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Assessment of humification degree of dissolved organic matter from different composts using fluorescence spectroscopy technology

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HIGHLIGHTS

- Eight mature composts from different sources in China were investigated.
- Analyze the characteristics of fluorescence spectroscopy of dissolved organic matter (DOM) among the compost samples.
- Characterize the correlation of fluorescence parameters of DOM.
- Identify humification degree of DOM using hierarchical cluster analysis (HCA) and projection pursuit regression (PPR).

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ABSTRACT

This study was conducted to assess the degree of humification in dissolved organic matter (DOM) from different composts, and their environmental impact after soil amending based on fluorescence measurements (emission, excitation, synchronous scan, and excitation-emission matrix [EEM]). The compost sources studied included dairy cattle manure (DCM), kitchen waste (KW), cabbage waste (CW), tomato stem waste (TSW), municipal solid waste (MSW), green waste (GW), chicken manure (CM), and peat (P). Conventional and EEM fluorescence spectroscopy indicated that the DOM of these composts contained compounds similar in structure but comparisons between conventional fluorescence parameters and fluorescence regional integration of EEM fluorescence spectra showed that the DOM was different in degree of humification. Regression analysis demonstrated significant corrections between major fluorescence parameters. In hierarchical cluster analysis, these composts were clustered into 2 groups and 4 subgroups, and projection pursuit regression analysis further ranked the compost sources as KW, CW, P > CM, DCM, TW, GW > MSW in their degree of humification in DOM.

1. Introduction

Composting is an environmentally friendly and economically viable alternative method for treating solid organic waste, such as municipal solid wastes (MSW) (Wei et al., 2007; Raut et al., 2008) and agricultural residues (Diasa et al., 2010; Yamamoto et al., 2010; Troy et al., 2012). Organic matter is partially transformed into more stable and complex macromolecules in the biological process of composting (Hsu and Lo, 1999). Humification and maturity are essential measures of compost when applied to soils, and numerous studies have been conducted to evaluate changes of these characteristics during composting (Marhuenda-Egea et al., 2007; He et al., 2011). However, few studies have examined the degree of humification in organic matter (dissolved organic matter [DOM], humic acid, etc.) of different composts.

Understanding the characteristic of the DOM formed during composting is important. Because most of the biologic activities occur in solid–liquid interface, changes in DOM during composting reflect transformation progress and compost stability (Said-Pullicino et al., 2007; Gómez-Brandón et al., 2008). After soil amending, the movement of DOM from composts through the soil profile influences the cycling of C and other nutrients and the microbial activities (Cronan et al., 1992). DOM also interacts with a number of inorganic and organic pollutants because of the presence of oxygen-containing and organic aromatic functional groups in its constituents (Plaza et al., 2009). The composition of the organic matter in composting is very complex due to the wide range of chemical compounds and the variety of decomposed and synthesized products (Marhuenda-Egea et al., 2007). In general, the aromatic and alkyl compounds in DOM increase during composting, resulting in an increase degree of humification and stability in mature compost DOM that is more resistant to biodegradation (He et al., 2011). Analysis of DOM usually includes composition, functionalities, and structural, chemical and spectroscopic

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characteristics using various techniques such as elemental assays, Vis, Fourier transform infrared (FTIR), and fluorescence spectra (Chefetz et al., 1998; Provenzano et al., 2001; Fuentes et al., 2006; Marhuenda-Egea et al., 2007; Caricasole et al., 2010; Santos et al., 2010). Specifically, fluorescence spectroscopy is used as a non-destructive tool to quantify composting humification and maturity (Hur et al., 2009). Parameters used to assess the degree of humification in DOM with fluorescence spectra include A_4/A_1, an area ratio of the last quarter (A_4: 570–641 nm) to the first quarter (A_1: 356–432 nm) in emission spectra (Zsolnay et al., 1999), I_{470}/I_{360}, a ratio between the fluorescence intensities at 470 and 360 nm in synchronous-scan excitation spectra (Kalbitz et al., 1999), and $r_{(A,C)}$, a ratio of peak A (fulvic acid-like substances) to peak C (humic acid-like) in Excitation emission matrix (EEM) fluorescence spectroscopy. It also includes fluorescence regional integration (FRI) (Chen et al., 2003) that has been used to quantitatively analyze all wavelength-dependent fluorescence intensity data from EEM spectra (Marhuenda-Egea et al., 2007).

The use of FTIR, Vis and fluorescence spectral techniques to characterize the same sample can generate a large amount of data that can be processed by chemometric methods (Santos et al., 2010). One of the important chemometric methods of data exploration is hierarchical cluster analysis (HCA), which considers the correlation between different variables. HCA allows easier interpretation of the results, and offers alternative analyses of fluorescence characteristics of compost DOM (He et al., 2011). Projection pursuit regression (PPR) is a nonlinear multivariate regression procedure, proposed by Friedman and Stuetzle (1981). Its basic idea is to project high dimension to low dimensional space and tries to find the intrinsic structural information hidden in the high dimensional data. At present it has been applied successfully to tackle some chemical problems (Ghasemi and Zolfonoun, 2013). Although the transformation of DOM during composting has been widely studied, most of the analyses have focused on compositions and structural characteristics of DOM during composting (Marhuenda-Egea et al., 2007; Said-Pullicino et al., 2007), and little has been revealed about the degree of humification in DOM of mature composts from different sources. The objective of this study was to use HCA and PPR to evaluate the degree of humification in DOM from different composts using data obtained through fluorescence spcetroscopy. As a result, some fluorescence parameters suitable for estimating the degree of humification in DOM were tested, the environmental impact of DOM from composts applied to soil was predicted.

2. Materials and methods

2.1. Sample collection and storage

Eight trapezoidal piles were prepared by Shanghai Songjiang Composting Plant, using dairy cattle manure (DCM), kitchen waste (KW), cabbage waste (CW), Tomato stem waste (TSW), MSW, green waste (GW), chicken manure (CM), and peat (P). Each composting pile contained approximately 2 t of raw material (1.5 m high with a 2×3 m base). The piles were turned over by forklift, when necessary, in order to improve the fermentation process. Composting was considered finished when the temperature of the pile became stable and germination index approached 80%, then, approximately 2 kg of samples (Table 1) were collected from mature composts, and stored at 4 °C for analysis of DOM.

2.2. Extraction of DOM

DOM was obtained as described by Said-Pullicino et al. (2007). Briefly, the compost samples were extracted with distilled water (solid to water at 1:10, w/v) for 24 h in a horizontal shaker at room temperature. The suspensions were centrifuged at 10000 rpm for 10 min, filtered through a 0.45 μm membrane filter, and freeze-dried.

2.3. Fluorescence spectroscopy

Fluorescence spectroscopy was recorded using a Perkin–Elmer model LS50B fluorescence spectrophotometer in a clear quartz cuvette. The slit width was 10 nm for both excitation and emission monochromators, and the scan speed was set at 500 nm min^{-1}. Emission spectra were measured over a range of 370–550 nm with excitation wavelength at 360 nm. Excitation spectra were obtained at 300–500 nm using an emission wavelength of 520 nm. Synchronous-scan spectra were acquired over 300–600 nm with a $\Delta\lambda$ of 55 nm (Kalbitz et al., 1999). EEM fluorescence spectra were obtained by subsequently scanning the emission spectra from 250 to 550 nm at 200–490 nm excitation wavelength with 5 nm increments. After regulating the scattering using interpolation in the areas affected by first- and second-order Ravleigh and Raman scatter (Bahram et al., 2006), the FRI technique was adopted for analysis (Chen et al., 2003).

2.4. Multivariate statistical analysis

SPSS version 17.0 was used for multivariate statistical analysis, i.e., correlation analyses, HCA, and PPR.

3. Results and discussion

3.1. Conventional fluorescence spectroscopy

Fluorescence emission spectra of DOM (Fig. 1a) were characterized by a broad band centered around 448 nm for P and 443 nm for CW, and between 436 and 439 nm for other composts. While the wavelength for P was similar to the wavelength of soil fulvic acid (450–460 nm), most of the wavelengths were close to that of compost fulvic acid (about 440 nm) (Provenzano et al., 1998). $f_{450/500}$, also called fluorescence index (FI, the ratio of emission intensity at 450 nm and 500 nm at 370 nm excitation), was initially used to distinguish sources of isolated aquatic fulvic acids (McKnight et al., 2001), but currently also denotes the aromaticity of DOM, i.e., the higher $f_{450/500}$ value is, the lower the aromaticity is. The $f_{450/500}$ varied from 1.81 to 2.55 among different samples (Table 2), suggesting that the organic matter contained in these composts was microbially derived (McKnight et al., 2001; Nam and Amy, 2008). The FI was highest for MSW and GW and lowest for CW and P, with intermediate values for the remaining compost samples.

Fluorescence excitation spectra exhibited a major peak between 390 and 400 nm for all samples, while MSW also showed a second peak at a lower wavelength (around 350 nm) (Fig. 1b). These spectra were similar to the excitation spectra of compost fulvic acid, but the shoulder at the shorter wavelength almost disappeared in soil fulvic acid (Provenzano et al., 1998). The ratio of fluorescence intensity at 436–383 nm (I_{436}/I_{383}) in excitation spectra, proposed by He et al. (2011) as the humification index, varied from 0.63 to 0.95 among the composts (Table 2), lowest for MSW and CM, and highest for KW and GW.

The synchronous-scan fluorescence spectra of DOM exhibited a major peak around 390 nm for all composts, and some samples showed minor peaks or shoulders at longer (around 430 nm for DCW, GW, KW, CW and P, 451 nm for P), or shorter (354 nm for MSW) wavelengths (Fig. 1c). The I_{454}/I_{399} index calculated from the spectra in the synchronous-scan excitation mode acquired