag from agroforestry biomass-fired power plants in China. *J. Agric. Resour. Environ.* **2019**, *36* (2), 127–139.
- (13) Wang, X.; Zhu, Y.; Hu, Z.; Zhang, L.; Yang, S.; Ruan, R.; Bai, S.; Tan, H. Characteristics of ash and slag from four biomass-fired power plants: Ash/slag ratio, unburned carbon, leaching of major and trace elements. *Energy Convers. Manage.* **2020**, *214*, 112897.
- (14) Tosti, L.; van Zomeren, A.; Pels, J. R.; Dijkstra, J. J.; Comans, R. N. Assessment of biomass ash applications in soil and cement mortars. *Chemosphere* **2019**, *223*, 425–437.
- (15) Vassilev, S. V.; Baxter, D.; Andersen, L. K.; Vassileva, C. G. An overview of the chemical composition of biomass. *Fuel* **2010**, *89* (5), 913–933.
- (16) Cruz, N. C.; Ródrigues, S. M.; Carvalho, L.; Duarte, A. C.; da Pereira, E.; Romkens, P. F. A. M.; Tarelho, L. A. C. Ashes from fluidized bed combustion of residual forest biomass: recycling to soil as a viable management option. *Environ. Sci. Pollut. Res.* **2017**, *24* (17), 14770–14781.
- (17) Krook, J.; Martensson, A.; Eklund, M. Sources of heavy metal contamination in Swedish wood waste used for combustion. *Waste Manage.* **2006**, *26* (2), 158–166.
- (18) Qin, J.; Hovmand, M. F.; Ekelund, F.; Ronn, R.; Christensen, S.; De Groot, G. A.; Mortensen, L. H.; Skov, S.; Krogh, P. H. Wood ash application increases pH but does not harm the soil mesofauna. *Environ. Pollut.* **2017**, *224*, 581–589.
- (19) Nurmesniemi, H.; Mäkelä, M.; Pöykiö, R.; Mankinen, K.; Dahl, O. Comparison of the forest fertilizer properties of ash fractions from two power plants of pulp and paper mills incinerating biomass-based fuels. *Fuel Process. Technol.* **2012**, *104*, 1–6.
- (20) Park, J.-H.; Wang, J. J.; Seo, D.-C. Agronomic and environmental performance of bottom ash discharged from biomass-based thermal power plant. *Sustainable Chem. Pharm.* **2023**, *33*, 101097.
- (21) Ondrasek, G.; Zovko, M.; Kranjčec, F.; Savić, R.; Romić, D.; Rengel, Z. Wood biomass fly ash ameliorates acidic, low-nutrient

hydromorphic soil & reduces metal accumulation in maize. *J. Cleaner Prod.* **2021**, *283*, 124650.

(22) Mendes, L. A.; Avellan, A.; Cruz, N. C.; Palito, C.; Römken, P. F.; Amorim, M. J.; Tarelho, L. A.; Rodrigues, S. M. Biomass ash formulations as sustainable improvers for mining soil health recovery: Linking soil properties and ecotoxicity. *Environ. Pollut.* **2021**, *291*, 118165.

(23) Tessier, A.; Campbell, P. G. C.; Bisson, M. Sequential extraction procedure for the speciation of particulate trace metals. *Anal. Chem.* **1979**, *51* (7), 844–851.

(24) Hakanson, L. An Ecological Risk Index for Aquatic Pollution Control – A Sedimentological Approach. *Water Res.* **1980**, *14* (8), 975–1001.

(25) You, M.; Hu, Y.; Yan, Y.; Yao, J. Speciation Characteristics and Ecological Risk Assessment of Heavy Metals in Municipal Sludge of Huainan, China. *Molecules* **2021**, *26*, 6711.

(26) Hu, Y.; You, M.; Liu, G.; Dong, Z. Characteristics and potential ecological risks of heavy metal pollution in surface soil around coal-fired power plant. *Environ. Earth Sci.* **2021**, *80* (17), 566.

(27) You, M.; Hu, Y.; Wang, Z.; Zhang, W. Characterization and Ecological Risk Assessment of Toxic Metal Contaminants in the Soil Around the Coal Gangue Hill in Huainan, Central China. *Water, Air, Soil Pollut.* **2023**, *234* (11), 667.

(28) You, M.; Yan, Y.; Hu, Y. Chemical speciation and risk assessment of trace elements in the soil of the agricultural area in huainan, China. *Appl. Ecol. Environ. Res.* **2024**, *22* (1), 901–915.

(29) Xu, S.; Zhou, C.; Fang, H.; Zhu, W.; Shi, J.; Liu, G. Characteristics of trace elements and potential environmental risks of the ash from agricultural straw direct combustion biomass power plant. *Chemosphere* **2023**, *333*, 138989.

(30) Li, X.; Rubaek, G. H.; Sorensen, P. High plant availability of phosphorus and low availability of cadmium in four biomass combustion ashes. *Sci. Total Environ.* **2016**, *557–558*, 851–860.

(31) You, M.; Hu, Y.; Meng, Y. Chemical speciation and bioavailability of potentially toxic elements in surface sediment from the Huaihe River, Anhui Province, China. *Mar. Pollut. Bull.* **2023**, *188*, 114616.

(32) Chuncai, Z.; Guijian, L.; Dun, W.; Ting, F.; Ruwei, W.; Xiang, F. Mobility behavior and environmental implications of trace elements associated with coal gangue: a case study at the Huainan Coalfield in China. *Chemosphere* **2014**, *95*, 193–199.

(33) Ting, F.; Wenxuan, L.; Guanjun, H.; Kai, C.; Xiuxia, Z.; Jing, L.; Kun, Y.; Suofei, J.; Yangyang, L.; Hui, L. Fractionation and ecological risk assessment of trace metals in surface sediment from the Huaihe River, Anhui, China. *Human Ecol. Risk Assess.* **2020**, *26* (1), 147–161.

(34) Izquierdo, M.; Querol, X. Leaching behaviour of elements from coal combustion fly ash: an overview. *Int. J. Coal Geol.* **2012**, *94*, 54–66.

(35) Camerani, M. C.; Steenari, B.-M.; Sharma, R.; Beckett, R. Cd speciation in biomass fly ash particles after size separation by centrifugal SPLITT. *Fuel* **2002**, *81* (13), 1739–1753.

(36) Maresca, A.; Hansen, M.; Ingerslev, M.; Astrup, T. F. Column leaching from a Danish forest soil amended with wood ashes: fate of major and trace elements. *Biomass Bioenergy* **2018**, *109* (2), 91–99.

(37) Tosti, L.; van Zomeren, A.; Pels, J. R.; Dijkstra, J. J.; Comans, R. N. J. Assessment of biomass ash applications in soil and cement mortars. *Chemosphere* **2019**, *223*, 425–437.

(38) Wu, Y.; Li, X.; Yu, L.; Wang, T.; Wang, J.; Liu, T. Review of soil heavy metal pollution in China: Spatial distribution, primary sources, and remediation alternatives. *Resour., Conserv. Recycl.* **2022**, *181*, 106261.