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Phytotoxicity and speciation of copper, zinc and lead during the aerobic composting of sewage sludge

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ABSTRACT

The content and speciation of heavy metals in composted sewage sludge is the main cause of negative impacts on environment and health of animal and human. An aerobic composting procedure was conducted to investigate the influences of some key parameters on phytotoxicity and speciation of Cu, Zn and Pb during sewage sludge composting. The pH value reached the optimal range for development of microorganisms, and content of organic matter (OM) and dissolved organic carbon (DOC) decreased with the composting age. The total amounts of Cu, Zn and Pb were much lower in the final compost. The results from sequential extraction procedure of heavy metals showed that composting process changed the distribution of five fractions of Cu, Zn and Pb, and reduced the total contents and sum percentages of four mobile fractions (exchangeable (EXCH), carbonate (CAR), reducible iron and manganese (FeMnOX), and organic matter bound (OMB)), indicating that the metal mobility and phytotoxicity decreased after aerobic composting. The seed germination and root growth of Pakchoi (*Brassica Chinensis* L.) were enhanced with composting age and reached the highest value at the end of compost. The decrease of OM and DOC was significantly correlated to changes of metal distribution and germination index (GI) of Pakchoi. Only for Cu in the compost, the GI could be predictable from the sum mobile metal fractions (EXCH + CAR + FeMnOX + OMB) ($R = -0.814^{*}$). For Zn and Pb, R value was significantly increased by use of other components, such as pH, OM and DOC, which suggested that the transformation of heavy metal speciation and phytotoxicity of sewage sludge during an aerobic composting was rather strongly dependent on multiple components than a single element.

1. Introduction

Land application of composted sewage sludge represents one of the most cost-effective methods for treatment and final disposal of sewage sludge, because the valuable components (N, P, K, organic matter (OM) and other necessary nutrients for plant growth) in stable sludge can be recycled and the properties of soil can be improved [1–3]. Unfortunately, the presence of non-biodegradable and toxic heavy metals limits agricultural application of composted sludge, which tends to accumulate along the food chains and bring potential risks to animal and human [4].

Total heavy metal concentration is an important indicator of pollution. It has been reported that total content of metals in sewage sludge was about 0.5–4% (on a dry weight basis) [5]. However, heavy metals associated with different fractions had different impacts on the environment [6] and their phytotoxicity would connect to some forms rather than the total concentration of metals [7]. The sequential chemical extraction procedures could provide an understanding of chemical fractions of heavy metals and was useful for predicting metal mobility, bioavailability and leaching rates [8].

Many researchers have focused on the heavy metal speciation and phytotoxicity of composted sewage sludge or raw sludge for agricultural use [9–13]. They found that heavy metals in the soils amended by composted sludge presented the higher stability and lower bioavailability [14,15]. Walter et al. [12] suggested that composting procedure changed the mobility of heavy metals and reduced the phytotoxicity of sludge.

The composting process accelerates decomposition of organic matter, especially in the stages with high temperature. Consequently, the significant variation of properties in compost materials occurred within a relatively short period, such as moisture, pH, ammonia, dissolved organic carbon and humus [16–20]. These changes could influence the distribution of heavy metal speciation and phytotoxic behavior of the compost materials. Some authors have studied the evolution of metal contents and fractions in the composting system [19–21]. However, the phytotoxicity of heavy metals was ignored, and the contribution of heavy metals in mobile

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speciation associated with other physicochemical parameters on the phytotoxic behavior is also needed to evaluate.

In the current study, an aerobic composting experiment was conducted on sewage sludge to evaluate the changes of heavy metals speciation and phytotoxic behavior in terms of Pakchoi seed germination. Meanwhile, the effects of some key parameters on metal phytotoxicity and speciation during composting were also investigated.

2. Materials and methods

2.1. Composting procedure

Dewatered anaerobically digested sewage sludge, collected from Sibao Wastewater Treatment Plant in Hangzhou, China, was mixed with sawdust as a bulking agent at 4:1 (w/w fresh weight) to obtain a water content of 60–70% and C/N ratio of 25. The composting reactor was cuboid and with inner dimension of 1.0 m × 0.8 m × 0.8 m (length × width × height). The mixture was composted for 42 days. Composting process was controlled by a forced-aeration static pile system and the air was supplied to the composting mass at 50 L min^{-1} and 12 times per day (15 min with intermission of 105 min per time, totally 3 h per day). At the depth of 0.3 m, temperature was monitored daily. Three phases were observed during composting: the mesophilic phase (32–50 °C, 0–4 days), the thermophilic phase (50–65 °C, 5–21 days, the highest value appeared on day 7) and the cooling phase (fall to room temperature, 22–42 days). About 200 g sample was collected from 5 positions in the composting reactor on days 0, 4, 7, 14, 21, 28 and 42, and mixed for chemical and biological testing by triplicate.

2.2. Chemical analysis

The moisture content of fresh compost sample was determined by oven-drying at 70 ± 5 °C [22]. The aqueous extracts of compost were obtained by shaking at 200 rpm with distilled water at a solid:water ratio of 1:10 (w/v) for 16 h at 20 °C. After the suspension was centrifuged at 10,000 rpm for 20 min and filtered through 0.45 μm membrane filter papers, the pH, EC and dissolved organic carbon (DOC) were determined by pH meter, conductivity meter and a total organic carbon analyzer (Apollo 9000, USA), respectively. Concentration of organic matter was determined by the Walkley and Black wet dichromate oxidation method [23]. For total N, the method of Kjeldahl digestion–distillation was used [24]. Total P was analyzed by the molybdenum blue color method after H_2SO_4–$HClO_4$ digestion [25]. Total Cu, Zn and Pb concentrations were analyzed by HF–HNO_3–$HClO_4$ digesting procedures [26] and measured by AAS (Thermo Solar MKII-6). The selected physicochemical properties of sewage sludge were listed in Table 1.

Table 1
Selected physicochemical properties of sewage sludge

Properties	Sewage sludge (SS)
Moisture (%)	82.4 ± 3.5[a]
pH	6.1 ± 0.07
Electrical conductivity (EC, ds m^{-1})	1.3 ± 0.1
Organic matter (%)	37.6 ± 1.4
Dissolved organic carbon (DOC, g kg^{-1})	10.0 ± 1.7
Total nitrogen (TN, g kg^{-1})	27.7 ± 0.9
Total phosphorus (TP, g kg^{-1})	15.4 ± 0.03
Cu (mg kg^{-1})	346.8 ± 10.6
Zn (mg kg^{-1})	3241.6 ± 52.9
Pb (mg kg^{-1})	194.6 ± 9.5

[a] The values are means ± standard deviations (n = 3).

2.3. Sequential extraction

Speciation of Cu, Zn and Pb in this study was conducted by using the procedure of Tessier et al. [27], which was widely used in the studies on heavy metals in sludge [12,21,28,29]. Five fractions of heavy metal were defined: (1) exchangeable (EXCH): 1 g air-dried sample was extracted with 1.0 M $MgCl_2$ at pH 7 with agitation at 220 rpm for 1 h at 25 °C; (2) carbonate (CAR): residue from (1) was extracted with 1.0 M NaOAc at pH 5 with agitation at 220 rpm for 5 h at 25 °C; (3) reducible iron and manganese (FeMnOX): residue from (2) was extracted with 0.04M NH_2OHHCl in 25% HOAc (v/v) for 6 h at 96 °C in water bath with occasional agitation; (4) organic matter bound (OMB): residue from (3) was extracted with 0.02 M HNO_3 and 30% H_2O_2 of pH 2 for 5 h at 85 °C, and then 3.2 M NH_4OAc in 20% HNO_3 (v/v) was added and agitated for 0.5 h at 25 °C; (5) residual (RES): residue from (4) was digested by HF–HNO_3–$HClO_4$ procedures [26]. After centrifugation and filtration, the supernatant from each extraction was analyzed by AAS (Thermo Solar MKII-6).

According to Tessier, the fraction of EXCH is readily influenced by changes of ionic composition in the liquid; CAR is susceptible to pH variations; FeMnOX is unstable in reductive conditions; OMB decomposes and changes under the oxidizing conditions; and RES permanently fixed in crystal lattice and not enter the food chain. In the normal conditions, fractions of EXCH and CAR mainly represent the heavy metal mobility in the short-term. During the composting, however, all of the fractions except RES make contributions to the metal mobility and bioavailability due to the rapid evolutions of compost properties.

2.4. Pseudo values of heavy metals

Since volatilization of gases and leaching of liquids following the decomposition and mineralization procedures of organic matter during composting, the Cu, Zn and Pb were concentrated in the compost mass [30]. To correct this excessive part of heavy metal contents during composting, all concentration values were normalized by the moisture content. The corrected pseudo values of heavy metals were evaluated using following formula as described similarly by Amir et al. [19]:

$$C_p = \frac{C_a \times (1 - m_0)}{1 - m_t} \,(\text{mg kg}^{-1}) \quad (1)$$

where C_a is the actually measured value of heavy metals (mg kg^{-1} dry compost); m_0 is moisture content in the compost sample of 0 day; m_t is the moisture content at each sampling time (0, 4, 7, 14, 21, 28 and 42 days).

2.5. Germination test for the pakchoi seeds

The germination assay was tested using Pakchoi (*Brassica Chinensis* L.) seed, which has a quick growth rate (harvest in about 2 months from sowing) and was popular to be used as a phytotoxic indicator to evaluate environmental risk of soil contamination by metals [31].

Compost extracts (three replicates for each sample) were prepared by shaking fresh samples with distilled water at a solid:water = 1:10 (w/v) for 1 h. The suspensions were then centrifuged, filtered and kept at 4 °C before testing. For germination tests, 5 mL of each extract were dispensed into a sterilized Petri-dish, which was lined with a filter paper. 50 seeds of Pakchoi were placed in one dish and incubated at 25 °C in the dark for 3 days. Distilled water was used as the control. Treatments were evaluated by counting the number of germinated seeds and measuring the length of the root. The percentage of relative seed germination