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Technical Note

Towards understanding the stabilization process in vermicomposting using PARAFAC analysis of fluorescence spectra

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HIGHLIGHTS

- PARAFAC can be used to monitor the organic transformation in vermicomposting.
- Vermicomposting degrade protein-like while increase humic acid-like compounds.
- The initial feedstock had impact on the composition and behavior of WEOM.
- Components 2 and 3 can be used as indicator for maturity.

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ABSTRACT

In this study, fluorescence excitation–emission matrix (EEM) combined with parallel factor analysis (PARAFAC) was employed to trace the behavior of water extractable organic matter and assess the stabilization process during vermicomposting of sewage sludge and cattle dung. Experiments using different mixing ratios of sewage sludge and cattle dung were conducted using *Eisenia fetida*. The results showed that vermicomposting reduced the DOC, DOC/DON ratio and ammonia, while increased the nitrate content. A three-component model containing two humic-like materials (components 1 and 2) and a protein-like material (component 3) was successfully developed using PARAFAC analysis. Moreover, the initial waste composition had a significant effect on the distribution of each component and the addition of cattle dung improved the stability of sewage sludge in vermicomposting. The PARAFAC results also indicated that protein-like materials were degraded and humic acid-like compounds were evolved during vermicomposting. Pearson correlation analysis showed that components 2 and 3 are more suitable to assess vermicompost maturity than component 1. In all, EEM–PARAFAC can be used to track organic transformation and assess biological stability during the vermicomposting process.

1. Introduction

Human activities generate large amounts of biodegradable organic waste, the treatment and disposal of which is one of the most critical environmental issues in the world (Vieyra et al., 2009). Vermicomposting is an alternative technique that uses the synergistic action of earthworms and microorganisms to greatly modify the physical and biochemical properties of the organic waste and accelerate the stabilization of organic matter (OM) (Lazcano et al., 2008). This method is simple, odorless, cost-effective, pathogen-free, and environmentally friendly (Lazcano et al., 2008; Khwairakpam and Bhargava, 2009), and has been considered as an option in the hierarchy of integrated solid waste management (Sharholy et al., 2008).

The evaluation of OM transformation and stability during composting or vermicomposting is very important to control the efficiency of the process (Benitez et al., 1999; Wei et al., 2007). As most of the OM is transformed by microorganisms in the water-soluble phase, water extractable organic matter (WEOM) is most subject to change and can directly reflect the OM transformation processes (Said-Pullicino et al., 2007a; Caricasole et al., 2010). Furthermore, the evolution of WEOM extracted from composting and vermicomposting has been regarded as a good indicator of the overall transformation and maturity of OM (Marhuenda-Egea et al., 2007; Zhu et al., 2011; Lv et al., 2013). Therefore, studying changes in WEOM is helpful not only for understanding of stabilization of organic wastes, but also for evaluation of biological stability.

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Fluorescence excitation–emission matrix (EEM) is a powerful tool for characterizing heterogeneous WEOM by providing an overall view of the composition and properties of WEOM in a selected spectral range (Henderson et al., 2009; Murphy et al., 2011). Because of its high sensitivity and simplicity, EEM has been widely used to study the behavior and transformation of OM in natural and engineered systems (Henderson et al., 2009; Stedmon et al., 2011). The application of fluorescence spectroscopy to trace the transformation of organic waste and assess maturity in composting and vermicomposting is also well documented (Marhuenda-Egea et al., 2007; Xing et al., 2012; Lv et al., 2013). However, because of the complexity of WEOM, fluorophores overlap in the EEM spectra, which often makes these spectra difficult for analysis (Yu et al., 2010a; Xing et al., 2012; Lv et al., 2013). Moreover, the commonly used "peak picking" technique is mainly dependent on the analysis of relevant peak locations and intensities. This method neglects a large quantity of data in EEM spectra and lacks the ability to capture the heterogeneity of samples (Ohno et al., 2007; Wu et al., 2012a).

Parallel factor analysis (PARAFAC) is a multivariate chemometric method that can decompose EEMs into various individual fluorescent components, thereby reducing the interference among fluorescent compounds (Stedmon et al., 2003; Stedmon and Bro, 2008). The combination of EEM and PARAFAC can provide a more accurate quantification of the composition and behavior of dissolved organic matter (DOM) (Wu et al., 2011). This new approach has been successfully used to evaluate the environmental dynamics (composition, source and fate) of DOM in diverse natural ecosystems (Stedmon et al., 2003; Singh et al., 2010). Fluorescence spectroscopy with PARAFAC analysis has also been applied in engineered systems. Lv et al. (2009) reported that PARAFAC was useful for tracking the fluorescent DOM fraction in landfill leachates. Furthermore, the results of Yu et al. (2010a), Wu et al. (2012a) also indicated that fluorescence EEM combined with PARAFAC could be employed to trace the properties and behavior of WEOM from landfilled municipal solid waste (MSW) and assess the biological stability of compost and MSW. However, to the best of our knowledge, there is no study to evaluate the transformation and stabilization of OM during vermicomposting process using the EEM–PARAFAC approach.

In light of the above facts, we hypothesize that fluorescence EEM combined with PARAFAC analysis may be suitable for monitoring changes in WEOM and tracking the stabilization process during vermicomposting. Therefore, this study aimed to: (1) obtain the chemical and fluorescence characteristics of the WEOM extracted from vermicomposting and (2) investigate the transformation of WEOM and assess the stabilization process during vermicomposting using EEM–PARAFAC.

2. Materials and methods

2.1. Vermicomposting process and sampling

Sewage sludge was obtained from a municipal wastewater treatment plant in Shanghai, China. Cattle dung was purchased from a farm in Pudong New Area, Shanghai, China. The raw materials were naturally dried under sunlight for 1 wk in order to avoid damages to earthworms as a result of the high moisture content and anaerobic fermentation. Specimens of *Eisenia fetida* maintained in the laboratory were randomly picked from several stock pots. This species was chosen because it has a wide tolerance to environmental variables and has been extensively employed in the treatment of various organic wastes (Khwairakpam and Bhargava, 2009).

Five circular plastic containers (15 cm diameter × 14 cm depth) were filled with 200 g feed mixture (dry weight) containing different proportions of sewage sludge and cattle dung (T_1, 100% + 0%; T_2, 75% + 25%; T_3, 50% + 50%; T_4, 25% + 75%; T_5, 0% + 100%). In addition, sawdust (30 g dry weight) was added to the feed mixture as a bulking material. The mixtures were manually turned over every 24 h for 14 d to avoid the damage of volatile toxic substances to earthworms. Subsequently, 25 non-clitellated earthworms with an average weight of 200–250 mg per unit were inoculated into each container. Three replicates were conducted for each treatment. The moisture content was maintained at 70 ± 10% by periodic sprinkling of distilled water during the whole process. The plastic containers were covered with perforated lids and placed in dark room with the temperature maintained at 23 ± 2 °C. Homogenized samples (about 50 g wet basis) were collected periodically up to 120 d. Subsamples were air-dried, ground to pass through a 1-mm sieve, and stored in a desiccator for further analysis.

2.2. Extraction of WEOM

Extraction of WEOM from the 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 8000 rpm for 10 min and filtered through a 0.45 μm pore-size membrane filter (Said-Pullicino et al., 2007b).

2.3. WEOM analysis

2.3.1. Chemical analysis

DOC and dissolved total nitrogen (DTN) of the extracts were measured using a TOC–VCPN analyzer (Shimadzu, Japan). The concentrations of ammonia and nitrate were determined following the standard procedure (APHA, 1998). The DON was calculated as the difference between DTN and inorganic-N.

2.3.2. Fluorescence spectra analysis

Fluorescence EEM spectra were recorded with an F-4600 (Hitachi, Japan) fluorescence spectrophotometer in a clear quartz cuvette. Emission and excitation slits were set at 5 nm band width, and the scan speed was fixed at 12 000 nm min^{-1}. The EEM spectra were collected by scanning the emission wavelength over the range 250–600 nm in 2 nm increments, while the excitation wavelength increased gradually from 200 to 500 nm in 10 nm increments (Yu et al., 2010b). The voltage of the photomultiplier tube was set at 600 mV for low level light detection. The temperature of the samples was maintained at room temperature (20 °C) during the analyses (Yu et al., 2010b).

2.4. PARAFAC analysis

A total of 40 EEMs (20 samples × 2 repetitions) were used to generate the dataset. The PARAFAC modeling was performed using MATLAB 2010b (Mathworks, Natick, MA) using the DOMFluor toolbox (http://www.models.kvl.dk/), following the procedure described by Stedmon and Bro (2008). Several preprocessing steps were used to correct and standardize the EEM landscape prior to PARAFAC modeling. First, the EEM of a control Milli-Q water was subtracted from each EEM from the studied samples to remove the lower-intensity Raman scatter lines; secondly, the higher Rayleigh and Raman scatters were corrected using the method recommended by Bahram et al. (2006); thirdly, the EEMs were normalized by dividing the spectra by the corresponding DOC concentration to reduce the effect of varying WEOM concentrations among the samples (Yu et al., 2010b). In addition, excitation wavelengths from 200 to 220 nm were deleted from each EEM because of random data fluctuations. The PARAFAC model was run with non-negativity constraints applied to each dimensions, and two