Evolution of Cr, Cu, Mn, and Zn during the composting process of chicken manure and their integrated potential ecological risk assessment

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Abstract. The aim of this study was to ascertain the evolution of Cr, Cu, Mn, and Zn during the composting process of chicken manure and their integrated potential ecological risk. This study detected the total amounts of Cr, Cu, Mn, and Zn in 4 samples collected at four different stages in the composting workshop of an intensive chicken farm in Chengdu, China. Furthermore, the chemical fractionation of the four heavy metals was analyzed by the BCR (European Community Bureau of Reference) three-step sequential extraction procedure for each sample. At last, the integrated potential ecological risk of Cr, Cu, Mn, and Zn in the compost at four different stages was evaluated by the procedure of potential ecological risk assessment based on its results of chemical fractionation of Cr, Cu, Zn, and Mn. During the composting process, the total amounts of Cr, Cu, Zn and Mn presented an increasing trend, significantly. Nevertheless, the residual fraction (Res-F) percentage of Cr, Zn, and Cu increased, and the acid extractable fraction (Aci-F) percentage of Mn decreased. The value of integrated potential ecological risk of the four heavy metals in the final product was 9.91. These results indicated the integrated potential ecological risk of the four heavy metals is low. This study provided a support on the promotion and utilization of compost for the intensive chicken farms in China.

1. Introduction

At present, China has a relatively high intensive level of chicken breeding. In this background, it is inevitable to intensively generate the chicken manure in large quantities. The amounts of chicken manure from intensive farm were 1.20×10^8 t just in 2015 in China [1, 2]. For such a large amount of chicken manure, it can generate serious pollution to environment if it is not be treated properly.

Composting was usually applied to dispose of animal manure due to its low-cost, effectivity, and sustainability [3]. Composting animal manure, on the one hand, can reduce manure volume, kill pathogenic microorganisms, and eliminate odour compounds [4]. On the other hand, it can acquire compost, which is the fundamental purpose of composting. For the compost, its application in
agriculture field can effectively promote the yields of crops. Nevertheless, the compost usually contained a certain amount of heavy metals, such as Cu, Zn, Mn, Hg, Ni, Pb, and Cr, which are added in feeds as the trace metals for promoting the growth of animal [5, 6]. Thus the application of the compost might cause the soil pollution by heavy metals [7]. In recent years, the study on heavy metals in the compost derived from animal manure has become research hotspot for ensuring the safety of ecological environment. However, these previous studies mainly focused on the compost derived from pig manure [8, 9, 10]. For the chicken manure, the reports are few.

In this study, we collected 4 samples at different stages (i.e., the initial stage (IS), the first composting stage (FCS), the second composting stage (SCS), and the end-product stage (EPS)) in the composting workshop of an intensive chicken farm in Chengdu, China. The total amount and chemical fractions of Cr, Cu, Zn, and Mn in the 4 samples were determined. Moreover, the integrated potential ecological risk of the four heavy metals in the compost at four different stages was evaluated by the procedure of potential ecological risk assessment based on its results of chemical fractionation of Cr, Cu, Zn, and Mn. The aim of this study is to ascertain the evolution of Cr, Cu, Mn, and Zn during the composting process and their integrated potential ecological risk. The study can provide a support on the promotion and utilization of compost for the intensive chicken farms in China.

2. Materials and methods

2.1. Materials

Four experimental samples were collected at the different stages (i.e., the initial stage (IS), the first composting stage (FCS), the second composting stage (SCS), and the end-product stage (EPS)) in the composting workshop of an intensive chicken farm in Chengdu, China. For the composting, the raw material was the mixture of fresh chicken manure (moisture content 70.0%), wheat bran (moisture content 11.3%) and bagasse (moisture content 23.1%) at a mass ratio of 5:3:2. The period of FCS, SCS and EPS is 14 days, 30 days and 10 days, respectively.

2.2. Detection of total amount and chemical speciation of heavy metal

3.0 g of a dry sample was digested with 28 mL of aqua regia [11]. The concentrations of Cr, Cu, Zn and Mn in the digestion were detected by an inductively coupled plasma spectrum analyzer (iCAP-6000, Thermo Fisher Scientific Inc., Waltham, MA, USA). The total amounts of Cr, Cu, Zn and Mn in the sample were calculated based on the above concentration results.

For the chemical fractionation of Cr, Cu, Zn, and Mn, 1.0 g of a dry sample was sequentially extracted by the BCR (European Community Bureau of Reference) three-step sequential extraction procedure [12]. According to BCR three-step sequential extraction procedure, the chemical speciation of heavy metal is divided into four fractions, i.e., acid extractable fraction (AcI-F), reducible fraction (Red-F), oxidizable fraction (Oxi-F) and residual fraction (Res-F). For the first three fractions, the concentrations of Cr, Cu, Zn, and Mn in the extract of each step were detected by the iCAP-6000 before used to calculate their contents in the sample, respectively. Based on the results, the percentage of each chemical fractions of heavy metal was calculated combining its total amount. The Res-F percentage of Cr, Cu, Zn, and Mn was respectively acquired by subtracting its percentages of the first three chemical fractions from 100%.

2.3. Integrated potential ecological risk assessment

The procedure of potential ecological risk assessment was used in this study to ascertain the integrated potential ecological risk of Cr, Cu, Zn, and Mn in the compost [13]. The assessment process is shown as the following equations (1)-(3).

\[ C_r = \frac{C_i}{C_n} \]  

(1)
\[ E_t = T_r C_f \]  
\[ RI = \sum E_t \]  

where \( C_f \) refers to the single heavy metal contamination degree index; \( C_i \) is the summation value of the contents of the first three chemical fractions of Cr, Cu, Zn, and Mn in compost (i.e., the content of Aci-F + the content of Red-F + the content of Oxi-F). \( C_n \) is the background value of heavy metal in the soils of China. The \( C_n \) value of Cr, Cu, Mn, Zn is 61 mg/kg, 23 mg/kg, 582 mg/kg, and 74 mg/kg, respectively [14]. \( E_t \) denotes the single heavy metal potential ecological risk index. \( T_r \) is the toxic coefficient of heavy metal, which is a constant value. The \( T_r \) value for Cr, Mn, Cu, Zn is 2, 1, 5, and 1, respectively [15]. RI refers to the integrated potential ecological risk index of heavy metals.

3. Results and discussion

3.1. Total amounts of heavy metals during composting process

Figure 1 shows the total amounts of Cr, Cu, Zn, and Mn at the different stages. In general, the total amounts of Cr, Cu, Mn, and Zn increased from IS to EPS indicating that the contents of heavy metal were concentrated (P<0.05). The results may be related to the decomposition of organic matter, loss of water and the mineralization of organic matter during the composting process [16]. However, the variation trends of the four heavy metals were different. For Cu and Zn, the total amounts presented the increasing trend from IS to SCS, and then tend to remain constant at the following stages. Unlike those of Cu and Zn, Cr showed an increasing trend throughout the composting process, while Mn firstly had a sharp increasing trend from FCS to SCS but decreased slightly from SCS to EPS. In the compost (at EPS), Mn (818.53 mg/kg) had the maximum total amount followed by Zn (707.37 mg/kg), Cu (84.00 mg/kg), and Cr (48.07 mg/kg). Table 1 shows the total amounts of Cr, Mn, Cu, Zn in different composts. Compared with different composts, the total amounts of Mn and Zn are high and the total amounts of Cr, Cu are at a moderate level in the chicken manure compost.

Table 1. The total amounts of Cr, Mn, Cu, Zn in different composts.

| Composting material                  | Cr (mg/Kg) | Mn     | Cu     | Zn     |
|--------------------------------------|------------|--------|--------|--------|
| Water hyacinth [18]                  | 54.50      | 1928.00| 54.10  | 177.10 |
| Swine manure [9]                     | -          | 330.00 | 976.00 | 1540.00|
| Sewage sludge [19]                   | -          | -      | 49.50  | 178.20 |
| Commercial manure composts [7]       | 74.60      | -      | 103.00 | 435.00 |
| This study                           | 48.07      | 818.53 | 84.00  | 707.37 |

*: Not mentioned in the research.
Figure 1. The total amounts of Cr, Cu, Zn, and Mn at the different stages during the composting process.

Table 2. The Chinese and European Union's acceptable content of Cr, Cu, Mn, Zn in compost.

|                | Limit value (mg/kg for dry matter) |
|----------------|-----------------------------------|
|                | Cr      | Cu | Mn | Zn |
| China<sup>a</sup> | 150     | -  | -  | -  |
| EU<sup>b</sup> (Organic agriculture) | 70      | 70 | -  | 200 |

<sup>a</sup> Chinese national standards of organic fertilizer (NY525-2012).
<sup>b</sup> EU Regulation on organic agriculture, 889/2008.

3.2. Heavy metal chemical fractionation during composting process

Figure 2 displays the percentage of each chemical fraction of Cr, Cu, Zn, and Mn at the different stages. For Cr (Figure 2a), the percentages of Aci-F, Red-F and Oxi-F decreased sharply from IS to FCS (p<0.05) and maintained stability at the following stages. Whereas the percentage of Res-F increased sharply form IS to FCS and then tended to be stabilized (P<0.05). The results indicated that the Aci-F, Red-F, Oxi-F of Cr were transformed into Res-F in the first composting period. For Mn (Figure 2b), the percentage of Aci-F raised from IS to FCS before decreased generally at the following stages (p<0.05) resulting in the percentage of Aci-F was reduced by 1.84% at EPS compared with that at IS. The percentage of Oxi-F increased gradually during composting process (P<0.05). Unlike the above two fractions, Red-F and Res-F had no significant changes during composting process (p>0.05). These changes indicated that Aci-F was transformed into Oxi-F and the transformation was mainly occurred after the first composting period. For Zn (Figure 2c), the significant percentage change of Aci-F was not observed (p>0.05). However, the percentages of Red-F and Oxi-F appeared a decreasing trend (p<0.05), while the percentage of Res-F increased sharply from IS to SCS and trended to be stable after SCS (p<0.05). According to the results, the conclusion can be drawn as that Red-F and Oxi-F was gradually transformed to Res-F during composting process and the first and second composting periods were the main transformation period. For Cu (Figure 2d), the percentages of all chemical fractions except for Red-F presented a significantly change (p<0.05). Specifically, the percentage of Aci-F increased marginally, and the percentage of Oxi-F decreased from IS to SCS and trended to be stable after SCS. The percentage of Res-F gradual raises generally before SCS and stabilized gradually at the following stages. For Cu, Oxi-F transformed gradually into Aci-F and Res-F
in the first and second composting periods during composting process. Overall, after composting, the dominated chemical fraction of Cr, Zn, and Cu in the compost (at EPS) was Res-F (89.85%, 49.49%, 75.97%, respectively), whereas the dominated chemical fraction of Mn was Aci-F (50.83%).

For the chemical fraction of heavy metal, Aci-F and Red-F are more bioavailable but Oxi-F and Res-F are more stable with low bioavailability [20]. In this study, the Res-F percentage of Cr, Zn, and Cu increased, and the Aci-F percentage of Mn decreased. The results indicated that the bioavailability of Cr, Cu, Zn, and Mn was decreased. Nevertheless, in the compost (at EPS), the dominated chemical fraction of Mn was Aci-F, indicating that the compost might arise a certain extend Mn pollution.

![Figure 2](image)

**Figure 2.** The percentage of each chemical speciation of Cr, Cu, Zn, and Mn at the different stages during the composting process.

### 3.3. Integrated potential ecological risk assessment of heavy metals in the compost

The values of $C_f$, $E_r$ and $RI$ in the process of integrated potential ecological risk assessment are listed in Table 3. According to Sungur et al., where $C_f < 1$, $1 < C_f < 3$, $3 < C_f < 6$, $6 < C_f < 9$, $C_f > 9$ represents clean level, low level, moderate level, considerable level and high level, respectively [21]. According to Xiao et al., where $E_r < 40$, $40 < E_r < 80$, $80 < E_r < 160$, $160 < E_r < 320$ and $E_r > 320$ represents low risk, moderate risk, considerable risk, high risk and very high risk, respectively [22]. And $RI < 150$, $150 < RI < 300$, $300 < RI < 600$, $RI > 600$ represents low risk, moderate risk, considerable risk and very high risk, respectively [22]. Table 3 shows that during the composting, the contamination grade of Cu changed from low level to clean level and the contamination grade of Zn changed from considerable level to moderate level based on the value of $C_f$. This results indicated that composting can decrease the contamination grade of heavy metals effectively. In addition, the results of $C_f$ indicates that the contamination grade of Cr, Cu, Zn, and Mn was the clean level, the clean level, the low level, and the moderate level in the compost (at EPS), respectively. Moreover, the $E_r$ value of
Cr, Cu, Zn, and Mn was 0.16, 4.39, 1.28, and 4.08, respectively, which revealed that the single potential ecological risk of each heavy metal was the low risk grade in the compost (at EPS). Taking all the four heavy metals into consideration, the calculated RI value was 19.16, 13.37, 9.77, 9.91 for IS, FCS, SCS, EPS, respectively. Compared with the results of Yan et al., the compost is safer [23]. According to the identification criteria of integrated potential ecological risk, the integrated potential ecological risk of Cr, Cu, Zn, and Mn belonged to the low risk level. According to the above results, the compost is safe for the environment.

| Heavy metals | C_y | E_r | RI     |
|--------------|-----|-----|--------|
| Cr           | 0.48| 0.13| 0.08   |
| Cu           | 1.68| 1.13| 0.90   |
| Mn           | 1.20| 1.30| 1.04   |
| Zn           | 8.62| 6.17| 4.04   |

4. Conclusion

For Cr, Cu, Mn, and Zn, the total amounts presented the increasing trend during the composting process of chicken manure. However, the Res-F percentage of Cr, Zn, and Cu increased, and the Aci-F percentage of Mn decreased, indicating that the bioavailability of Cr, Cu, Mn, Zn in chicken manure reduced through composting. The integrated potential ecological risk assessment of Cr, Cu, Mn, Zn in the compost revealed that the compost is safe for the environment.

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