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Impact of fly ash and phosphatic rock on metal stabilization and bioavailability during sewage sludge vermicomposting

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HIGHLIGHTS

- Earthworm activity increased in vermibeds with fly ash (FA) and phosphoric rock (PR).
- Cu and Zn bioavailabilities were decreased the most in sewage sludge with 20% FA.
- Pb, Cd, and As bioavailabilities were decreased the most in sewage sludge with 20% PR.
- Metal bioavailability was predicted by total organic carbon, but not always by pH.

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ABSTRACT

Sewage sludge (SS) was mixed with different proportions of fly ash (FA) and phosphoric rock (PR), as passivators, and earthworms, *Eisenia fetida*, were introduced to allow vermicomposting. The earthworm growth rates, reproduction rates, and metal (except Zn and Cd) concentrations were significantly higher in the vermireactors containing FA and PR than in the treatments without passivators. The total organic carbon (TOC) and total metal concentrations in the mixtures decreased, and the mixtures were brought to approximately pH 7 during vermicomposting. There were significant differences in the decreases in the metal bioavailability factors (BFs) between the passivator and control treatments, and adding 20% FA (for Cu and Zn) or 20% PR (for Pb, Cd, and As) to the vermicompost were the most effective treatments for mitigating metal toxicity. The BF appeared to be dependent on TOC in the all treatments, but was not closely dependent on pH in the different vermibeds.

1. Introduction

Increasing urbanization leads to new sewage treatment plants being established, producing more sewage sludge (SS). This material contains a lot of organic matter (OM), a variety of trace elements, pathogens, toxic organic compounds, and heavy metals, so sludge disposal and utilization have been paid much attention. Sludge composting is the most common treatment, and it renders the pathogens harmless, causes organic matter (OM) humification and stabilization, and reduces the bioavailability of heavy metals, through high temperature fermentation. Composting is a process in which organic waste is decomposed into humic material by a number of different microorganisms (Nomeda et al., 2008). Sewage sludge is not conducive to aerobic fermentation because it is not porous and easily agglomerates. Therefore, adding straw or sawdust to the SS, to aid composting, has been studied, and each additive acted as a conditioning and expansion agent and increased the fermentation substrates (Xiong et al., 2010). Aside from conditioning and expansion agents, passivators, such as phosphoric rock (PR) and fly ash (FA), have been used as immobilizing amendments, to reduce the mobility and bioavailability of heavy metals in SS (Lee and Pandey, 2012).

The variation in heavy metal speciation with sludge composition and sludge conditions has been determined (He et al., 2009; Nomeda et al., 2008), and the addition of PR and FA was found to play an important role in changing the heavy metal forms. It has been shown that applying PR to materials polluted by heavy metals can increase the residual (i.e., non-bioavailable) fractions of Pb, Cu, and Zn in the final material by 53%, 13%, and 15%, respectively (Cao et al., 2003). Wang et al. (2001) found that the effective concentrations of Pb, Cu, Zn, and Cd were reduced by 99%, 97%, 96%, and 98%, respectively, by the addition of phosphate to a contaminated site. Metal stabilization with FA has brought the mobility of Pb, Cr, As and Hg down by strengthening the adsorption abilities of the substrate (Dermatas and Meng, 1996). Recently, Xu et al. (2012)

Abbreviations: SS, sewage sludge; PR, phosphoric rock; FA, fly ash; BF, bioavailability factor; OM, organic matter; TOC, total organic carbon; EC, electrical conductivity; F1, exchangeable; F2, carbonate-bound; F3, Fe/Mn oxide-bound; F4, organic matter/sulfide-bound; F5, residual.

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showed that treatment with a 14% SS and 6% FA mixture reduced the eco-toxicity of metals more than other mixtures, and also gave the highest yield of Manila grass.

In addition to traditional composting processes, vermicomposting technology has been used in recent years for the effective enrichment of heavy metals in the SS and for the stabilization of SS. Vermicomposting uses earthworms' special ecological functions in combination with environmental microorganisms to reduce secondary pollution from SS and to recycle it more effectively (Singh et al., 2011). Bakar et al. (2011) reported that heavy metal (Cr, Cd, Pb, Cu, and Zn) concentrations in vermicompost were 0.25–11.57 times higher than the initial concentration because of the mineralization and excretion of non-accumulated heavy metals by the earthworms. Similar results found by Yadav and Garg (2009) showed that heavy metal concentrations in vermicomposts were higher than in initial feed mixtures. Conversely, a reduction in heavy metal (Cu, Mn, Zn, and Pb) concentrations through vermicomposting of SS was found by Khwairakpam and Bhargava (2009), and concentrations of each metal in the vermicompost were found to be within the permissible limits for its application to agricultural soils.

Previous studies have concentrated primarily on mitigating the metal toxicity from SS by mixing the SS with a range of agents before vermicomposting it (Suthar, 2008a, 2009; Vig et al., 2011). However, the quality of vermicomposted sludge amended with PR and FA, based on the characteristics of the metals, especially their speciation, in the SS, has not yet been studied. A more detailed understanding of the redistribution of Cu, Zn, Pb, Cd, and As in SS vermicomposted with PR and FA is needed to understand how to suppress metal toxicity. The study presented here was carried out with the following aims: (1) to estimate the growth and reproduction rate of the composting earthworms, and to measure the concentrations of the metals (Cu, Zn, Pb, Cd, and As) in earthworm tissues and the SS with different proportions of PR and FA added, both before and after vermicomposting; (2) to investigate the effects of vermicomposting with PR and FA on the distribution and bioavailability of Cu, Zn, Pb, Cd, and As in SS; and (3) to examine the correlation of the BF of the metals in SS with pH and TOC during vermicomposting, for different treatments.

2. Methods

2.1. Substrates, earthworms, passivator, and the vermicomposting process

Samples of SS with 70–85% moisture content were taken from the Suojincun Wastewater Treatment Plant, in the Xuanwu District of Nanjing, China, where an activated sludge process is used to treat urban sewage. *Eisenia fetida* (Savigny), one of the best suited species for vermicomposting SS under all climatic conditions (Sinha et al., 2010), were obtained from One Viewpoint Biological Technology Co., Ltd. (Nanjing, China). Fly ash and PR were obtained from the Huaneng Power Plant (Nanjing, China) and the Changgu Phosphate Fertilizer Plant (Nanjing, China), respectively. The substrates and passivators were left outside to dry, in the sun, for 20 days, turning them twice each day. The physicochemical properties of the SS, PR, and FA are listed in Table 1.

Four vermicomposting treatments were prepared, each using the same earthworm species but different proportions (on a weight/weight basis) of SS, PR, and FA (T1 = 100% SS; T2 = 80% SS + 20% FA; T3 = 80% SS + 20% PR; T4 = 80% SS + 10% FA + 10% PR). Each vermicomposting reactor (35 cm diameter × 40 cm deep) contained 7.0 kg of waste mixture, and each test was performed in triplicate. The mixtures in the reactors were manually turned every day for 20 days before adding the earthworms, to reduce the accumulation of volatile and other substances that are toxic to earthworms (Vig et al., 2011). After that period, about 70 mature earthworms, with a total live weight of 50 g, were introduced into the four reactors to allow vermicomposting. The reactors were covered with nonwoven material to stop the earthworms escaping, and they were placed in the dark in a room kept at a constant temperature (23 ± 0.6 °C). The moisture content of the mixture was maintained at 70–85% by periodic sprinkling with distilled water, to maintain good earthworm functions. The mixtures were vermicomposted for 70 days, after which the earthworms, worm casts, and cocoons were separated from the composts by hand. The earthworm weights, growth, and reproduction rates were measured following the method described by Suthar (2009).

Table 1
Initial physico-chemical properties of sewage sludge, fly ash, and phosphoric rock used for vermicomposting.[a]

Parameters	Sewage sludge	Fly ash	Phosphoric rock
pH	7.2 ± 0.16	9.3 ± 0.31	3.0 ± 0.24
TOC (g/kg)	352 ± 9.7	ND[b]	ND[b]
EC (ds/m)	4.2 ± 0.21	0.3 ± 0.02	0.7 ± 0.05
N (g/kg)	10.7 ± 0.54	4.3 ± 0.12	TQ[c]
P (g/kg)	3.9 ± 0.26	1.2 ± 0.11	336 ± 7.8
K (g/kg)	7.9 ± 0.67	1.5 ± 0.24	TQ[c]
C/N	26.7	104 ± 3.2	ND[b]
Cu (mg/kg)	178 ± 4.3	12.8 ± 0.05	4.0 ± 0.03
Zn (mg/kg)	781 ± 13.5	149 ± 10.2	334 ± 16.7
Pb (mg/kg)	231 ± 6.2	7.6 ± 0.21	TQ[c]
Cd (mg/kg)	12.7 ± 0.32	1.1 ± 0.12	1.4 ± 0.09
As (mg/kg)	47.2 ± 2.87	14.8 ± 1.32	TQ[c]

[a] Values (mean ± standard deviation) are the averages of three replicates.
[b] Not detected.
[c] Trace quantity.

2.2. Analytical methods

Each SS sample was air-dried at room temperature, and then thoroughly ground, homogenized, and passed through a 100 mesh sieve. Electrical conductivity (EC) was determined in a 10% (w/v) aqueous solution using a digital EC meter. The pH and TOC of the raw materials and the vermicomposted mixtures were measured according to the method published by Vig et al. (2011). Total carbon was analyzed using an elemental analyzer (Elementar Vario EL III, Germany), and the method published by Black et al. (1965) was used for measuring total N, P, and K. The metals in the vermicomposted mixture were fractionated using a sequential extraction procedure described by Nomeda et al. (2008), and the total metal (Cu, Zn, Pb, Cd, and As) concentrations were the sum of the exchangeable (F1), carbonate-bound (F2), Fe/Mn oxide-bound (F3), organic matter/sulfide-bound (F4), and residual (F5) fractions. The heavy metal concentrations were determined by atomic absorption spectrophotometry (AAS) (Z-8100, Japan).

Three earthworms were taken for analysis before and after vermicomposting. The worms were washed in distilled water, frozen, and dried in a ventilated oven at 60 °C for 72 h. The dried earthworms from each treatment group were analyzed for Cu, Zn, Pb, Cd, and As after being passed through a 20 mesh sieve. Sample digestion procedures were selected (from tests performed before the study reported here, data not shown) to obtain the most accurate metal concentrations, with total heavy metals (Cu, Zn, Pb, and Cd) being analyzed using the $HF–HNO_3–HClO_4$ digestion procedure (Carter, 1993) and total As being analyzed using the $HNO_3–H_2SO_4$ digestion method (Frank et al., 1983), and the same procedures were used to analyze the metals in the SS. The mean initial heavy metal concentrations in the earthworms were: Cu, 13.6 mg kg^{-1};