Fluorescence characteristics of molecular weight fractions of dissolved organic matter derived from composts

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ABSTRACT

A study was conducted to determine the fluorescence characteristics of various molecular weight (MW) fractions of dissolved organic matter (DOM) derived from different composts based on fluorescence regional integration (FRI) and parallel factor (PARAFAC) modeling of excitation-emission matrix (EEM) fluorescence spectra. The significant differences in the locations of EEM peaks indicated that there were differences in the molecular structures of the MW >5 kDa fraction and the other fractions. FRI indicated that the degree of humification increased with increasing MW for all of the MW fractions, except for the MW >5 kDa fraction, suggesting that FRI was not suitable for analyzing MW fractions with differences in their molecular structures. PARAFAC modeling resulted in three components for the MW >5 kDa fraction and two components for the other MW fractions. Red-shifting occurred in components 1 (Microbial Humic-like) and 2 (Terrestrial Humic-like) as the MW increased. And component 3 was categorized as a protein-like substance. PARAFAC modeling of the MW fractions can isolate more components and resolve more fluorophores than can DOM analysis.

1. Introduction

Composting is an environmentally friendly and economically viable alternative method for treating solid organic wastes (Wei et al., 2007, 2014a; Troy et al., 2012). Because most of the biological activities occur in the solid–liquid interface, changes in the DOM during composting reflect the progress of the transformation and the compost stability (He et al., 2011). The MW and size of the DOM derived from composts applied to cropland influence the cycling of C and other nutrients as well as the microbial activities in the soil ecosystem (Spaccini et al., 2009).

Analysis of the DOM usually includes the determination of the composition, functionalities, and structural, chemical and spectroscopic characteristics (Chefetz et al., 1998; Provenzano et al., 2001; Santos et al., 2010; He et al., 2011; Wei et al., 2014b). The structures of DOM can reflect the degree of humification and composting process. Furthermore, the fluorescence characteristics is also effective to analyze DOM (Provenzano et al., 2001). Yu et al. (2010) demonstrated that the composting progress was characterized by a degradation of the original tyrosine-like (i.e., Ex/Em = 225–237/309–321 nm; & Ex/Em = 275/310 nm) and tryptophan-like (i.e., Ex/Em = 225–237/340–381 nm; & Ex/Em = 275/340 nm) substances and a formation of the humic-like (i.e., Ex/Em = 300–370/400–500 nm) and fulivc-like (i.e., Ex/Em = 237–260/400–500 nm) substances of samples. In addition, Senesi and Plaza (2007) also suggested that as composting time increases, a decrease of molecular heterogeneity and an increase of aromatic polycondensation, level of conjugated chromophores and humification degree were observed by fluorescence EEM spectra. Therefore, fluorescence EEMs spectra of the DOM from composts could be used as a monitoring tool for assessing the maturity of compost. Specifically, EEM fluorescence spectroscopy has been widely used to characterize DOM derived from different sources (Chen et al., 2003; Singh et al., 2010), and FRI proposed by Chen et al. (2003) has been used as a tool to quantify the EEM spectra

of compost DOM (He et al., 2011, 2014). In FRI, EEM spectra are divided into five regions, and the composition and transformation characteristics of the DOM are evaluated by calculating the relative volume. Additionally, to overcome the difficulty in identifying fluorescent components in DOM, chemometric methods such as PCA (Boehme et al., 2004), HCA (He et al., 2011; Wei et al., 2014b), and PARAFAC (Andersen and Bro, 2003; Singh et al., 2010) have been used. HCA and PCA have unique applications in revealing the structural changes of the DOM in composts that are unable to be observed from fluorescence parameters alone (Zbytniewski and Buszewski, 2005; Wei et al., 2014b). Multivariate analyses have the drawback of not taking full advantage of the information inherent in the EEM spectra, while PARAFAC can segregate a suite of complex EEM landscapes into meaningful spectral components (Andersen and Bro, 2003).

The EEM, in conjunction with PARAFAC (EEM-PARAFAC), has recently been used to characterize the DOM derived from different compost sources (Andersen and Bro, 2003; Singh et al., 2010). Two primary fluorescing groups in DOM have been identified, and they are humic-like and protein-like substances. Humics are a complex mixture of aromatic and aliphatic compounds derived from the decay of organic matter, while protein-like substances are formed as a result of biological activities (Singh et al., 2010). The use of PARAFAC to characterize the fluorescence properties of DOM has been accelerated by the development of a MATLAB-based tutorial and toolbox specifically for the PARAFAC analysis of DOM fluorescence (Stedmon and Bro, 2008; Zhang et al., 2011). However, despite the use of EEM-PARAFAC in assessing the biological transformation of DOM during composting (He et al., 2014), there has been a lack of research other than characterizing the compositions of different MW fractions in DOM derived from different composts using EEM-PARAFAC.

The objective of this study was to quantify the EEM spectra of MW fractions based on FRI and characterize the composition of MW fractions in DOM derived from different composts using EEM-PARAFAC analysis. Furthermore, the use of FRI to quantitate different MW fractions was demonstrated, and the similarities and differences of the components of DOM and its MW fractions analyzed using EEM-PARAFAC were discussed.

2. Materials and methods

2.1. Sample collection and storage

Ten trapezoidal piles of DCM, KW, CW, P, TSW, MSW, GW, CM, S, and MCW were prepared by the Shanghai Songjiang Composting Plant. Composting was considered finished when the temperature of the pile became stable and the germination index approached 80%. Approximately 2 kg of each of the mature composts was collected and stored at 4 °C for analysis of the DOM. Details of the composting and DOM properties were described in previous papers (Wei et al., 2014a, 2014b).

2.2. Extraction of the DOM

Briefly, the compost samples were extracted with distilled water (solid to water ratio of 1:10, w/v) for 24 h in a horizontal shaker at room temperature. The suspensions were centrifuged at 10 000 rpm for 10 min, filtered through a 0.45 μm membrane filter. All samples were stored in the dark at 4 °C before fluorescence spectra analysis.

2.3. Chemical characterization analysis

All chemical analyses were carried out in triplicate and using chemicals of analytical grade. In addition, the methods were determined following the standard procedure (APHA, 1998).

2.4. Ultrafiltration

A TFF system equipped with membrane packages of 1 kDa, and 5 kDa (Pall Corporation) was used to separate fractions of MW <1 kDa, 1 kDa < MW < 5 kDa, and MW > 5 kDa.

2.5. EEM fluorescence spectroscopy

The WEOC of all samples was adjusted to 6.0 mg l^{-1} with distilled water. Fluorescence spectra were recorded using a Hitachi model F-7000 luminescence spectrophotometer. EEM fluorescence spectra were obtained by subsequently scanning the emission spectra from 250 to 550 nm at excitation wavelengths from 200 to 490 nm using 5 nm increments. Raman scattering effects were removed by subtracting a Milli-Q EEM. Finally, the fluorescence intensity was corrected to the area under the Milli-Q water Raman peak (excitation 350 nm) run the same day (Lawaetz and Stedmon, 2009). After the scattering was calibrated using interpolation in the areas affected by first- and second-order Ravleigh and Raman scattering (Bahram et al., 2006), the FRI analysis was conducted (Chen et al., 2003).

2.6. PARAFAC analysis

In this study, all EEM spectra data of each MW fraction comprised a three-dimensional data array (30 samples × 41 Ex × 45 Em). PARAFAC analysis was carried out in Matlab using the DOM Fluor toolbox (Stedmon and Bro, 2008), and split half analysis was used to validate the identified components (Stedmon et al., 2003). The model was constrained to non-negative values. No outlier EEMs were identified during the analysis. Fluorescence components can be separated by PARAFAC. And according to the shape and the location of the peak, the definition of the components identified in this study is based on the previous reports (Cory and Mcknight, 2005; Fellman et al., 2009).

2.7. Multivariate statistical analysis

Statistical analysis was carried out using the software SPSS version 18.0 for Windows (SPSS, Chicago, IL). One-way analysis variance (ANOVA) was used to test the significantly difference of $P_{i, n}$ in the EEM fluorescence spectra of different regions and different MW fractions. Box charts were plotted by Origin 8.0.

3. Results and discussion

3.1. Characteristics of different wastes in composting

The Characteristics of samples at initial and final stage of composting were presented in Table 1.

The properties of samples at initial and final stage of composting are showed in Table 1. The initial pH values of different materials vary from each other. The higher pH values in CM (8.01), DCM (8.07), and MCW (8.23) were caused by higher ammonia concentration in them. However, the final pH values of these composts are not significantly different from each other. Furthermore, there were significant differences in the concentrations of TOC and DOC among all samples at initial as well as final stage of composting. The large variation was a result of the presence of various organic components in these composts. The higher concentrations of TOC and the lower concentrations of DOC mainly occurred in GW, MCW, and TSW, which contained a high distribution of macromolecular organic