

# Bioremediation of polycyclic aromatic hydrocarbons (PAHs)-contaminated sewage sludge by different composting processes

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## Abstract

The efficiency of four different composting processes to bioremediate polycyclic aromatic hydrocarbons (PAHs)-contaminated sewage sludge was investigated. Prior to composting, sewage sludge coming from the Datansha wastewater treatment plant, Guangzhou, China, was mixed with rice straw to obtain a C/N ratio of 13:1. After 56 days of composting, the total concentrations of 16 PAHs ( $\Sigma_{\text{PAHs}}$ ) ranged from 1.8 to 10.2 mg kg<sup>-1</sup> dry weight, decreasing in order of inoculated-manual turned compost (IMTC) > manual turned compost (MTC) > continuous aerated compost (CAC) > intermittent aerated compost (IAC), exhibiting removal rates of 64%, 70%, 85% and 94%, respectively. Individual PAHs were generally removed in similar rates. IAC treatment showed a higher removal rate of high molecular weight PAHs and carcinogenic PAHs comparing to the other composting processes.

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## 1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are widespread pollutants, which enter the environment as a result of the incomplete combustion or pyrolysis of organic material and from the spilling of mineral or tar oils. Due to their toxic, mutagenic and carcinogenic properties, 16 PAH compounds have been identified as priority pollutants both by China and the United States Environmental Protection Agency (USEPA) and seven of them are considered as carcinogenic [1]. Because of their hydrophobic nature, most PAHs bind to particles of soils and sediments, and

hence are widely distributed at various levels in soils, sediments and sewage sludges [2–7].

Sewage sludge is a product of the wastewater treatment process, which is rich in organic materials as well as in nitrogen and phosphorous. In China, the rapid development of industrial and agricultural activities, and subsequently the increased use of chemicals have seriously impacted the environmental quality over the last decades. To face this problem, more than 600 wastewater treatment plants (WWTPs) have been established till now countrywide, producing annually around 5000 million kg of sewage sludge, a production that is expected to exceed 8000 million kg by 2010 [8]. The current main disposal routes for sludge are incineration, sanitary landfill, or use in agriculture as soil amendment.

Sewage sludge is considered a sink for organic contaminants originating both from domestic and industrial sources, including toxic and/or carcinogenic compounds like PAHs [2,4–6,9–12].

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They constitute a group of contaminants that have been detected by many authors in sewage sludge, exhibiting mean total concentrations of 16 PAHs from 1 to 2000 mg kg<sup>-1</sup> dry weight (d.w.) [2,5,6,9–12]. In China, the total concentrations of 16 PAHs have been found to range from 1.4 to 144 mg kg<sup>-1</sup> d.w. in sewage sludges collected from 11 WWTPs in nine cities [5].

The application of sludge to agricultural land implies exposure of soil microbial, plant, and animal life, including humans, to contaminants contained in the sludge [6]. Thus, prior to agricultural recycling of sludges, a treatment is needed to ensure their stability, to reduce the concentration of hazardous pollutants, and to increase their beneficial effect for soils. A process that can achieve the above requirements is composting, an *ex situ* biotreatment technology [13,14] that leads to the formation of mineralization products CO<sub>2</sub> and H<sub>2</sub>O and the stabilization of organic matter in the form of humic substances containing competitive microbial biomass [15]. Numerous studies have shown that composting has an enormous potential for bioremediation through sustaining microbial populations of a wide range of microorganisms, which are able to degrade a variety of organic contaminants at the laboratory and/or field scales [13–23]. Composting has been proven to degrade PAHs, in rates that exceed 80% in some cases and require treatment time shorter than land-farming [16].

Another agricultural residual causing serious effect on environment is rice straw. In China, in 2004, the growth area of rice (*Oryza sativa* L.) reached 31 million hectares and yielded about 16.5 billion kg of rice straw residues [24]. In China as well as in many other developing countries, rice straw is usually disposed of by *in situ* burning, which has a harmful impact on the environment (global addition of carbon dioxide) and on the local population (e.g. respiratory or allergic disorders) [25]. Recently, various approaches have been described for the utilization of rice straw such as paper production, construction materials, compost, animal food, etc. Until now, only a limited part of the produced rice straw is used for these purposes. Given that rice straw contains a large amount of organic material and nutrients [26], its conversion into value-added compost, similarly to the sewage sludge, may have the potential to improve productivity of crops and reduce environmental pollution. Previous investigations clearly indicate that the operational parameters are of crucial importance during composting treatments of contaminated wastes, and thus their optimisation will result in beneficial environmental and economic practices. High temperature, good availability of nutrients, good oxygenation, and increased microbial variety can affect the biodegradation rate of organic contaminants. The low ratio of carbon to nitrogen (C/N) and the high phosphorus (P) content indicates that sewage sludge is an important source of N and P for the aerobic microorganisms responsible for the composting process [26]. For sewage sludge to be composted, it is generally necessary to incorporate a second material as a structuring agent that must have complementary properties, such as a high C/N ratio as well as balancing moisture. Rice straw is rich in organic matter (80%) and oxidizable organic C (34%) and has a high C/N ratio, which can vary from 50 to 150 [26].

Currently, Chinese legislation lacks concrete act that deal with tolerable levels of organic micropollutants in composts and only limited research has focused on the removal rate of organic contaminants such as PAHs in composts of sewage sludge with rice straw. For this reason, the objectives of this study were to investigate the concentrations of 16 PAHs in compost of sludge with rice straw under four different approaches and to compare the removal rates of PAHs between these four processes.

## 2. Material and methods

### 2.1. Composting

Secondary dewatered sludge was taken from Datansha wastewater treatment plant in Guangzhou, China. It contained organic carbon of 173 g kg<sup>-1</sup> d.w., 25 g N kg<sup>-1</sup> d.w. (C/N, 6.9:1), and the moisture content was 81.7%.

Rice (*O. 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 in length. It contained organic carbon of 312 g kg<sup>-1</sup> d.w., 5.8 g N kg<sup>-1</sup> d.w. (C/N, 54:1), and the moisture content was 12.2%.

Inoculation mixture comprised of microorganisms, enzymes and growth promoting agents was supplied by Organica Company, Hong Kong.

The composting experiment was conducted out in South China Agricultural University, Guangzhou. Four different piles were prepared by mixing thoroughly sewage sludge with rice straw to obtain a C/N ratio of 13:1 as shown in Table 1. Wood chips (4–20 cm × 2–4 cm) were added as bulking agent at 10% (w/w) to the piles of continuous aerated compost (CAC) and intermittent aerated compost (IAC). Tap water and faecal sewage were added to maintain the moisture contents of the initial mixtures at 60% (w/w). The four different composts were prepared on four purpose-built platforms (2.0 m × 1.5 m × 2.0 m, *L* × *W* × *H*). The volume of the initial mixture was 2.0–2.3 m<sup>3</sup> of each pile. Inoculation mixture was spiked in the initial mixture of inoculated-manual turned compost (IMTC). The heaps were turned and mixed every 5 days to provide oxygen for the piles of manual turned compost (MTC) and IMTC, 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<sup>-1</sup> in the morning, while IAC was aerated 16 times during 15 min with intermission of 75 min (total 4 h day<sup>-1</sup>). The temperatures were recorded daily at a depth of 35 cm composting piles. Samples were collected at day 0 (after mixing sewage sludge with rice straw) for determining the initial concentration of PAHs. At the end of the composting process (day 56), samples were taken from different sites of each pile for analysis. Subsamples were air-dried, ground to <1 mm, and refrigerated in closed alumina containers until analysis.

### 2.2. Chemicals and materials

A composite stock standard solution (1000 μg mL<sup>-1</sup> in dichloromethane, 99.8% purity) contained 16 PAHs (Table 2).

Table 1  
Mixture of sewage sludge and rice straw used for composting and treatments of experiment<sup>a</sup>

Treatments	Components						Volume of mixture (m <sup>3</sup> )
	Sewage sludge (kg)	Rice straw (kg)	Wood chip (kg)	Tap water (kg)	Faecal sewage (kg)	Inoculant (mL) <sup>b</sup>	
Manual turned compost (MTC)	750	160	–	20	25	–	2.3
Inoculated manual turned compost (IMTC)	750	160	–	45	–	200	2.3
Continuous aerated compost (CAC)	600	130	73	18	20	–	2.0
Intermittent aerated compost (IAC)	600	130	73	18	20	–	2.0

<sup>a</sup> C/N ratio is 13:1 for the four different composts.

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

The working standard solutions in dichloromethane were prepared by diluting appropriate volumes of the stock standard solution. Internal standard solution (4000 µg mL<sup>-1</sup> in dichloromethane, 99.8% purity) contained naphthalene-*d*<sub>8</sub>, acenaphthene-*d*<sub>10</sub>, phenanthrene-*d*<sub>10</sub>, chrysene-*d*<sub>12</sub> and perylene-*d*<sub>12</sub>. Surrogate standard solutions (4000 µg mL<sup>-1</sup> in dichloromethane, 99.8% purity) contained nitrobenzene-*d*<sub>5</sub> and *p*-terphenyl-*d*<sub>14</sub>, respectively. These standards were purchased from Ultra Scientific (North Kingstown, RI, USA).

Analytical grade organic solvent (Guangzhou Chemical Reagent Co., purity >99%) including dichloromethane, acetone and *n*-hexane were redistilled before use. Silica gel (80–200 mesh, Guangzhou Chemical Reagent Co.) and neutral alumina (80–100 mesh, Guangzhou Chemical Reagent Co.) were Soxhlet extracted with dichloromethane and *n*-hexane, respectively, for 24 h, then activated at 180 and 250 °C, respectively, for 12 h, deactivated with 3% redistilled water, and kept in *n*-hexane before use. Anhydrous sodium sulfate (Guangzhou Chemical Reagent Co., purity >99%) was dried at 450 °C for 6 h and stored in a sealed desiccator.

All the glass apparatus were washed with K<sub>2</sub>CrO<sub>4</sub>–H<sub>2</sub>SO<sub>4</sub> solution, washed with tap water and redistilled water, then dried

at 120 °C. Glass apparatus except for Soxhlet extract-tube were furnace at 300 °C for 8 h before use.

### 2.3. Physico-chemical analysis

pH was measured using 10 g air-dried compost (1 mm) suspended in 25 mL redistilled water using a pH meter (PH3-3C, Shanghai Instrument Co., China). The organic carbon was measured using Walkley-Black titration [27]. The humic substances were extracted by 0.1 M NaOH solution and measured after oxidation by KMnO<sub>4</sub> [28]. 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.

### 2.4. PAH extraction and separation

Sample extraction and cleanup were performed according to methods of USEPA 3540C and 3630, respectively. Compost samples (approximately 20 g) were weighed onto Whatman

Table 2  
Abbreviation of PAH compounds, detection limits, octanol–water partition coefficients and vapor pressure

Compounds	Abbreviation	N <sup>a</sup>	Detection limits (µg kg <sup>-1</sup> )	log K <sub>ow</sub> <sup>b</sup>	Vapor pressure (Pa, 25 °C) <sup>c</sup>
Naphthalene	Nap	2	0.21	3.37	10.9
Acenaphthylene	Acy	3	0.22	4.08	5.96 × 10 <sup>-1</sup>
Acenaphthene	Ace	3	0.20	4.22	5.96 × 10 <sup>-1</sup>
Fluorene	Fl	3	0.45	4.38	8.86 × 10 <sup>-2</sup>
Phenanthrene	Phe	3	0.44	4.46	1.8 × 10 <sup>-2</sup>
Anthracene	Ant	3	0.78	4.54	2.0 × 10 <sup>-4</sup>
Fluoranthene	Fla	4	0.99	5.20	2.54 × 10 <sup>-1</sup>
Pyrene	Pyr	4	1.4	5.30	8.86 × 10 <sup>-4</sup>
Benzo[ <i>a</i> ]anthracene <sup>d</sup>	BaA	4	0.71	5.91	7.3 × 10 <sup>-6</sup>
Chrysene <sup>d</sup>	Chr	4	0.84	5.61	5.7 × 10 <sup>-7</sup>
Benzo[ <i>b</i> ]fluoranthene <sup>d</sup>	BbF	5	1.3	5.78	–
Benzo[ <i>k</i> ]fluoranthene <sup>d</sup>	BkF	5	1.1	6.20	–
Benzo[ <i>a</i> ]pyrene <sup>d</sup>	BaP	5	0.61	6.35	1.5 × 10 <sup>-5</sup>
Dibenzo[ <i>a,h</i> ]anthracene <sup>d</sup>	DahA	5	0.68	6.51	1.8 × 10 <sup>-6</sup>
Indeno[1,2,3- <i>cd</i> ]pyrene <sup>d</sup>	InP	6	0.75	6.75	–
Benzo[ <i>ghi</i> ]perylene	BghiP	6	0.78	6.90	2.0 × 10 <sup>-5</sup>

<sup>a</sup> Number of rings.

<sup>b</sup> According to Huckins et al. [29].

<sup>c</sup> According to ISPAC [30].

<sup>d</sup> Carcinogenic PAH compounds.

cellulose extraction thimbles, which were pre-extracted with *n*-hexane/dichloromethane (1:1, v/v) for 24 h and extracted in a Soxhlet extractor (Guangzhou, China) for 24 h with 100 mL acetone/dichloromethane (1:1, v/v). Sulfur was removed from the extracts by adding activated copper (activated with 10% hydrochloric acid) into dichloromethane before extraction.

The extracts were reduced to 5.0 mL in a rotating evaporator (Yarong, China) at 50 °C. The concentrated extracts were loaded on a combined column of silica gel and alumina. The glass chromatography column (25 cm × 1 cm, length × I.D.), fitted with a PTFE stopcock, was packed up from the bottom with cotton-wool (Soxhlet extracted with dichloromethane for 72 h before use), 3 cm alumina, 10 cm extracted silica, followed by 2 cm anhydrous sodium sulfate. Two fractions (*n*-hexane and dichloromethane) were used for separation. The collected fractions were blown down to 0.5 mL by a gentle stream of nitrogen. The internal standard was added to adjust variation in sample volumes before GC–MS analyses.

### 2.5. GC–MS analysis and quantification of PAH compounds

Analysis of individual PAH compound was performed by GC–MS according to method of USEPA 8270C. GC–MS analyses were carried out with Hewlett-Packard 5890 Series II gas chromatograph equipped with a mass spectrometer (Hewlett-Packard 5972, Agilent Technology). A HP-1 25 m × 0.20 mm I.D. × 0.11 μm film (Agilent Technology) fused silica capillary column was used. The oven temperature of GC was programmed as follows: 45 °C hold for 1 min, raised at 6.0 °C min<sup>-1</sup> to 200 °C, then at 8.0 °C min<sup>-1</sup> to 300 °C (held for 5 min). The solvent delay was 3.0 min and the flow velocity of carrier gas helium was 0.615 mL min<sup>-1</sup>. The injection was set on a splitless mode at 250 °C, and the injection volume was 1.0 μL. MS transfer line temperature was 280 °C. Before sample analysis, the instrument was tuned with decafluorotriphenylphosphine. Mass spectra were compared with reference compounds in mass spectral libraries (Pripol.L and Nbs75k.L). Identification of individual compounds was based on the comparison of retention time data between samples and the standard solution containing 16 PAHs. Quantification was performed by integration of the selected ion chromatograms extracted from the total ion current. Internal calibration was used for quantification. The retention time of the internal standard was used to correct for variation in retention time. This operation was performed automatically by the Hewlett-Packard MS chemstation.

### 2.6. QA/QC measures and performances

The instruments were calibrated daily with calibration standards and the relative percent difference between the five-point calibration and the daily calibrations were <20% for all of target analyses. Method blanks (solvent), spiked blanks (standards spiked into solvent), matrix spiked duplicates, sample duplicates were routinely analyzed with compost samples. In addition, surrogate standards were added to the

samples to monitor matrix effects and quality control of the sample preparation and analysis procedures. Recoveries of nitrobenzene-*d*<sub>5</sub> and *p*-terphenyl-*d*<sub>14</sub> varied from 75.0% to 89.5% and from 82.6% to 88.3%, respectively. None of the PAH compounds was detected in blank experiments. Detection limits and abbreviations of PAHs are presented in Table 2.

## 3. Results and discussions

### 3.1. Concentrations of PAHs before and after composting

The concentrations of PAHs in the sewage sludge, the initial mixture (day 0) and the final composts (day 56) are summarized in Table 3. Total PAH concentration ( $\Sigma_{\text{PAHs}}$ ) was 32.7 mg kg<sup>-1</sup> d.w. in the sewage sludge and decreased to 28.6 mg kg<sup>-1</sup> d.w. after mixing with rice straw. Similarly, concentrations of Phe, Ant and Fl, which were predominant in the Datansha sewage sludge, decreased in the initial mixture indicating that rice straw contained low concentrations of these PAHs. Ace and Acy were not detectable in the sludge, but their concentrations of 0.03 and 0.01 mg kg<sup>-1</sup> d.w. in the initial mixture (day 0), respectively, show that these contaminants derived from rice straw. Total concentrations of seven carcinogenic PAHs ( $\Sigma_{\text{PAHscarce}}$ ) in the sewage sludge and the initial mixture (day 0) were 10.1 and 9.1 mg kg<sup>-1</sup> d.w. (Fig. 1a), respectively. The concentration of PAHs in the sewage sludge is considered quite high, given that the maximum permissible limit proposed by the European Union for land application is 6 mg kg<sup>-1</sup> (calculated as the sum of Ace, Phe, Fl, Fla, Pyr, BbF, BjF, BkF, BaP, InP and BghiP) [31] and the respective of the USA for the sum of the seven carcinogenic PAHs (BaA, Chr, BbF, BkF, BaP, DahA and InP) is 4.6 mg kg<sup>-1</sup> [32]. Such high levels of contaminations highlight

Table 3  
Concentrations of PAHs in sewage sludge, the initial mixture ( $C_i$ , day 0) and the final composts ( $C_f$ , day 56) (mg kg<sup>-1</sup> d.w.)

Compounds	Sludge	Initial	MTC	IMTC	CAC	IAC
Nap	0.06	0.42	1.3	0.75	0.43	0.12
Acy	ND <sup>a</sup>	0.03	ND	0.03	0.04	ND
Ace	ND	0.01	ND	ND	ND	ND
Fl	4.8	4.0	0.63	1.7	0.37	0.65
Phe	6.6	5.6	2.7	3.5	1.3	0.36
Ant	6.1	5.0	1.1	0.62	0.21	0.07
Fla	3.0	2.7	1.6	2.1	1.05	0.14
Pyr	1.5	1.4	0.21	0.18	0.21	0.12
BaA	3.9	3.7	0.20	0.12	0.21	0.11
Chr	2.2	2.1	0.07	0.05	0.41	0.18
BbF	0.95	0.81	0.01	0.01	0.06	0.04
BkF	1.7	1.4	0.22	0.03	0.29	0.19
BaP	0.65	0.62	0.71	1.1	0.14	0.06
DahA	0.22	0.18	0.003	ND	ND	ND
InP	0.48	0.28	0.003	0.003	0.007	0.007
BghiP	0.57	0.38	0.007	0.001	0.005	0.008
$\Sigma_{\text{PAHs}}^b$	32.7	28.6	8.6	10.2	4.7	1.8
$\Sigma_{\text{PAHs} \leq 3/\geq 4}^c$	1.2	1.1	2.0	1.9	1.0	1.9

<sup>a</sup> Not detectable.

<sup>b</sup> Sum concentration of 16 PAH compounds.

<sup>c</sup> Ratio of sum concentration of low molecular weight PAHs ( $\leq 3$  rings) to that of high molecular weight PAHs ( $\geq 4$  rings).

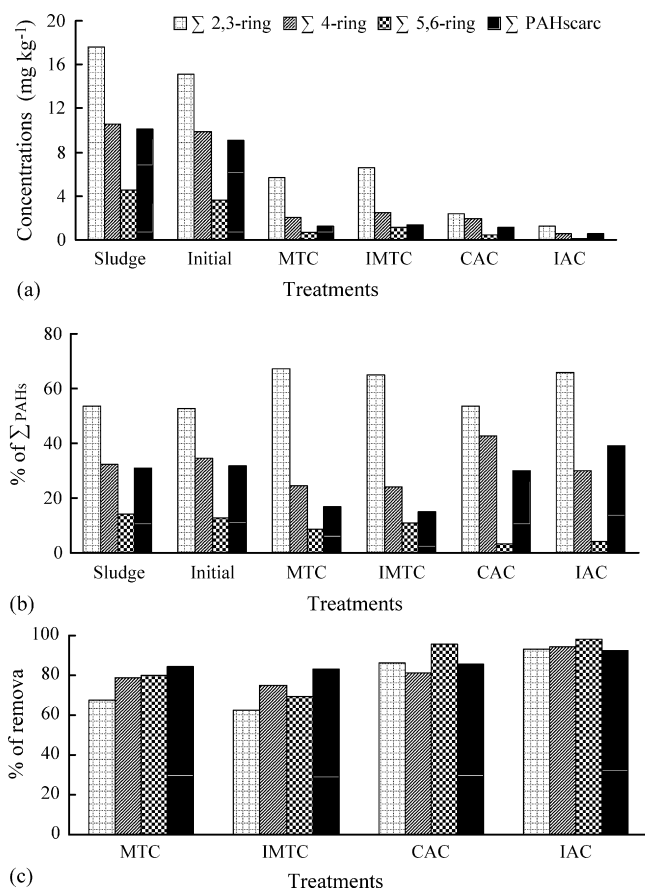


Fig. 1. Distribution and removal of different categories of  $\Sigma$ PAHs in sewage sludge, initial mixture and final composts. (a) Concentrations in  $\text{mg kg}^{-1}$  d.w., (b) % of different categories of  $\Sigma$ PAHs compared to  $\Sigma$ PAHs and (c) % of removal.

the need for extra treatment of Datansha sewage sludge before this is further disposed of.

After 56 days of composting, almost all PAHs were still detectable, except for Ace that was not found in any compost, Acy (in the MTC and IAC treatments) and DahA (in the IMTC, CAC and IAC treatments).  $\Sigma$ PAHs in the final composts varied from 1.8 to  $10.2 \text{ mg kg}^{-1}$  d.w., decreasing in order of  $\text{IMTC} > \text{MTC} > \text{CAC} > \text{IAC}$  (Table 3). In other studies dealing with sludge composts, the  $\Sigma$ PAHs have been found to range between 0.21 and  $1556 \text{ mg kg}^{-1}$  [16–19,33,34].

Concerning the concentrations of PAHs with different rings, dominant compounds in sewage sludge, initial mixture and all final composts were those with 3 and 4 rings (Table 3), which is consistent with the results reported by other authors in compost samples [9]. It appears that the total concentrations of 2 and 3 rings ( $\Sigma_{2,3\text{-ring}}$ ), 4 rings ( $\Sigma_{4\text{-ring}}$ ), 5 and 6 rings ( $\Sigma_{5,6\text{-ring}}$ ), and  $\Sigma_{\text{PAHscarce}}$  decreased in the final composts (Fig. 1a). It is of particular interest to note that  $\Sigma_{\text{PAHscarce}}$  ranged from 0.59 to  $1.3 \text{ mg kg}^{-1}$  d.w. being significantly lower than the European Union and United States limits given above.

The percent distributions of  $\Sigma_{2,3\text{-ring}}$ ,  $\Sigma_{4\text{-ring}}$ ,  $\Sigma_{5,6\text{-ring}}$  and  $\Sigma_{\text{PAHscarce}}$  to  $\Sigma_{\text{PAHs}}$  changed a lot after the 56 days of composting, being similar only between MTC and IMTC (Fig. 1b), showing that some composting processes had different effects on the different categories of PAHs. The ratios of sum concentration of

Table 4  
Removal rates of PAHs in composts of sewage sludge with rice straw (%)<sup>a</sup>

Compounds	MTC	IMTC	CAC	IAC
Nap	+ <sup>b</sup>	+	+	71
Acy	100	+	+	100
Ace	100	100	100	100
Fl	84	58	91	84
Phe	52	38	77	94
Ant	78	88	96	99
Fla	40	22	61	95
Pyr	85	87	85	91
BaA	95	97	94	97
Chr	97	98	80	91
BbF	99	98	93	95
BkF	84	98	79	86
BaP	+	+	77	90
DahA	98	100	100	100
InP	99	99	98	98
BghiP	98	100	99	98
$\Sigma$ PAHs <sup>c</sup>	70	64	85	94

<sup>a</sup> Removal rate (%) =  $((C_i - C_f)/C_i) \times 100$ , in which,  $C_i$  is the initial concentration of PAHs at the start of composting of sewage sludge with rice straw (day 0) (Table 3) and  $C_f$  is the final concentration of PAHs at the end of composting (day 56) (Table 3).

<sup>b</sup> Concentration of PAHs in the final compost (day 56) is greater than the initial one (day 0), see text for explanation.

<sup>c</sup> Removal rate (%) calculated with sum concentration of 16 PAH compounds.

low molecular weight PAHs ( $\leq 3$  rings) to those of high molecular weight PAHs ( $\geq 4$  rings) ( $\Sigma_{\text{PAHs} \leq 3} / \Sigma_{\text{PAHs} \geq 4}$ ) were about 1.0 in the initial mixture and sewage sludge, and increased to about 2.0 in MTC, IMTC and IAC which implied the dominant accumulation of low molecular weight PAHs in these composts, whereas the ratio of 1.0 (in CAC) indicated the accumulation of high molecular weight PAHs especial 4-ring PAHs.

### 3.2. Removal of PAHs during composting

Table 4 summarizes the removal rates of individual and total PAHs during the four composting processes. Almost all PAHs exhibited removal rates of more than 70%, with the exceptions of Fla in IMTC, MTC and CAC (22%, 40% and 61%, respectively), Phe in IMTC and MTC (38% and 52%, respectively) and Fl in IMTC (58%). In few cases, an increase in the concentration took place (Nap in MTC, IMTC and CAC; Acy in IMTC and CAC; and BaP in MTC and IMTC). The range of removal rates reported in previous studies is quite broad and values of –133% to 100% [35]. Guerin [36] suggested that the increase in concentration of certain PAHs might be due to the heterogeneous nature of the compost. In general, lighter PAHs (2–3 rings) are expected to be removed in higher rates, because of their increased solubility and their higher volatility, whereas heavier PAHs (5–6 rings) could be biodegraded or strongly bound to the composting organic matrix, due to their strong lipophilic character (Table 2). These two phenomena can only be distinguished with labelled substances [37]. The 4-ring PAHs should normally have an intermediate behaviour between 2–3 rings and 5–6 rings; however, in some studies they have been shown to exhibit removal rates lower than heavier PAHs [13,35,38].

Table 5  
Chemical properties of the initial mixture and the final composts

	Initial	MTC	IMTC	CAC	IAC
pH (water/compost = 2.5/1)	7.45	7.24	7.52	7.14	7.12
C/N	13.0	11.7	12.1	10.9	12.0
Organic carbon (g kg <sup>-1</sup> d.w.)	197	235 (19.3) <sup>a</sup>	236 (19.8)	234 (18.8)	238 (20.8)
Humic substance (g kg <sup>-1</sup> d.w.)	154	193 (25.3)	175 (13.0)	205 (33.1)	203 (31.8)
Ash (%)	37.6	57.5	55.7	58.1	56.5

<sup>a</sup> Number in parenthesis is the percentage of increase compared to respective initial values.

In some cases, the increases of high molecular weight PAHs or low molecular weight PAHs have been reported by other authors in the past [17,35]. This enrichment could be attributed to the mass reduction that takes place during composting (around 40–60% [37]) and to the very low degradation/volatilisation rates of the high molecular weight contaminants during composting due to their physico-chemical properties (Table 2). The amounts of organic carbons and humic substances in the final composts of the present study increased by 18.8–20.8% and 13.0–33.1%, comparing to the initial values, respectively (Table 5), something that confirms the mass reduction of the composts.

Concerning the different composting approaches, the highest removal rate of  $\Sigma_{\text{PAHs}}$  was observed in IAC (94%), followed by CAC (84%), substantially higher than those in MTC (70%) and IMTC (64%) (Table 4). The removal rate of  $\Sigma_{\text{PAHs}}$  in the present study was similar to other composts of sewage sludge or soil contaminated [15,22,23,39]. Moreover, the removal rates of Phe, Ant, Fla and BaP in the static piles (IAC and CAC) were higher than those in the piles turned (MTC and IMTC), and also the highest ones were observed in IAC and the lowest ones in IMTC (Table 4). These results confirm that IAC treatment was the best process.

The different removal rates in the different composts are directly related to the composting processes, which affected the composting temperature, diversity of the microflora and bioavailability of PAHs. Fig. 2 displays the temperature trend during the composting processes. In the pile of IAC the temperature raised from 27 to 67 °C during the first 7 days, dropped and remained at approximately 50 °C for about 4 weeks for the thermophilic phase, whereas that in the pile of CAC raised from 27 to 63 °C during the first 7 days and

remained at approximately 50 °C for about 3 weeks, and then decreased to 35 °C after 45 days and reached a constant level with ambient temperature after 50 days. The temperatures in the piles of MTC and IMTC increased to 55 °C during the first 10 days and remained at around 50 °C for about 2 weeks for the thermophilic phase, then dropped to 40 °C at 35 days and finally reached a constant level with ambient temperature after 46 days marking stabilization phase. High temperatures will typically increase the solubility and mass transfer rates of the contaminants, thereby making them more available to metabolism [13]. That might be an explanation for the higher removal rates achieved in IAC and CAC treatments. In addition to the elevated temperature, the pile of IAC provides oxygen that facilitates the degradation of PAHs. The highest temperatures in the piles turned (MTC and IMTC) were considerably lower than those in the static piles (IAC and CAC) because in the former two, temperature increases were avoided due to the turning and mixing the compost every 5 days. The temperature increase is not always a factor that enhances removal of PAHs. As a matter of fact, Antizar-Ladislao et al. [38] reported that removal rates of PAHs at 38 °C were higher than the respective at 55 and 70 °C. Temperature increase might lead to decrease removal rates due to the inhibition of the microbial diversity and hence of the enzymatic potential of the system. Moreover, the moisture contents in the piles turned (MTC and IMTC) were higher than those in the static piles (IAC and CAC) in the same day, something that affects the microbial activity and PAHs bioavailability [14].

Concerning the pile of IMTC, it should be noted that its  $\Sigma_{\text{PAHs}}$  removal rate was lower than those in the others. Similarly, some results in other reports showed that the removal rates of PAHs in composts with known PAH degraders were lower than those with soil native microbes [35,40], while the use of the autochthonous microflora, with no introduction of foreign microorganisms, offers the greatest potential for PAHs degradation [41]. It seems therefore, in certain process, that inoculation of the compost with microorganisms did not speed up the process [42].

The composting of sludge with rice straw in the present study was performed in a lower ratio of C/N (13:1). This ratio was chosen to reduce the cost of operations. The removal rates of  $\Sigma_{\text{PAHs}}$  in this study were similar to other studies, even higher [14,16,23]. Iranzo et al. [26] reported that the lower the C/N ratio (17:1–24:1) was, the more rapid the increase in microbial activity was. Moreover, a low C/N ratio provides a better homogeneity of mixture and consequently a great microbial attach, which is useful for a composting remediation strategy. Bernal et al. [43] suggested that one maturity index was a C/N < 12 ratio in compost of sewage sludge, poultry

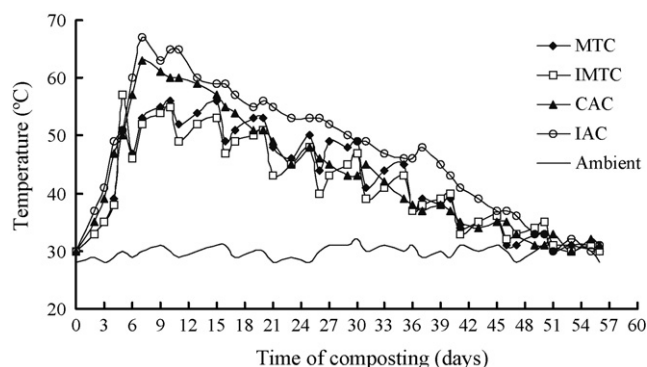


Fig. 2. Temperature change during composting.

manure and maize straw. According to their proposal, the final composts in this study reached the maturity phase (Table 5). Hence, it could be proposed that a composting strategy at a low C/N ratio for remediation of PAHs in sewage sludge with rice straw is practical and sustainable, especially the IAC approach.

Regarding PAHs with different rings, removal rates of  $\Sigma_{2,3\text{-ring}}$ ,  $\Sigma_{4\text{-ring}}$  and  $\Sigma_{5,6\text{-ring}}$  varied from 56% to 92%, 75% to 94%, and 69% to 98%, respectively, decreasing in the same way as  $\Sigma_{\text{PAHs}}$  in the four different composting processes (Table 4 and Fig. 1c). Several studies have shown that removal of  $\Sigma_{2,3\text{-ring}}$ ,  $\Sigma_{4\text{-ring}}$  and  $\Sigma_{5,6\text{-ring}}$  decreases in order of  $\Sigma_{2,3\text{-ring}} > \Sigma_{4\text{-ring}} > \Sigma_{5,6\text{-ring}}$  [14,16,22,23], whereas one study has reported that the removal of  $\Sigma_{5,6\text{-ring}}$  are higher than those of  $\Sigma_{4\text{-ring}}$  [35]. On the other hand, 86–94% of  $\Sigma_{\text{PAHscarce}}$  were removed in the final composts and the highest one was observed in IAC treatment, indicating its great bioremediation potential of carcinogenic PAHs in sewage sludge.

#### 4. Conclusions

The composting processes applied to the mixture of sewage sludge with rice straw at a low C/N ratio (13:1) met the duration of thermophilic phase and reached maturity. Suitable composting of sludge with rice straw at a low C/N ratio was practical to bioremediate PAHs-contaminated sewage sludge. In fact, after composting (56 days),  $\Sigma_{\text{PAHs}}$  and  $\Sigma_{\text{PAHscarce}}$  found in composts are lower than the limits proposed by the European Union and the USA legislation. In all composting treatments,  $\Sigma_{2,3\text{-ring}}$  accounted for more than 65% of  $\Sigma_{\text{PAHs}}$  while  $\Sigma_{5,6\text{-ring}}$  less than 10%, but the accumulation of high molecular weight PAHs especially 4-ring PAHs in CAC treatment was high compared to those observed in the three other processes used in this study.

Whatever the treatment was, removal rates ranged from 64% to 94% and from 86% to 94% for  $\Sigma_{\text{PAHs}}$  and  $\Sigma_{\text{PAHscarce}}$ , respectively. Aerated composting approaches (the static piles) especially IAC treatment were more efficient to remove PAHs than the other approaches.

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