Bioresource Technology 151 (2014) 306–313

Contents lists available at ScienceDirect

Bioresource Technology

journal homepage: www.elsevier.com/locate/biortech

Evaluation of hydrothermal treatment in enhancing rice straw compost stability and maturity

Bakhtiyor Nakhshiniev [a,*], Muhammad Kunta Biddinika [a], Hazel Bantolino Gonzales [b], Hiroaki Sumida [c], Kunio Yoshikawa [a]

[a] Department of Environmental Science and Technology, Interdisciplinary Graduate School of Science and Engineering, Tokyo Institute of Technology, 4259 Nagatsuta-cho, Midori-ku, Yokohama, Kanagawa 226-8503, Japan
[b] Innovative Platform for Education and Research, Interdisciplinary Graduate School of Science and Engineering, Tokyo Institute of Technology, 4259 Nagatsuta-cho, Midori-ku, Yokohama, Kanagawa 226-8503, Japan
[c] Laboratory of Soil Science, Department of Chemistry and Life Science, Nihon University, 1866 Kameino, Fujisawa, Kanagawa 252-8510, Japan

HIGHLIGHTS

- Bin-scale composting (90 L) was performed following a pilot-scale (200 L) HTT.
- HTT with mild reaction condition (180 °C, 1.0 MPa, 30 min) enhanced rice straw composting process.
- Rice straw compost with HTT can reach stability within 6 weeks of composting.
- Rice straw compost with HTT may be phytotoxic if used as growing media for EC sensitive plants.

ARTICLE INFO

Article history:
Received 5 September 2013
Received in revised form 23 October 2013
Accepted 26 October 2013
Available online 1 November 2013

Keywords:
Hydrothermal treatment
Rice straw
Compost
Stability and maturity

ABSTRACT

In order to evaluate the hydrothermal treatment (HTT) in enhancing compost stability and maturity of lignocellulosic agricultural residues, a bin-scale (90 L) composting of rice straw with and without "HTT" was performed. The rice straw compost product with "HTT" after 6 weeks of composting can be considered stable and adequate for field application as expressed by pH of 8.4, "EC value" of 2.96 dS m^{-1}, C/N ratio of 12.5, microbial activity of <8.05 mg CO_2 g^{-1} OM d^{-1}, NH_4^+—N content of 93.75 mg kg^{-1} DM and finally, by "GI" of >83%. However, compost may prove phytotoxic if used as growing media for EC sensitive plants. As for rice straw compost product without "HTT", the high microbial activity (>12.28 mg CO_2 g^{-1} OM d^{-1}) even after 14 weeks of composting suggests that the residue has not stabilized yet and is far away from stability and maturity, although a higher GI (>100%) was observed.

1. Introduction

The growth of global food production, increased price of energy coupled with increased production of biofuels from food crops are causing the high price of chemical fertilizers (Mueller et al., 2011). On the other hand, large volumes of crop residues which could have been converted into valuable organic fertilizers are regarded as waste each season almost everywhere in the world (Yadvinder-Singh et al., 2005). Rice (*Oryza sativa*), although the world's second most-grown crop, produces the largest amount of crop residues. According to FAO (2013), over the past ten years, the global paddy rice output on an average was about 664.3 million Mt. As rice generates about one Mt of straw per each Mt of grain, large amount of residue is accumulated annually. Rice straw is unique relative to other crop residues; it has limited use as an animal feed because of its high silica content (Van Soest, 2006). Direct incorporation of the rice straw into the soil is also limited as it may cause certain agronomic problems such as temporary immobilization of nutrients and associated crop yield reduction (Yadvinder-Singh et al., 2005). As a result, a large amount of produced straw is left unutilized, which is mostly burnt on-farm (Gadde et al., 2009), although burning of the straw *in situ* is the most discouraged option as it emits air pollutions (Gadde et al., 2009) and causes loss of valuable nutrients into atmosphere (Yadvinder-Singh et al., 2005). Fortunately, composting offers a low-cost and environmentally friendly option for recovery and recycling of nutrients in the crop residues. Composting is a process of controlling and enhancing the biological decomposition of organic residues into usable end product such as organic fertilizer (Kluczek-Turpeinen, 2007). The C/N ratio, moisture content, particle size, airflow and temperature are the key

---

* Corresponding author. Tel.: +81 8058931645; fax: +81 459245518.
E-mail addresses: bakhtiyor_nr@yahoo.com, bakhtiyor.n.aa@m.titech.ac.jp (B. Nakhshiniev).

0960-8524/$ - see front matter © 2013 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.biortech.2013.10.083

parameters influencing the process. Successful optimization of these parameters may shorten the process and result in quality product i.e. stable and mature compost (Guo et al., 2012). Nevertheless, ordinary composting of rice straw is a too slow process for farmers, and may require at least 90 days to allow transformation of the residue into stable and mature compost (Goyal and Sindhu, 2011). This is because, microbial access to cellulose (a major biodegradable component of crop residue), is known to be inhibited by hemicellulose–lignin association during the decomposition process. In native lignocellulose i.e. rice straw, lignin is intermeshed and chemically bonded with hemicellulose polysaccharides, which together form a barrier that becomes even more resistant to microbial degradation (Malherbe and Cloete, 2002). Therefore, enhancement of rice straw composting process requires disruption of this physicochemical barrier. It has been suggested that at least 50% of hemicellulose should be removed to significantly increase cellulose degradability (Agbor et al., 2011).

In order to enhance the composting process, an innovative hydrothermal treatment (HTT) technology with mild reaction conditions (180 °C, 1.0 MPa, 30 min) was selected as a pretreatment step for solubilization of hemicellulose before subsequent composting of rice straw. The HTT reaction conditions were selected from our previous bench-scale work in which a reaction temperature of 180 °C was the most favorable for solubilization of the major portion of hemicellulose polysaccharides (Nakhshiniev et al., 2012). However, stability and maturity are also the important aspects of compost quality, in particular in relation to its agronomic application. Therefore, it is essential to evaluate the stability and maturity of the compost to ensure effectiveness of the pretreatment technology.

A large variety of physical, chemical and biological parameters have been proposed for the evaluation of compost stability and maturity (Wichuk and McCartney, 2010). Biological stability index evaluated by respirometric measurements based either on CO_2 production rate, O_2 uptake or release of heat has been frequently applied in compost stability determination (Komilis and Kletsas, 2012). Compost maturity, on the other hand, which implies no toxicity to plants upon immediate application of compost, is still best determined using the plant phytotoxicity tests, such as seed germination and/or plant growth bioassays (Wang et al., 2004). In practice, phytotoxicity can also be induced by factors such as high amounts of free ammonia, excess soluble salts or certain organic acids. Therefore, the change in chemical parameters during the composting process such as pH, electrical conductivity (EC), C/N ratio, $NH_4^+{-}N$ formation and the ratio of $NH_4^+{-}N$ to $NO_3^-{-}N$ have been found as the useful indicators in compost maturity determination (Wang et al., 2004). Integrated use of these parameters and indices has been shown to result in better evaluation of compost stability and maturity (Mondini et al., 2003). The objective of this research, therefore, was to measure the changes in physical, chemical and biological parameters and indexes during composting of rice straw residue with and without HTT, and evaluate HTT in enhancing the compost stability and maturity of the rice straw residue.

2. Methods

2.1. Material and HTT process

In this study, rice straw was used as the model lignocellulosic agricultural residue. It was purchased from the local gardening store. Since, the residue was already cut into small pieces ranging from 2 to 4 cm no additional cutting was required. In order to obtain sufficient amount of material for subsequent bin-scale composting experiment a pilot-scale HTT facility with reactor capacity of 200 L was employed in this study. Schematic and overall view of the HTT facility is shown in Fig. 1. First, the rice straw (about 8 kg in dry weight) was fed into the reactor, and then, saturated steam supplied from the boiler was injected into the reactor until the pre-set hydrothermal conditions (180°C, 1.0 MPa) were reached. The blades installed inside the reactor then started to mix the residue for about 30 min. After the treatment was complete, the reactor was decompressed immediately by flashing the steam through the condenser and the moist treated residue (with around 68% MC) was discharged by rotating the blades, which also act as a screw conveyor. Four batches were performed. The treated products cooled down, mixed and were preserved (10 °C) until the next experimental procedure. The chemical properties of the residue with and without HTT are shown in Table 1.

2.2. Compost substrate preparation

The rice straw residues, with and without HTT, were then spread on separate blue plastic sheets and microbial inoculums were applied using a bottle with water spray nozzle. Since, the residue obtained after the HTT had already a moisture content of 68%, no correction of the moisture content was required. As for the untreated residue, however, it was initially soaked in the water for 48 h to constitute the moisture content of 68%. Because the initial C/N ratios of both substrates were higher than the range considered optimum (25–30) for starting composting process, necessary amount of nitrogen was added to the substrates (8 g per each kg of DM) in order to bring the C/N ratios within the recommended range. The nitrogen was added in the form of urea solution (17% w/v) and was applied (100 ml per each kg of substrate) soon after the application of microbial inoculums. All preparations were conducted outdoor when the ambient temperature was below 15 °C, so no special care was taken to prevent the water or nitrogen loss. The amount of substrates loaded in each composting reactor was about 18 kg (wet basis). While the substrate was being loaded into each reactor, original samples were withdrawn (bottom, middle, top) immediately for subsequent analyses, and the composting process was begun; the composting time was noted as week zero (Week 0).

2.3. Microbial inoculum preparation

Compost microbial inoculum was prepared by means of shaking a 1:25 (w/v) compost/water mixture for 15 min in a warm water bath (32 °C). Compost was commercially produced (Wakayama Organic Productive Union, Japan) and prior to shaking, it was supplemented with glucose solution (5% w/v) and pre-incubated at 32 °C for 3 days in air-tight collapsible container in order to active the microbes. Produced gas was released and compost was mixed once daily. Because, the hydrothermally treated residue had undergone a ‘sterilization’ process, rice straw rinse water was also prepared in similar way to include ‘native’ microbial inoculums presented naturally in the untreated residue. The prepared suspensions were then mixed and diluted with 5 parts of pure water before it was applied as a compost inoculum.

2.4. Composting setup

Plastic dust bins with a volume of 90 L (Fig. 2) were modified and used as composting reactors. The bins were externally insulated with two layers of glass wool and aluminum foil thermal insulators to minimize the convective heat loss. A removable airtight lid was put on top of each reactor to facilitate intermittent mixing and sampling of substrate during the course of composting. The lids, however, were insulated from the inner side (foam rubber) in order to minimize the occurrence of the reflux condition.

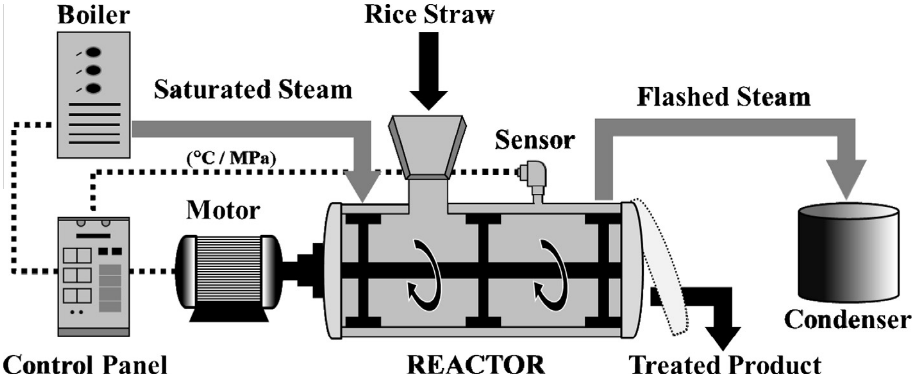

Fig. 1. Schematic view of the pilot-scale HTT facility used in this research.

Table 1
Chemical properties of the rice straw residue before and after HTT.

Parameters	Before HTT	After HTT
Hot water extractives, %	10.30	18.00
Hemicellulose, %	29.60	7.35
Cellulose, %	36.46	43.45
Lignin, %	13.97	19.91
Ash (550 °C, 2 h), %	9.8	11.5
Moisture content, %	14.0	68.0
OM (100%-Ash), %	90.2	88.5
pH	6.81	3.86
EC, dS m^{-1}	2.20	4.75
Total C, %	42.49	45.25
Total N, %	0.85	0.98
C/N ratio	49.99	46.17

One thermocouple (K-Type) connected to data logger (TM-947SD) was fitted at the center of each reactor to record the temperature of the composts at the interval of 30 min. The temperature in the laboratory was maintained at 24 °C. In order to have the air flow uniformly distributed throughout the compost substrate, the material was placed on the stainless punch plate installed at the bottom of the reactors. The air was supplied continuously by compressor pump and the flow rate was fixed at 0.48 L kg^{-1} DM min^{-1} in every reactor (Jiang et al., 2011). The compost was mixed manually at 1- or 2-weeks interval throughout the composting process.

2.5. Sample collection

Besides the samples taken at the beginning of composting (Week 0), seven more solid samples (about 250 g) were taken from each reactor throughout the composting process, specifically during the turning at Weeks 2, 4, 6, 8, 10, 12 and 14. Samples were taken from three parts (top, middle, bottom) of the reactor and after homogenization (considering the MC) were divided into two parts; with one part kept fresh at 4 °C, and another part air-dried and grounded to pass through 0.25 mm sieve. The air-dried and ground samples were used to analyze the total carbon (Total C), total nitrogen (Total N), ash and organic matter (OM) contents. The fresh samples were used to analyze the dry matter (DM), pH, electric conductivity (EC), ammonium nitrogen (NH_3^+—N) and nitrate nitrogen (NO_3^-—N). The fresh samples were also used in microbial stability and phytotoxicity tests.

2.6. Analytical methods

The Total C and Total N contents were determined using an automatic high sensitive NC-analyzer (Sumigraph NC-220F, SCAS, Japan). The DM content was assessed by oven-drying at 105 °C for 24 h and the ash was determined by combustion of 3 g oven-dried sample at 550 °C for 2 h in a muffle furnace. Subsequently, the difference between DM and ash was considered the OM content. The pH and EC were analyzed in a 1:10 (w/v) compost/water (distilled) solution following a 30-min shaking in the water bath (25 °C). The NH_4^+—N and NO_3^-—N were extracted with 0.5 M K_2SO_4 (1:10 w/v) solution and analyzed by steam distillation using MgO-Devarda's alloy followed by back titration of the boric acid distillates using 0.0025 M H_2SO_4 solution.

2.7. Evolution of carbon dioxide

Microbial stability index was evaluated by the microbial respiration test based on CO_2 evolution rate (mg CO_2 g^{-1}OM d^{-1}), which is similar to the procedure described in CCQC (2001). Approxi-

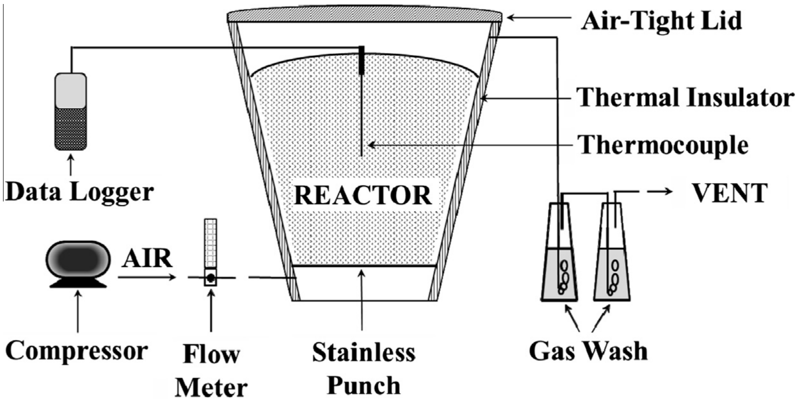

Fig. 2. Diagram of the composting reactor.

mately 10 g of sample conditioned at 50% moisture content was sealed in a 3.0 L vessel along with a vial containing a known volume of 1 M NaOH solution. The vessel was sealed and incubated at 37 °C for 4 days. The amount of CO_2 trapped by NaOH was determined daily over a 4-day period by back titration with 1 M HCl to phenolphthalein endpoint, after adding excess amount of $BaCl_2$. All measurements were performed in three replications, including a jar without compost as a blank.

2.8. Phytotoxicity test

A phytotoxicity test employing seed germination index (GI) was used to evaluate compost maturity in this study (Zucconi et al., 1981). The fresh sample was mixed with distilled water to attain a 1:10 (w/v) compost/water mixture, and after shaking for 6 h at 25 °C the aqueous extracts were obtained by centrifugation (5040*g*-force, 20 min) followed by filtration through a 0.45 μm membrane filter. A commercial germination test sheet (Tanepita, FHK, Japan) pasted orderly with 50 seeds of Komatsuna (*Brassica rapa* var. *peruviridis*), was placed inside a UV-sterilized petri dish and was wetted with 5 ml of compost extract. Komatsuna seeds have been widely used in Japan in germination tests (Hase and Kawamura, 2012). The Petri dishes were then incubated for 4 days at 25 °C in the dark. After 4-day incubation the germination was stopped (by adding 5 ml of ethanol) and the germinated seeds were counted and the root length was measured. Three replicates (with total seeds number of 150) were set out for each treatment, including distilled water that was used as a control. The GI was then calculated according to the expression $\mathrm{GI}(\%) = (A \times C)/(B \times D) \times 100\%$ in which, A and C represent the number of seeds germinated in extract-treated and control dishes, respectively; and B and D represent the average root length of extract-treated and control seeds, respectively (Zucconi et al., 1981).

2.9. Statistical analyses

The statistical analysis of data was performed using the Data Analysis ToolPak of the Excel (Microsoft Office 2010). A *t*-Test was used for testing statistical significant differences of the sample means among composting times. Two-tail and a 95% confidence (or alpha of 0.05) was assumed for all tests. The relationships between the parameters were defined by correlation and regression analysis.

3. Results and discussion

3.1. Evolution of composting temperature

Monitoring of compost temperature is important for the stability and maturity determination. Evolution of temperature has been found to strongly reflect metabolic activity of microorganisms during the composting process (Tiquia et al., 1996). The final decrease in temperature to reach an ambient temperature without reheating upon mixing may indicate the maturation phase (Tang et al., 2007). In addition, compost must experience the temperature exceeding 55 °C for at least 3 days in order to eliminate pathogens and weeds. Fig. 3 shows the evolution of temperature during the composting process of the rice straw residue with and without HTT. During the composting experiment the room temperature fluctuated between 23 (night) and 25 °C (day), therefore 24 °C was assumed a mean. As can be seen, the temperature in the compost reactors began to rise soon after establishing the composting conditions as well as after each turning during the active stages (seen as the sharp drops in temperature curves). The compost temperature of the residue with HTT reached a maximum of 63 °C (on day 9) and remained above 55 °C for more than 15 days. Then, the temperature decreased rapidly and remained between 34 and 37 °C until Week 6. Afterward, the temperature diminished and became close to room temperature, thus, composting entered a maturation phase. However, the compost temperature of the residue without HTT only reached a maximum of 51 °C (on day 10) so the required temperature for pathogens and weed destruction was not fulfilled. The temperature then decreased and was maintained at the lower levels between 35 and 40 °C until Week 4. After Week 4, a further slight decreased led to the compost temperature to range between 30 and 35 °C until Week 10. Then, it dropped and stayed close to room temperature until the end of composting process.

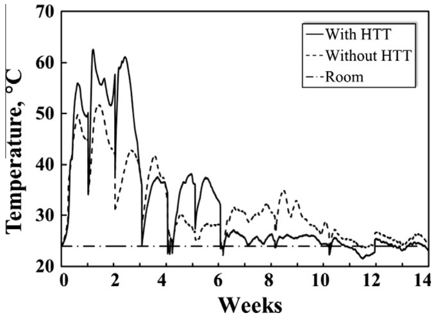

Fig. 3. Evolution of temperature during composting process of rice straw with and without HTT.

3.2. Variations in pH and EC

Variations in pH and EC are useful parameters for monitoring the composting process (Hosseini and Aziz, 2013). In addition, pH and EC are considered important compost parameters because they can affect the quality and suitability of the final product for plant growth. The compost pH value ranging from 5.5 to 8.5 is considered acceptable and the EC higher than 1.5 dS m^{-1} and 4.0 dS m^{-1}, respectively, are considered the upper limit values for growing media, and tolerable by plants of medium sensitivity (Silva et al., 2013). The variations of pH and EC during the composting process of the rice straw residue with and without HTT are shown in Fig. 4a and b, respectively.

The pH value of the rice straw compost with HTT at the start of composting (Week 0) was about three units lower than the rice straw compost without HTT (Fig. 4a). This pH difference can be attributed to the presence of organic acids formed normally during the HTT of lignocellulosic residues. Nevertheless, the pH of rice straw compost with HTT increased rapidly and alkaline value of 8.2 was observed on Week 2. This could be explained both by decomposition of organic acids by microorganisms as well as by the release of ammonia (Fig. 4c) from mineralization of organic nitrogen. After Week 2, the pH did not change significantly and stayed near 8.0 until the end of experiment (Table 2). The pH variation in rice straw composting without HTT, followed a similar pattern; in particular, an increase to around 8.2 on Week 2 and the final value of around 7.8. A natural pH drop typical in the early stage of composting process was not seen because the conversion of OM to acidic compounds probably, occurred sooner than sampling the compost on Week 2.

Unlike the pH, the initial EC value in rice straw compost with HTT was higher than the EC value in rice straw compost without HTT (Fig. 4b): the respective values were 4.75 and 2.2 (dS m^{-1}). This difference was apparently due to the presence of soluble organic compounds. As these soluble organic compounds were consumed by microorganisms, the EC reduced to 2.9 (dS m^{-1}) on

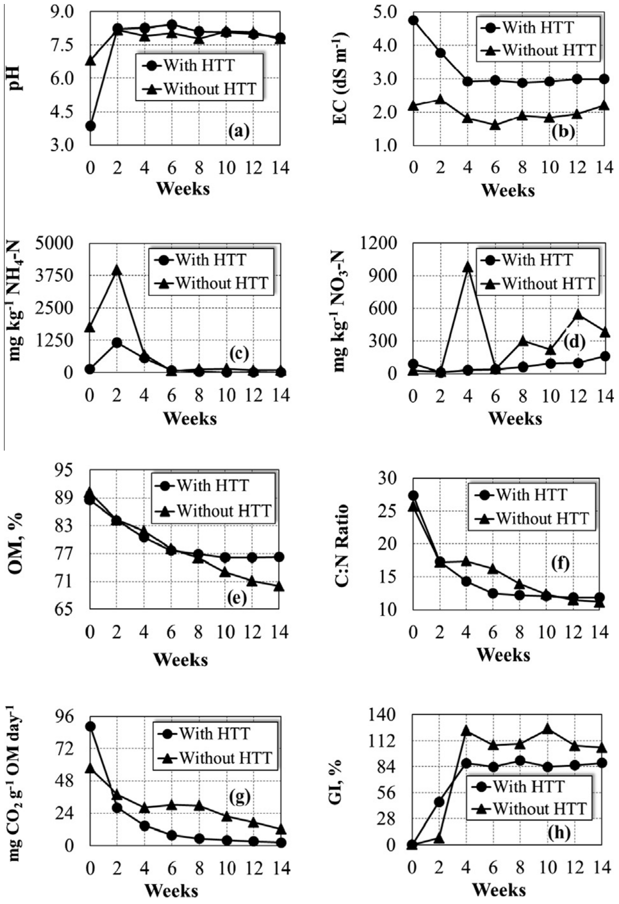

Fig. 4. Changes in pH (a), EC (b), NH_4^+—N (c), NO_3^-—N (d), OM (e), C/N ratio (f), microbial activity (g) and germination index of Komatsuna seeds (h) during the composting process of rice straw with and without HTT.

Week 4. Afterwards, the EC stabilized and the final value was 3.0 (dS m^{-1}). As for the rice straw compost without HTT, statistical analyses (Table 2) showed that no significant change occurred and therefore, the EC value similar to the initial one (2.2 dS m^{-1}) was observed at the end of process.

3.3. Evolution of NH_4^+—N and NO_3^-—N

During the composting process, organic nitrogen is usually decomposed during the active phase of composting resulting in the release of relatively high levels of NH_4^+—N; as composting process continues and maturation phase is reached, ammonia is eventually reduced through volatilization or nitrification to form the NO_3^-—N (Haug, 1993). According to CCQC (2001), mature compost should not have the NH_4^+—N content of more than 500 mg kg^{-1}, or the NH_4^+—N / NO_3^-—N ratio of > 3. The variations of the NH_4^+—N and the NO_3^-—N during composting of rice straw with and without HTT are shown in Fig. 4c and d, respectively.

The initial NH_4^+—N content in the rice straw compost with HTT was only 135.1 mg kg^{-1}, but soon it reached 1167 mg kg^{-1} (or 4.9% of TN) on Week 2. This was probably, the reason for rapid increase of pH on Week 2. As composting proceeded, immobilization of NH_4^+—N by microorganisms occurred and the NH_4^+—N content in compost product decreased to reach the lower level of 93.8 mg kg^{-1} on Week 6. This decrease in NH_4^+—N was related to microbial immobilization because no significant nitrification (Fig. 4b) or NH_3 volatilization (data not presented) were observed during this period. After Week 6, the NH_4^+—N content continued decreasing and only 16.7 mg kg^{-1} was measured at the end of experiment. An intensive NH_4^+—N formation was observed in the rice straw compost without HTT. This can be examined from the high NH_4^+—N content of 1747 mg kg^{-1} (or 10.8% of TN) on Week 0. According to Ndegwa et al. (2008), urea can be converted to NH_3 in a matter of hours to few days by the extracellular urease enzyme, which is found in many microorganisms during the compost process. In this experiment, the rice straw residue initially, was soaked in the water for 48 h and it is likely that this pretreatment promoted the development of urease activity of the microorganisms (naturally present in the residue), which in turn, promoted rapid decomposition of urea at such early stage of composting process. The NH_4^+—N content then increased again and reached 3965 mg kg^{-1} (17.5% of TN) on Week 2. After this peak, the NH_4^+—N content in the substrate decreased rapidly and only 66.2 mg kg^{-1} was measured on Week 6, which was apparently due to the transformation to NO_3^-—N (Fig. 4d) as well as volatilization of NH_3 (data not presented). After Week 6, the NH_4^+—N content followed a gradual increase to reach a value of 155.6 mg kg^{-1} on Week 10 before to decrease again and stabilize at 88.9 mg kg^{-1} until the end of experiment.

The NO_3^-—N contents in both compost substrates were very low at the early stage of composting (Fig. 4d). In the rice straw compost with HTT, the NO_3^-—N content was about 87.8 mg kg^{-1} on Week 0 and the value soon decreased to 12.9 mg kg^{-1} on Week 2. After Week 2, the NO_3^-—N content did not show significant change until Week 6 (Table 2). Probably, relatively high temperature (over 55 °C) during the active phase of composting suppressed the growth of nitrifying bacteria. After Week 6, when temperature became close to the room temperature, the NO_3^-—N contents started to increase slowly but consistently. The reason for such slow rate in the NO_3^-—N formation could be slow rate of organic nitrogen remineralization that has had been immobilized by microorganism during the active phase. In fact, it is said that when nitrogen is incorporated into microbial cellular substances it becomes relatively stable (Marumoto et al., 1977). The NO_3^-—N contents in the rice straw compost without HTT were highly dynamic. If the NO_3^-—N contents were about 31.7 and 17.9 mg kg^{-1} on respective Week 0 and Week 2, relatively high content was detected on Week 4 (979.9 mg kg^{-1}). This could be favored by the presence of high ammonia as well as temperature drop in compost to around 40 °C. The later one could be affected by the coarse structure of the untreated substrate, which might permit 'good' aeration of compost. The available NO_3^-—N was then immediately lost through denitrification process as relatively low content of the NO_3^-—N (44.4 mg kg^{-1}) was measured on Week 6. This was concluded because there was still a large net loss in total N (data not presented) although no leaching or ammonia volatilization occurred during this period. In the following weeks, the NO_3^-—N contents increased but fluctuated between 220 and 550 mg kg^{-1}.

From the NH_4^+—N/NO_3^-—N ratio, the compost products in both reactors should have entered maturation phase at Week 6, since from this point the ratio for both cases did not exceed the established value (i.e. >3). However, the NH_4^+—N/NO_3^-—N ratios cannot be used as an indicator of maturity in this research because, the NH_4^+—N and NO_3^-—N contents in either composts were not sufficiently high, i.e. >250 mg kg^{-1} OM (CCQC, 2001).

3.4. Variations in OM content

During the composting process, part of OM in the substrate is converted to CO_2, H_2O and energy, while the remainder is eventually converted to stable organic compounds (Insam and de Bertoldi, 2007). Therefore, the content of OM should decrease during composting process. The losses of OM content during composting of the rice straw with and without HTT are illustrated in Fig. 4e.

Table 2
Variations in selected biochemical properties during composting of rice straw with and without HTT.

Parameters	Composting periods (weeks)							
	0	2	4	6	8	10	12	14
pH	3.86 ± 0.12a [6.81 ± 0.08a]	8.23 ± 0.25b [8.18 ± 0.23b]	8.26 ± 0.20b [7.91 ± 0.14b]	8.41 ± 0.16b [8.04 ± 0.17b]	8.11 ± 0.12b [7.78 ± 0.13b]	8.08 ± 0.16b [8.12 ± 0.09b]	7.99 ± 0.14b [8.08 ± 0.12b]	7.84 ± 0.08b [7.77 ± 0.10b]
EC (dS m^{-1})	4.75 ± 0.05a [2.20 ± 0.06a]	3.78 ± 0.03b [2.38 ± 0.17a]	2.92 ± 0.15c [1.82 ± 0.11a]	2.96 ± 0.07c [1.62 ± 0.20a]	2.88 ± 0.10c [1.90 ± 0.15a]	2.92 ± 0.07c [1.84 ± 0.11a]	3.02 ± 0.08c [1.95 ± 0.16a]	3.00 ± 0.05c [2.21 ± 0.18a]
NH_4^+—N (mg kg^{-1} DM)	135.1 ± 9.0a [1747 ± 12a]	1167 ± 21b [3965 ± 44b]	565.2 ± 5.4c [700.0 ± 20.7c]	93.75 ± 5.51a [66.18 ± 3.90d]	39.77 ± 5.68d [137.5 ± 8.86e]	16.67 ± 3.06d [155.6 ± 6.1e]	22.22 ± 5.56d [88.89 ± 5.56d]	16.67 ± 5.56d [88.89 ± 5.00d]
NO_3^-—N (mg kg^{-1} DM)	87.80 ± 0.01a [31.71 ± 3.66a]	12.89 ± 5.37b [17.91 ± 5.37a]	32.85 ± 5.47b [979.9 ± 11.0b]	38.84 ± 0.04b [44.44 ± 5.56a]	60.36 ± 1.12c [302.9 ± 17.9c]	94.03 ± 8.9ac [222.4 ± 6.6c]	98.45 ± 5.53a [544.3 ± 35.4d]	161.50 ± 2.2d [384.2 ± 0.01e]
OM (%)	88.54 ± 0.02a [90.19 ± 0.15a]	84.12 ± 0.08b [84.23 ± 0.25b]	80.52 ± 0.10c [81.88 ± 0.07c]	77.66 ± 0.12d [78.03 ± 0.15d]	76.91 ± 0.15de [76.07 ± 0.08e]	76.16 ± 0.17de [72.96 ± 0.05f]	76.12 ± 0.07e [71.11 ± 0.05g]	76.24 ± 0.24d [70.11 ± 0.05h]
Total C (%)	43.51 ± 0.40a [42.96 ± 0.06a]	41.25 ± 0.42b [39.10 ± 0.10b]	41.90 ± 0.01b [39.32 ± 0.10b]	40.83 ± 0.16c [37.82 ± 0.04c]	40.69 ± 0.02c [36.27 ± 0.03d]	40.89 ± 0.07d [35.68 ± 0.06e]	40.61 ± 0.05e [34.22 ± 0.01f]	40.47 ± 0.06e [33.71 ± 0.02g]
Total N (%)	1.59 ± 0.002a [1.67 ± 0.01a]	2.38 ± 0.03b [2.27 ± 0.03b]	2.93 ± 0.01c [2.26 ± 0.01b]	3.27 ± 0.02d [2.33 ± 0.01c]	3.34 ± 0.02e [2.61 ± 0.01d]	3.39 ± 0.02f [2.89 ± 0.01e]	3.43 ± 0.01f [2.98 ± 0.003f]	3.42 ± 0.003f [3.02 ± 0.004 g]
C to N ratio	27.37 ± 0.25a [25.72 ± 0.18a]	17.33 ± 0.37b [17.23 ± 0.19b]	14.30 ± 0.03c [17.40 ± 0.08b]	12.49 ± 0.05d [16.23 ± 0.04c]	12.18 ± 0.07e [13.90 ± 0.06d]	12.06 ± 0.04e [12.35 ± 0.01e]	11.84 ± 0.01f [11.49 ± 0.01f]	11.83 ± 0.02f [11.16 ± 0.01g]
CO_2 evolution (mg g^{-1} OM d^{-1})	88.59 ± 0.14a [57.35 ± 1.33a]	28.25 ± 0.62b [38.01 ± 0.37b]	14.83 ± 0.15c [28.25 ± 0.30c]	8.05 ± 0.10d [30.29 ± 0.48c]	5.19 ± 0.17e [29.81 ± 0.47c]	4.08 ± 0.05f [21.80 ± 0.31d]	3.33 ± 0.05 g [17.19 ± 0.29e]	2.42 ± 0.16 h [12.28 ± 0.10f]
Germination index (%)	0.00 ± 0.00a [0.00 ± 0.00a]	46.07 ± 1.1b [7.25 ± 0.80b]	87.66 ± 2.3 cd [122.8 ± 5.3ce]	83.73 ± 2.3ce [107.5 ± 7.0d]	92.05 ± 3.0d [108.6 ± 4.1d]	83.91 ± 2.0e [124.8 ± 1.1e]	85.47 ± 4.4e [106.7 ± 1.6d]	88.11 ± 2.4de [104.7 ± 1.5d]

The results are the means of three replicates ± standard error. Values within the same row followed by the same letter(s) do not differ significantly according to *t*-Test ($\alpha = 0.05$).
A [B], where A = with HTT and [B = without HTT].

The initial OM contents were approximately equal in both compost reactors. The contents decreased during the course of composting from 88.54 to 76.24% in the rice straw compost with HTT, and from 90.19 to 70.11% in the rice straw compost without HTT. The loss of OM in the rice straw compost with HTT occurred predominantly during the active stage, specifically, between Week 0 and Week 6, when the temperature (Fig. 3) and microbial activity (Fig. 4g) were high. This can be explained by the idea that most of the OM in the substrate was depleted by microorganism at this stage. Subsequently, the loss of OM in the rice straw with HTT slowed down and became fairly stable after Week 6. This behavior in OM loss coincided well with the evolution of the C/N ratio (Fig. 4f) and microbial activity (Fig. 4g), which may suggest that the compost have indeed reached stability. However, the loss of OM in the rice straw compost without HTT occurred throughout the composting process, reflecting the high rate of biodegradation in the substrate. The high rate of degradation was also reflected by high microbial activity in the compost (Fig. 4g), although a greater loss in OM content was achieved at the end of the process (20.18% compared to 12.29% in the rice straw compost with HTT). In this experiment, in fact, the rice straw residue during the HTT process was enriched in lignin fraction (Table 1) because of partial losses of hemicellulose polysaccharides. Therefore, this difference in OM mineralization is attributed mainly to the higher content of lignin in the rice straw compost with HTT (Komilis and Ham, 2003).

3.5. Variations in C/N Ratio

The C/N ratio is an important agronomic parameter of final compost product as it was found to affect immobilization and release of nitrogen and other important crop nutrients in the soil (Ahmad et al., 1969). Because of higher loss of carbon compounds generally, decreasing trend in C/N ratio is expected. The C/N ratio smaller than 25 is indicative of an acceptable maturity (CCQC, 2001), a ratio of 15 or even less being most preferable (Jimenez and Garcia, 1989). The trends in C/N ratio of the rice straw composts with and without HTT are illustrated in Fig. 4f.

The major reduction in the C/N ratio of the rice straw compost with HTT occurred during the active phase of decomposition, i.e. Week 0 and Week 6. The C/N ratio values at Week 0 and Week 6 were 27.4 and 12.5, respectively. This can suggest that biodegradation rate of the rice straw was enhanced with HTT. After Week 6, the C/N ratio leveled off and stabilized around 12, which could indicate stability of the compost. Indeed, the compost could be stable from this point, since this value is very close to the C/N ratio of many humic substances found in stable soil organic matters (Kuwatsuka et al., 1978). As for the C/N ratio of the rice straw compost without HTT, considerable decrease from the initial value of 25.7–17.2 occurred between Week 0 and Week 2. One of the possible reasons for this rapid drop could be the decomposition of easily available carbons by microorganisms. Then, the C/N ratio remained unchanged until Week 4, implying that the loss of nitrogen from the system was also substantial during this period. After Week 4, the C/N ratio started to decrease again and the compost had a C/N ratio of about 11.2 on Week 14. However, continuous decrease in the profile of the C/N ratio suggests that the substrate is rich in some carbon materials that are yet to be degraded. Therefore, as stated by Jimenez and Garcia (1989), a C/N ratio cannot be considered indicative of compost maturity until stability in the C/N ratio change is not seen.

3.6. Evolution of carbondioxide

As compost approaches stability microbial activity decreases and the CO_2 evolution rate is expected to decline (Wichuk and

Table 3
Pearson correlation coefficient between measured parameters of rice straw compost with and without HTT.

	pH	EC	NH_4^+—N	NO_3^-—N	OM	C/N ratio	CO_2 evolution	GI
pH	–	−0.882** [ns]	ns [ns]	ns [ns]	ns [ns]	ns [ns]	ns [ns]	0.872** [ns]
EC		–	ns [ns]	ns [ns]	0.937** [ns]	0.975** [ns]	0.968** [ns]	−0.997** [−0.753*]
NH_4^+—N			–	ns [ns]	ns [ns]	ns [ns]	ns [ns]	ns [−0.849**]
NO_3^-—N				–	ns [ns]	ns [ns]	ns [ns]	ns [ns]
OM					–	0.954** [0.940**]	0.934** [0.926**]	−0.943** [−0.770*]
C/N ratio						–	0.998** [0.960**]	−0.976** [−0.736*]
CO_2 evolution							–	−0.969** [−0.797*]
GI								–

ns, not significant.
A [B], where A = with HTT and [B = without HTT].
* Significant at $p < 0.05$.
** Significant at $p < 0.01$.

McCartney, 2010). According to CCQC (2001), a compost product with microbial activity of less than 8.0 mg CO_2 g^{-1}OM d^{-1} is stable and mature. Fig. 4g shows the evolution of CO_2 as an indication of stability during the composting of rice straw with and without HTT.

In the early stages of the process, the CO_2 evolution rate for the rice straw compost with HTT was about 1.7 times higher than for the rice straw compost without HTT because of the enhancement of the rice straw digestibility after pretreatment (Thomsen et al., 2009). The CO_2 evolution rate then decreased rapidly and the threshold stability value of 8.0 mg CO_2 g^{-1}OM d^{-1} was reached soon on Week 6. This result corresponds well with the change of other measured parameters and further confirmed that the rice straw compost with HTT reached an obvious stabilization phase on Week 6. However, there was no clear trend in the CO_2 evolution rate for the rice straw compost without HTT. Initially, the CO_2 evolution rate decreased to reach a value of 28.25 mg CO_2 g^{-1}OM d^{-1} on Week 4, and then no significant change occurred (Table 2) until Week 8. It is likely that microbial activity during Week 4 and Week 8 was supported by the release of carbon from cellulose that was largely unavailable until Week 4 due to protective effect of hemicellulose–lignin association (Malherbe and Cloete, 2002.). In the following weeks, the CO_2 evolution rate started to decrease again, but the value measured at the end of experiment (Week 14) was still high (12.28 mg CO_2 g^{-1}OM d^{-1}). Such a high microbial activity could suggest that the residue had not stabilized yet and is far away from stability phase.

3.7. Germination index

While organic materials decompose, a variety of metabolic compounds are released during composting and these compounds can be toxic to plants (Zucconi et al., 1985). The GI was a sensitive indicator and its increase corresponded with the decreases in concentrations of phytotoxic compounds as compost aged (Tiquia and Tam, 1998). Compost with GI of ⩾80% is considered phytotoxic-free and adequately matured (CCQC, 2001). Fig. 4h shows the change of GI percentage during the composting of rice straw with and without HTT.

The initial GI was 0% for both compost products. Then, soon both composts overcame the threshold value (⩾80%) and yielded high GI (87.7–122.8%) on Week 4, which may indicate the disappearance of phytotoxic compounds (Tiquia and Tam, 1998). The GI in rice straw compost with HTT on Week 0 and Week 2 could be controlled by high EC value, since the increases in GI values corroborated well with the decreases in EC values during this period. The low GI in rice straw compost without HTT probably was due to the phytotoxic effect of urea and associated NH_4^+—N release during the early stage of composting (Fig. 4c). The GI fluctuations observed for both compost products after Week 4 onwards, are in agreement with the finding of Zucconi and de Bertoldi (1987). The higher GI (104.7–124.8%) found after Week 4 for rice straw compost without HTT suggests that the high content of NO_3^-—N (Fig. 4d) might exert a positive influence on GI (Tiquia and Tam, 1998). However, these results demonstrated that the compost would not have any phytotoxic effects, even if the microbial activity was still high and that stability and maturity are different compost properties.

3.8. Correlation between stability and maturity parameters

The Pearson correlation coefficient (r) among measured parameters was calculated in order to find a simplest indicator(s) which could be used to assess the stability and maturity of the compost with and without HTT. Table 3 indicates that there was very strong statistical correlation (at $p < 0.01$) among various stability and maturity parameters of rice straw compost with HTT. Specifically, the CO_2 evolution had very strong positive correlation with the EC (*0.968*), OM (*0.934*) and C/N ratio (*0.998*). On the other hand, the GI had very strong but negative correlation with the EC (−*0.997*), OM (−*0.943*) and C/N ratio (−*0.976*). There was also very strong negative correlation between the GI and the CO_2 evolution (−*0.969*). According to these statistical results, the EC and C/N ratio (or OM) may be used to evaluate stability and maturity of rice straw compost with HTT. As for rice straw compost without HTT, the CO_2 evolution correlated well (at $p < 0.01$) with OM (*0.926*) and C/N ratio (*0.960*). A strong negative correlations (at $p < 0.05$) were also calculated between the GI and the EC (−*0.753*), OM (−*0.772*), C/N ratio (−*0.736*) and the CO_2 evolution (−*0.797*). However, it appears that the use of the parameters such as the EC, C/N ratio and OM is not sufficient for determination of both the stability and maturity of rice straw compost without HTT. For example, compost had the GI as high as an indicative of mature compost but resulted in the high CO_2 evolution, which is indicative of unstable compost. Therefore, conducting respirometric test is also necessary in order to ensure an adequate evaluation of stability and maturity of rice straw compost without HTT.

4. Conclusion

Bin-scale composting of rice straw following the pilot-scale of HTT was performed in order to adequately evaluate the novel HTT technology in enhancing stability and maturity of rice straw compost. According to the results, the HTT (180 °C, 1.0 MPa) can efficiently enhance rice straw compost process. The compost product can be considered stable and adequate for field application after 6 weeks. Furthermore, the compost end product is like free of weeds, pests and pathogens because of 'sterilization' during the pretreatment process. However, compost with HTT may prove phytotoxic if used as growing media for EC sensitive plants.

References

Agbor, V.B. et al., 2011. Biomass pretreatment: fundamentals toward application. Biotechnol. Adv. 29, 675–685.

Ahmad, Z., Kai, H., Harada, T., 1969. Factors affecting immobilization and release of nitrogen in soil and chemical characteristics of the nitrogen newly immobilized. Soil Sci. Plant Nutr. 15 (6), 252–258.

CCQC (The California Compost Quality Council), 2001. Compost Maturity Index. Nevada, CA, USA.

FAO (Food and Agriculture Organization of the United Nations), 2013. FAOSTAT. Available at: http://faostat3.fao.org/faostat-gateway/go/to/home/E (Verified on 15.10.2013).

Gadde, B., Bonnet, C., Menke, C., Garivait, S., 2009. Air pollutant emissions from rice straw open field burning in India, Thailand and the Philippines. Environ. Pollut. 157, 1554–1558.

Goyal, S., Sindhu, S.S., 2011. Composting of rice straw using different inocula and analysis of compost quality. Microbiol. J. 1 (4), 126–138.

Guo, R. et al., 2012. Effect of aeration rate, C/N ratio and moisture content on the stability and maturity of compost. Bioresour. Technol. 112, 171–178.

Hase, T., Kawamura, K., 2012. Evaluating compost maturity with a newly proposed index based on a germination test using Komatsuna (*Brassica rapa* var. *peruviridis*) seeds. J. Mater. Cycles Waste Manag. 14 (3), 220–227.

Haug, R.T., 1993. The Practical Handbook of Compost Engineering. Lewis Publishers, Boca Raton, ISBN 0873713737.

Hosseini, S.M., Aziz, H.A., 2013. Evaluation of thermochemical pretreatment and continuous thermophilic condition in rice straw composting process enhancement. Bioresour. Technol. 133, 240–247.

Insam, H., de Bertoldi, M., 2007. Microbiology of composting process. In: Diaz, L.F., de Bertoldi, M., Bidlingmaier, W., Stentiford, E. (Eds.), Compost Science and Technology. Waste Management Series. Elsevier Science, p. 26.

Jiang, T., Schuchardt, F., Li, G.X., Guo, R., Zhao, Y.Q., 2011. Effect of C/N ratio, aeration rate and moisture content on ammonia and greenhouse gas emission during the composting. J. Environ. Sci. 23 (10), 1754–1760.

Jimenez, E.I., Garcia, V.P., 1989. Evaluation of city refuse compost maturity: a review. Biol. Waste. 27, 115–142.

Kluczek-Turpeinen, B., 2007. Lignocellulose degradation and humus modificationby the fungus *Paecilomyces inflatus*. Acad. Diss. Microbiol., University of Helsinki, Helsinki.

Komilis, D.P., Ham, R.K., 2003. The effect of lignin and sugars to the aerobic decomposition of solid wastes. Waste Manag. 23, 419–423.

Komilis, D., Kletsa, C., 2012. Static respiration indices to investigate compost stability: effect of sample weight and temperature and comparison with dynamic respiration indices. Bioresour. Technol. 121, 467–470.

Kuwatsuka, Sh., Tsutsuki, K., Kumada, K., 1978. Chemical studies on soil humic acids: I. Elemental composition of humic acids. Soil Sci. Plant Nutr. 24 (3), 337–347.

Malherbe, S., Cloete, T.E., 2002. Lignocellulose biodegradation: fundamentals and applications. Rev. Environ. Sci. Biotechnol. 1, 105–114.

Marumoto, T., Kai, H., Yoshida, T., Harada, T., 1977. Chemical fractions of organic nitrogen in acid hydrolysates given from microbial cells and their cell wall substances and characterization of decomposable soil organic nitrogen due to drying. Soil Sci. Plant Nutr. 23 (2), 125–134.

Mondini, C., Dell'Abate, T.M., Leita, L., Benedetti, A., 2003. An integrated chemical, thermal, and microbiological approach to compost stability evaluation. J. Environ. Qual. 32, 2379–2386.

Mueller, S.A., Anderson, J.E., Wallington, T.J., 2011. Impact of biofuel production and other supply and demand factors on food price increases in 2008. Biomass Bioenerg. 35, 1623–1632.

Nakhshiniev, B., Gonzales, H.B., Yoshikawa, K., 2012. Hydrothermal treatment of date palm lignocellulose residue for organic fertilizer conversion: effect on cell wall and aerobic degradation rate. Compost Sci. Util. 20 (4), 245–253.

Ndegwa, P.M., Hristov, A.N., Arogo, J., Sheffield, R.E., 2008. A review of ammonia emission mitigation techniques for concentrated animal feeding operations. Biosyst. Eng. 100, 453–469.

Silva, M.E.F., Lemos, L.T., Bastos, M.M.S.M., Nunes, O.C., 2013. Recovery of humic-like substances from low quality composts. Bioresour. Technol. 128, 624–632.

Tang, J.C., Shibata, A., Zhou, Q., Katayama, A., 2007. Effect of temperature on reaction rate and microbial community in composting of cattle manure with rice straw. J. Biosci. Bioeng. 1044, 321–328.

Thomsen, M.H., Thygesen, A., Thomsen, A.B., 2009. Identification and characterization of fermentation inhibitors formed during hydrothermal treatment and following SSF of wheat straw. Appl. Microbiol. Biotechnol. 83, 447–455.

Tiquia, S.M., Tam, N.F.Y., 1998. Elimination of phytotoxicity during co-composting of spent pig-manure sawdust litter and pig sludge. Bioresour. Technol. 65, 43–49.

Tiquia, S.M., Tam, N.F.Y., Hodgkiss, I.J., 1996. Microbial activities during composting of spent pig-manure sawdust litter at different moisture contents. Bioresour. Technol. 55 (3), 201–206.

Van Soest, P.J., 2006. Review - rice straw, the role of silica and treatments to improve quality. Anim. Feed Sci. Tech. 130, 137–171.

Wang, P. et al., 2004. Maturity indices for composted dairy and pig manures. Soil Biol. Biochem. 36, 767–776.

Wichuk, K.M., McCartney, D., 2010. Compost stability and maturity evaluation: a literature review. Can. J. Civ. Eng. 37 (11), 1505–1523.

Yadvinder-Singh, Bijay.-Singh., Timsina, J., 2005. Crop residue management for nutrient cycling and improving soil productivity in rice- based cropping systems in the tropics. Adv. Agron. 85, 269–470.

Zucconi, F., de Bertoldi, M., 1987. Compost Specification for the Production and Characterization of Compost from Municipal Solid Waste. In: de Bertoldi, M., Ferranti, M.P., L'Hermite, P., Zucconi, F. (Eds.), Compost Production Quality and Use. Elsevier, Applied Science, pp. 30–50.

Zucconi, F., Pera, A., Forte, M., De Bertoldi, M., 1981. Evaluating Toxicity of Immature Compost. Biocycle. 22, 54–57.

Zucconi, F., Monaco, A., Forte, M., Beritodi, M., 1985. Phytotoxins during the stabilization of organic matter. In: Gasser, J.K.R. (Ed.), Composting of Agricultural and other Wastes. Elsevier, London, pp. 73–86.