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Research article

Effects of different straws on heavy metal release and bioavailability in coal gangue

Xiuyue Xu[1,2], Jun Ren[1,2,*], Ningning Wang[3,4] and Huilin Dong[1,2]

[1] School of Geography and Resources, Guizhou Education University, Guiyang, 550018, China
[2] Guizhou Provincial Key Laboratory of Geographic State Monitoring of Watershed, Guizhou Education University, Guiyang, 550018; China
[3] Chongqing Key Laboratory of Exogenous Minerals and Mine Environment, Chongqing, 401120; China
[4] College of Resources and Environmental Engineering, Guizhou University, Guiyang, 550025, China

* **Correspondence:** Email: renjun@gznc.edu.cn; Tel: +0086085113339619920; Fax: +0086085186277219.

Abstract: The purpose of this study was to investigate the effects of the addition of rice straw (RIS), corn straw (CS), pepper straw (PS), and rape straw (RAS) on the release and speciation of heavy metals in coal gangue. Results showed that the addition of rape straw and corn straw significantly increased the pH value of the leachate. Straw addition increased the iron (Fe), manganese (Mn), copper (Cu), zinc (Zn), and cadmium (Cd) concentrations in leachate but inhibited the release of lead (Pb) from coal gangue, with RIS having a particularly significant inhibitory effect. Straw addition promoted the transformation of heavy metals from a reducible to an oxidizable state in coal gangue, with significant differences in the impact on exchangeable heavy metals. Rape straw reduced the exchangeable Fe and Mn concentrations, whereas RIS decreased the exchangeable Zn concentration. The results of the RAC risk assessment indicated that by the end of the trials, RAS significantly reduced the ecological risks of Fe, Mn, Cu, Pb, and Cd. In summary, when using straw to remediate and improve coal gangue, dynamic changes in the activity of heavy metals need to be considered, and the use of RAS should be prioritized to avoid potential secondary environmental pollution.

Keywords: straw; coal gangue; heavy metal; release; bioavailability; ecological remediation

1. Introduction

China is one of the largest producers of agricultural crops in the world, also having the highest production of straw globally. It is estimated that China produces approximately 8.56 million tons of straw annually [1]. As of 2023, China has successfully maintained a comprehensive straw utilization of over 86%, achieving a utilization pattern that primarily focuses on fertilizer use, supplemented by substrate and raw material additions [2]. However, straw waste and the occasional scattered burning not only cause a waste of resources but also exacerbate environmental pollution, posing a threat to human health [3].

Coal is the main energy source and an important industry in China. The development of coal resources plays an important supporting role in economic construction and social development [4]. According to National Bureau of Statistics data, coal consumption in China in 2022 reached 45.6 billion tons, representing a 10.5% increase from the previous year, maintaining its position as the largest coal consumer. In the process of coal mining, a large amount of coal gangue is produced, and its output accounts for approximately 15% of the overall coal production [5]. The accumulated stock of coal gangue in China exceeds 7 billion tons, with more than 2600 gangue hills and about 1600 large gangue hills [6,7], most being located in southwest China. The main uses of coal gangue include the recovery of heat for power generation, construction materials, and as a filling raw material for subsidence mines [8]. However, these applications utilize less than 30% of the annual stockpile. Furthermore, there are several challenges in the utilization of coal gangue, including severe environmental issues, low utilization rates of valuable elements, high treatment costs, substantial capital investment requirements, and insufficient consumption capacity, which collectively limit the rapid development of coal gangue resource utilization [9]. With the increase in stacking time, weathering, leaching, and other processes enhance the release of heavy metals and other harmful substances, leading to ecological problems such as soil acidification, salinization, and fertility decline [10,11], which further threaten human health [12,13]. The mean contents of copper (Cu), chromium (Cr), nickel (Ni), zinc (Zn), and mercury (Hg) in the soil around a coal gangue stockpile in Guizhou Province, China, all exceeded the standard to varying degrees [14]. In the Chengcun mining area in Huixian City, Henan Province, the cadmium (Cd) pollution risk level of wheat in the reclaimed farmland from coal gangue reached a moderate risk [15]. Ren et al. [16] measured the lead (Pb), Zn, Cr, and Cu concentrations in the soil around a coal gangue stockpile in Huozhou, Shanxi Province, and found that, by taking the background value of the soil in Shanxi Province as a reference, all four heavy metals were enriched to different degrees, and soil quality standards were exceeded. Therefore, the restoration of coal gangue-contaminated soil around mining areas is of great significance.

It has been reported that the ecological restoration of coal gangue can not only reduce the ecological harm to the environment surrounding the mining area but will also optimize the landscape and natural features of the mining area. This restoration process is a crucial step in improving the ecological environment of the coal mine area [17]. The greatest challenge in achieving the ecological restoration of coal gangue is the lack of nutrients in the gangue hills, which restricts the growth of the plants used in restoration. Most plants are unlikely to survive if they are planted directly on the gangue hills, and even if they do survive, they are difficult to maintain and manage. Consequently, nutrient supplementation is essential for the gangue hills prior to phytoremediation to meet the growth requirements of the restoration plants.

Straw is a valuable biomass resource, rich in nutrients essential for plant growth. When returned to the field, straw plays a critical role in enhancing soil quality by improving soil structure, promoting aggregate formation, and increasing fertility [18,19]. These benefits are largely mediated by soil microorganisms, which decompose the straw, converting its photosynthetic carbon into stable soil organic carbon and stimulating microbial activity and biomass [20]. Beyond its agricultural benefits, straw has recently gained attention as a potential material for environmental remediation due to its unique physicochemical properties. Xu et al. [21] demonstrated that rice and wheat straw can increase soil pH, reduce Cd bioavailability, and decrease Cd uptake by ryegrass. Similarly, rice and soybean straw were found to enhance Cd accumulation in hyperaccumulator plants, achieving a Cd removal rate of 29.8%–50.7% from contaminated soils [22]. Meanwhile, studies have shown that straw entering the soil also poses a risk of activating heavy metals. The addition of rice straw can significantly increase the content of available lead (Pb) in the soil [23], while the addition of corn straw (CS) and bean straw can also significantly enhance the content of available Cd [24]. However, it has not been reported whether different types of straw can be used for the ecological restoration of coal gangue or whether the addition of different types of straw will increase the ecological risk of heavy metals. Therefore, this study explored the effect of straw type on the release of heavy metals in the leachate of coal gangue by adding four different straw species (rice, corn, pepper, and rape). Furthermore, by analyzing the occurrence forms of heavy metals, the effect of straw species on the transformation of heavy metal forms in coal gangue was determined. This research not only provides a theoretical basis for the in-situ remediation of coal gangue but also achieves the goals of treating waste with waste and the utilization of waste resources, reducing the pressure of pollution control, and achieving a win-win outcome.

2. Materials and methods

2.1. Test materials

Coal gangue was obtained from a gangue dump site in Qingzhen City, Guizhou Province, China. The collected coal gangue samples were immediately transported to the laboratory for processing. Coal gangue was spread flat on kraft paper to air dry naturally. After air drying, the gangue was crushed with a wooden stick and passed through a 5-mesh nylon sieve for later use. The physicochemical properties of the coal gangue are shown in Table 1. Rice straw (RIS), corn straw (CS), pepper straw (PS), and rape straw (RAS) were all collected from unpolluted farmland in Guiyang City, China. The various straws were washed with deionized water to remove dust and impurities, dried at 70 °C, and then cut into 5 mm pieces for use.

Table 1. Physicochemical properties of the coal gangue.

pH	EC	Organic matter	Fe	Mn	Cu	Zn	Pb	Cd
2.76	2219	96.52	37200.00	112.00	118.60	199.10	67.90	0.75

2.2. Experimental design

A 100 g weathered coal gangue sample was placed into a 500 mL plastic cup. Four treatment groups were set up based on the type of straw, including rice straw, corn straw, pepper straw, and rape straw. A control group without straw addition (CK) was also established, and each treatment group was set up with three replicates. The water content of each treatment group was adjusted to 65% of the maximum field water capacity by the weighing method. During the experiment, water was added by the weighing method every 5 days to maintain the water content of each group at 65% of the field water capacity.

2.3. Sample collection and determination

Samples were collected in batches on days 0, 1, 7, 15, 90, and 180 during straw decomposition. The leaching test was conducted in accordance with the solid waste–extraction procedure for leaching toxicity-horizontal vibration method (HJ 557-2010). The pH, Eh, and EC values of the leachate were determined on the same day using a pH meter (SH2601, Shanghai Dapu, China), a potentiometric titrator (DZ-2, Shanghai Hongyi, China), and a conductivity meter (DDS11A, Shanghai Leici, China), respectively. The different chemical forms of heavy metals in coal gangue were extracted using the European Community Bureau of Reference (BCR) sequential extraction method, as reported in Zhang et al. (2012), with the extracted forms being in the order of exchangeable, reducible, oxidizable, and residual states. The specific extraction steps are shown in Table 2. The residual state of heavy metals was determined following digestion with nitric acid–hydrofluoric acid–perchloric acid. The leachate and various extracted states of Mn, Cu, Zn, Pb, and Cd were measured using inductively coupled plasma mass spectrometry (iCAP RQ, Thermo Fisher Scientific, Waltham, MA, USA), while Fe was determined using atomic absorption spectrophotometry (WFX-110, Beijing Rayleigh, China).

Table 2. Improved BCR sequential extraction method.

Procedure	Chemical form	Method	Constituent
1	Exchangeable state	Add 40 mL of 0.11 mol/L acetic acid to 1 g of soil sample, shake at room temperature for 16 h at 4000 rpm, and centrifuge for 20 min.	Exchangeable state and carbonate binding state
2	Reducible state	Add 40 mL of 0.5 mol/L hydroxylamine hydrochloride ($NH_2OH·HCl$), shake at room temperature for 16 h at 4000 rpm, and centrifuge for 20 min.	Iron-manganese oxide binding state
3	Oxidizable state	Add 10 mL of 8.8 mol/L H_2O_2, leave at room temperature for 1 h, and dissolve in a water bath for 1 h. Add another 10 mL of 8.8 mol/L H_2O_2 and dissolve in a water bath to about 1 mL. Add 40 mL of 1 mol/L ammonium acetate (NH_4Ac), shake at room temperature for 16 h at 4000 rpm, and centrifuge for 20 min.	Organic and sulfide binding state
4	Residual state	Nitrate–hydrofluoric acid–perchloric acid digestion	

2.4. Potential ecological risk assessment of heavy metals

Heavy metal potential ecological risk assessment (risk assessment code, RAC) is a procedure that has emerged from morphological research, mainly analyzing the active forms of heavy metals present in the environment [25,26]. When the proportion of the active form of heavy metals to the total amount of all forms is very high, the risk of heavy metals to the environment is greater. The relationship between the proportion of active forms of heavy metals and the degree of pollution is shown in Table 3.

Table 3. Relationship between the degrees of pollution and the proportion (%) of the active form of a heavy metal [25,26].

%	<1	1–10	10–30	30–50	≥50
Degree of pollution	None	Mild	Moderate	Severe	Extremely serious

2.5. Data processing and analysis

For data statistics and analysis, IBM SPSS Statistics 25 was employed, whereas Origin 2023 was utilized for mapping purposes.

3. Results

3.1. The impact of various types of straw on the pH, Eh, and EC of leachates

The changes in pH, Eh, and EC values of coal gangue leachate in different treatment groups are shown in Figure 1. With the decomposition of different straws, the pH of the leachate in each treatment group exhibited a trend of first decreasing and then increasing. In all groups, the pH at the later stage of the experiment was higher than at the early stage. Moreover, the pH values in the corn straw and rape straw treatments were significantly higher than those in other treatment groups. At the end of the experiment, the pH values of the leachate in the CS and RAS treatment groups were 1.74 and 1.82 times that of the CK group, respectively. In the CK group, the Eh in the leachate gradually increased. After adding different straw types to the coal gangue, the Eh of the leachate showed a trend of first decreasing and then increasing. The Eh in all treatment groups decreased to the lowest at 7–15 d; the Eh in the CS and RAS groups decreased more than that of other treatment groups. The Eh at 15 days in the CS and RAS treatment groups dropped to 114 and 88 mV, respectively, which were significantly lower than the CK treatment group at 262 mV. Except for RAS, the EC value of the leachate exhibited a general trend of gradual increase, with the increase in the CS being greater than that of other treatment groups. At the end of the experiment, the EC value in the CS treatment group reached 4077.00 μm/cm, which was 1.80 times that of the CK group, while the EC in the RAS treatment group was 1.28 times that of the CK group.

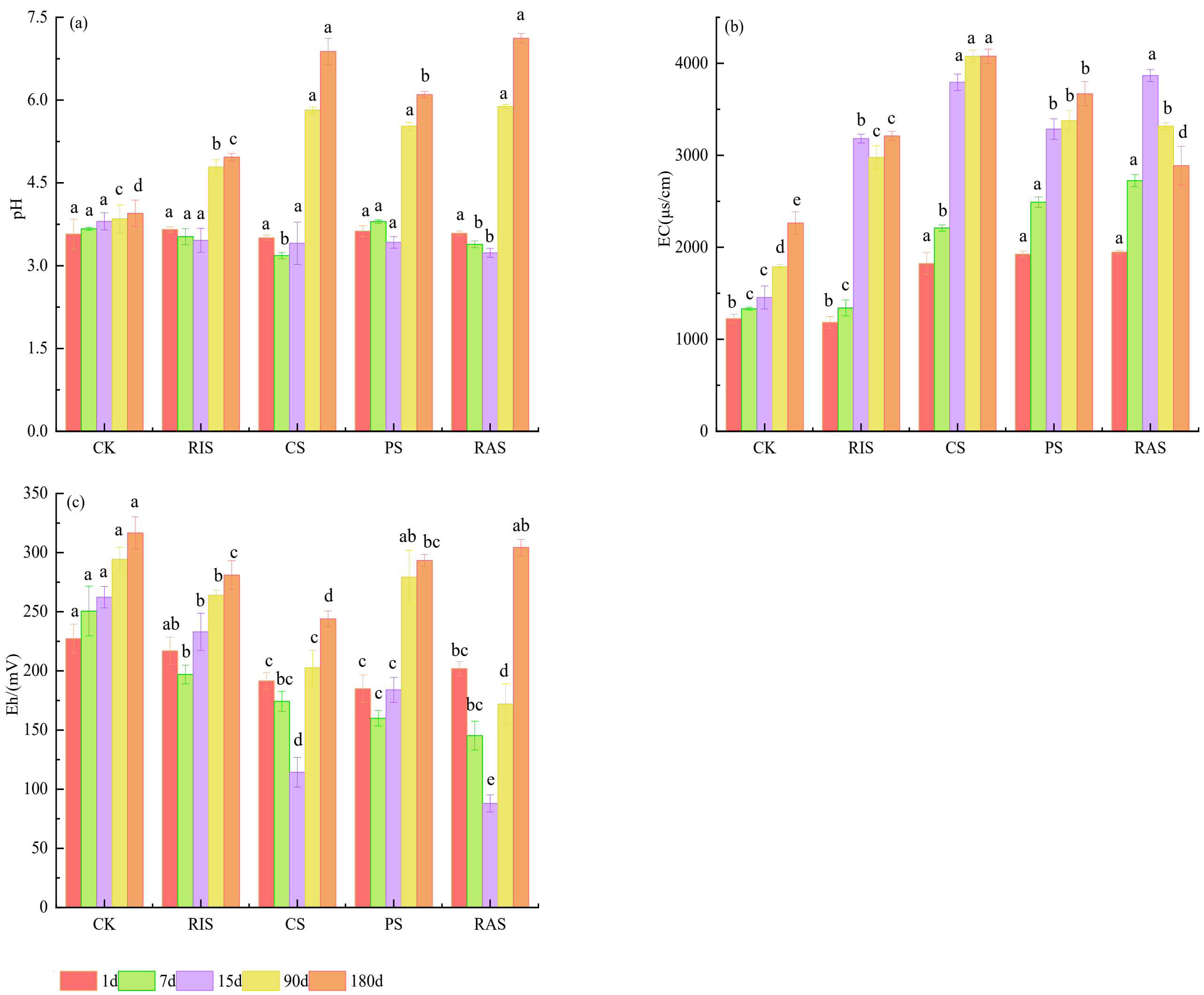
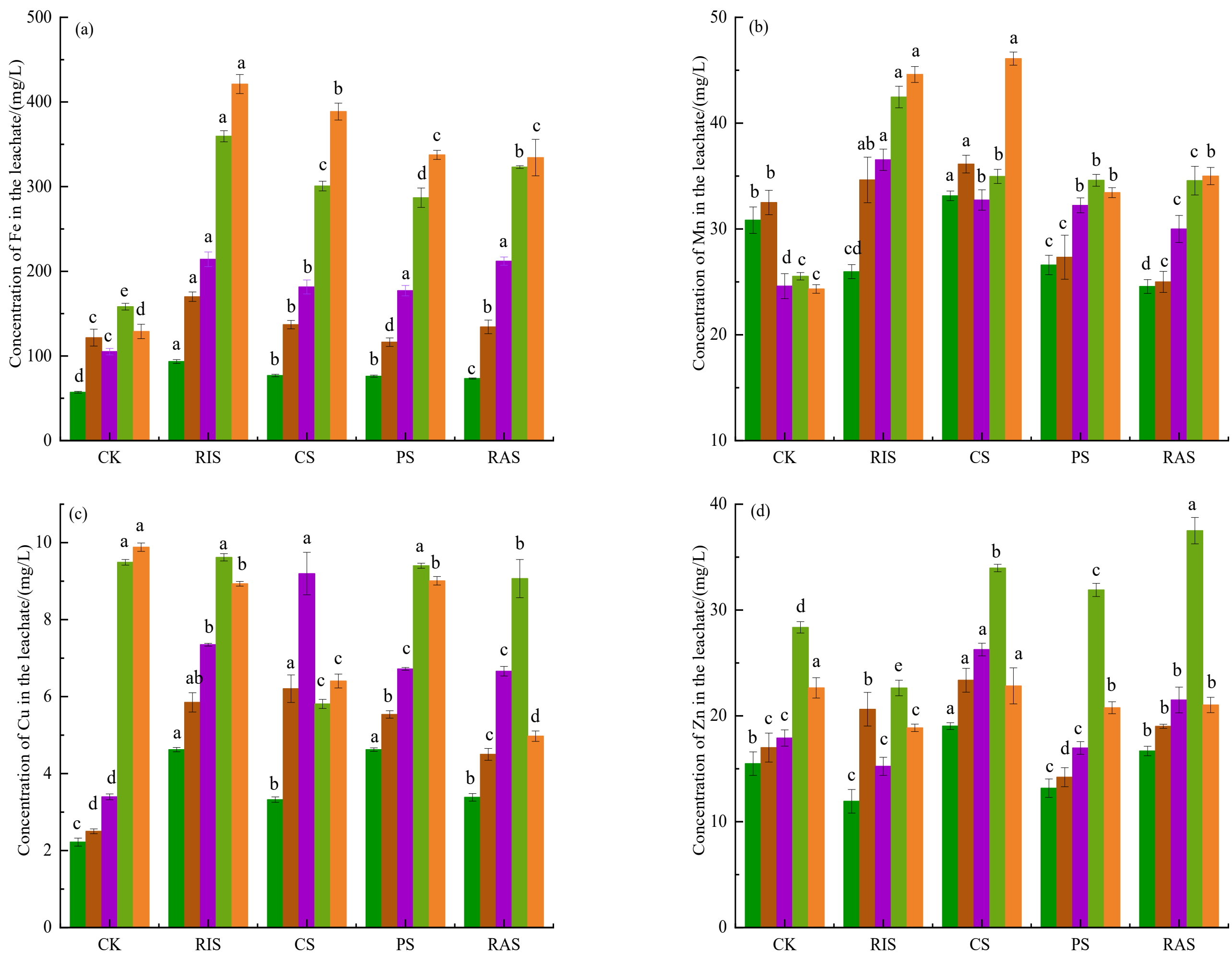


Figure 1. The effect of straw addition on the physicochemical properties of the leaching solution. Different lowercase letters indicate a significant difference among the different treatments at the same time ($P < 0.05$).

3.2. The effect of different straws on the release of heavy metals in coal gangue

The decomposition of the different types of straw significantly increased the mass concentrations of Fe and Mn in the leachates of each treatment group ($P < 0.05$). As shown in Figure 2(a) and 2(b), the Fe and Mn concentrations in the leachates of the same treatment group gradually increased with straw decomposition time. The Fe concentration in the RIS treatment group was significantly higher than in the other straw treatment groups. The Fe concentration in the RIS treatment group increased from 93.42 mg/L on day 1 to 421.21 mg/L on day 180. Compared with the other treatment groups, the leachate concentration in the PS treatment group was significantly lower than in the other treatment groups. At the end of the experiment, the Fe concentrations in the RIS, CS, PS, and RAS treatment groups were 3.27, 3.02, 2.62, and 2.59 times that of the CK group, respectively. Similarly to Fe, as the experiment progressed, the Mn concentration in the leachate gradually increased. However, the Mn concentration in the RAS treatment group was significantly lower than in the other treatment groups.

In each treatment group, the Cu concentration in the leachate first increased and then decreased. Except for CS, the Cu concentration in the leachate of each treatment group reached a maximum after day 90, with a decrease then observed in all treatment groups. At the end of the experiment, the Cu concentrations in the RIS, CS, PS, and RAS treatment groups were 90.82%, 65.31%, 91.94%, and 50.71% of that in the CK group, respectively. The Cu concentration in the RAS treatment group was significantly lower than in the other treatment groups. As shown in Figure 2(d), similarly to the variation of Cu, the Zn concentration in each treatment group also exhibited a trend of first increasing and then decreasing, and all reached a maximum value by day 90. The Zn concentration in the PS treatment group at day 90 was 1.32 times that of the CK group. Subsequently, the Zn concentration in each treatment group decreased to varying degrees, and the Zn concentration in the RIS treatment group decreased by 16.65% compared to the CK group. Compared with the CK group, the addition of the different types of straw inhibited the release of Pb from coal gangue, with RIS having the most significant inhibitory effect. Over the 180 days, RIS, CS, PS, and RAS inhibited the release of Pb by 38.99%, 49.50%, 33.38%, and 33.67%, respectively, compared with the CK. Except for the RAS treatment group, the Cd concentration in the leachates of each treatment group was significantly lower than that of the CK treatment group in the early stage of the experiment (days 1–15). In the later stage of the experiment (days 90–180), the Cd concentration in the leachates of each treatment group was higher than that in the CK treatment group, and the Cd concentration significantly increased, with the growth rate of the RIS treatment group being higher than the other groups.



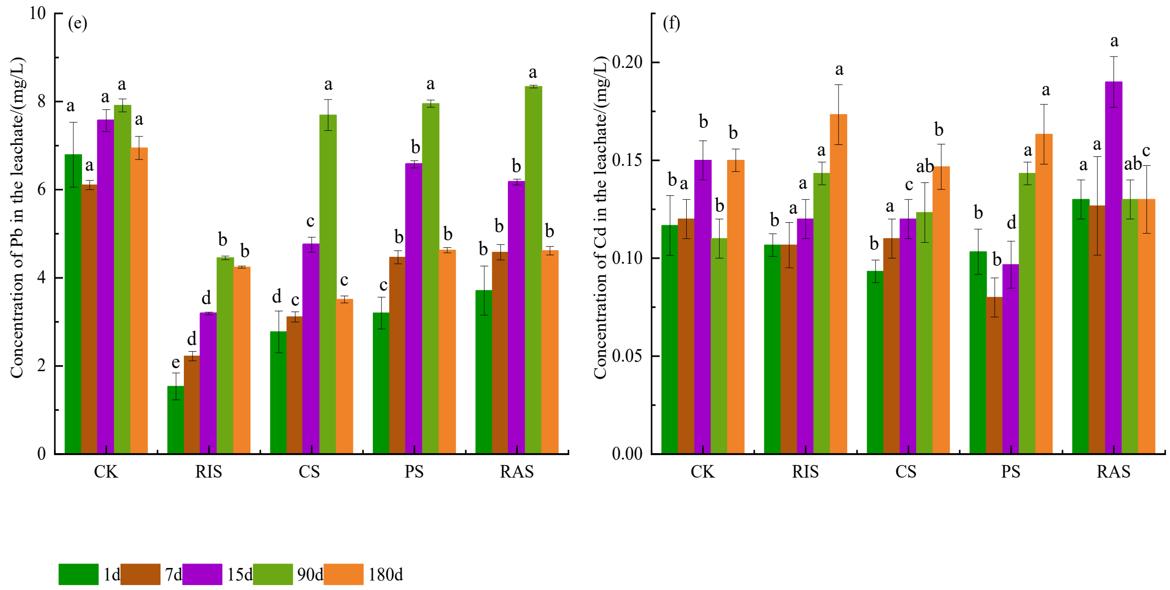


Figure 2. The effect of straw addition on heavy metal release from coal gangue. Different lowercase letters indicate a significant difference among the different treatments ($P < 0.05$).

3.3. The effect of the different straws on the speciation of heavy metals in coal gangue

The speciation of heavy metals determines their environmental behavior and bioavailability, directly affecting their migration and cycling in environmental media. By applying the BCR sequential extraction method, heavy metals in coal gangue were divided into four forms: exchangeable, reducible, oxidizable, and residual. The exchangeable form has a higher activity and toxicity, whereas the reducible, oxidizable, and residual forms pose relatively less harm [27]. The changes of heavy metal forms in coal gangue after the addition of the different straws are shown in Figure 3. As shown in Figure 3(a), compared with the CK group, the proportion of exchangeable Fe in the same treatment group generally exhibited a trend of first increasing and then decreasing with the continuous decomposition of straw. The RAS treatment group exhibited a more significant change in the content of exchangeable Fe. The proportion of exchangeable Fe in the RAS treatment group decreased from 8.66% (straw decomposition on day 15) to 2.60% (at the end of the experiment). On day 15, the concentration of reducible Fe in the RAS treatment group displayed a significant decrease of 51.84% compared to the CK group. Concurrently, there was a notable increase in the proportion of oxidizable Fe. By the end of the experiment, the exchangeable Fe in the CS treatment group accounted for the largest proportion, reaching 5.89%, which was a 34.17% increase compared to the CK group. The addition of CS caused the concentration of reducible Fe to continuously decrease. By the end of the experiment, its concentration in the CS group dropped to 3.66%, a decrease of 63.16% compared to the CK group.

Manganese in coal gangue mainly exists in the form of residue and oxidizable states. As the experiment progressed, the proportion of exchangeable Mn in the CS treatment group increased gradually, while in the PS treatment group, the proportion of exchangeable Mn continued to decrease. By the end of the experiment, compared with the CK, the concentration of exchangeable Mn in the PS treatment group decreased by 20.79%. The addition of PS promoted the conversion of exchangeable and reducible Mn to oxidizable and residue states.

Cu in coal gangue mainly exists in the form of residue, with a content of 61.81 mg/kg, accounting for 52.12% of the total Cu content in coal gangue, followed by the oxidizable state, accounting for 29.70%. As shown in Figure 3(c), straw decomposition gradually reduced the proportion of exchangeable and reducible Cu in each group and gradually increased the content of oxidizable and residual Cu. Compared with other treatment groups, the change in Cu forms in the CS group was more pronounced. Compared to CK, at the end of the experiment, the exchangeable and oxidizable Cu decreased by 80.41% and 64.40%, respectively.

As the experiment progressed, the reducible Zn gradually decreased, and the reduction in reducible Zn was most pronounced in the CS treatment group. At day 180, the concentration of reducible Zn in the CS decreased by 69.31% compared to the CK, while the concentration of exchangeable Zn in the RIS treatment group decreased by 19.90%.

In the raw coal gangue, Pb is predominantly found in the residual state, with a content of 62.07 mg/kg, accounting for 91.42% of the total Pb present. This indicates that the residual form is the dominant speciation of Pb in the coal gangue. The addition of straw promoted the decrease in the proportion of exchangeable Pb in coal gangue. In the same treatment group, with the continuous decomposition of straw, the proportion of exchangeable Pb in coal gangue continued to decrease. The proportion of exchangeable Pb in the raw coal gangue was 2.12%, and at the end of the experiment, the proportions of exchangeable Pb in the RIS, CS, PS, and RAS groups decreased to 1.76%, 0.93%, 1.33%, and 1.55%, respectively. In all treatment groups, the proportion of reducible Pb decreased, while the proportion of oxidizable Pb increased, and the changes in each form were more pronounced in the CS treatment group. At the end of the experiment, the proportion of reducible Pb in the CS group decreased from 6.12% to 3.89%. In summary, the addition of straw promoted the transformation of Pb from exchangeable and reducible states to an oxidizable state, enhancing the stability of Pb in coal gangue.

The residual fraction is the main form of Cd present in raw coal gangue, with the proportion of residual Cd in raw coal gangue being 58.43%. The effect of straw addition on the Cd forms in coal gangue is shown in Figure 3(f). Compared with CK, the addition of straw generally reduced the proportion of exchangeable and reducible Cd in all treatment groups, while increasing the proportions of oxidizable and residual Cd, with the changes in Cd forms being more pronounced in the CS treatment group. The proportion of exchangeable Cd in raw coal gangue was 8.43%; at the end of the experiment, it decreased to 6.31% in the CK group and to 3.63% in the CS group, which was 57.53% of the CK group. The proportion of reducible Cd in the CS treatment group was 20.51% lower than that in the CK group, while the proportion of oxidizable Cd increased to 26.77%.

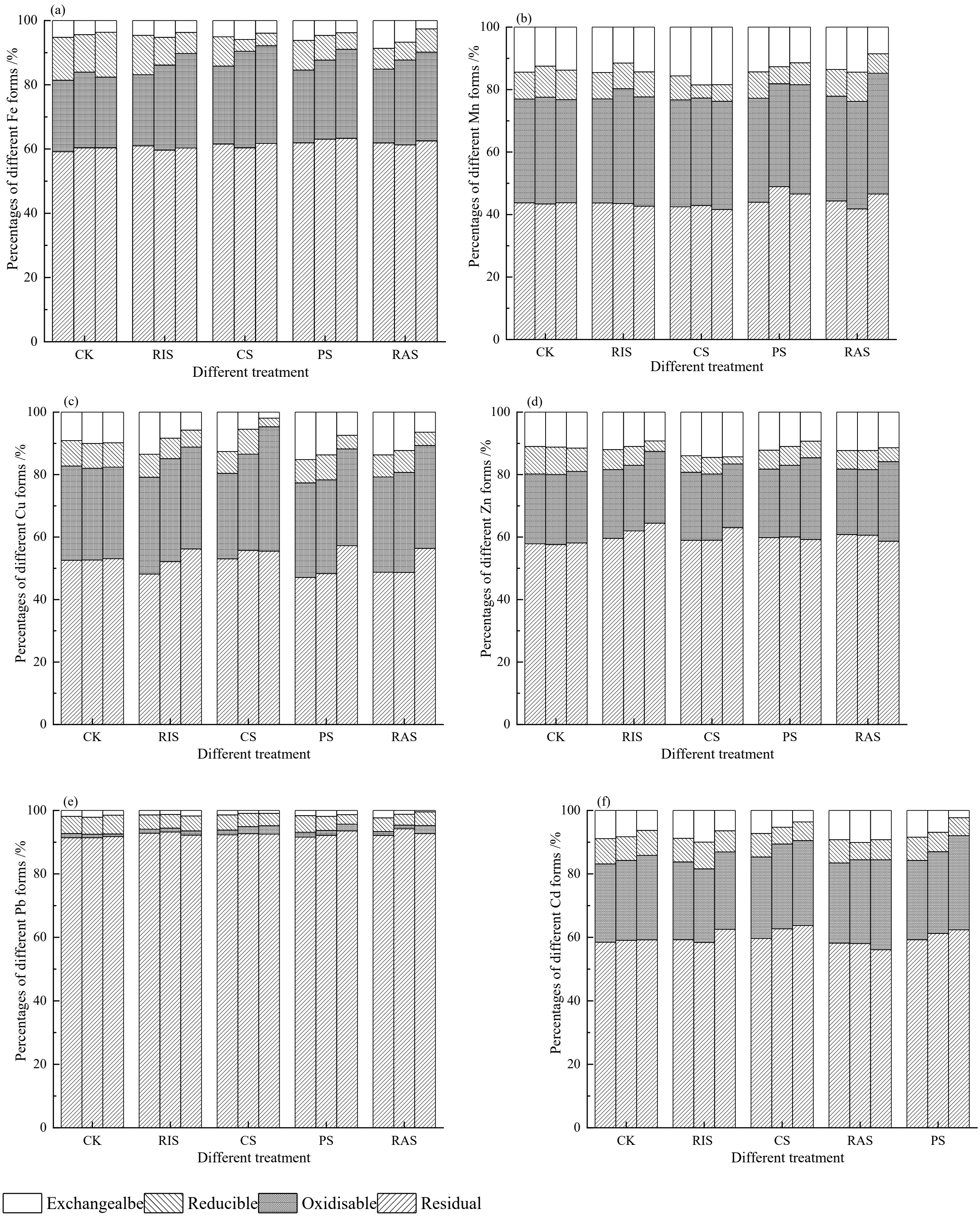


Figure 3. Effect of straw addition on the form variation of heavy metals in coal gangue.

3.4. Ecological assessment of heavy metals after the addition of straw to coal gangue

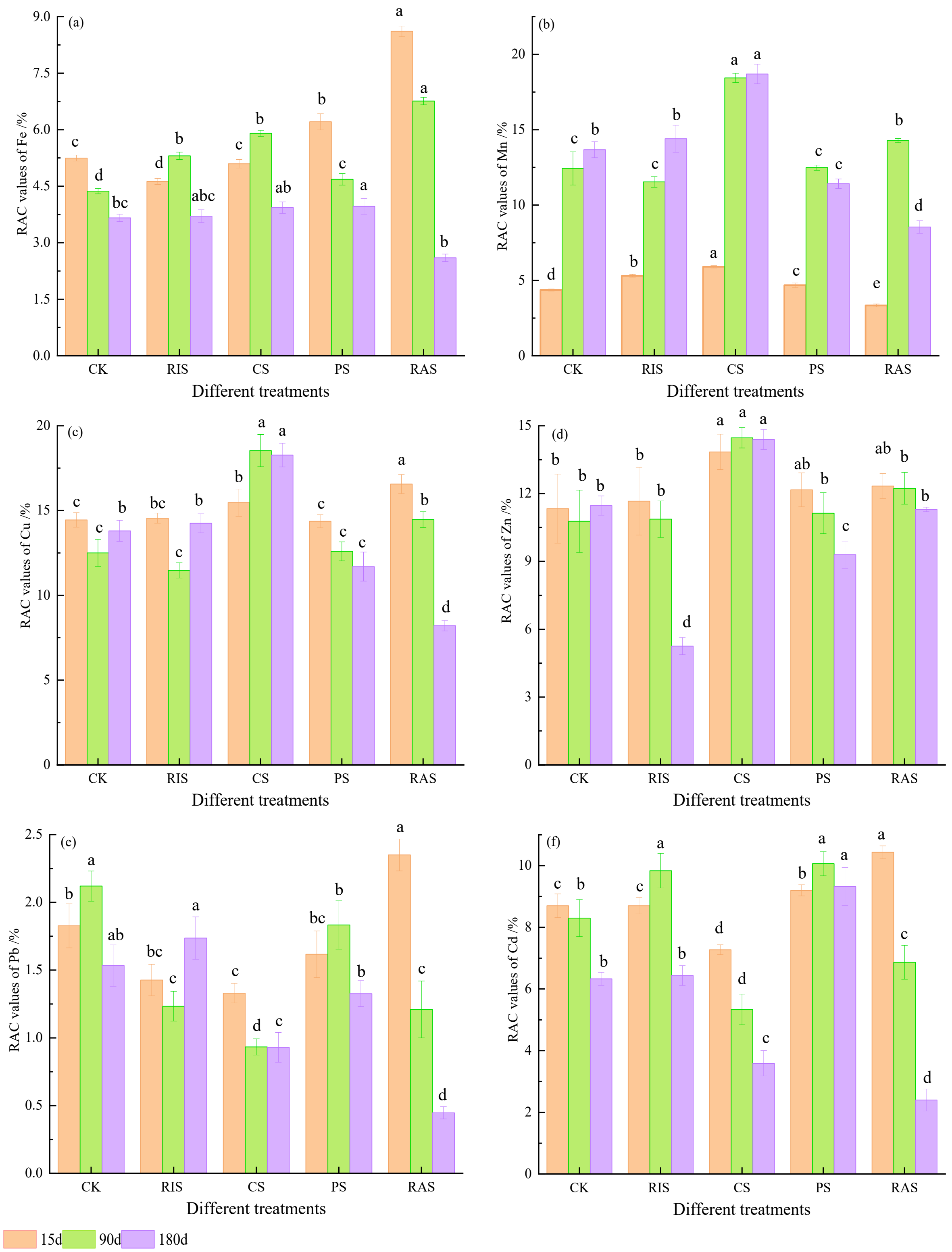


Figure 4. RAC values of heavy metals in different treatments.

The degree of harm that heavy metals pose to the environment is related to their total concentration in the environmental media; however, to a greater extent, it depends on the distribution of the different forms of heavy metals. The RAC is an assessment method based on morphological research. The higher the proportion of the fraction of the active form of heavy metals to the total, the stronger the migration capacity of the heavy metals, and the greater the potential risk to the ecological environment. The proportions of the active forms of heavy metals in coal gangue at the end of the experiment are shown in Figure 4. The proportion of active forms followed the order of Mn > Zn > Cu > Fe > Cd > Pb. After adding different straws, the RAC values of Fe were less than 10%, indicating that the potential ecological risk of Fe in coal gangue was *mild*. By the end of the experiment, the RAC value was 2.60%, which was significantly lower than in other treatment groups. Similar to Fe, by day 180, the RAC values of Mn in the RAS treatment group were lower than in the other treatment groups. The addition of CS enhanced the activity of Mn in the gangue, and RAC values increased from 5.90% (15 days) to 18.70% (180 days), indicating that the ecological risk of Mn in the CS group has risen from *Mild* to *Moderate*. The addition of PS reduced the activity of Cu in coal gangue, while the decomposition of CS significantly reduced the activity of Pb and Cd in coal gangue. In the early stage of the experiment (15 days), RAS increased the activity of Pb and Cd. In the later stage of the experiment, the activity of Pb and Cd in the RS treatment group was significantly lower than in the other treatment groups. In summary, in the early stage of the experiment (before day 15), the addition of straw promoted the bioactivity of Fe, Cu, Pb, and Cd in coal gangue. In the later stage of the experiment, RAS reduced the activity of these four elements, significantly lowering their potential ecological risks.

4. Discussion

When straw enters the environment, the easily soluble substances it contains will produce low-molecular-weight organic acids after biodegradation [28]. Previous research indicates that there is a highly significant negative correlation between the pH value and the content of organic acids produced during straw decomposition [29]. This may be the reason why the pH in the leachate of each treatment group was lower than that of the CK group. In the later stages of the experiment, the pH values in each treatment group were higher than those in the CK group, which is consistent with the findings of Yuan et al. [30]. This phenomenon may be attributed to the presence of various alkaline base ions, such as calcium and magnesium, in the straw. When these ions enter the soil, they are released and can react with active acids in the soil, including H^+, Al^{3+}, and CO_2. These reactions reduce the content of exchangeable H^+ and Al^{3+} in the soil, thereby increasing the pH [31]. The increase in EC values in treatment groups may be attributed to two main factors. First, previous studies have shown that the decomposition of straw generates significant amounts of soluble organic matter with strong metal-chelating properties, facilitating the release of heavy metals from coal gangue [32]. Second, straw is known to contain abundant nutrients (N, P, K, Ca, Mg) and organic matter [33], and microbial decomposition of these components has been documented to increase solution conductivity [34].

During the experiment, the concentrations of Fe, Mn, Cu, and Zn in the leachate were higher than those in the CK group. This may be attributed to the fact that straw decomposition in the initial stage produces a large amount of low-molecular-weight organic acids, which lower the pH and increase the solubility of heavy metals. Furthermore, dissolved organic carbon (DOC) derived from straw degradation contains abundant functional groups (e.g., carboxyl, hydroxyl, and carbonyl), which exhibit strong metal-complexing capabilities and can enhance the mobilization of heavy metals in soil systems [35]. Consistent with these mechanisms, our experimental results showed significantly higher concentrations of Fe, Mn, Cu, and Zn in the leachate compared to the CK group. Studies have shown that RAS has a lower C/N ratio and a higher content of easily decomposable components compared to other straws, with its mineralization intensity and decomposition rate being significantly higher than those of other straws [36]. Therefore, it is possible that during the initial stages of the experiment, the soluble organic matter produced reacted with the heavy metals in coal gangue, causing the concentrations of heavy metals in leachates in the RAS treatment group to be greater than in the other treatment groups. Studies have shown that with the decomposition of straw, the content of easily degradable organic matter in straw during the decomposition process displays a downward trend, while the content of humus-like substances displays an upward trend, and the humic acid concentration increases [36]. Humic acid can form large, water-insoluble complexes with heavy metals through chelation, which can passivate heavy metals [37,38]. This might be the reason why the concentration of Cu, Zn, Pb, and Cd in the leachate decreases in the later stage of the experiment.

The biological toxicity of heavy metals is not only related to their total amount, but to a greater extent, it is determined by the proportion of their forms. Different forms have different environmental effects, which directly impact the toxicity, mobility, and cycling of heavy metals in nature [39]. Studies have shown that organic matter from straw returned to the soil can change over time, with the products of its degradation and humification processes in the soil including DOC and humus. Dissolved organic carbon has a low molecular weight and contains several functional groups, such as carboxyl, hydroxyl, and carbonyl, which have strong complexation abilities for heavy metals in the soil. This can promote the activation of heavy metals in the soil. The formation of humus can also increase the adsorption and fixation of active heavy metals in the soil, thereby reducing the bioavailability of heavy metals [40]. In this study, the decomposition of different types of straw accelerated the transformation of reducible Fe and Mn in coal gangue to exchangeable Fe and Mn forms. Zhang et al. [41] found that the addition of glucose promotes soil microbial activity and accelerates the reduction processes of Fe and Mn. In the early stages of the experiment, the contents of exchangeable Fe and Mn increased, while in the later stages, the oxidizable Fe and Mn contents in each treatment group were higher than those in the CK group. This may be attributed to the enhanced activity of dissimilatory metal-reducing bacteria in the microbial community, leading to the gradual reduction and dissolution of iron and manganese minerals in the soil. Consequently, Fe and Mn were released into the soil, thereby increasing the proportion of exchangeable Fe and Mn [42]. In the later stages of the experiment, as straw continued to decompose, the dissolved organic carbon in each treatment group gradually degraded, while the proportion of humus increased [43]. Research indicates that after humus combines with mineral surfaces, it forms complexes or chelates with Fe and Mn ions [44], acting as a bridge to facilitate the immobilization of Fe and Mn. This promotes an increase in the proportion of oxidizable Fe and Mn in each treatment group while simultaneously reducing the bioavailability of heavy metals [45,46]. Except for the RIS treatment group, the addition of the straws promoted the release of Zn from coal gangue. Previous research showed that most Zn compounds are readily soluble in water, leading to the released Zn not easily forming stable compounds, but rather easily forming exchangeable Zn [47]. Therefore, the addition of straw in this study promoted the reduction of reducible Zn and an increase in the proportion of exchangeable Zn. In the early stages of the experiment, the addition of straw had a minor effect on the forms of Cd in each treatment group. In the later stages of the experiment, as the straw continued to decompose, the forms of Cd in each treatment group shifted from reducible to oxidizable states, and the increase in oxidizable Cd in the RAS treatment group was greater than in the other treatment groups. This may be due to the abundance of thiol compounds in the straw of cruciferous plants such as rape, which can chelate with Cd, thereby increasing the content of oxidizable Cd in the soil [48,49].

Studies show that as straw is continuously decomposed, the concentration of humic acid gradually increases [50,51]. Humic acid can promote the transformation of Pb and Cd from the weak acid-extractable state with high activity to the residual state in contaminated soil, further reducing the bioactivity of Pb and Cd [52]. However, some studies have shown that with the extension of the straw decomposition time, metal ions adsorbed in the manganese oxide combined state and organic matter combined state will be released and transformed into the exchangeable state with the decomposition of organic matter, increasing Mn activity [49]. The inconsistent conclusions of previous studies may be related to the type and structure of the straws used, as well as the differences in the decomposition products. At the same time, the physical and chemical characteristics of coal gangue and organic matter concentration may also lead to differences in the transformations among the various forms of heavy metals.

5. Conclusions

(1) After adding different types of straw to coal gangue, the pH of the leachate generally displayed a trend of first decreasing and then increasing, with the impact on pH being more significant for RAS and CS. At the end of the experiment, the pH values for the CS and RAS treatment groups were 1.74 and 1.82 times that of the CK group, respectively. After straw addition, the Eh of the leachate reached a minimum between days 7 and 15, with the greatest decrease in Eh observed in the CS and RAS treatment groups.

(2) As the straw decomposition time increased, the Fe and Mn concentrations in the leachate gradually increased. The Fe concentration in the RIS treatment group was significantly higher than in the other treatment groups, increasing from 93.42 mg/L (day 1) to 421.21 mg/L (day 180), while the Fe concentration in the PS treatment group remained at the lowest level. The Mn concentration in the leachate of each treatment group also gradually increased with the progress of the experiment, but the increase in the Mn concentration in the RAS treatment group was significantly lower than in the other treatment groups.

(3) The addition of straw promoted the transformation of heavy metals from a reducible state to an oxidizable state in coal gangue, while there was a significant difference in the impact on exchangeable heavy metals. The addition of RAS reduced the concentration of exchangeable Fe and Mn, whereas the addition of RIS led to a decrease in the concentration of exchangeable Zn. The RAC risk assessment results showed that by the end of the experiment, the addition of RAS significantly reduced the ecological risks of Fe, Mn, Cu, Pb, and Cd, while CS exacerbated the ecological risks of Mn and Zn in coal gangue.

In summary, incorporating different types of straw into coal gangue ecological restoration efforts serves a dual purpose: it improves the recycling efficiency of the various straws and also plays a role in immobilizing heavy metals in coal gangue. The passivation effect of RAS was stronger than the other straws. However, while conducting restoration, the dynamic changes in the activity of various heavy metals in coal gangue should be taken into account, and the use of RAS should be prioritized to avoid potential secondary environmental pollution.

Use of AI tools declaration

The authors declare they have not used Artificial Intelligence (AI) tools in the creation of this article.

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Conflict of interest

The authors declare that they have no competing interests

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