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Chemical and spectroscopic characterization of water extractable organic matter during vermicomposting of cattle dung

Baoyi Lv, Meiyan Xing *, Jian Yang, Wensheng Qi, Yongsen Lu

Key Laboratory of Yangtze River Water Environment , Ministry of Education, State Key Laboratory of Pollution Control and Resources Reuse, College of Environmental Science and Engineering, Tongji University, Shanghai 200092, China

HIGHLIGHTS

- Vermicomposting degraded the protein-like groups while increased the humic acid-like compounds in the WEOM.
- Fluorescence regional integration (FRI) can reveal the transformation and humification process during the vermicomposting.
- WEOM is very useful to monitor the organics transformation and assess the maturity in the vermicomposting.

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ABSTRACT

This work illustrated the characteristics and transformation of water extractable organic matter (WEOM) during vermistabilization (*Eisenia fetida*) of cattle dung by means of chemical and spectroscopic methods. The independent experiment conducted in triplicate was sampled at the 0, 7, 14, 21, 35, 60 and 90 days. Results showed that the DOC kept steady around 2.7 g kg^{-1} after day 60 and the DOC/DON ratio decreased from 19.77 to 5.26 till the end of vermicomposting. On the other hand, vermicomposting decreased the aliphatic, proteinaceous, carbohydrates components and increased the aromaticity and oxygen-containing functional groups in the WEOM. Moreover, fluorescence spectra and fluorescence regional integration (FRI) results indicated that protein-like groups were degraded and fulvic and humic acid-like compounds were evolved during the vermicomposting process. In all, this study suggested the suitability of WEOM for monitoring the organics transformation and assessing the maturity in the vermicomposting.

1. Introduction

In China, the intensification of cattle breeding has resulted in an increase in the production of biodegradable organic wastes, which need to be efficiently recycled due to the environmental problems associated with their indiscriminate application to agricultural fields (Bernal et al., 2009). Vermicomposting is a popular technique characterized by the combined action of earthworms and microorganisms, thereby accelerating the stabilization of organic matter and greatly modifying its physical and biochemical properties (Aira et al., 2002; Lazcano et al., 2008). This method is easy to operate, odorless, cost effective, pathogen free and environmental friendly (Khwairakpam and Bhargava, 2009; Lazcano et al., 2008; Li et al., 2011). Additionally, the significant higher nitrogen, phosphorus and humic contents in the end products of vermicomposting can help to improve soil fertility and stimulate plant growth (Arancon et al., 2005).

Although earthworms accelerate the vermicomposting process by modifying the substrate and stimulating the microbial metabolic activity (Lazcano et al., 2008), the biochemical degradation of the organic matter is carried out by the microorganisms, either living free and/or dwell in the earthworm gut (Aira et al., 2002; Benitez et al., 1999). Since most of the organic matter is transformed by microorganisms in the water-soluble phase (Caricasole et al., 2010), WEOM stands for the most active fraction of the organic waste. Moreover, WEOM was most subject to change and it could directly reflect the organic matter transformation processes (Said-Pullicino et al., 2007; Caricasole et al., 2010). Consequently, the composition of WEOM has been suggested as a better indicator

Abbreviations: WEOM, water extractable organic matter; DOC, dissolved organic carbon; DTN, dissolved total nitrogen; DON, dissolved organic nitrogen; DOC/DON, the quotient of dissolved organic carbon and dissolved organic nitrogen; FCD, fresh cattle dung; $SUVA_{254}$, specific UV absorption at 254 nm; FRI, fluorescence regional integration; FT-IR, Fourier transform infrared; EEM, excitation–emission matrix; E_4/E_6, the quotient of absorbance at 465 and 665 nm; GFC, gel filtration chromatography; SFI, specific fluorescence intensity.

* Corresponding author. Tel./fax: +86 21 65984275.
E-mail addresses: xingmeiyan@tongji.edu.cn, xmy5000@163.com (M. Xing).

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of stability for the organic matter than that of the solid phase (Caricasole et al., 2010). For example, the evolution of WEOM extracted from aerobic composting has been regarded as a good indicator of the overall transformation and maturity of organic matter (Said-Pullicino et al., 2007). Therefore, studying the changes of WEOM is very helpful to understand the bio-stabilization process.

Previous studies on vermicomposting focused on the stabilization of various solid wastes, the application of vermicompost as a soil organic amendment or fertilizer and the earthworm population dynamics (Garg et al., 2006; Aira et al., 2007; Renuka Gupta, 2008). In addition, the characteristics of WEOM in the initial and final vermicomposts of sewage sludge and cow dung were also reported (Xing et al., 2012). However, the chemical and spectroscopic behaviors of WEOM during vermicomposting process have not been fully understood.

WEOM consists of a heterogeneous mixture of compounds with different molecular sizes and complexities, ranging from simple sugars and organic acids to complex proteins and humic colloids (Traversa et al., 2010). An integration of various techniques is a prevalent way to characterize the features of WEOM. Many indices, including dissolved organic carbon (DOC), specific ultra-violet absorbance (SUVA), and fluorescence excitation–emission matrix (EEM) spectroscopy etc., were used to investigate the properties of WEOM (Shao et al., 2009; He et al., 2011a). DOC can act as a general indicator of WEOM, while $SUVA_{254}$, E_4/E_6 and Fourier transform infrared spectra (FT-IR) can provide more detailed information on WEOM, such as the aromaticity and humification degree of derived compounds (Weishaar et al., 2003; Saadi et al., 2006; He et al., 2011a). Furthermore, fluorescence excitation–emission matrix (EEM) spectroscopy combining with fluorescence regional integration (FRI) technique can provide an overall view of fluorescent properties of WEOM in a selected spectral range, which has been employed in structural identification and stability assessment of organic wastes (Zhu et al., 2011).

Keeping in light of the above facts, we hypothesized that the WEOM could show obvious changes during the vermicomposting process and be also very helpful to understand the stabilization process in the vermicomposting. Therefore, the aims of this study were to examine the chemical and spectroscopic characteristics of WEOM at different stages during vermicomposting of cattle dung by using various analytical approaches, as well as to investigate the transformation of WEOM and the vermicompost stability based on the WEOM information obtained.

2. Methods

2.1. Vermicomposting process and sampling

The fresh cattle dung (FCD) was obtained from a cattle farm in Pudong district, Shanghai, China. In order to avoid the damage of the high moisture content and anaerobic fermentation to earthworms, the cattle dung was naturally dried under sunlight for 1 week with periodic turning over before used. *Eisenia fetida* maintained in the laboratory with cattle dung as culturing substrate were randomly picked from several stock cultures. *E. fetida* was chosen because it had wide tolerance of environmental variables and had been extensively applied in the vermicomposting of organic matter such as animal manures (Khwairakpam and Bhargava, 2009; Suthar, 2009).

A lab-scale vermicomposting experiment was carried out in plastic containers (40 cm diameter × 25 cm depth) with 2 kg cattle dung (dry basis) as substrate, followed by manually turning over every 24 h for 7 days to eliminate toxic volatile substances. Subsequently, 250 non-clitellated earthworms (*E. fetida*) with an average weight of 200–250 mg per unit were inoculated into the container. Triplicate vermireactors were established in this study. Moisture content was maintained at 80 ± 10% by periodic sprinkling of distilled water during the whole process. The plastic containers were covered with perforated lids and settled in dark with temperature kept at 23 ± 1 °C. Homogenized samples (about 50 g wet basis) were collected at 0, 7, 14, 21, 35, 60 and 90 days of each experiment. Subsamples were air-dried, ground to pass through a 20 meshes sieve and stored in a desiccator for further analysis.

2.2. Extraction of WEOM

The extraction of WEOM from vermicompost samples was performed in a horizontal shaker with deionized water (solid to water ratio of 1:20, w/v) for 24 h at room temperature. The suspensions were centrifuged at 10,000*g* for 10 min and filtered through a 0.45-μm pore-size membrane filter (Said-Pullicino et al., 2007). Part of the extract was freeze-dried and placed in sealed plastic containers.

2.3. WEOM analysis

2.3.1. Organic matter contents analysis

Dissolved organic carbon (DOC) and dissolved total nitrogen (DTN) of the extracts were measured by a TOC-VCPN analyzer (Shimadzu, Japan). The dissolved organic nitrogen (DON) content was calculated as (DTN) − (NH_4^+–N + NO_3^-–N). UV absorption at 254 nm of the WEOM was measured using a UV 765 spectrophotometer (Shanghai Precision & Scientific Instrument Co., Ltd., Shanghai, China). Before measurement, all solutions were diluted to DOC concentrations <10 mg L^{-1}. The specific UV absorption ($SUVA_{254}$) was determined by normalizing UV absorbance at 254 nm to the corresponding concentration of dissolved organic carbon. The E_4/E_6 was given as the ratio of absorbance which measured at 465 and 665 nm.

2.3.2. FT-IR spectra

The Fourier transform infrared (FT-IR) spectra can reveal the major functional groups of organic matters and predict the major components (He et al., 2011a). In the present study, about 1 mg freeze-dried WEOM sample was mixed thoroughly with 200 mg of dried spectrometry grade KBr and pressed to a pellet under reduced pressure. The pellet was immediately measured after preparation using a Nicolet 5700 FT-IR spectrophotometer (Madison, WI) (Xing et al., 2011). The spectra were recorded in the range of 4000–400 cm^{-1} with a 2 cm resolution.

2.3.3. GFC analysis

Molecular weight distribution of the WEOM was analyzed by a Gel Filtration Chromatography analyzer (LC-10ADVP, Shimadzu, Japan) using TSKgel G4000PWXL column (TOSOH, Japan) equipped with RID-10A detector on elution with aqueous Milli-Q water. Polyethylene glycol with molecular weight (1,169,000; 771,000; 128,000; 11,840; 4020; 620 and 194 Da) was used for the calibration standards (Shao et al., 2009). 50 μL sample was injected into the column and the flow rate was 0.5 mL min^{-1}. The elution of elements at each time interval was collected by an automatic fraction collector and automatically analyzed using UV spectroscopy and dissolved organic matter analyzer (Xing et al., 2011).

2.3.4. Fluorescence spectra analysis

Fluorescence EEM spectra was recorded using an F-4600 (Hitachi, Japan) fluorescence spectrophotometer in a clear quartz cuvette. Emission and excitation slits were set at a 5-nm band width, and a scan speed of 12,000 nm min^{-1} was selected. The EEM spectra were recorded by scanning the emission wavelength over the range 250–600 nm at 2 nm increments, while the