# Effects of maize stovers and sewage sludge co-pyrolysis on characteristics and heavy metals in biochar

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**Abstract**: Maize stovers were mixed with sewage sludge at different proportions (0, 25%, 50% and 75%) and treated in a pyrolysis device up to 600 ℃ via a co-pyrolysis process. Four kinds of biochars ($SCB_0$, $SCB_{25}$, $SCB_{50}$ and $SCB_{75}$) were obtained respectively. The properties of biochars, heavy metals (Cu, Zinc, Pb, Ni, Cr, Mn and As) contents, BCR forms and TCLP leaching toxicity characteristics were studied and the potential ecological risks were evaluated. The results showed that with the increase of maize stover content, the biochar yield, ash content, H/C and N/C ratios were significantly reduced while the pH value and the aromatization degree of biochar were significantly increased. After co-pyrolysis with maize stovers, the morphology of heavy metals in the resultant biochar changed significantly. The residue fraction ratio of Cu, Zn, Ni and Cr was significantly increased, indicating that pyrolysis might promote the transformation of heavy metals into more stable forms. All the heavy metals leached from biochars obtained by mixed pyrolysis did not exceed the limit stipulated by GB5085.3-2007 leaching toxicity identification standard and the overall potential risk index was further reduced . The ecological risk was significantly reduced from the moderate to the slight risk level and the minimum risk level reached when the addition amount of maize stover was 50%. The current study might provide a theoretical basis for the resource utilization and harmless utilization of sewage sludge and maize stovers.

**Keywords**: straw; sludge; heavy metals; co-pyrolysis; speciation analysis; risk assessment
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## 0 Introduction

Sewage sludge (SS) is the solid waste generated during wastewater treatment by activated sludge method in sewage treatment plant. With the continuous progress of urbanization and the gradual increase of water environment treatment, the production of SS increases day by day, according to the growth rate of SS, the annual output of SS is likely to reach or even exceed 60 million tons in 2020[1-2]. SS contains a lot of organic compounds, salts and heavy metals, as well as a variety of pathogenic bacteria and microorganisms. Direct disposal of SS into the environment might cause the release of pollutants into soil and water, which might be migrated into the food chain and finally threatening human health[3]. Therefore, how to realize SS resource utilization and harmless treatment at low cost has become the focus of attention.

SS pyrolysis technology refers to the endothermic decomposition reaction of SS under the high temperature at about 600 ℃ without oxygen, which is a chemical decomposition process produces mixed combustible gases, tar and biochars etc[4]. Pyrolysis is an environmentally friendly SS treatment technology, which not only completely kill parasitic eggs and pathogenic microorganisms, fully lyse organic pollutants, but also achieve carbon fixation, nutrient recovery and biomass energy (biological oil and pyrolysis gas) extraction, and greatly reduce the volume of SS[5]. Pyrolysis treatment can also realized the solidification and stabilization of heavy metals and the retention of N, P, K and other effective elements in sludge. Biochars with good properties can be used as soil improver or biochar fertilizer[6-7].

The addition of external materials and co-pyrolysis with sludge can not only improve the quality of sludge biochars, but also significantly change the content and availability of heavy metals in biochars, so that heavy metals in SS biochars can exist in a more stable form. China

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is abundant in agricultural and sideline product waste, which can be used as external materials to co-pyrolysis with SS. In the researches of mixed pyrolysis of activated sludge and agricultural sideline product waste, more studies have been conducted on the co-pyrolysis of activated sludge and rice husk[8-9]. China is rich in maize stovers (MS) resources, most of which are not properly used. If the addition of MS to SS during the co-pyrolysis process could create a synergistic enhancement effect on the immobilization of metals in the biochar end product and consequently allow a further substantial decline in environmental risk compared with the pyrolysis of sludge alone, it might provide a better way for safe disposal for both SS and MS. At present, studies on the co-pyrolysis of MS and SS mainly focus on the effects of biological carbon on the physical and chemical properties of soil and the adsorption of toxic and harmful substances, etc.[10-12]. However, the effects of co-pyrolysis of MS with different mass ratios on heavy metal morphology, leaching toxicity and ecological risk in biochar were not investigated.

The purpose of the present study was to investigate the total amount, morphological changes and leaching toxicity of heavy metals in solid phase products after co-pyrolysis of SS with different proportion(0, 25%, 50%, 75%) of MS and the ecological risks was also evaluated. The data obtained from this study might provide a theoretical basis for SS "reduction, stabilization, harmless and resource" treatment.

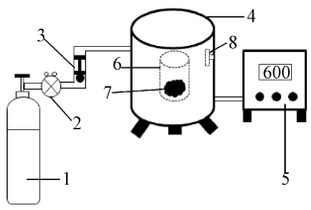
## 1 Materials and methods

### 1.1 Experimental materials

Multi-point sampling was used to collect centrifugal SS from a sewage treatment plant in Xiamen city in which the Triple Ditch mode was applied. The collected SS and CS samples were first air-dried at room temperature (25 ℃) and then dried in an oven at 105 ℃ to constant weight. The dried SS and MS were then ground by high-speed pulverizer, passed through 200-mesh sieve, sealed in plastic bags and then kept in a vacuum desiccator for future use.

### 1.2 Co-pyrolysis of SS and MS

The dried MS and SS were mixed at 4 different proportions with mass ratios of 0∶1, 1∶3, 1∶1 and 3∶1 (adding ratio of MS was 0, 25%, 50% and 75%), respectively. 50.00 g of each mixed sample was weighed and put into a pyrolysis device furnace (as shown in Fig.1). The flow rate of nitrogen gas (purity 99.99%) was 50 mL/min and the pyrolysis was conducted under anaerobic environment. The furnace was heated to 600 ℃ at a heating rate of 10 ℃/min and then hold for 60 min at 600 ℃. After the reaction, the high purity nitrogen gas was still applied until the furnace was cooled down to room temperature. The biochar products were then collected (recorded as $SCB_0$, $SCB_{25}$, $SCB_{50}$ and $SCB_{75}$, respectively) and then stored in a desiccator for further analyses.




1. Nitrogen gas； 2. Pressure regulator； 3. Flow meter； 4. Pyrolysis furnace； 5. Temperature controller； 6. Internal reaction zone； 7. Produced solid phase；8. Exhaust port

Fig.1 Schematic diagram of pyrolysis device

### 1.3 Sample analysis

#### 1.3.1 Basic property analysis

The ash contents of SS and biochar samples were determined according to 《Industrial Analysis Methods of Coal(GB /T 212-2008)》.Elemental analyzer（Vario EL III, Hanau, Germany） was used to analyze and determine the elements C, H, N and S in sludge and biochar samples, $CaCO_3$ and sulfanilic acid standard materials were selected for quality control[13]. pH value (1:10, w/v) was detected by pH meter (FE20K, mettler Toledo).

#### 1.3.2 Analysis of heavy metal total amount

The untreated and pyrolyzed samples were digested with a mixture of concentrated acid ($HNO_3$:$HClO_4$:HF = 1:1:1, v / v) by using the microwave digestion instrument (Milestone Ethos 1, Italy). Each of the digestion solutions was filtered and diluted for concentration analysis. The heavy metals (Cu, Zn, Pb, Ni, Cr, Mn and As)concentrations in the untreated and pyrolyzed samples were determined by inductively coupled plasma-mass spectrometry (ICP-MS) (Agilent 7700x).

#### 1.3.3 Heavy metal BCR extraction and determination

The sample was firstly treated using the modified BCR continuous extraction method and the heavy metals in the sample were then determined by ICP-MS. The pretreatment procedures[14] were as follows:

F1 (weak acid fraction): 0.500 g sample was weighed in a 50 mL centrifuge tube, 0.11 mol/L acetic acid solution was added, which was oscillated continuously for 16 hours in a shaking bed at (22±5) ℃ and 200 r/min and then centrifuged at 8 000 r/min for 10 minutes. The supernatant was then removed, filtered into a 50 mL volumetric flask through a 0.22 $\mu$m filter membrane and then filled up to 50 mL by using 2% $HNO_3$. 10 mL solution was stored for further testing.

F2 (reducible fraction): The solid phase residue in F1 was placed in an oven for drying treatment at 85℃. After drying, 20 mL 0.5 mol/L hydro xylamine chloride solution was added, which was subjected to oscillation, centrifugation and volume determination under the same conditions as described in F1. 10 mL solution was taken and stored for further testing.

F3 (oxidation fraction) : Place the solid residue of F2 in an oven for drying treatment at 85℃. After drying, 5 mL of 30% $H_2O_2$ was added in. The mixture was heated at (85±2) ℃for 1 hour after it was let stand for 1 hour. 5 mL more

$H_2O_2$ was added in and continued beating until the mixture was nearly dry. 25 mL of ammonium acetate solution (1 mol/L) was added in, which was subjected to oscillation, centrifugation and volume determination under the same conditions as described in F1. 10 mL solution was taken and stored for further testing.

F4 (residue fraction) : Solid residue in F3 was determined by 1.3.2 total heavy metal analysis method.

1.3.4 Analysis of heavy metal leaching toxicity

TCLP[15] method was used to detect the heavy metal leaching toxicity of the produced biochar obtained by mixing different proportions of MS and SS. 1.000 g sample was weighed and put into a 50 mL centrifuge tube, 20 mL leaching solution (5.7 mL glacial acetic acid was diluted to 1 L, solution pH value was kept at (2.88±0.05) and the ratio of sample to leaching solution was 1∶20) was added , the mixture was oscillated for 18 hours at 200 r/min, then centrifuged at 8 000 r/min for 10 min. The supernatant wasobtained and filtered with 0.22 $\mu$m filter membrane to a 50 mL volumetric flask, and then fill up to the calibration using 2% $HNO_3$. 10 mL was taken for ICP-MS inspection.

1.3.5 Potential ecological risk assessment

Potential ecological risk index （RI） was used to evaluate the potential pollution risk of heavy metals in SS and biochars[16]. The calculation formula is as follows:

$$C_f = W_s / W_n \quad (1)$$

$$E_r = T_f \cdot C_f \quad (2)$$

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

Where $C_f$ is the pollution coefficient of a single metal; $W_s$ is the content of F1+F2+F3; $W_n$ is the content of F4; $T_f$ is the biotoxic response factor of heavy metals, where As(10)>Ni (6)>Pb(5)=Cu(5)>Cr(2)>Zn(1)= Mn(1)[16-17]; $E_r$ is the single potential ecological risk coefficient; RI is the potential ecological risk index of heavy metals. The indicators of potential ecological risk assessment are shown in table 1.

Table 1 Potential ecological risk evaluation indices[7]

| Single potential ecological risk coefficient $E_r$ | Potential ecological risk index RI | Degree of potential ecological risk |
|---|---|---|
| $E_r \leqslant 40$ | RI≤150 | Slight |
| $40 < E_r \leqslant 80$ | 150<RI≤300 | Medium |
| $80 < E_r \leqslant 160$ | 300<RI≤600 | Relatively high |
| $160 < E_r \leqslant 320$ | RI>600 | High |
| $E_r > 320$ | | Very high |

1.3.6 Data analysis

Microsoft Excel 2010 and SPSS18.0 were used for data processing and analysis, and LSD method was used for mean difference analysis. The significance difference level was $P< 0.05$.

## 2 Results and analysis

### 2.1 Physico-chemical analysis

The physico-chemical properties of pure SS and biochars (SS and MS co-pyrolyzed biochar, SCB) with different proportion of MS adding were shown in Table 2. After the pyrolysis of SS, the content of C, H, N and O elements significantly decreased, indicating that during the pyrolysis process, these elements were mainly transferred to pyrolysis gas in the form of CO, $CO_2$, $H_2O$ and hydrocarbon compounds[18]. When the added MS increased from 0 to 75%, the biochar yield decreased 23.11% and the ash content decreased significantly with the increase of MS. The pH value of pure sludge was close to neutral; however, the pH value of SCB increased significantly with the increase of MS adding in. Generally, H/C molar ratio reflects the aromatization level of sludge biochar[19-20]. With the increase of MS ratio, the content of element C in SCB basically showed an upward trend, which was due to the higher content of C in corn stalks. The content change of element H in SCB was not significant and therefore the H/C molar ratio of biochar gradually decreased which indicating that the addition of MS was benefit for increasing the aromatization level of biochar. It should be noted that there was a negative correlation between the pH value of biochar and the H/C molar ratio, which indicated that the high aromatization level of biochar had a significant impact on its pH value [21]. With the increase of MS, the biochar C/N molar ratio increased significantly, suggesting that the number of functional groups related to N on the surface of biochar decreased significantly[22]. This was consistent with the findings of Yuan et al[23]. that the loss of N in the pyrolysis process led to the increase of C/N ratio. When biochar was applied into soil, the C/N molar ratio could be used as an indicator of the ability of organic matter to release inorganic N[24-25]. Therefore, it could be predicated that compared with the pure sludge applied to the soil, biochar had less inorganic N release.

Table 2 Physicochemical properties of raw materials and biochars

| Sample | Yield/% | C/% | H/% | N/% | S/% | O/% | H/C | N/C | pH value | Ash/% |
|---|---|---|---|---|---|---|---|---|---|---|
| SS | / | 23.14±0.02d | 5.07±0.05a | 3.65±0.04a | 1.22±0.19b | 21.58±1.22b | 2.63 | 0.14 | 6.86±0.05e | 46.93±0.16e |
| MS | / | 48.35±0.01a | 5.56±1.46a | 0.39±0.01e | 0.11±0.02d | 41.65±1.65a | 1.38 | 0.01 | ND | 19.66±0.17f |
| $SCB_0$ | 61.23 | 16.89±0.14f | 1.05±0.04b | 1.88±0.05c | 1.43±0.08a | 1.32±0.04c | 0.75 | 0.10 | 8.64±0.12d | 83.12±1.07a |
| $SCB_{25}$ | 52.69 | 21.57±0.24e | 1.32±0.02b | 1.84±0.09c | 1.29±0.03ab | 0.98±0.02c | 0.73 | 0.07 | 10.22±0.03c | 77.78±0.23b |
| $SCB_{50}$ | 44.98 | 33.46±0.11c | 0.96±0.02b | 2.07±0.13b | 0.86±0.02c | 0.86±0.05c | 0.34 | 0.05 | 11.18±0.06b | 68.46±0.36c |
| $SCB_{75}$ | 38.12 | 39.78±0.16b | 0.87±0.00b | 1.21±0.02d | 0.75±0.03c | 0.79±0.02c | 0.26 | 0.03 | 11.33±0.04a | 65.32±0.52d |

Note: SCBx: mixed biochar; X: percentage of MS; ND: not detected. The letters after each data indicate whether there was a significant difference in the data in the same column.

### 2.2 Analysis of heavy metal content

The contents of Cu, Zn, Pb, Ni, Cr, Mn and As in the raw materials and biochars were shown in Table 3. As shown in table 3, the order of heavy metal content in SS from high to low was Zn> Cu> Mn> Ni> Cr> Pb>As, in which Zn, Cu, Mn and Ni were relatively high (1 385.26, 1 121.67, 368.87 and 188.42 mg/kg, respectively), while Cr, Pb and As were relatively low (68.59, 57.17 and 10.86 mg/kg, respectively). After pyrolysis, heavy metals in SS were gathered and kept in biochars. Pyrolyzed with different proportions of MS created biochars with different heavy metal contents. Compared with pure SS, the content of each heavy metal in $SCB_0$ increased significantly and reached to the maximum. On one hand high temperature was conducive to the accumulation of heavy metals[26] and on the other hand, $SCB_0$ was composed of pure SS with no addition of MS, the content of each heavy metal would reach the maximum after pyrolysis. With the increase of MS amount, the content of heavy metals in samples decreased after pyrolysis. It mostly due to that MS had much lower heavy metal contents and thus had a dilution effect for the heavy metal contents in the yielded biochars. As the proportion of MS increased, it would dilute the content of heavy metals to some extent. The similar results were reported by Pan et al[27]. The existing forms of heavy metals in SS and biochars played a key role in its environmental impact and bioavailability. Therefore, only taking the content of heavy metals as a single consideration factor could not fully reflect its real environmental impact[28]. In this study, the environmental risks of heavy metals were further comprehensively investigated from the morphology of heavy metals.

Table 3 Contents of heavy metals in raw materials and biochars (mg·kg$^{-1}$)

| Sample | Cu | Zn | Pb | Ni | Cr | Mn | As |
|---|---|---|---|---|---|---|---|
| SS | 1 121.67±5.17d | 1 385.26±60.05d | 57.17±2.34d | 188.42±6.16e | 68.59±1.58c | 368.87±0.25c | 10.86±1.02c |
| MS | 21.82±1.32f | 5.38±0.82e | 0.62±0.11e | 0.31±0.08f | 3.12±0.65e | 6.16±0.76d | 0.23±0.02e |
| $SCB_0$ | 1 985.76±16.35a | 2 386.15±53.69a | 121.38±2.19a | 768.36±8.18a | 109.57±3.14a | 683.48±26.01a | 22.55±3.21a |
| $SCB_{25}$ | 1 703.31±21.36b | 2 068.33±49.53b | 96.43±2.69b | 589.66±19.86b | 82.33±5.03b | 464.59±15.46b | 13.59±1.07b |
| $SCB_{50}$ | 1 253.69±18.95c | 1 656.49±26.88c | 69.69±3.13c | 559.48±22.46c | 52.28±2.05d | 394.58±12.49c | 8.09±0.27d |
| $SCB_{75}$ | 1 021.53±22.69e | 1 409.34±34.35d | 53.49±2.02d | 315.78±12.98d | 51.49±4.22d | 437.56±20.43b | 7.68±0.38d |

### 2.3 Morphological analysis of heavy metals

The risk of heavy metal is not only related to its content but also its form[29]. At present, BCR continuous extraction method (supported by the European standard test and analysis committee) is widely used in the study of the morphology of heavy metals in sludge and biochar. Among them, the exchangeable fraction (F1) is adsorbed on the surface of particles or exists in the form of binding carbonate, which is easily affected by the change of ion composition in water and the adsorption and desorption process. The reducible fraction (F2), which is combined with iron and manganese oxides, is extremely unstable under hypoxia condition. The oxidizable fraction (F3) is the combination of metal ions with organic matter and sulfide. The residue fraction (F4) is a combination form with silicate mineral and crystalline iron magnesium oxidation state, which is regarded as a stable heavy metal form[29-30]. Heavy metals in (F1+F2) forms have direct ecological toxicity and bioavailability. Heavy metals in the form of F3 have potential ecological toxicity and bioavailability. However, the heavy metals in the F4 form basically have no ecological toxicity and biological availability[31]. Therefore, BCR morphological analysis was used to evaluate the stability and safety of heavy metals, the results are shown in figure 2.

As shown in Figure 2, in SS, the F4 fraction ratios (F4/(F1+F2+F3+F4)) of the 7 heavy metals decreases in the following sequence Pb>As>Cr>Mn>Zn>Cu>Ni. In $SSB_0$, the sequence is Cr > Pb > As > Cu > Zn >Mn> Ni. After SS was pyrolyzed without adding MS, heavy metals was changed dramatically. The F4 fraction ratios for all the 6 heavy metals increased except Mn, among them, the F4 fraction ratios of Cu, Zn, Ni and Cr increased from 7.71%, 10.36%, 6.57% and 52.50% to 61.66%, 57.07%, 20.72% and 98.13%, respectively, indicating that pyrolysis promotes the transformation of heavy metals into more stable forms[32]. With the gradual increase of the MS addition, the F4 fraction ratios of Mn and Ni residues showed a trend of first increasing and then decreasing, which reached the highest in $SSB_{50}$, saying 50.70% and 34.46% respectively. In $SSB_0$, the F4 fraction ratios of Cu, Zn, Cr and As residues were the highest, reaching 66.66%, 57.07%, 98.13% and 76.8%, respectively. This indicated that MS had a good passivation effect on heavy metals in SS. Because MS biochar had a highly poroused structure and contained silicon and aluminum oxides, which could form aluminate compounds under alkaline conditions and had a strong adsorption capacity for heavy metal ions[12]. In the process of pyrolysis, MS co-pyrolysis with SS created a synergistic effect. The heavy metals in the SS such as exchangeable state and oxidation state of iron and manganese, which were in relatively unstable state, would partially dissolved in the pores formed by MS. Also, with the formation of the

pyrolytic polymers, they were re-fixed in its polymer and transferred to more stable metal forms[8]. Furthermore, with the gradual increase of the MS addition, the F4 fraction ratio of Pb increased slowly. In $SSB_{75}$, the F4 fraction ratio reached 98.50%; however, the F4 fraction ratio in SS was still very high, 95.63%. Therefore, pyrolysis had no significant impact on Pb in SCB and the F4 fraction remains dominant.

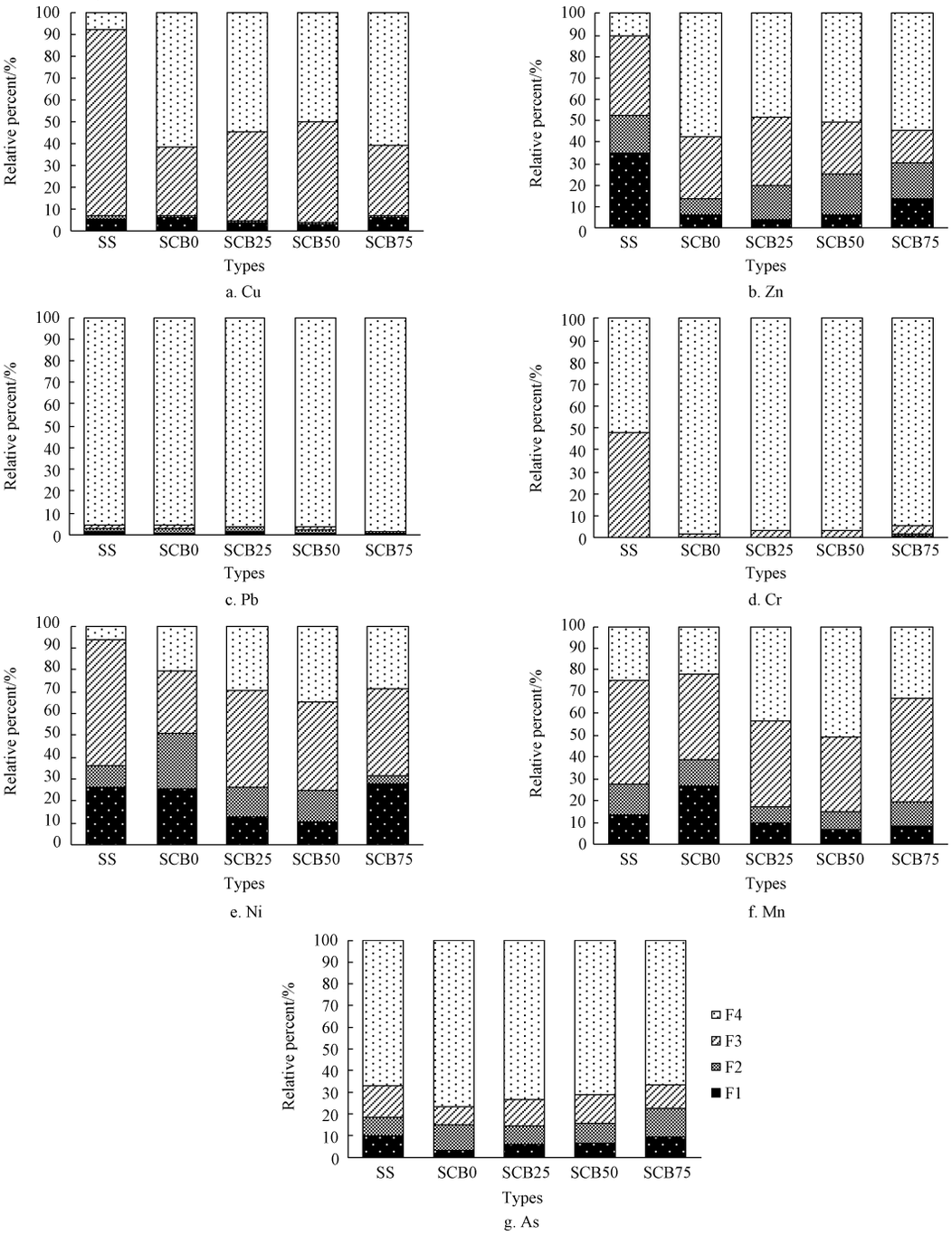



Fig. 2　Morphological distribution of heavy metals in SS and biochars

## 2.4　Analysis of leaching toxicity

The characteristics of heavy metals TCLP leaching for SS and biochars are shown in table 4. As can be seen from Table 4, the leaching amounts of Zn and Ni in SS are relatively high, reaching 25.26 and 16.34 mg/L respectively. Among them, the leaching amount of Ni exceeds the limit set by GB5085.3-2007 leaching toxicity identification standard[33]. Therefore, the direct application of SS in environment might have potential environmental pollution risks. After the pyrolysis, the leaching amount of Ni from $SCB_0$ is 1.48 mg /L, which had been reduced below the limit specified by the leaching toxicity identification standard, and has a very low environmental safety risk when applied. With the increase of the addition proportion of MS, the leaching concentrations of Cu, Zn, Pb, Ni, Cr, Mn and As in biochars gradually decrease. There is no significant difference between 50% and 75% of the addition quantities which have been reduced to a very low level and all below the threshold specified in the standard. Therefore, no new environmental risks will be brought.

Table 4 Amounts of heavy metals leached from SS and biochar

| Sample | Concentration $c$/(mg·L$^{-1}$) | | | | | | |
|---|---|---|---|---|---|---|---|
| | Cu | Zn | Pb | Cr | Ni | Mn | As |
| SS | 3.96±0.53b | 25.26±4.63a | 0.01±0.00a | 0.36±0.01a | 16.34±1.02a | 4.96±1.03a | 0.07±0.01b |
| $SCB_0$ | 5.14±0.08a | 24.13±2.62a | 0.00±0.00a | 0.18±0.02a | 1.48±0.05b | 2.64±0.08b | 0.09±0.01a |
| $SCB_{25}$ | 2.03±0.01c | 24.88±1.03a | 0.01±0.00a | 0.09±0.02a | 0.64±0.03bc | 2.66±0.05b | 0.00±0.00d |
| $SCB_{50}$ | 1.16±0.01d | 10.98±0.98b | 0.00±0.00a | 0.03±0.01a | 0.06±0.01c | 1.89±0.06bc | 0.02±0.01c |
| $SCB_{75}$ | 1.56±0.03d | 11.46±1.02b | 0.00±0.00a | 0.05±0.00a | 0.18±0.01c | 1.22±0.05c | 0.01±0.00cd |
| Limits value[33] | 100 | 100 | 5 | 15 | 5 | - | 5 |

### 2.5 Potential ecological risk assessment

In order to better investigate the potential ecological risk of heavy metals in biochars, table 5 lists the potential ecological risk indies of different biochar heavy metals. As shown in Table 5, the potential ecological risk coefficient of heavy metals in SS is high, reaching 163.83, and the risk degree is medium. The risk coefficient of Ni in SS reaches 85.31, which was a high risk level. The risk coefficient of Cu reaches 59.88, which is a medium risk level. Direct discharge of pure SS will cause environmental pollution. After pyrolysis without MS, the overall potential risk index decreased from 163.83 (SS) to 33.60 ($SCB_0$), reducing 79.49%, which is a slight level, and direct discharge has little impact on the environment. Adding $SCB_{25}$, $SCB_{50}$ and $SCB_{75}$ obtained by mixed pyrolysis of MS and SS in different proportions further reduces the overall potential risk index to 24.53, 22.69 and 26.35, respectively reducing 85.03%, 86.15% and 83.92%, and the ecological risk significantly reduces to the level of slight risk. In conclusion, compared with direct pyrolysis of SS, the addition of mixed pyrolysis with MS can further reduce the overall potential risk degree of heavy metals in biochars, and a 50% addition amount of MS will create a minimum risk level, which provides a theoretical basis for the resource utilization and harmless utilization of SS and MS.

Table 5 Potential ecological risk assessment

| Sample | Single potential ecological risk coefficient $E_r$ | | | | | | | Potential ecological risk index RI | Potential ecological risk |
|---|---|---|---|---|---|---|---|---|---|
| | Cu | Zn | Pb | Cr | Ni | Mn | As | | |
| SS | 59.88 | 8.65 | 0.23 | 1.81 | 85.31 | 3.03 | 4.92 | 163.83 | Moderate |
| $SCB_0$ | 3.11 | 0.75 | 0.22 | 0.04 | 22.95 | 3.50 | 3.02 | 33.60 | Low |
| $SCB_{25}$ | 4.14 | 1.08 | 0.20 | 0.07 | 14.07 | 1.32 | 3.65 | 24.53 | Low |
| $SCB_{50}$ | 5.02 | 0.99 | 0.17 | 0.07 | 11.41 | 0.97 | 4.05 | 22.69 | Low |
| $SCB_{75}$ | 3.26 | 0.84 | 0.08 | 0.11 | 15.04 | 1.99 | 5.03 | 26.35 | Low |

## 3 Conclusions

1）With the increase of MS content from 0 to 75%, the biochar yield, ash content, H/C and N/C ratios of biochar decreased significantly, while the pH value increased significantly. The addition of MS can tremendously improve the aromatization of biochar which is beneficial for the improvement of sludge charcoal quality.

2） Because high temperature is conducive to the accumulation of heavy metals in SS, the content of heavy metals in biochar after pyrolysis is significantly higher than that in the original SS. With the increase of the MS addition quantity, the content of heavy metals in pyrolyzed samples decreases, mainly due tothat heavy metals content in MS are relatively low compared with that in SS, which will dilute the heavy metals content to some extent.

3）After mixed pyrolysis with MS, the morphology of heavy metals in the resultant biochar changed significantly. The F4 fraction ratio of Cu, Zn, Ni and Cr was significantly increased, indicating that pyrolysis might promote the transformation of heavy metals into more stable forms. All the heavy metals leached from biochars obtained by mixed pyrolysis did not exceed the limit stipulated by GB5085.3-2007 leaching toxicity identification standard, the overall potential risk index was reduced further. The ecological risk was significantly reduced from the moderate to the slight risk level and the minimum risk level was reached when the addition amount of MS was 50%. The current findings might provide a theoretical basis for the resource utilization and harmless utilization of SS and MS.

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# 玉米秸秆与污泥混合热解对生物碳特性及重金属的影响

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**摘　要**：利用热解装置开展不同质量比例玉米秸秆 （0，25%，50%和 75%）与污泥混合热解实验，分别得到4种生物炭（SCB0，SCB25，SCB50 和 SCB75），研究了生物炭性质、重金属（Cu，Zn，Pb，Ni，Cr，Mn 和 As）含量、BCR 形态和TCLP 浸出毒性特征，并开展潜在生态风险评估。结果表明，随着玉米秸秆添加比例的增加，生物炭产率、灰分、H/C 和 N/C 比显著降低，pH 值显著增大，生物炭芳香化程度明显提高。添加玉米秸秆与污泥混合热解可以促进重金属向更稳定的形态（F4 态）转化。4种生物碳中重金属浸出均未超出 GB5085.3-2007 浸出毒性鉴别标准规定的限值，生态风险均明显降低至轻微风险水平，在玉米秸秆添加量为50%时达到最低风险水平，该研究为污泥与玉米秸秆资源化和无害化利用提供了理论依据。

**关键词**：秸秆；污泥；重金属；混合热解；形态分析；风险评价