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A further inquiry into co-pyrolysis of straws with manures for heavy metal immobilization in manure-derived biochars

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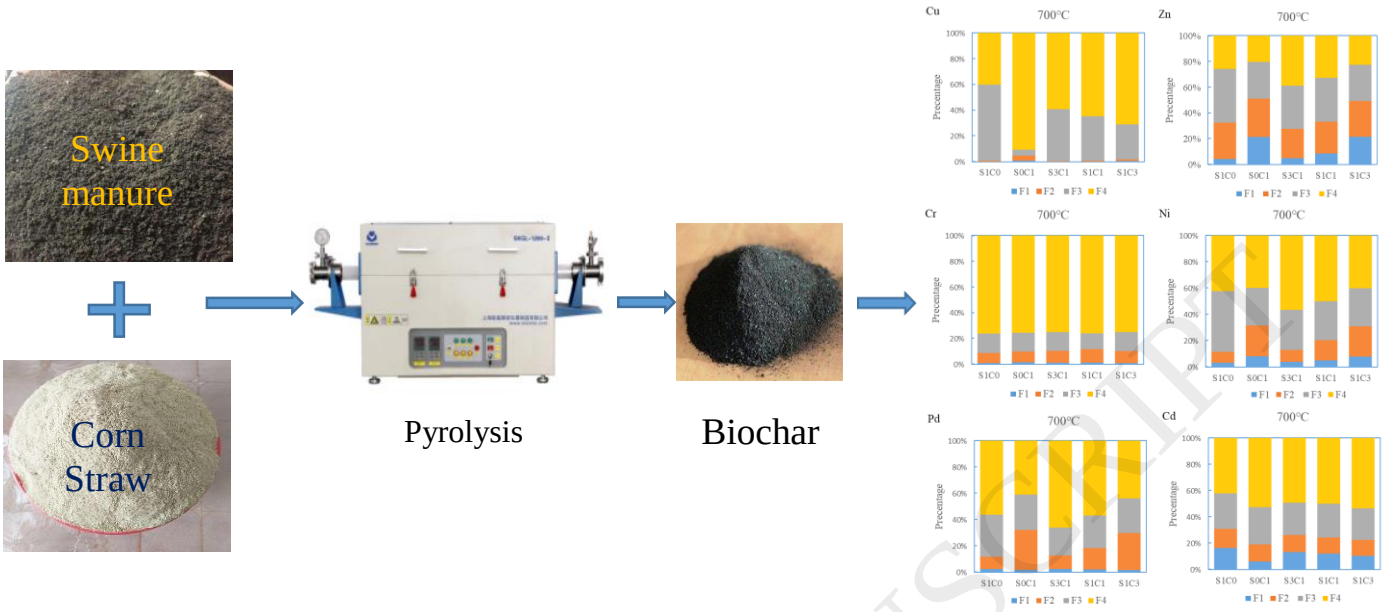
Graphatic abstract



Highlights

- Co-pyrolysis of CS with SM reduced total Cu, Zn, Pb, Ni, Cd and Cr of SM biochars.
- Higher CS addition ratio and higher pyrolysis temperature favored Cd and Cu immobilization.
- Higher temperature and lower addition ratio immobilized Zn, Ni and Pb better.
- The ecological risks of SM and single pyrolysis SM biochars were dominated by Cd, Cu and Zn.
- Pyrolysis at CS/SM ratio 3:1 and 700 ℃ was optimal to reduce environmental risks of SM biochars.

Abstract

Co-pyrolysis of straws with manures has been found effective to mitigate heavy metal risks in manure-derived biochars. This study further investigated co-pyrolysis strategy on the levels, species and risks of metals (Cu, Zn, Cr, Ni, Pb, and Cd) carried by manure-based biochars through co-pyrolyzing swine manure (SM) and corn straw (CS) with different mixture ratios (1:0, 0:1, 3:1, 1:1, and 1:3, w/w) at 300 ℃, 500 ℃ and 700 ℃. The total heavy metals in SM biochars were significantly reduced by CS addition except when SM/CS ratio was 3:1 at 300 ℃. Notably, CS addition increased stable Ni, Zn, Cu, Pb and Cd, but simultaneously mobilized part of Ni, Zn, Cu and Pb in SM biochars, especially at higher CS ratio and higher temperature. Co-pyrolysis converted less stable Cd to more stable Cd at all pyrolysis conditions, with higher CS ratio and higher temperature more effective. Overall, higher temperature (700℃) and

higher addition ratio of CS (SM/CS 1:3) were more favorable for mitigating the potential ecological index of biochar-bearing Cd, Cu and Zn, the dominating risky contributor to SM biochars, hence more effective to mitigate the overall environmental risks of heavy metals in the derived SM biochars.

Keywords: Co-pyrolysis; Heavy metals; Speciation; Swine manure; Biochar

1. Introduction

In China, the annual production of livestock and poultry manures is estimated to be about 3.2 billion tons [1]. The direct application of animal manures into farmland are effective to improve soil fertility and increase crop yield [2, 3]. Nevertheless, the amount of total heavy metals in animal manures are generally high, originating from feedstock additives for animal disease prevention and growth promotion [4]. Long-term application of animal manures bearing high-level heavy metals can lead to elevating concentrations of soil heavy metals, which subsequently harms crop and humans through the food chain [5-7]. Therefore, alternative and safe ways to use animal manures have been a matter of great concern.

Pyrolysis is a promising method for disposing and utilizing various biomass wastes including animal manures. This process can reduce the volume of animal manures, kill intrinsic pathogens and parasites, and produce value-added bio-energy (e.g. liquid biofuel and syngas) and carbon-rich solids (biochars) [8, 9]. Heavy metals in animal manures can be redistributed into the liquid (bio-oil), gas and solid (biochar) phases during pyrolysis, and this redistribution of heavy metals is dependent on experimental conditions [10]. Moreover, the chemical speciation of heavy metals has been shown to be altered from less to more stable states during pyrolysis, suggesting heavy metals in animal manure were immobilized by pyrolysis [11-13]. On the contrary, pyrolysis tends to increase the total concentrations of heavy metals in post-pyrolysis manures due to considerable decrease in volume, suggesting potential environmental risks of the generated biochars as environmental amendments. Therefore, efficient reduction and immobilization of heavy metal in animal manures during pyrolysis need to be explored.

Recently, some researchers showed that the addition of biomass wastes with low levels of heavy metals into animal manures or sludge that tends to have higher contents of heavy metals during pyrolysis triggered a significant drop of the total heavy metal amount of derived biochars due to "dilution effect" [14-16]. Nevertheless, in comparison with single pyrolysis, co-pyrolysis process exhibited inconsistent effects on the mobility, chemical speciation and bioavailability of heavy metals in the blended biochars. For instance, Huang et al. reported that a minimal effect of co-pyrolysis of sewage sludge with rice straw/sawdust on the mobility of Cu, Zn, Ni, Cr, Pb and Mn in sludge biochars [14]. In contrast, Jin et al. reported that co-pyrolysis of sewage sludge and bamboo sawdust transformed the unstable toxic metals (Cu, Zn, Cr, Ni, Pb and Mn) into more stable fractions, and reduced the environmental risk of these metals in sludge biochars [15]. Meng et al. reported that addition of rice straw into pig manure could reduce the bioavailable (CH_3COONH_4 extractable) and potentially releasable (indicating environmental risk) Cu and Zn, however this only occurred when pyrolysis was below a certain temperature (vary between adding ratios and evaluation endpoints) and the reverse effects were observed when temperature was higher beyond [16]. These inconsistent findings can be the result of varying feedstock types and operating conditions, such as pyrolysis temperature, heating rate, residence time, and blending ratio. According to our knowledge, these are the only available reports on the effects of the co-pyrolysis strategy on lowing the total and bioavailable metal levels and reducing the inherent metal-associated environmental risks. More work is needed to confirm the feasibility of this risk-alleviating strategy for biochar-carrying metals, covering a wide range of heavy metals and pyrolysis conditions.

In this work, swine manure (SM) and corn straw (CS) were chosen as representatives of animal manures and non-manure biomass wastes. The two feedstocks were selected due to their large volume and urgency of proper disposal in China. Co-pyrolysis of SM and CS at different mixture ratios (1:0, 0:1, 3:1, 1:1, and 1:3) was

conducted at different temperature (300℃, 500℃, and 700℃). The aims of this study were to (1) assess the properties of biochars generated by single pyrolysis of SM and co-pyrolysis of SM and CS; (2) investigate the total levels and fractionation of heavy metals in produced biochars; (3) evaluate the potential environmental risk of heavy metals in biochars by introducing the potential ecological risk index.

2. Methodology

2.1 Sample collection and biochar production

Swine manure was sorted out from a swine farm in Shijiazhuang City, Hebei Province, China. Corn straw was collected from a farmland in Langfang City, Hebei Province, China. These feedstocks were oven dried at 60℃ until constant weights were recorded. The dried samples were then grounded and sieved to below 250 μm before being stored in enclosed plastic bags.

The pretreated SM and CS were fully mixed using an agitator in the following mass ratios of 1:0, 0:1, 3:1, 1:1 and 1:3, for which the produced biochars were hereafter referred to as S1C0, S0C1, S3C1, S1C1, and S1C3, respectively. Then, these samples were placed into a porcelain crucible and thermally treated in a vacuum tube furnace under a 300 mL/min N_2 flow condition. The furnace was heated to the designated temperature (300 ℃, 500 ℃, or 700 ℃) at a heating rate of 10 ℃/min and maintained for 2h. The produced biochars were cooled and packed in sealed plastic bags for analysis.

2.2 Analysis of samples

The elemental composition (C, N, and H) of derived biochars were determined using an elemental analyzer (Vario EL cube, Elementar, Germany). The standard method (GB/T28731-2012) was followed to determine the ash contents of biochar samples, and mass difference (O% = 100% – [C %+ H% + N% + Ash%]) was adopted to calculate the O content. The pH of SM, CS and biochars (sample/deionized water, 1:10, w/v) were measured using a pH meter (PHS-3C, Sanxin, China).

The total heavy metals of feedstock and biochar samples were determined by digesting 0.5 g samples with HNO_3-HF -$HClO_4$ (4: 2: 1, v/v/v) mixture. The chemical speciation of heavy metals in the samples were performed by a modified three-step BCR sequential extraction procedure initially developed by the Commission of the European Communities Bureau of Reference (BCR). The details of extraction approaches were reported previously [17]. This procedure divided heavy metals into exchangeable and acid-soluble fraction (F1), reducible fraction (F2), oxidizable fraction (F3), and residual fraction (F4). Heavy metals from both digestion and BCR extraction were detected by inductively coupled plasma-optical emission spectrometer (ICP-OES, Optima 2000DV, Perkin Elmer, USA).

2.3 Environmental risk assessment of heavy metals in SM and biochars

In this study, the modified potential ecological risk index (*RI*) was introduced to evaluate the potential environmental risk of heavy metals in SM and biochars [18, 19]. These indices were calculated by the following equations:

$$C_f = C_i / C_n, \quad (1)$$

$$E_r = T_r \cdot C_f, \quad (2)$$

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

where C_f is the contamination factor for each metal, Ci is the concentrations of active heavy metals fraction (F1 + F2) , C_n is the reference background value for heavy metals in soils form Jiangsu Province (Cu, Zn, Cr, Ni, Pb, and Cd are 22.3, 62.6, 77.8, 26.7, 26.2, 0.13 mg/kg, respectively)[20], E_r is the potential ecological index for each heavy metals, Tr is the toxic factor of corresponding heavy metals (Cu, Zn, Cr, Ni, Pb, and Cd are 5, 1, 2, 6, 5 and 30, respectively). The criteria used for risk ranking was in accordance with the C_f, E_r and *RI* thresholds listed in Table 1.

3. Results and discussion

3.1 Biochar yield

The higher biochar yield was observed at lower pyrolysis temperature (Table 2). An obvious decrease in yields of all biochars occurred between 300 °C and 500 °C, which resulted from the destruction of lignocellulosic components in SM and CS [21].

In comparison, only a slight decrease in biochar yield happened between 500 °C and 700 °C, which is likely attributable to the decomposition or volatilization of inorganic matter at above 500°C [22]. The yield of S0C1 was lower than that of S1C0, owing to higher content of organic components and lower content of ash in CS. As expected, the yields of blended biochars were higher than that of S0C1 and lower than that of S1C0.

The theoretical yields of blended biochars were calculated from the following equation:

$$Y_{theoritical} = W*Y_{SM} + (1-W)*Y_{CS}$$

where $Y_{theoretical}$ (%) represents the theoretical yields of blended biochars; Y_{SM} (%) represents the yield from SM pyrolysis alone; Y_{CS} (%) represents the yield from CS pyrolysis alone; W (%) represents the weight percentage of SM in the SM/CS mixtures.

The interactive effect analysis by the comparison between the experimental and theoretically calculated yields of the blended biochars is shown in Table 2. The experimental yields of the blended biochars at 300℃ were obviously lower than the theoretical values, suggesting the antagonistic effect between SM and CS on the producing of solid phase during co-pyrolysis at 300℃. It might be because the co-pyrolysis of SM with CS decreased the external energy requirement for pyrolysis [23], thus the release of volatile matter was accelerated, and the speed of weight loss increased [24]. The difference between experimental values and theoretical values of biochar yield was bigger at low pyrolysis temperature (300 ℃) than that at high pyrolysis temperatures (500 ℃ and 700 ℃), and it decreased with increasing ratios of CS/SM, suggesting that the interactive effect was strongly affected by the proportion of added CS and pyrolysis temperature. Wang et al. also observed antagonistic effect of sewage sludge and wheat straw co-pyrolysis on the yield of the blended biochar [25].

3.2 Characteristics of feedstocks and biochars

Characteristics of feedstocks and biochars, including ultimate analysis, ash content and pH are summarized in Table 3. The N, H, and O contents of all biochars decreased with rising pyrolysis temperature, which resulted from the more thorough decomposition of organic matter at high temperature. In addition, pyrolysis increased the C content of CS, with higher pyrolysis temperature increasing more. Contrastingly, S1C0 generated at 300 °C had higher C content, while their counterparts generated at 500 °C and 700 °C displayed lower C contents than the raw SM. Given that CS was dominated by organic constituents (94.09%) while SM contains considerable proportion of inorganic compositions (ash, 31.73%), more organic C accumulated in CS biochars at higher temperature while more ash remained in SM biochars produced from higher temperature diluted the C content. Normally, the lower H/C and O/C molar ratios indicate the higher organic aromaticity of biochars [26, 27]. Biochars with higher aromaticity are commonly more resistant to decomposition and hence more stable in the environment [14]. Pyrolysis led to a decrease in molar H/C and O/C ratios of SM and CS, and this two ratios decreased with rising pyrolysis temperature, implying higher aromaticity and stability of biochars derived at higher temperature. The C, H and O contents in blended biochars increased with CS addition, whereas the ash and N contents showed an opposite trend. After the addition of CS, the molar H/C and O/C ratios of blended biochar decreased, indicating an increase in their aromaticity and stability. Our studies echoed previous finding that co-pyrolysis of bamboo sawdust with sludge at 400 °C decreased H/C ratio of sludge biochars [15], while inconsistent with the finding showing little effect of rice straw and sawdust addition on the H/C ratios of sewage sludge biochars [14].

The pH values of raw SM and CS were 8.05 and 7.37, respectively. Pyrolysis led to an increase of pH of both SM and CS, and the higher pyrolysis temperature produced biochars with higher alkalinity. This was because of the decomposition of organic components and accumulation of alkali salts during pyrolysis [22]. The variation of pH among produced biochars was in line with the change of ash content. Under the same pyrolysis temperature, S1C0 had the higher pH than S0C1, and thus the co-pyrolysis of

CS with SM generated biochars with lower pH than pyrolysis of SM alone. The pH values of S1C0 and S0C1 at 700°C were about 12. Such high alkalinity of biochars is promising to alleviate soil acidification and favor the immobilization of positively charged heavy metals ions. However, the soil alkalinity induced by such highly alkaline biochars needed to be controlled not to harm soils and plants.

3.3 Heavy metal levels in feedstocks and biochars

Regarding the total heavy metal concentrations in the SM and its biochars (Fig. 1), Zn was highest, followed by Cu, Cr, Ni, Pb, and Cd. Seriously, the total Cu and Zn concentration of SM exceeded the limitations of manure compost in Germany (Cu =100 mg/kg and Zn = 400 mg/kg) [28]. This can be due to the extensive use of copper and zinc salts as feed additives in swine rations [29]. As a result, total Cd, Cr, Pb, and Ni concentrations in the generated biochars were within safe levels, while Zn and Cu concentrations were above the threshold limit values recommended by the International Biochar Initiative (143 and 416 mg/kg for Cu and Zn, respectively) [30]. As expected, the total levels of six heavy metals in CS were lower than in SM, and the difference was more significant for Cu and Zn.

After pyrolysis of SM, the total Cu, Cr and Ni concentrations gradually increased with rising pyrolysis temperature, indicating most of these metals remained in biochars. Nevertheless, the concentrations of total Zn, Cd, and Pb tended to decline at higher temperature (500 ℃ for Pb and Zn; 400 ℃ for Cd) after an initial increase in lower temperature range. Previously, Zeng et al. also observed the percentage of Zn, Pb and Cd remained in biochars increased first from 200-700℃ and then slightly declined at 800 ℃ during the pyrolysis of swine manure and goat manure [10]. The reason for higher remaining of Cu, Cr and Ni in biochars may due to their low vapor pressures and high boiling temperatures, while less retention of Zn, Pb, Cd in biochars can be due to the high volatility of these metals or formation of metal chlorides ($CdCl_2$, $ZnCl_2$, and $PbCl_2$) that are highly volatile [31].

The total concentrations of the six heavy metals in the blended biochars, except for S3C1 at 300 ℃, were lower compared to the S1C0 at the same temperature, which resulted from a "dilution effect" induced by the added CS that was with lower heavy metal levels. Thus, within the studied blending ratios, the higher percentage of added CS, the lower the total heavy metals concentrations in the blended biochars. Similar result was also found by Meng et al. [16]. Overall, co-pyrolysis of SM with higher percentage of CS addition at low pyrolysis temperature appeared to be better in lowering the total heavy metal levels of blended biochars.

3.4 Speciation of heavy metals in feedstocks and biochars

The toxicity and environmental risk of heavy metals are related to the mobile/bioavailable fraction rather than the total concentrations. This study obtained four heavy metal fractions with the mobility and bioavailability in the order of F1 (exchangeable and acid soluble) > F2 (reducible) > F3 (oxidizable) > F4 (residual) [19]. The F1+F2, F3 and F4 fraction is often regarded as directly bioavailable, potentially bioavailable (under highly acidic and oxidizing conditions) and non-bioavailable, respectively [10, 32].

Results in Fig. 2 displayed that over 70% of Cu and Zn in SM were F1+F2 fraction, and Ni, Cd and Pb were also primarily distributed to F1+F2 fraction (>50%). In comparison, more than 80% of Cr in SM remained in F3 + F4 fraction, which was in accord with previous findings [10, 33]. This indicated a high potential environmental risk of the raw SM from Cu, Zn, Ni, Cd and Pb which was relatively higher than that from Cr. A remarkable decline of the F1+F2 fraction of all targeting metals was observed when SM was converted into biochar by pyrolysis, and this decrease was more significant at higher temperature. In contrast, the percentage of F4 fraction increased with rising pyrolysis temperature, suggesting the conversion of unstable (F1 + F2)

heavy metals into stable (F4) status in SM during pyrolysis. Previous studies also observed increased percentage of stable fraction of heavy metals in various types of animal manure-derived biochars as pyrolysis temperature rose [10, 12, 13]. When pyrolysis temperature increased, metals in SM could be trapped and occluded by the formed carbon matrix as organometallic complex or associate with the mineral and crystal lattices to form insoluble inorganic forms like metal-phosphate and metal-silicate [34-36].

Although the stability of all heavy metals increased when SM was converted into biochar by pyrolysis, the distribution patterns of different metals in biochars varied. For example, F3 and F4 fractions (59.00% and 40.16%, respectively) were the main forms of Cu in S1C0 at 700 ℃, while F1+F2 fractions was minimal (0.83%). For Ni in S1C0 at 700℃, F3 and F4 (46.11% and 42.32%, respectively) were also the main fraction, while F1+F2 still make up a small fraction (11.57%). The reason for the low proportion of mobile (F1+F2) Cu and Ni at 700 ℃ could be that metal salts (carbonate, sulfate, chlorate, phosphate, etc.) could decompose into metal oxides (CuO and NiO) at lower temperature (<500℃), and then reduced to lower valence (Cu(I) and Ni (I)) and further to crystal Cu^0 and Ni^0 that are less soluble by the reducing gas (CO and H_2, etc) or biochar at higher temperature (550-750℃) [37, 38]. Similar results of Cu and Ni fractionations were observed on biochars derived from municipal sewage sludge [39], swine and goat manures [10]. For Pb in S1C0 made from 700℃, F3 accounted for 31.93% and F4 contributed as high as 56.26% to the total content. This might be due to the fact that SM is relatively rich in phosphorus, and thus easily leading to stable lead phosphates formation during pyrolysis [40]. The F4 fraction of Cr was highest among six heavy metals (76.12%), with F1+F2 fraction accounting for 9.25%. This might be due to the formation of free CaO through the thermal decomposition of $CaCO_3$ above 650 ℃ [41], which could fix Cr(VI) through forming stable compound $CaCrO_4$ [42]. Despite the decrease of F1+F2 fraction of Zn and Cd with pyrolysis, still 32.54% and 30.92% existed as F1+F2 fraction for Zn and Cd in S1C0 at 700 ℃, respectively, indicating that Zn and Cd in S1C0 had a higher mobility and hence potential risk than other heavy metals in the derived biochars. Similarly, Meng et al. also found that a considerable percentage (about 30%) of Zn in F1+F2 fractions in biochar derived from pig manure at 700 ℃ [13]. It was also noted that the distribution patterns of six heavy metals in the four fractions of S0C1 were different from that in S1C0. For instance, the proportion of F1+F2 (4.85%) and F4 (90.61%) fraction of Cu in S0C1 at 700 ℃ were obviously higher than that in S1C0 (0.83% and 40.16% for F1+F2 and F4, respectively). The F1+F2 fraction of Zn, Ni and Pb was higher while F4 fraction was lower in S1C0 than in S0C1. In contrast, Cd showed an opposite trend to that of Zn, Ni and Pb. This might result from different organic and inorganic elemental compositions in SM and CS, which could lead to formation of different organometallic or inorganic-metallic complexes for different metals during pyrolysis. The exact mechanisms regarding this needs a further study. No significant differences of distribution pattern of Cr were observed between S1C0 and S0C1.

After CS addition, the change of distribution patterns of six heavy metals varied. Overall, at all pyrolysis temperatures, F1+F2 fractions of Cu, Zn, Pb and Ni were mostly higher in the blended biochars than in S1C0 and they increased with increasing CS/SM ratios, except Zn with a slightly decrease in biochars derived at 300 ℃. For the F4 fraction at 300 and 500 ℃, stable (F4) Cu and Ni increased after CS addition with higher increase observed at higher addition ratio, while CS addition showed negligible effect on stable (F4) fraction of Zn and Pb. In contrast, at 700 ℃, the F4 fraction of Cu increased with increasing CS addition ratio while stable (F4) Zn, Ni and Pb increased when CS/SM ratio was 1:3 and 1:1, but decreased when the CS/SM ratio increased to 3:1. Hence, for Cu, Zn, Pb, Ni, especially at higher pyrolysis temperature, though CS addition mostly transformed part of their potentially bioavailable fractions (F3) to stable forms (F4), it also unfavorably mobilized part of the potentially bioavailable (F3) metal into bioavailable species (F1+F2). Higher pyrolysis temperature (700 ℃) did

favor the generation of stable fractions of Cu, Zn, Pb, Ni, but these were mostly transformed from F3. No significant change in the distribution pattern was observed for Cr after CS addition. Notably, at all three temperatures, the percentages of Cd in F1+F2 clearly decreased with rising proportion of CS addition, while F4 fractions exhibited an opposite trend. Both changes of F1+F2 and F4 fractions of Cd were more significant at higher CS addition ratio and higher pyrolysis temperature. The largest increase (17.66%) of stable Cd by CS addition was for S1C3 at 300 ℃. At 300 ℃ and 500 ℃, both the mobile (F1+F2) Cd and potentially bioavailable (F3) Cd were converted to stable (F4) fraction after CS addition, while the more bioavailable (F1+F2) Cd transformed to both potentially bioavailable (F3) and non-bioavailable (F4) Cd at 700 ℃. Around 53.53 % of Cd occluded in F4 fraction and 23.93% in the F3 fraction in S1C3 at 700 ℃. Overall, we can clearly see that the impact of CS addition on the distribution patterns of heavy metals in the blended biochars were associated with the types of heavy metals and the proportion of added CS. Also, the optimal addition ratio of CS to achieve best effectiveness on different metals varied. For example, considering the largest decrease of F1+F2 fraction, largest increase of the F4 fraction as well as largest F4 fraction, the optimal effect of CS on Cu and Cd are S1C3 at 700 ℃ while best SM/CS combination for Zn, Pb, Ni was at S3C1 of 700 ℃. Hence, when looking at effect of co-pyrolysis on mitigating the metal releasing potentials from manure-based biochars, selecting pyrolysis conditions and addition ratios that favors more types of metals, and most importantly the most hazardous metals, would have to be considered. Furthermore, there was a significant (p<0.05) correlation between heavy metals fractions, with except of Ni and Pb in F3 Fraction and Ni in F4 fraction, and biochar characteristics, especially H/C, O/C and pH (Table 4). This suggested that changes of heavy metal speciation were greatly related with the formation of aromatic structures and increased alkalinity in biochars. Another study also found correlation between available and/or stable fractions of heavy metals (Cu, Mn, Cd, Cr, As and Zn) with biochar characteristics, i.e., pH, organic carbon, electrical conductivity, fixed carbon, and specific surface area [43]. The detailed mechanisms for redistribution of heavy metals in the blended biochars need further investigation.

3.5 Environmental risk assessment

The C_f (contamination factor), E_r (potential ecological index for individual heavy metal) and *RI* (potential ecological risk index) values of heavy metals in SM and biochars are displayed in Fig.3. The criteria used for risk ranking for heavy metals based on C_f, E_r and *RI* are in Table 1. The C_f value of Zn (13.79) and Cu (6.11) in SM indicated high and moderate Cu and Zn contamination, respectively. The C_f of other heavy metals (Cr=0.07, Ni=0.22, Pb=0.13, and Cd=3.17) in SM implied a negligible or low contamination from these metals. The E_r values of metals in SM suggested a considerable environmental risk from Cd (E_r=94.96) and low potential ecological risks from other heavy metals (E_r<40). The comprehensive *RI* value of SM reached 141.42, suggesting a considerable environmental risk to apply to soils and water. This high *RI* of SM was contributed mainly from Cd (67.15%), followed by Cu (21.62%) and Zn (9.75%) (data not shown). Pyrolysis reduced the C_f, E_r and *RI* for all metals in SM, apart from C_f and E_r for Zn in S1C0 of 300 ℃ and 500 ℃ and C_f, E_r and *RI* of Cd in S1C0 of 300 ℃. However, compared to *RI* of pre-pyrolysis SM, pyrolysis increased the contribution of Cd (increased to 73.80%, 81.66% and 77.88% in S1C0 at 300, 500 and 700℃, respectively) and Zn (increased to 10.47%, 16.39% and 18.98% in S1C0 at 300, 500 and 700℃, respectively) and decreased that of Cu (decreased to 15.04%, 1.20% and 1.60% in S1C0 at 300, 500 and 700℃, respectively) to the *RI* of derived biochars. The ecological index of Cr, Ni, Pb were minimal or very low in both SM and generated biochars (Fig. 3). Additionally, it can be noted that the C_f, E_r and *RI* values in S0C1 were lower than that of S1C0 for all major contaminating metals. Hence, after addition of CS to the SM for co-pyrolysis, the C_f, E_r and *RI* values of the mixed biochars further

declined to below those of S1C0 derived at the corresponding temperatures. The C_f, E_r and *RI* of blended biochars decreased with increasing ratio of CS/SM and increasing pyrolysis temperature, indicating co-pyrolysis with high CS addition ratio at higher temperature was a better technique for reducing the potential environmental risk of heavy metals in SM. Noteworthy, due to low risk contribution of Cu, Zn, Ni and Pb to the *RI* of SM biochars, the unfavorable mobilization of part of these metals made little influence to the *RI* of SM biochars. Meanwhile, since Cd, Cu and Zn were the dominating contributor to the high risk (*RI*) of SM and SM biochars, the reduction of *RI* of SM by pyrolysis and CS addition were mainly driven by Cu, Zn and Cd, especially at higher temperature.

4. Conclusions

In this work, a study was conducted about feasibility of adding corn straw (CS) into swine manure (SM) for co-pyrolysis to lower the environmental risk of SM biochar-bearing heavy metals. As expected, the reduction of total heavy metals (Cu, Zn, Cr, Ni, Pb, and Cd) levels were generally observed in the blended biochars, which resulted from the dilution effect from CS. Pyrolysis and CS addition increased stable fractions of Cu, Zn, Ni, Pb and Cd but also unfavorably mobilized part of Cu, Pb, Ni and Zn in SM and SM biochars, mostly with more obvious effects at higher temperature. The additions of CS favored Cd immobilization best, and converted the less stable (F1+F2 or F1+F2+F3) fractions of Cd into more stable (F3+F4 or F4) Cd, with higher CS addition ratio and higher temperature more favorable. The optimal condition for Cu and Cd immobilization was CS/SM 3:1 at 700 ℃ while that for Zn, Pb and Ni was CS/SM 1:3 at 700 ℃. The calculated potential ecological risk index (*RI*) suggested that the ecological risk of SM and derived SM biochars was mainly contributed by Cd (67.15% to SM and 73.80%-81.66% to S1C0), Cu (21.62% to SM, 15.03% to S1C0 at 300 ℃) and Zn (9.75% to SM, 10.47-19.08% to S1C0). Hence, the reduction effect of pyrolysis and CS addition on the *RI* of SM and derived biochars was driven by the considerably reduced potential ecological index (*Er*) of these major risky metals. Overall, this study demonstrated feasibility of co-pyrolysis strategy to obtain manure-based biochars with acceptable environmental risks from heavy metals. The optimal condition to reduce the metal mobility and metal-relevant environmental risks of derived SM biochars was higher CS addition rate (CS/SM ratio 3:1) and higher pyrolysis temperature (700 ℃).

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Figure lists

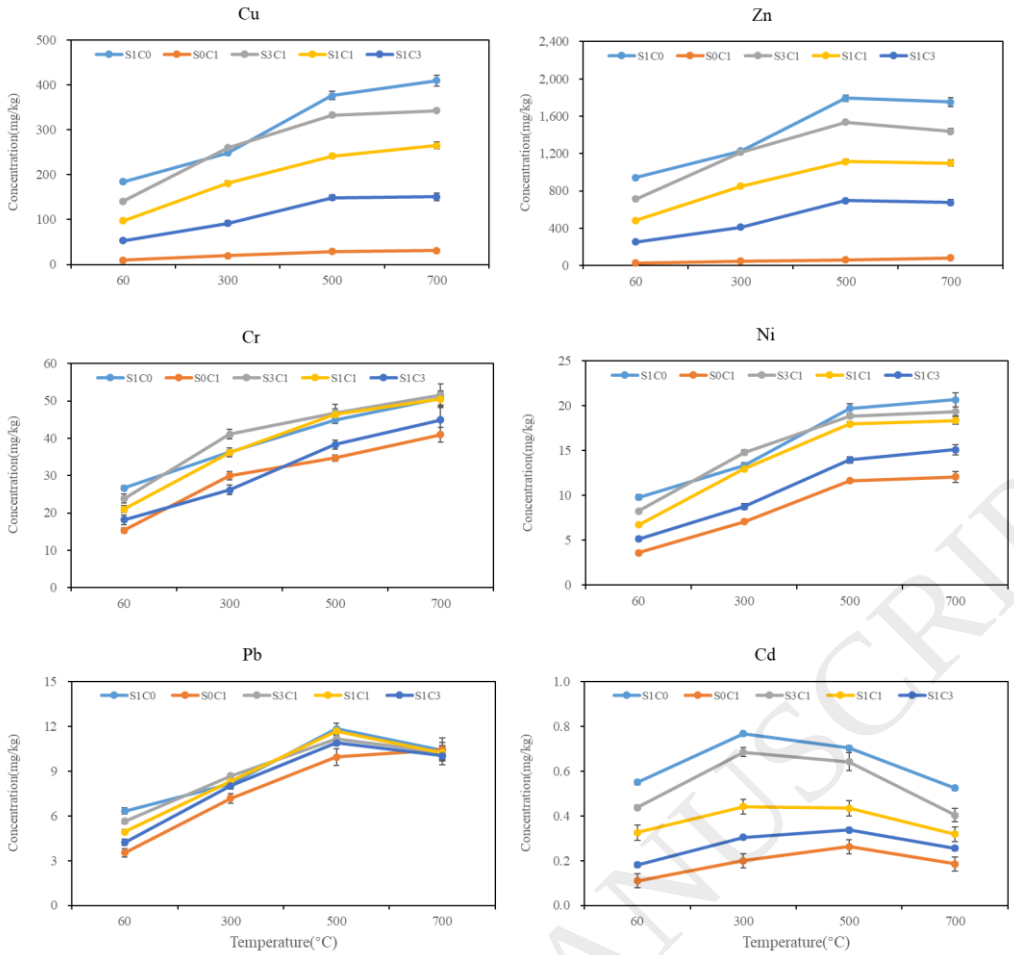

Fig. **1.** The total concentrations of Cu, Zn, Cr, Ni, Pb, and Cd in SM and biochars.

Fig. 2. Changes in the speciation of Cu, Zn, Cr, Ni, Pb, and Cd in SM and biochars

Notes: F1, F2, F3, F4-Exchangeable and acid-soluble, reducible, oxidizable and residual metal fraction.

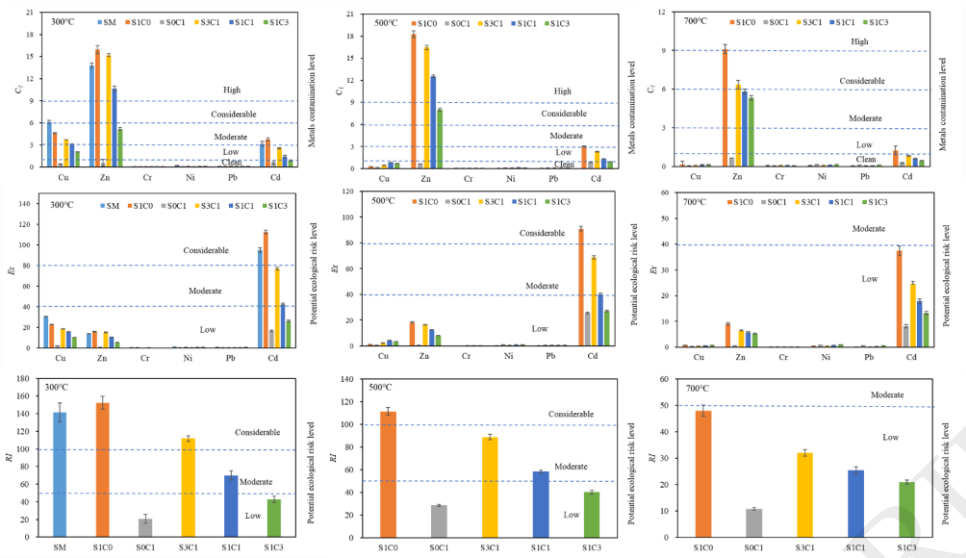

Fig. 3. Ecological risk assessment of the heavy metals in SM and its biochars.
Notes: C_f -Contamination factor of each metal, E_r -Potential ecological index for each metal, RI-Potential ecological risk index of heavy metals in SM and biochars.

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Table 1. The criteria used for risk ranking for heavy metals

C_f	Metal contamination	E_r	Environmental risk levels	*RI*	Environmental risk levels
< 1	Clean	<40	Low	<50	Low
1-3	Low	40-80	Moderate	50-100	Moderate
3-6	Moderate	80-160	Considerable	100-200	Considerable
6-9	Considerable	160-320	High	⩾200	High
⩾9	High	⩾320	Very high		

Notes: C_f -Contamination factor of each metal, E_r -Potential ecological index for each metal, RI- Potential ecological risk index of heavy metals in SM and biochars;

Table 2. The yields of biochar obtained at different pyrolysis temperatures

Items	300℃		500℃		700℃	
	Experimental value (%)	Theoretical value (%)	Experimental value (%)	Theoretical value (%)	Experimental value (%)	Theoretical value (%)
S1C0	73.82±0.47	-	47.47±0.22	-	43.82±0.11	-
S0C1	50.63±0.21	-	31.85±0.17	-	28.95±0.05	-
S3C1	58.38±0.30	68.03±0.34	41.16±0.13	43.56±0.20	38.60±0.12	40.10±0.06
S1C1	55.58±0.18	62.23±0.12	38.04±0.07	39.66±0.16	35.74±0.10	36.39±0.13
S1C3	53.17±0.09	56.43±0.16	35.63±0.17	35.75±0.14	32.66±0.07	32.67±0.17

Notes: Data is present as mean value ± standard deviation (triplicate).

Table 3. Properties of the feedstocks and biochars

Items		Elemental composition (%)				Molar ratio		Ash	pH
		C	H	N	O	H/C	O/C	(%)	
SM		30.55 ±0.35	4.89 ±0.06	4.11 ±0.04	28.72 ±0.62	1.92 ±0.03	0.71 ±0.02	31.73 ±0.84	8.05 ±0.05
CS		51.97 ±0.48	5.96 ±0.06	2.28 ±0.02	33.88 ±0.84	1.38 ±0.04	0.49 ±0.01	5.91 ±0.06	7.37 ±0.06
300℃	S1C0	32.58 ±0.51	3.60 ±0.08	2.80 ±0.06	14.51 ±0.45	1.33 ±0.05	0.33 ±0.01	46.52 ±1.41	9.11 ±0.04
	S0C1	56.57 ±1.20	4.69 ±0.12	1.27 ±0.01	23.88 ±0.28	0.99 ±0.01	0.32 ±0.01	13.59 ±0.08	8.45 ±0.09
	S1C3	38.84 ±0.74	3.44 ±0.07	2.32 ±0.05	15.16 ±0.13	1.06 ±0.03	0.29 ±0.00	40.25 ±0.28	8.90 ±0.08
	S1C1	43.91 ±0.44	3.77 ±0.13	2.19 ±0.07	17.38 ±0.18	1.03 ±0.02	0.30 ±0.00	32.75 ±0.74	8.86 ±0.11
	S3C1	50.56 ±0.61	4.27 ±0.18	1.58 ±0.03	21.69 ±0.26	1.01 ±0.01	0.32 ±0.01	21.91 ±0.34	8.53 ±0.11
500℃	S1C0	28.43 ±0.30	1.58 ±0.05	2.21 ±0.09	5.46 ±0.07	0.67 ±0.01	0.14 ±0.00	62.33 ±0.46	11.02 ±0.08
	S0C1	64.01 ±0.46	2.54 ±0.04	1.12 ±0.07	10.56 ±0.09	0.48 ±0.02	0.12 ±0.00	21.79 ±0.19	10.49 ±0.14
	S1C3	34.72 ±0.21	1.55 ±0.07	2.12 ±0.05	6.33 ±0.04	0.53 ±0.01	0.14 ±0.00	55.29 ±0.23	10.92 ±0.16
	S1C1	43.62 ±0.39	1.77 ±0.04	1.98 ±0.06	7.83 ±0.05	0.49 ±0.02	0.14 ±0.00	44.80 ±0.42	10.73 ±0.10
	S3C1	56.50 ±0.58	2.27 ±0.02	1.41 ±0.04	9.59 ±0.32	0.48 ±0.02	0.14 ±0.00	30.23 ±0.16	10.52 ±0.13
700℃	S1C0	28.23 ±0.16	0.79 ±0.03	1.42 ±0.05	2.48 ±0.007	0.34 ±0.01	0.07 ±0.00	67.09 ±1.45	12.64 ±0.17
	S0C1	70.76 ±0.59	1.65 ±0.04	1.03 ±0.01	4.13 ±0.09	0.28 ±0.01	0.04 ±0.00	22.44 ±0.46	11.90 ±0.14
	S1C3	36.22 ±0.36	0.95 ±0.06	1.35 ±0.02	3.10 ±0.04	0.31 ±0.01	0.06 ±0.00	58.38 ±0.36	12.31 ±0.08
	S1C1	46.46 ±0.74	1.17 ±0.05	1.29 ±0.04	3.50 ±0.06	0.30 ±0.01	0.06 ±0.00	47.59 ±0.67	12.20 ±0.09
	S3C1	60.32 ±1.06	1.48 ±0.03	1.09 ±0.01	4.08 ±0.06	0.29 ±0.01	0.05 ±0.00	33.03 ±0.25	11.93 ±0.10

Notes: Data is present as mean value ± standard deviation (triplicate).

Table 4. Pearson correlation between heavy metals speciation and properties of the feedstocks and biochars

		C (%)	H (%)	N (%)	O (%)	H/C	O/C	Ash (%)	pH
F1+F2 (%)	Cu	0.063	0.975**	0.346	0.969**	0.896**	0.951**	-0.550*	-0.932**
	Zn	0.107	0.833**	0.525*	0.809**	0.796**	0.824**	-0.513	-0.913**
	Cr	0.899**	0.464	-.585*	0.455	0.008	0.131	-0.936**	-0.309
	Ni	0.628*	0.750**	0.056	0.695**	0.505	0.566*	-0.863**	-0.715**
	Pb	-0.547*	0.422	0.869**	0.394	0.731**	0.642**	0.214	-0.580*
	Cd	-0.158	0.672**	0.592*	0.663**	0.750**	0.767**	-0.226	-0.746**
F3(%)	Cu	-0.711**	-0.206	0.606*	-0.154	0.098	0.050	0.636*	-0.015
	Zn	-0.277	-0.920**	-0.351	-0.875**	-0.813**	-0.851**	0.679**	0.909**
	Cr	-0.734**	0.141	0.917**	0.128	0.534*	0.435	0.498	-0.342
	Ni	-0.299	-0.353	0.316	-0.353	-0.163	-0.235	0.409	0.188
	Pb	0.390	0.116	-0.422	0.174	-0.186	-0.046	-0.384	-0.063
	Cd	0.048	0.384	0.300	0.421	0.318	0.378	-0.257	-0.515*
F4(%)	Cu	0.566*	-0.545*	-0.779**	-0.585*	-0.749**	-0.748**	-0.141	0.704**
	Zn	-0.002	-0.676**	-0.548*	-0.666**	-0.681**	-0.699**	0.355	0.794**
	Cr	0.102	-0.639*	-0.650**	-0.613*	-0.718**	-0.707**	.249	.756**
	Ni	-0.295	-0.354	-0.296	-0.308	-0.298	-0.293	0.406	0.456
	Pb	0.516*	-0.500	-0.867**	-0.483	-0.771**	-0.705**	-0.144	0.663**
	Cd	-0.007	-0.493	-0.400	-0.524*	-0.452	-0.509	0.280	0.626*

Notes: F1, F2, F3, F4-Exchangeable and acid-soluble, reducible, oxidizable and residual metal fraction. * - Significant level of $p<0.05$, **- Significant level of $p<0.01$.