Waste Management xxx (2016) xxx–xxx

Contents lists available at ScienceDirect

Waste Management

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

Analysis of volatile organic compounds in compost samples: A potential tool to determine appropriate composting time

Fengxiang Zhu [a], Zaifa Pan [b], Chunlai Hong [a], Weiping Wang [a], Xiaoyang Chen [a], Zhiyong Xue [a,*], Yanlai Yao [a,*]

[a] Institute of Environment, Resource, Soil and Fertilizer, Zhejiang Academy of Agricultural Sciences, Hangzhou 310021, PR China
[b] College of Chemical Engineering and Materials Science, Zhejiang University of Technology, Hangzhou 310014, PR China

ARTICLE INFO

Article history:
Received 23 March 2016
Revised 12 June 2016
Accepted 13 June 2016
Available online xxxx

Keywords:
Compost
Composting time
Volatile organic compounds
Pig manure
SPME
GC/MS

ABSTRACT

Changes in volatile organic compound contents in compost samples during pig manure composting were studied using a headspace, solid-phase micro-extraction method (HS-SPME) followed by gas chromatography with mass spectrometric detection (GC/MS). Parameters affecting the SPME procedure were optimized as follows: the coating was carbon molecular sieve/polydimethylsiloxane (CAR/PDMS) fiber, the temperature was 60 °C and the time was 30 min. Under these conditions, 87 compounds were identified from 17 composting samples. Most of the volatile components could only be detected before day 22. However, benzenes, alkanes and alkenes increased and eventually stabilized after day 22. Phenol and acid substances, which are important factors for compost quality, were almost undetectable on day 39 in natural compost (NC) samples and on day 13 in maggot-treated compost (MC) samples. Our results indicate that the approach can be effectively used to determine the composting times by analysis of volatile substances in compost samples. An appropriate composting time not only ensures the quality of compost and reduces the loss of composting material but also reduces the generation of hazardous substances. The appropriate composting times for MC and NC were approximately 22 days and 40 days, respectively, during the summer in Zhejiang.

1. Introduction

Large amounts of manure are produced each year around the world, including more than 2 billion tons of animal manure produced in China alone (Lin et al., 2012). Composting is a sustainable option for manure management. Organic matter is decomposed, mineralized, humified, harmlessly treated, and reached a stable level during composting. Considerable amounts of effective nitrogen, phosphorus and potassium are generated. Humic-like substances and some new small molecular organic materials are synthesized during the process. Moreover, pathogenic microorganisms, eggs, weed seed and substances harmful to crops are effectively eliminated or killed. Maturity indicators determine the degree of maturity of compost, and these include physical parameters, chemical parameters, biological activity, etc. (Raj and Antil, 2011; Shen et al., 2012). The degree of compost maturity is based on whether there was flora and fauna damage during composting. Generally, longer compost times result in higher compost maturity. However, many studies have shown that large amounts of harmful gases are produced during the composting process, including nitrogen- and sulfur-based compounds, volatile fatty acids, hydrocarbons, trepans, esters, ethers, alcohols, and aldehydes/ketones (Nasini et al., 2016; Smet et al., 1999; Wang et al., 2012). Volatile organic compounds have a warming potential approximately 2000 times higher than CO_2 (Nasini et al., 2016). Therefore, determining an appropriate composting time that reduces the production of harmful gases is a question worth studying and the focus of environmental protection issues.

There have been many previous studies of volatile organic compounds. Currently, research methods that consider volatile organic compounds include nuclear magnetic resonance (NMR) spectroscopy and gel permeation chromatography. HS-SPME followed by GC/MS (HS-SPME-GC–MS) was developed to detect volatile components during composting. Most reports that have used HS-SPME-GC–MS to study volatile organic compounds during composting have mainly focused on the analysis of individual compost samples and the total amount of volatile organic compounds

* Corresponding authors at: Institute of Environment, Resource, Soil, and Fertilizer, Zhejiang Academy of Agricultural Sciences, Hangzhou 310021, PR China.

E-mail addresses: xzyhjwsw@126.com (Z. Xue), yaoyl0679@hotmail.com (Y. Yao).

http://dx.doi.org/10.1016/j.wasman.2016.06.021
0956-053X/

in the entire composting process for online monitoring. There are few reports on specific compounds and the analysis of volatile organic compounds during the whole composting process (Li and Huang, 2006; Nasini et al., 2016; Shen et al., 2012; Tiquia and Tam, 1998). HS-SPME-GC–MS has strong analytical capabilities for volatile organic substances and has qualitative and quantitative analysis applications in medical (Gentili et al., 2004; Kamysek et al., 2011), environmental (Higashikawa et al., 2013; Kotowska et al., 2012; Menendez et al., 2004), agricultural (Soto et al., 2015; Sun et al., 2015; Zhang et al., 2010), micro-organism (Stoppacher et al., 2010; Strobel et al., 2008), soil (Durovic et al., 2012; Eriksson et al., 2001), water (Ma et al., 2012; Martínez et al., 2013; Morales et al., 2012), cosmetics (Ortiz and Tena, 2006; Yang et al., 2010), and food safety fields (Sang et al., 2013; Silva et al., 2015; Tait et al., 2014).

In this study, changes in the main volatile compounds during composting were studied, and the main parameters affecting the micro-extraction process, including the type of fiber coating, extraction temperature and time, were optimized. Our goal was to provide a scientific basis for selecting a suitable composting time through observing changes in volatile organic substances produced during the composting process using HS-SPME-GC–MS.

2. Methods

2.1. Materials and instruments

Commercial, manual SPME holders and fibers coated with 100 μm PDMS, 65 μm polydimethylsiloxane/polydivinylbenzene PDMS/DVB and 75 μm CAR/PDMS were purchased from Supelco (Bellefonte, PA, USA). The fibers were conditioned by heating in the injection port of the GC according to the manufacturer. A heating block thermostat C-MAG HS4 (IKA company, Germany) was used for temperature control of HS-SPME extraction.

All analyses were performed by placing 1.5 g samples into 15 ml clear glass vials sealed with PTFE septum and bored aluminum caps. The GC/MS analysis was carried out on a GC/MS system [ThermoFinnigan (Austin, TX, USA), trace DSQ] operating in electron impact (EI) mode at 70 eV. A fused-silica capillary column (30 m × 0.25 mm inner diameter) coated with 50% diphenyl–50% dimethylpolysiloxane and with a 0.25 μm film thickness (CP-Sil 24 CB) was used. The carrier gas was helium at a flow rate of 1 ml/min, with a split ratio of 1/15. An initial temperature was set to 40 °C for 2 min followed by an increase in the column temperature to 100 °C at a rate of 5 °C min^{-1}. The temperature was then increased to 250 °C at a rate of 10 °C min^{-1} and maintained at this temperature for 5 min. The transfer line temperature was set at 250 °C. SPME desorption was performed in the GC/MS injector, and the desorption temperature and time were set at 250 °C and 5 min, respectively. Samples were analyzed by full scan MS from 40 to 500 amu. The peaks in the resulting chromatograms were identified through direct comparison to a commercially available mass spectra database using the dedicated library searching system together based on the interpretations of their mass spectral fragmentation patterns.

2.2. Composting experiment

The composting experiment was performed from May 23rd to August 25th in Zhejiang. Two composting treatments were designed, namely, maggot-treated compost (MC) and natural compost (NC). For MC, first, about eighteen million neonate maggots (<24 h after hatch) were added to 1.8 tons of pig manure flatly piled to an approximate thickness of 7 cm in three large cement trays (7.3 × 2.3 × 0.2 m). Second, late instar maggots were harvested on day 7, and all the manure residue from the trays was placed in a peak-shaped pile (4.5 m in length, 2.2 m in width, and 0.8 m in height) in a rainproof workshop without walls and covered with a plastic film for 24 h to kill the residual maggots, after which it was allowed to compost. Fig. 1 showed the performance of the composting treatment for MC (Fig. 1). For NC, a natural compost was constructed via the same method, using 1.8 tons of manure composted for 7 days in three trays without the addition of maggot inoculum. Then, all the manure residue from the trays was placed in a peak-shaped pile and covered with plastic film for 24 h to kill any naturally developed maggots, after which it was allowed to compost. Both composts were turned upside down every 3 days for the first month and every 5 days thereafter. This process lasted 12 weeks when both composting temperature reduced to near room's. Three 1 kg samples were randomly taken from each tray daily during the first stage and from MC or NC at 40 cm below the surface at intervals of 3–6 days during the second stage. All samples were preserved at −10 °C prior to analysis.

2.3. Optimization of SPME conditions

SPME conditions were optimized on a GC instrument equipped with flame ionization detection (FID, Thermo Scientific (Milan, Italy), Trace GC Ultra) by analyzing the NC sample composted for 39 days. First, the types of fiber (100 μm PDMS, 65 μm PDMS/DVB, and 75 μm CAR/PDMS) were examined. Second, the extraction was optimized for temperature (50, 60, 70 and 80 °C) and then for time (20, 30, 40 and 50 min). The desorption time was set at 5 min. Optimal conditions were determined by achieving the maximum response based on the summation of the analytical peak area.

2.4. SPME conditions of samples

The type of fiber was 75 μm CAR/PDMS, the extraction temperature was 60 °C, and the time was 30 min.

3. Results and discussion

3.1. Optimization of SPME conditions

3.1.1. Choice of fiber

The amount and type of extracted compound depend mainly on the partition coefficient of the analyte between the fiber coating and the sample matrix, and therefore depend on the polarity and thickness of the fiber coating. Three commercially available fibers (100 μm PDMS, 65 μm PDMS/DVB, and 75 μm CAR/PDMS) were evaluated concerning their extraction efficiencies. Extractions were performed by exposing the fibers to the headspace of the sample for 30 min at 60 °C. The chromatogram obtained from the 75 μm CAR/PDMS fiber showed a high extraction efficiency (Fig. 2), and this fiber was selected for further experiments because the compost consists of different polar compounds, and the CAR/PDMS fiber is capable of extracting both polar and non-polar compounds.

3.1.2. Optimization of the extraction temperature

The extraction temperature plays an important role in the absorption of analytes on the fiber because it influences the rates of mass transfer. Different temperatures (50, 60, 70 and 80 °C) were tested for extraction efficiency (Fig. 3). After the extraction process, the analyte was thermally desorbed into the GC injector port at 250 °C for 5 min. The summation of the peak area increased as temperature increased from 50 °C to 60 °C, and decreased when the temperature further increased to 70 and 80 °C (Fig. 4). Moreover, too high a temperature may result in the loss of fiber-coating components. To directly view the influence of the peak areas of the

Please cite this article in press as: Zhu, F., et al. Analysis of volatile organic compounds in compost samples: A potential tool to determine appropriate composting time. Waste Management (2016), http://dx.doi.org/10.1016/j.wasman.2016.06.021