

Concentration and speciation of heavy metals in six different sewage sludge-composts

Quan-Ying Cai^a, Ce-Hui Mo^{b,*}, Qi-Tang Wu^a, Qiao-Yun Zeng^a, Athanasios Katsoyiannis^{c,1}

^a College of Resources and Environment, South China Agricultural University, Guangzhou 510642, China

^b Department of Environmental Engineering, Jinan University, Guangzhou 510632, China

^c EU-Joint Research Center; Institute for Health and Consumer Protection, Physical and Chemical Exposure Unit, Ispra (VA), TP-281, Via E. Fermi 1, I-21020, Italy

Received 11 October 2006; received in revised form 31 December 2006; accepted 31 January 2007

Available online 6 February 2007

Abstract

This study presents the concentrations and speciation of heavy metals (HMs) in six different composts of sewage sludges deriving from two wastewater treatment plants in China. After 56 days of sludge composting with rice straw at a low C/N ratio (13:1), cadmium (Cd), copper (Cu), lead (Pb) and zinc (Zn) were enriched in sludge composts, exhibiting concentrations that varied from 0.75 to 2.0, 416 to 458, 66 to 168 and 1356 to 1750 mg kg⁻¹ dry weight (d.w.), respectively. The concentrations increased by 12–60% for Cd, 8–17% for Cu, 15–43% for Pb and 14–44% for Zn compared to those in sewage sludges. The total concentrations of individual or total elements in the final composts exceeded the maximum permissible limits proposed for compost or fertilizer. In all the final composts, more than 70% of total Cu was associated with organic matter-bound fraction, while Zn was mainly concentrated in exchangeable and Fe–Mn oxide-bound fractions which implied the high mobility and bioavailability. Continuously aerated composting treatment exhibited better compost quality and lower potential toxicity of HMs, whereas inoculant with microorganism and enzyme spiked during composting had no obvious advantage on humification of organic matter and on reducing HM mobility and bioavailability.

© 2007 Elsevier B.V. All rights reserved.

Keywords: Heavy metals; Speciation; Compost; Sewage sludge; Rice straw

1. Introduction

The rapid development of industrial and agricultural activities in China, and the subsequent increase in the use of chemicals have seriously impacted on the environment during the past decades. To face this ecological risk, more than 600 wastewater treatment plants (WWTPs) are currently operating, and consequently, about 5000 million kg of dry sewage sludge are produced annually [1]. Land application of sewage sludge is the most cost-effective option of sludge disposal because of its advantages over traditional means such as landfilling or incineration. However, land application of sludge represents

also a potential threat to the environment because of the presence of pathogens and of toxic pollutants (i.e., heavy metals or organic pollutants). This threat is aggravated when toxic metals are accumulated or mobilised in the soils [2–5].

Composting is a stabilization process of aerobic decomposition, which has been widely used for different types of wastes. It leads to the development of microbial populations which causes numerous physico-chemical changes in the mixture. Composting can reduce the mixture volume by 40–50%, effectively destroy the pathogens by the metabolic heat generated by the thermophilic phase, degrade a big number of hazardous organic pollutants and provide a final product that can be used as a soil amendment or fertilizer [6]. Composting, when followed by land application, is considered as one of the most economical ways for the treatment and final disposal of sewage sludge because it combines material recycling with sludge disposal at the same time [7].

During the last decades, the researches on heavy metal (HM) concentrations and their bioavailability in sludge and/or

* Corresponding author. Tel.: +86 20 85226615; fax: +86 20 85226615.

E-mail addresses: cai_quanying@yahoo.com (Q.-Y. Cai), tchmo@jnu.edu.cn (C.-H. Mo), wuqitang@scau.edu.cn (Q.-T. Wu), qiaoyunzeng@126.com (Q.-Y. Zeng), athanasios.katsoyiannis@jrc.it (A. Katsoyiannis).

¹ Currently at EU-JRC.

compost have received increased scientific attention. It has been reported that the total HM content in sewage sludges is about 0.5–2.0% on a dry weight basis and in some cases may rise up to 4%, especially for metals such as Cu and Zn [8,9]. The total concentrations of HMs indicate the extent of contamination, but they provide little information about the forms in which HMs are present, or about their potential for mobility and bioavailability in the environment [10]. HMs are non-biodegradable and occur in various forms in sewage sludge and its compost. Their mobility and bioavailability in a given medium are very important, and thus in order to assess their environmental impact it is not sufficient to determine only their total concentrations, but also their chemical speciation in sludge and compost.

Chemical speciation can be defined as the process for identifying and quantifying different species, forms or phases present in a material. Many studies have been performed on the HM speciation in sewage sludge and its compost [11–18]. During composting process, the HM distribution is influenced through the release of HMs during organic matter mineralization or the metal solubilization by the decrease of pH, metal biosorption by the microbial biomass or metal complexation with the newly formed humic substances or other factors [12,19]. Some studies have shown that the available fraction of HMs mainly decides their mobility, bioavailability or phytotoxicity in soils [2,5]. Assessment of concentrations and chemical speciation of HMs in composts enables one to evaluate their bioavailability and suitability for land application.

In China, compost is used in agriculture, forestry and horticulture [20]. With the increased production of sewage sludge, there is a great need to develop low cost and high efficiency composting technologies, compatible with China's conditions, as well as a need for environmental monitoring. The need of good quality compost, free of hazardous substances, is even higher for China, where the concentrations of HMs in 36,000 ha investigated (out of 300,000 ha basic agricultural protecting cropland) in 2000, exceeded the maximum permissible values for cropland [21]. The present study aimed at investigating the concentrations of four HMs (Cd, Cu, Pb and Zn) in the composts from different composting processes of sewage sludge with rice straw at a low C/N ratio and at evaluating their suitability for land application. The speciation of the most abundant HMs is also presented.

2. Materials and methods

2.1. Composting

Secondary dewatered sludges were taken from Datansha WWTP in Guangzhou city and Zhen'an WWTP in Foshan city, Guangdong Province (Canton), China. Rice (*Oriza sativa* L.) straw was collected from the experimental farm of South China Agricultural University, Guangzhou. It was air-dried and chopped into small pieces, about 5–6 cm of length. The selected chemical characteristics of sludge and rice straw are presented in Table 1. Inoculation mixture comprised of microorganisms, enzymes and growth promoting agents was supplied by Organica Company, Hong Kong.

The composting experiment was conducted in South China Agricultural University, Guangzhou. Six different processes were prepared by mixing thoroughly sewage sludge with rice straw to obtain an initial C/N ratio of 13:1 as shown in Table 2. Wood chips (4–20 cm × 2–4 cm) were added as bulking agent at 10% (w/w) to the piles of continuously aerated composting (CAC) and intermittently aerated composting (IAC). Tap water and faecal sewage were added to maintain the moisture contents at nearly 70% (w/w). Five different piles were prepared on five purpose-built platforms (2.0 m × 1.5 m × 2.0 m, length × width × height). The volume of the initial mixture was 2.0–2.3 m³ of each pile. The pile of manual-rotated composting (MRC) was prepared in a round sealed reactor (250 L) with six holes (2 cm, i.d.). The inoculation mixture was diluted with water and then spiked in the initial mixture of inoculated-manual turned composting (IMTC). The heaps were turned and mixed every 5 days to provide oxygen for the piles of manual-turned composting (MTC), IMTC and Foshan sludge-manual-turned composting (FS-MTC), respectively. CAC and IAC were performed as the static pile approaches and were aerated using a forced aeration system (aerator, 500 W, Guangzhou Hengyang Electric Co., China). CAC was aerated continuously for 4 h day⁻¹ in the morning, while IAC was aerated 16 times during 15 min with intermission of 75 min (total 4 h day⁻¹). MRC was rotated 3–5 rotations every day. The temperature was recorded daily at a depth of 35 cm in the composting piles. After mixing of sewage sludge with rice straw (day 0)

Table 1
Physico-chemical properties of sewage sludges, rice straw and initial mixture

Parameter	Guangzhou sludge (GS)	Foshan sludge (FS)	Rice straw	Initial mixture	
				GS with rice straw	FS with rice straw
Organic carbon (g kg ⁻¹)	173	205	312	— ^a	—
Total N (g kg ⁻¹)	25.0	29.6	5.8	22.1	24.3
Total P (g kg ⁻¹)	13.4	26.8	—	15.8	23.4
Total K (g kg ⁻¹)	21.4	10.3	—	17.3	15.0
C/N	6.9	6.9	54	13.0	13.0
Humic substance (g kg ⁻¹)	—	—	—	154	173
Ash (%)	—	—	—	37.6	30.9
EC ₂₅ ^b (mS cm ⁻¹)	1.9	2.3	—	2.0	2.4
pH ^b	6.48	6.36	—	7.45	7.14
Moisture content (%)	81.7	80.7	12.2	71.8	71.2

^a Not measured.

^b Water/sample = 2.5/1.

Table 2
Treatments of experiment, mixture of sewage sludge and rice straw used for composting

Treatments	Components						Volume of mixture (m ³)
	Sewage sludge ^a (kg)	Rice straw ^a (kg)	Wood chip (kg)	Tap water (kg)	Faecal sewage (kg)	Inoculant ^b (mL)	
Guangzhou sludge (GS) with rice straw							
Manual-turned composting (MTC)	750	160	–	20	25	–	2.3
Inoculated manual-turned composting (IMTC)	750	160	–	45	–	200	2.3
Continuously aerated composting (CAC)	600	130	73	18	20	–	2.0
Intermittently aerated composting (IAC)	600	130	73	18	20	–	2.0
Manual-rotated composting (MRC)	115	25	–	3	3	–	0.3
Foshan sludge (GS) with rice straw							
Foshan sludge-manual-turned composting (FS-MTC)	750	160	–	20	25	–	2.3

^a Wet weight.

^b Inoculant is a mixture of microorganisms, enzymes and growth promoting agents (supplied by Organica Company, Hong Kong).

and at the end of the composting process (day 56), samples were collected from different points of each pile to ensure representative sampling. Subsamples were air-dried, ground, and passed through a 1 mm sieve. Portions of the samples (approximately 20 g) were further ground to pass through a 100-mesh sieve, and refrigerated in closed containers until analysis.

2.2. Chemicals and materials

Multi-element stock solution containing Cd, Cu, Pb and Zn ($1000 \pm 2 \text{ mg L}^{-1}$ in 5% HNO_3) was obtained from Merck (Darmstadt, Germany). Calibration standard solutions were prepared by appropriate dilution of the stock solution with 0.1 mol L^{-1} HNO_3 prior to use. Suprapure acids and deionized water were used for the preparation of samples, extraction solutions and standard solutions. All the other reagents used in this study were of analytical grade or better.

All glassware were cleaned by soaking for 24 h in diluted nitric acid, followed by rinsing three times with deionized water to remove any adhered impurities.

2.3. Analysis of total metal concentration

The modified method presented by Tessier et al. [22] was applied to determine the total concentrations of HMs (Cd, Cu, Pb and Zn) in sewage sludge, the initial mixtures (day 0) and final composts (day 56). Approximately 0.20 g (100-mesh) of each sample was weighed out and placed into pre-cleaned Pyrex test tube. Then they were digested twice with a mixture (1:5, v/v) of 2 mL concentrated HClO_4 (Guangzhou Chemical Co.) and 10 mL HF (Guangzhou Chemical Co.) (the mixtures were evaporated to near dryness each time). Finally, HClO_4 (1 mL) alone was added and the sample was evaporated until the appearance of white fumes. The residue obtained was dissolved with 0.1 mol L^{-1} HNO_3 , transferred into polyethylene volumetric flask (25 mL) through $0.45 \mu\text{m}$ filter and then diluted to the mark. Water blanks were used to con-

trol that the presence of metals was lower than the limit of $0.5 \mu\text{g L}^{-1}$.

2.4. Sequential extraction of Cu and Zn

The conventional method of Tessier et al. [22] with modification was used for the sequential extraction. One gram of each compost sample was weighed on a 50 mL polycarbonate centrifuge tube and the following fractions obtained:

- (1) Exchangeable including water soluble fraction. Compost sample was extracted at room temperature with 20 mL of 0.11 mol L^{-1} HOAc by shaking for 5 h.
- (2) Fe–Mn oxide-bound fraction. The residue from (1) was extracted with 0.1 mol L^{-1} ($\text{NH}_2\text{OH}\cdot\text{HCl}$) in 25% acetic acid (v/v) for 16 h by shaking.
- (3) Organic matter-bound fraction. To the residue from (2), 5 mL of H_2O_2 (30%) at pH 2.0 was added at 30 min interval to prevent from foaming. The mixture was heated to 85°C for 5 h with occasional agitation. After cooling, 2 mL of 2 mol L^{-1} NH_4OAc in 20% HNO_3 (v/v) was added and the sample was diluted to 20 mL and agitated continuously for 30 min.
- (4) Residual. The residue from (3) was digested with a mixture of HF and HClO_4 (5:1, v/v) according to the procedure described above for analysis of total metal concentration.

After each successive extraction, separation was accomplished by centrifuging at 5000 rpm for 30 min. The supernatant was removed, filtered and analyzed for Cu and Zn concentrations.

The concentrations of Cu and Zn in the extracts were determined by inductively coupled plasma atomic emission spectrophotometer and those of Cd and Pb by graphite furnace atomic absorption spectrometry (Hitachi model, Japan) under optimised measurement conditions. For quality control, reagent blanks and samples in duplicate were analyzed to detect contamination and to assess precision and bias. The analytical results

showed no signs of contamination and that the precision and bias of the analysis were generally <10%.

2.5. Physico-chemical analysis

The moisture content was determined by oven-drying at 105 °C for 24 h. The pH was measured using 10 g air-dried sample (1 mm) suspended in 25 mL deionized water using a pH meter (PH3-3C, Shanghai Instrument Co., China). Electrical conductivity (EC) (1:2.5, w/v, solid:water) was measured using an electrical conductivity meter (DDB-303, Shanghai Instrument Co.). Total N and P in samples were extracted by the micro-Kjeldahl method for N and Molybdenum Blue method for P [23]. The organic carbon was measured using the Walkley–Black titration method [24]. The humic substances were extracted by 0.1 M NaOH solution and measured after oxidation by KMnO₄ [25]. Ash content was determined using a loss-on-ignition (LOI) procedure. Briefly, 5 g samples were dried at 110 ± 2 °C for 24 h, and then transferred to a muffle furnace (SX-4-10, Shanghai Electric Stove Co., China) held at 550 ± 2 °C for 20 h. Ash content was calculated from the ratio of pre- and post-ignition sample weights.

2.6. Statistical analysis

Experimental results are expressed on a dry weight basis. Statistical analysis including a multiple comparison (Duncan test, $P < 0.05$) and correlation analysis was performed using the Statistical Analysis System (SAS, Version 8.0) for Windows.

3. Results and discussion

3.1. Physico-chemical properties of different composts

Fig. 1 shows that, during the composting process, in the static piles (IAC and CAC treatments) the temperatures reached the maximum values (67 and 63 °C, respectively) during the first 7 days and that the thermophilic phases remained (at higher than 50 °C) for 25 days; the temperature in FS-MTC treatment increased to 61 °C in the first 9 days and the thermophilic phases remained for 20 days around; whereas, the highest temperatures in the other piles (MTC, IMTC and MRC treatments) were approximately 55 °C and then decreased to 40 °C after 35 days.

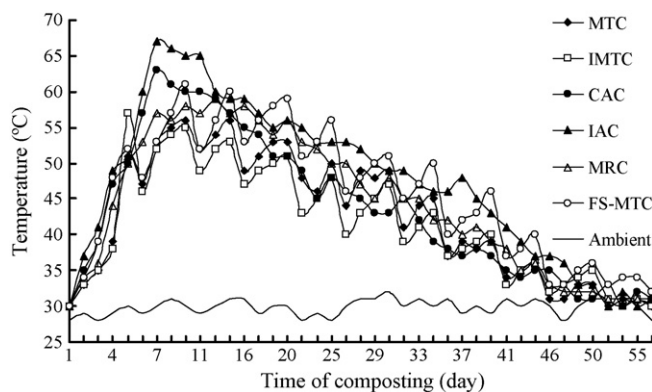


Fig. 1. Temperature change during composting.

The thermophilic duration in the different piles was long enough to meet the requirements of the sanitary standard.

The physico-chemical properties of the initial mixture and final composts are presented in Tables 1 and 3, respectively. The pH values in the final composts varied from 6.85 to 7.52, being within the optimal range for development of bacteria (6.0–7.5) and fungi (5.5–8.0) [19]. The ash content increased from 37.6% (initial mixture) to 55.7–58.1% for GS composts and from 30.9 to 46.7% for FS compost, respectively. Regarding the humic substances in the final composts, their concentrations increased by 13.6–33.1% for GS composts and by 24.9% for FS compost compared to the ones in the initial mixture. The C/N ratio decreased slightly from 13.0 to different levels varying between 10.9 and 12.1. Bernal et al. [25] suggested that one of the maturity indices was the ratio $C/N < 12$ in the composts of sewage sludge, poultry manure and maize straw. The change in the C/N ratio, the amounts of ash and humic substances reflect microbial decomposition of organic matter and the final composts in this study reaching the maturity phase.

3.2. Occurrence of HMs in sewage sludge and in the final composts

The HM concentrations of Guangzhou sludge (GS) and Foshan sludge (FS) are given in Table 4. The most abundant HM was Zn (1213 and 1190 mg kg⁻¹ for GS and FS, respectively), followed by Cu (396 and 357 mg kg⁻¹ for GS and FS, respectively), Pb (57 and 134 mg kg⁻¹ for GS and FS, respectively) and finally

Table 3
Chemical properties of the final composts

	MTC	IMTC	CAC	IAC	MRC	FS-MTC
Organic C (g kg ⁻¹)	235	236	234	238	246	269
Total N (g kg ⁻¹)	20.1	19.6	21.5	19.8	19.6	22.0
Total P (g kg ⁻¹)	15.7	17.1	15.6	14.7	16.4	31.9
Humic substance (g kg ⁻¹)	193	175	205	203	204	216
Ash (%)	57.5	55.7	58.1	56.5	56.0	46.7
C/N	11.7	12.1	10.9	12.0	12.6	12.2
pH ^a	7.24	7.52	7.14	7.12	7.52	6.85
EC ₂₅ ^a (mS cm ⁻¹)	2.79	2.78	3.21	3.08	3.03	2.97

^a Water/compost = 2.5/1.

Table 4

Total concentrations of heavy metals in sewage sludges, initial mixture and Chinese legal limits (mg kg^{-1})

	Cd	Cu	Pb	Zn
Guangzhou sludge (GS)	0.54	396	57	1213
Foshan sludge (FS)	1.74	357	134	1190
Initial mixture				
GS with rice straw	0.42	225	33	760
FS with rice straw	1.1	206	82	744
Standard (GB 4284-84) ^a				
Limit (soil pH <6.5)	5.0	250	300	500
Limit (soil pH \geq 6.5)	20	500	1000	1000
Standard (GB 18918-2002) ^b				
Limit (soil pH <6.5)	5.0	800	300	2000
Limit (soil pH \geq 6.5)	20	1500	1000	3000
Range (mean) in soil of the Pearl River Delta ^c	ND–1.8 (0.48)	1.4–190 (230)	7.7–180 (35)	11–280 (66)

^a Control Standards for Pollutants in Sludges for Agricultural Use (GB 4284-84).^b The discharge standard of pollutants for municipal wastewater treatment plant (GB 18918-2002).^c According to Wong et al. [26].

by Cd (0.54 and 1.7 mg kg^{-1} for GS and FS, respectively). The Cu and Zn concentrations were within the discharge standard of pollutants for municipal WWTP (GB 18918-2002, enforced since 2003), but exceeded the control standards of pollutants in sludges for agricultural use (GB 4284-84, enforced since 1984), and also markedly higher than the mean concentrations of HMs in soils of the Pearl River Delta, China (Table 4) [26], highlighting the need for efficient treatment before disposal.

After composting (56 days) of sewage sludge with rice straw, the total metal concentrations in the final composts showed a wide variation (Table 5). The dominant HM was Zn, followed by Cu and Pb, and Cd, being in good agreement with their distribution profiles in the initial sludges and with other studies dealing with composts [2,27,28]. Zinc concentrations varied from 1356 (FS-MTC) to 1750 mg kg^{-1} (IAC) and Cu from 41 (FS-MTC) to 458 mg kg^{-1} (MRC). Concerning the least abundant HMs, Cd and Pb, their concentrations ranged from 0.75 (CAC) to 2.0 mg kg^{-1} (FS-MTC) and from 66 (MRC) to 168 mg kg^{-1} (FS-MTC), respectively.

Compared to the respective values of HMs in sludge and the initial mixture, the total concentrations of HMs in the final composts increased remarkably (Table 5). For example, in the GS composts, compared to the concentrations of HMs in GS, an increase of 39–60% for Cd and 32–44% for Zn were observed, while 8–17% for Cu and 15–43% for Pb. The increase percentage would reach 88–148% if compared to those in the

initial mixture of GS with rice straw. Similar increases in the total metal concentrations were found in many relevant studies [12,15,18,29,30], where even 3-fold enrichment of Cu and Zn in the mature compost compared to the initial values was observed [12]. Composting may concentrate or dilute the HMs content of the sewage sludge [19,31]. The change of metal concentration is generally attributed to the metal loss through leaching and to organic matter destruction [31,32]. In this study, the composting trials were performed in the purpose-built platforms, and thus there was no leaching and runoff during composting. HMs are non-biodegradable. Moreover, in order to reduce the cost of operations, the composting of sludge with rice straw in the present study was conducted at a low ratio of C/N (13:1) (Table 1). It is therefore concluded that the increase in the concentration of HMs was mainly due to the weight loss of materials following organic matter decomposition and mineralization processes during the composting period [12,31,32]. On the other hand, the increase percentages of four metals in the different composts were not constant. Among the five composting processes of GS, the higher increase percentages of Pb and Zn were found in IAC and CAC treatments, and the lowest increase percentages of Cd, Cu, Pb and Zn were observed in CAC, IAC, MRC and IMTC, respectively. The results demonstrate that the composting approaches had effects on the metal condensation. As previously shown, the static piles (CAC and IAC) reached the higher temperature and remained longer in the thermophilic

Table 5

Concentrations (mg kg^{-1}) of HMs in final composts and their increase percentage (%)

Treatments	Cd	Cu	Pb	Zn
MTC	0.86 (59 ^a , 105 ^b)	434 (10, 93)	67 (17, 103)	1710 (41, 125)
IMTC	0.79 (46, 88)	445 (12, 98)	73 (29, 121)	1597 (32, 110)
IAC	0.81 (50, 93)	428 (8, 90)	82 (43, 148)	1750 (44, 130)
CAC	0.75 (39, 79)	431 (9, 92)	79 (39, 139)	1734 (43, 128)
MRC	0.87 (60, 107)	458 (16, 104)	66 (15, 100)	1723 (42, 127)
FS-MTC	1.95 (12, 77)	416 (17, 102)	168 (26, 105)	1356 (14, 82)

^a The increase percentage of concentration compared to the value in sewage sludge.^b The increase percentage of concentration compared to the value in the initial mixture.

Table 6
Limit values of HMs in compost of some countries (mg kg^{-1})

Country	Regulation	Cd	Cu	Pb	Zn
Netherlands ^a	Compost	<1	<60	<100	<200
	Clean compost	<0.7	<25	<65	<75
Canada ^b	Class A	3	100	150	500
	Class B	20	757	500	1850
Poland ^c	Standard for compost	5	300	350	1500
Spain ^c	Fertilizer and related materials	10	450	300	1100
UK ^c	Composting association quality label	1.5	200	150	400
EC (European Commission) ^c	Draft W.D. biological treatment of biowaste (class 1)	0.7	100	100	200
	Draft W.D. biological treatment of biowaste (class 2)	1.5	150	150	400
Australia ^c	ARMCANZ limits for biosolids	3	200	200	250
US ^d	Rodale organic seal of compost quality	4	300	150	400

^a Legal requirements for heavy metals in compost and clean compost originating from so-called other organic fertilisers in the Netherlands [33].

^b Class A of composts “which have no restrictions in use” and Class B of compost “which can be used on forest lands and road sides and for other landscaping purposes”, according to Canadian normalization [34].

^c According to Hogg et al. [35].

^d According to Brinton [36].

phases than the other treatments. In addition to the elevated temperature, forced aeration in the static piles provided oxygen which might affect the mineralization processes and thereby behavior in the mixture. Additionally, the increase percentages of Cd and Zn in the GS composts were significantly higher than those in the FS compost, indicating that the metal condensation was also affected by the properties of raw sludge used for composting. Similarly, Hsu and Lo [12] suggested that the types of composting and raw materials are of major importance to metal condensation.

Currently, Chinese legislation lacks concrete act that deals with the maximum permissible limit of HMs in the compost. Compared to the respective limits of other countries (Table 6), the only one that was met by all composts was the Canadian class B “which can be used on forest lands and roadsides and for other landscaping purposes” [34]. Briefly, most exceedances were because of the high Zn and Cu values. Lead concentrations in the composts exceeded in all cases the limit for “clean compost” of Netherlands, but in all other cases (except the FS compost), they were below limits. However, if the values in the report of Hogg et al. [35] including the ones proposed by European Commission are adopted, it can be seen that all composts of the present study would be classified as improper. Special attention, therefore, should be given if the final compost is intended for agricultural purpose.

3.3. Speciation of Cu and Zn in the final composts

Because the concentrations of both Cu and Zn in sludges exceeded the acceptable values for agricultural use (GB 4284-84), the chemical speciation of Cu and Zn in the final composts was of great interest. According to the fractionation scheme used, Cu and Zn were categorized as “exchangeable”, “Fe–Mn oxide-bound”, “organic matter-bound” and “residual” fractions.

Concerning Cu, after the composting period (56 days), it was mainly converted to the organic matter-bound fraction, ranging from 301 (FS-MTC) to 341 mg kg^{-1} (MRC) (Table 7), and accounting for more than 70% of total Cu (Fig. 2a). The high stability of organic matter-bound complexes of Cu was also observed in the compost of swine manure [12] or sludge compost [13,15,30]. Concentrations of residual fraction accounted for 18–23% of total Cu and were followed by the exchangeable and Fe–Mn oxide-bound fractions. Walter et al. [30] observed the same distribution pattern of four fractions in sludge compost. These results indicate that Cu has higher affinity for organic matter, which is consistent with the speciation profile of Cu in sewage sludge [12,13,16].

Concerning Zn in the GS composts, the highest concentration was found in Fe–Mn oxide-bound fraction (except IMTC treatment), varying from 607 (IMTC) to 685 mg kg^{-1} (MRC)

Table 7
Copper fractions in the final composts (mg kg^{-1})

Treatments	Exchangeable	Fe–Mn oxide-bound	Organic matter-bound	Residual	Total ^a
MTC	14 c ^b (c) ^c	3.1 c (c)	326 a (abc)	92 b (ab)	435 (ab)
IMTC	33 c (a)	18 c (a)	316 a (abc)	83 b (b)	450 (a)
CAC	10 c (e)	1.9 c (c)	312 a (bc)	98 b (a)	422 (ab)
IAC	14 c (c)	4.7 c (b)	333 a (ab)	82 b (b)	434 (ab)
MRC	21 c (b)	5.3 d (b)	341 a (a)	81 b (b)	448 (ab)
FS-MTC	13 c (d)	2.2 d (c)	301 a (c)	97 b (a)	413 (b)

^a Sum concentration of the four fractions.

^b Mean followed by the same letters within a row were not significantly different ($P > 0.05$).

^c Mean followed by the same letters within a column in parentheses were not significantly different ($P > 0.05$).

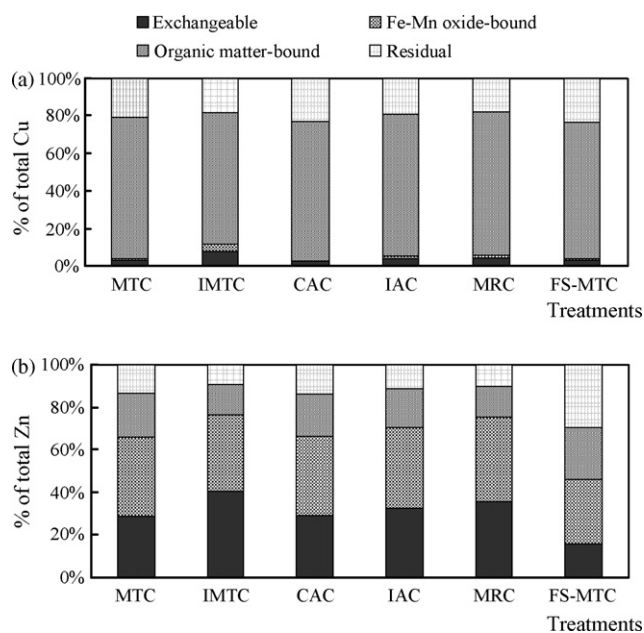


Fig. 2. Distribution of different metal fractions in sludge composts: (a) Cu and (b) Zn.

and being significantly higher than those of organic matter-bound and residual fractions (Table 8). The concentrations of exchangeable fraction, ranged from 493 (MTC) to 614 mg kg⁻¹ (IMTC), and were also significantly higher than those of organic matter-bound and residual fractions, and the lowest concentration was observed at the residual fraction. With respect to Zn in the FS compost, Fe–Mn oxide-bound and residual fractions showed very close concentrations, 413 and 408 mg kg⁻¹, respectively, being significantly higher than those of the other two fractions. The lowest concentration was observed in the exchangeable fraction. The different chemical fractions, expressed as the percentage of their total concentrations at the final composts, varied considerably for Zn (Fig. 2b). In the FS compost, the percentage of total Zn decreased in order of Fe–Mn oxide-bound > residual > organic matter-bound > exchangeable fraction. Contrarily, in the GS composts, exchangeable or Fe–Mn oxide-bound fraction accounted for more than 30% of total Zn (except exchangeable fraction in MTC treatment), organic matter-bound fraction accounted for 14–21%, while residual fraction accounted for about 10%. Zinc is the most mobile and bioavailable HM in sewage sludge [5,16]. Some

studies show that, among different chemical fractions of metals in sludge compost, exchangeable fraction represents the form with the highest mobility, the most readily bioavailable and thereby the most potentially toxic in soils [11,29]. The high percentage of exchangeable fraction for Zn in the GS composts suggested its great availability [12]. Similarly, Walter et al. [30] found that, in sludge compost, 59 and 37% of total Zn were mainly distributed in the organic matter-bound and the DTPA-extracted fractions, respectively; Zorpas et al. [37] reported that, in a sludge composting process with kaoline addition, 25–29% of total Zn was soluble and leachable. These values imply a great potential environmental threat by Zn. Thus, though the amounts of exchangeable HMs in the final composts were lower compared to their total contents (e.g., Cu), land application of sludge compost, especially of the GS compost, should be controlled, or certain agent such as lime [17] or natural zeolite [37] is suggested to be added in the sewage sludge during composting to reduce HM availability (especially Zn) associated with the compost.

As illustrated in Fig. 2, the speciation pattern of Cu is remarkably different from that of Zn in the same treatment. In GS composts, exchangeable fraction of Zn accounted for 29–40% of total Zn which was higher by two to three times than the respective percentage of Cu, indicating that the mobility and bioavailability of Zn in sludge compost was higher compared to Cu. Apparently, Cu was mainly associated with organic matter-bound fraction in all compost samples, whereas the percentages of both exchangeable and Fe–Mn oxide-bound forms for Zn were above 30%, but that of organic matter-bound fraction was less than 20%, demonstrating that the behavior of Cu and Zn during composting were different. Copper has higher affinity for organics and is less labile in sludge compost than Zn [38]. The sequence of reacting metals with humic substances was Cu > Zn [38]. Amir et al. [14] reported that, during composting of sewage sludge, the formation of humic substances seems to transform Zn and particularly Cu from sulfide fraction to organic fraction. Similarly, Gao et al. [15] showed that, after forced aerated composting of sludge, residual fraction of Zn in sewage sludge was transformed to the Fe–Mn oxide-bound and organic matter-bound fractions. Residual fraction of Zn was the least abundant fraction in all GS composts and also had relatively lower percentage of Zn compared to that of Cu (Fig. 2).

The distribution profiles of the four fractions of Cu in the GS composts were similar to those in the FS compost, while those

Table 8
Zinc fractions in the final composts (mg kg⁻¹)

Treatments	Exchangeable	Fe–Mn oxide-bound	Organic matter-bound	Residual	Total ^a
MTC	493 b ^b (c) ^c	636 a (a)	354 c (a)	228 d (bcd)	1711 (ab)
IMTC	678 a (a)	607 b (a)	241 c (c)	157 d (b)	1682 (b)
CAC	517 b (c)	658 a (a)	349 c (a)	251 d (bc)	1776 (a)
IAC	580 b (b)	668 a (a)	332 c (ab)	195 d (cde)	1775 (a)
MRC	614 a (b)	685 a (a)	262 b (c)	170 b (de)	1731 (a)
FS-MTC	219 c (e)	413 a (b)	332 b (ab)	408 a (a)	1373 (c)

^a Sum concentration of the four fractions.

^b Mean followed by the same letters within a row were not significantly different ($P > 0.05$).

^c Mean followed by the same letters within a column in parentheses were not significantly different ($P > 0.05$).

Table 9
Pearson correlation coefficients of HM fractions and total concentration with selected chemical properties of the final composts

	Organic C	Humic substances	Ash	pH
Cu				
Exchangeable		−0.80*		0.77*
Fe–Mn oxide-bound		−0.87*		0.66*
Organic matter-bound			0.60*	0.61*
Residual				−0.72*
Total	−0.50*	−0.71*		0.95**
Zn				
Exchangeable	−0.81*	−0.72*	0.81*	0.87*
Fe–Mn oxide-bound	−0.86*		0.95**	0.66*
Organic matter-bound		0.55*		−0.77*
Residual	0.80*	0.70*	−0.82*	−0.88*
Total	−0.92**		0.98**	0.58*

* Statistically significant at the $P < 0.05$.

** Statistically significant at the $P < 0.01$.

of Zn were considerably different. In the FS compost, the Zn proportion of exchangeable fraction was lower, while those of organic matter-bound and residual fractions were higher than those in the GS composts (Fig. 2b). Petruzzelli et al. [11] suggested that the speciation of HMs in the sludge compost depends on its initial chemical state in the sewage, the adsorption and precipitation mechanisms in sludge, and the effect of stabilization and humification processes of the material during composting on the HM chemical forms. During composting, the mobility and bioavailability of HMs depend on the physico-chemical properties of the medium (i.e., decomposition of organic matter, pH, or affinity of metals for various chemical forms [14]). The organic carbon content in FS (205 g kg^{-1}) was higher by 19% than in GS (173 g kg^{-1}) (Table 1). Organic matter is decomposed and transformed to stable humic substances which have a capacity to interact with metal ions [14]. Furthermore, the decrease of the soluble fraction of Cu was in agreement with the increase of humic substances and the decrease of pH in sludge compost [14]. After composting, the contents of organic carbon and humic substance in the FS compost were higher, but in a lower pH, than in GS composts (Table 3), which might affect the speciation distribution of Cu and Zn in the final composts.

The different composting processes, exhibited different effects on the speciation of Cu and Zn. For Cu in GS composts, organic matter-bound form the highest percentage of total Cu was in MRC and decreased in the order of MRC > IAC > MTC > IMTC > CAC ($76.7\% > 76.0\% > 74.8\% > 74.0\% > 70.0\%$) (Fig. 2a). The highest concentration of residual form was observed in CAC treatment, where it was significantly higher than in IMTC, IAC and MRC treatments. Contrarily, the highest concentrations of both exchangeable and Fe–Mn oxide-bound forms were found in IMTC treatment, being significantly higher than those in the other treatments, and the lowest ones were observed for the CAC treatment (Table 6). Regarding Zn in GS composts, its concentration at the exchangeable fraction decreased in the order of IMTC > MTC > IAC > CAC > MTC (Table 8). The significantly lower concentration of Zn in this fraction of CAC and MTC treatments implies relatively lower

potential toxicity. The concentrations of organic matter-bound fraction for Zn in MTC and CAC treatments were significantly higher than in IMTC and MRC treatments, and the concentration at the residual fraction in CAC treatment was also significantly higher than in IMTC and MRC treatments. Apparently, both Cu and Zn showed the relatively lower mobility and bioavailability in the MTC and CAC treatments. This, in combination with the fact that CAC treatment has demonstrated the highest removal rate for polycyclic aromatic hydrocarbons (PAHs) [39], suggests that the compost that derives from the CAC treatment is the least potential toxic among these five composting processes.

It can also be assumed that among the five composting processes of GS, IMTC treatment is the most potentially toxic, due to the highest percentage of exchangeable fraction (by 38% and 1.4-fold higher than MTC treatment for Zn and Cu, respectively) and the lower percentage of residual fraction. Similarly, Garcia et al. [40] reported that, during composting of sewage sludge, HM contamination did influence the microbial populations and led to decreased mineralization and humification. In this study, IMTC treatment was spiked with inoculant containing microorganisms while faecal sewage was not added, and thus its humic substance content was markedly lower (by 10.3–17.1%) than in the other treatments (Table 3). This result demonstrates that this inoculant has no obvious advantage on the mineralization and humification of the sludge combined with rice straw and on the reduction of the toxicity of Cu and Zn.

3.4. Influence of compost chemical properties on metal distribution

The composting of organic wastes is considered as a biological decomposition process of organic materials. HM distribution and bioavailability after composting depends on the metal itself and the physico-chemical properties of the medium. The chemical properties of composting products such as humic substances, organic carbon (C), ash and pH influence the HM speciation transformation and distribution in compost [12,14,15]. Pearson

correlation matrices of metal fractions with organic C, humic substances, ash content and pH were explored to determine the effect of these selected parameters on HM speciation distribution in the final composts (Table 9).

For Cu, there is a strongly negative correlation between the humic substance content and the exchangeable fraction ($R^2 = -0.80$, $P < 0.05$) and with the Fe–Mn oxide-bound fraction ($R^2 = -0.87$, $P < 0.05$), while organic matter-bound fraction was significantly positively correlated with ash contents ($R^2 = 0.60$, $P < 0.05$), which is similar to those in the compost of swine manure [12]. Moreover, exchangeable fraction of Cu showed a strong positive correlation with pH ($R^2 = 0.77$, $P < 0.05$), which was also observed in sludge composting performed by Amir et al. [14]. This is in good agreement with the high affinity of Cu to organic acid, something that contributes to the formation of humic substances [29].

For Zn, exchangeable fraction was significantly negatively correlated to the contents of organic C and humic substances ($R^2 = -0.81$ and -0.72 , respectively, for both $P < 0.05$), and significantly positively correlated to the ash content and the pH ($R^2 = 0.81$ and 0.87 , respectively, $P < 0.05$). Fe–Mn oxide-bound fraction presented significantly positive correlation with the ash content ($R^2 = 0.95$, $P < 0.01$) and the pH ($R^2 = 0.66$, $P < 0.05$) but was negatively correlated with the organic C ($R^2 = -0.86$, $P < 0.05$). In contrast to the exchangeable fraction, the residual fraction showed a good positive correlation with the contents of organic C and humic substances, and a negative correlation with the ash content and the pH. Generally, the pH has a great effect on the chemical fractions of HMs. Wang et al. [28] reported that, in neutral sludge, Zinc had a higher percentage in the acid soluble/exchangeable and organic matter-bound fraction, while humic substances in the compost contain various organic functional groups that can sorb metal ions through ionic force [20,38]. In this study, pH and humic substances of the final composts ranged from 6.85 to 7.52 and from 175 to 216 g kg⁻¹ (Table 3), respectively. The pH value and the transformation of organic matter to humic substances during composting process might affect the transformation of Zn and consequently the speciation distribution.

On the other hand, the degree of stabilization achieved by organic matter seems to be important in determining the potential mobility of HMs [29]. As discussed earlier, the final composts (day 56) in this study generally reached maturation as indicated by the contents of ash and humic substances, C/N ratios (except MRC treatment) (Table 3). Furthermore, CAC treatment showed the lowest C/N ratio, slightly higher concentrations of total N, humic substances and ash content, but lower potential mobility of HMs compared to the other treatments.

4. Conclusions

After composting (56 days) by different approaches, the mixture of sewage sludge with rice straw at a low C/N ratio (13:1) reached maturity. The total concentrations of HMs in the final composts varied, exhibiting different percent increases in all treatments. Concentrations of HMs and especially of Zn exceeded the proposed limits. Cu presented more affinity to the

organic matter while most of Zn was in exchangeable and Fe–Mn oxide-bound fractions. Concentration and speciation of HMs in the final composts were affected by the properties of the sludge, the composting process, and thereby, by the physico-chemical properties of the final compost, like the organic C, the humic substance content and the pH. The CAC treatment showed the lowest HM potential toxicity, while IMTC present higher HM mobility and bioavailability compared to the other composting processes.

Most of the studies on composting approaches concern organic pollutants, which are biodegradable and thus, the composting approaches appear satisfactory and are suggested for agricultural use as soil amendment. The increase in relative concentrations of non-degradable pollutants, like HMs, during composting appears to be of even greater importance and suggests that the need for strict limits and for continuous monitoring is imperative.

Acknowledgements

This work was supported by the Natural Science Foundation of China (No. 39870435, 30471007), Key Scientific Research Project of Ministry of Education of China (No. 02112), Natural Science Foundation of Guangdong Province (No. 021011, 036716, 043005970) and Project of Department of Science & Technology of Guangdong Province (No. 01C21202, 03A20504, 03C34505). Thanks are also due to Datansha and Zhen'an wastewater treatment plants in Guangzhou and Foshan, respectively, for supplying sewage sludges.

References

- [1] X. Tang, L. Zhao, The development of sludge disposal strategy, *Environ. Sci. Manag.* 30 (68–70) (2005) 90.
- [2] S.R. Smith, *Agricultural Recycling of Sewage Sludge and the Environment*, CAB International, Wallingford, 1996.
- [3] P. Mantovi, G. Baldoni, G. Toderi, Reuse of liquid, dewatered, and composted sewage sludge on agricultural land: effects of long-term application on soil and crop, *Water Res.* 39 (2005) 289–296.
- [4] F.A. Nicholson, S.R. Smith, B.J. Alloway, C. Carlton-Smith, B.J. Chambers, An inventory of heavy metals inputs to agricultural soils in England and Wales, *Sci. Total Environ.* 311 (2003) 205–219.
- [5] E. Daelsch, B. Deroche, V. Van de Kerchove, Impact of sewage sludge spreading on heavy metal speciation in tropical soils (Réunion, Indian Ocean), *Chemosphere* 65 (2006) 286–293.
- [6] E. Epstein, *The Science of Composting*, Technomic Publishing Co. Inc., Lancaster, PA 17604, USA, 1997.
- [7] M. Fang, J.W.C. Wong, Effects of lime amendment on availability of heavy metals and maturation in sewage sludge composting, *Environ. Pollut.* 106 (1999) 83–89.
- [8] D.K. Jain, R.D. Tyagi, Leaching of heavy metals from anaerobic sewage sludge by sulfur-oxidizing bacteria, *Enzyme Microb. Technol.* 14 (1992) 376–383.
- [9] M. Karvelas, A. Katsoyiannis, C. Samara, Occurrence and fate of heavy metals in the wastewater treatment process, *Chemosphere* 53 (2003) 1201–1210.
- [10] D.L. Lake, Chemical speciation of heavy metals in sewage sludge and related matrices, in: J. Lester (Ed.), *Heavy Metals in Wastewater and Sludge Treatment Processes, Sources, Analysis and Legislation*, vol. 1, CRC Press, Boca Rotan, FL, USA, 1987.
- [11] G. Petruzzelli, L. Ottaviani, E. Veschetti, Characterization of heavy metal mobile species in sewage sludge for agricultural utilisation, *Agrochimica* 38 (1994) 277–284.

- [12] J.H. Hsu, S.L. Lo, Effect of composting on characterization and leaching of copper, manganese, and zinc from swine manure, *Environ. Pollut.* 114 (2001) 119–127.
- [13] J.W.C. Wong, K. Li, M. Fang, D.C. Su, Toxicity evaluation of sewage sludges in Hong Kong, *Environ. Int.* 27 (2001) 373–380.
- [14] S. Amir, M. Hafidi, G. Merlina, J.C. Revel, Sequential extraction of heavy metals during composting of sewage sludge, *Chemosphere* 59 (2005) 801–810.
- [15] D. Gao, G.D. Zheng, T.B. Chen, W. Luo, W. Gao, Y.A. Zhang, Y.X. Li, Changes of Cu, Zn, and Cd speciation in sewage sludge during composting, *J. Environ. Sci.* 17 (2005) 957–961.
- [16] A. Fuentes, M. Lloréns, J. Sáez, M. Aguilar, J.F. Ortuño, V.F. Meseguer, Phytotoxicity and heavy metals speciation of stabilised sewage sludges, *J. Hazard. Mater.* 108 (2004) 161–169.
- [17] J.W.C. Wong, A. Selvam, Speciation of heavy metals during co-composting of sewage sludge with lime, *Chemosphere* 63 (2006) 980–986.
- [18] G.D. Zheng, D. Gao, T.B. Chen, W. Luo, Stabilization of nickel and chromium in sewage sludge during aerobic composting, *J. Hazard. Mater.* 142 (2007) 216–221.
- [19] A.A. Zorpas, D. Arapoglou, K. Panagiotis, Waste paper and clinoptilolite as a bulking material with dewatered anaerobically stabilized primary sewage sludge (DASPSS) for compost production, *Waste Manag.* 23 (2003) 27–35.
- [20] Y.S. Wei, Y.B. Fan, M.J. Wang, J.S. Wang, Composting and compost application in China, *Resour. Conserv. Recy.* 30 (2001) 277–300.
- [21] Environment Protection Administration (EPA), PR China, Chinese Bulletin of Environment of 2000, 2001.
- [22] A. Tessier, P.G.C. Campbell, M. Bisson, Sequential extraction procedure for the speciation of particulate trace metals, *Anal. Chem.* 51 (1979) 844–858.
- [23] Z.X. Zhu, Soil Science, China's Agricultural Press, Beijing, 1983.
- [24] D.H.W. Nelson, L.E. Sommers, Total carbon, organic carbon and organic matter, in: A.L. Page, R.H. Miller, D.R. Keeney (Eds.), *Methods of Soil Analysis. Part II. Chemical and Microbiological Properties*, American Society of Agronomy, Madison, WI, 1982, pp. 539–580.
- [25] M.P. Bernal, A.F. Navarro, A. Roig, J. Cegarra, D. Garcia, Carbon and nitrogen transformation during composting of sweet sorghum bagasse, *Biol. Fert. Soil* 22 (1996) 141–148.
- [26] S.C. Wong, X.D. Li, G. Zhang, S.H. Qi, Y.S. Min, Heavy metals in agricultural soils of the Pearl River Delta, South China, *Environ. Pollut.* 119 (2002) 33–44.
- [27] T. Chen, Q. Huang, D. Gao, Y. Zheng, J. Wu, Heavy metal concentrations and their decreasing trends in sewage sludge of China, *Acta Sci. Circumstantiae* 23 (2003) 561–569.
- [28] C. Wang, X. Hu, M.L. Chen, Y.H. Wu, Total concentrations and fractions of Cd, Cr, Pb, Cu, Ni and Zn in sewage sludge from municipal and industrial wastewater treatment plants, *J. Hazard. Mater.* 119 (2005) 245–249.
- [29] L. Leita, M. De Nobili, Water-soluble fractions of heavy metals during composting of municipal solid waste, *J. Environ. Qual.* 20 (1991) 73–78.
- [30] I. Walter, F. Martínez, V. Cala, Heavy metal speciation and phytotoxic effects of three representative sewage sludges for agricultural uses, *Environ. Pollut.* 139 (2006) 507–514.
- [31] D.J. Wagner, G.D. Bacon, W.R. Knocke, M.S. Switzenbaum, Changes and variability in concentration of heavy metals in sewage sludge during composting, *Environ. Technol.* 11 (1990) 949–960.
- [32] C. Ciavatta, M. Govi, A. Simoni, P. Sequi, Valuation of heavy metals during stabilization of organic matter in compost produced with municipal solid wastes, *Bioresour. Technol.* 43 (1993) 147–153.
- [33] SDU, Law concerning the quality and use of so-called other organic fertilisers (so-called BOOM decree), *Staatblad van het Koninkrijk der Nederlanden, 's Gravenhage*, 613 (1991) 1–45.
- [34] CCME (Canadian Council of Ministers of the Environment), Proposed compost standards for Canada, 1993, Cited in the Composting Council of Canada, *Composting Technologies and Practices*, 1995.
- [35] D. Hogg, J. Barth, E. Favoino, M. Centemero, V. Caimi, F. Amlinger, W. Devliegher, W. Brinton, S. Antler, Comparison of Compost Standards Within the EU, North America and Australasia, The Waste and Resources Action Programme, Banbury, 2002 (<http://www.wrap.org.uk>).
- [36] W. Brinton, Compost Quality Standards & Guidelines: an International View, Final Report to the New York State Association of Recyclers, Woods End Laboratory, 2000.
- [37] A.A. Zorpas, E. Kapetanios, G.A. Zorpas, P. Karlis, A. Vlyssides, I. Haralambous, M. Loizidou, Compost produced from organic fraction of municipal solid waste, primary stabilized sewage sludge and natural zeolite, *J. Hazard. Mater.* 77 (2000) 149–159.
- [38] S.W. Chang Chien, M.C. Wang, C.C. Huang, Reactions of compost-derived humic substances with lead, copper, cadmium, and zinc, *Chemosphere* 64 (2006) 1353–1361.
- [39] Q.Y. Cai, C.H. Mo, Q.T. Wu, Q.Y. Zeng, A. Katsoyiannis, J.F. Férard, Bioremediation of polycyclic aromatic hydrocarbons (PAHs)-contaminated sewage sludge by different composting processes, *J. Hazard. Mater.* 142 (2007) 535–542.
- [40] C. Garcia, J.L. Moreno, T. Hernandez, F. Costa, Effect of composting on sewage sludges contaminated with heavy metals, *Bioresour. Technol.* 53 (1995) 13–19.