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Changes in the chemical characteristics of water-extracted organic matter from vermicomposting of sewage sludge and cow dung

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ABSTRACT

The chemical changes of water-extractable organic matter (WEOM) from five different substrates of sewage sludge enriched with different proportions of cow dung after vermicomposting with *Eisenia fetida* were investigated using various analytical approaches. Results showed that dissolved organic carbon, chemical oxygen demand, and C/N ratio of the substrates decreased significantly after vermicomposting process. The aromaticity of WEOM from the substrates enhanced considerably, and the amount of volatile fatty acids declined markedly, especially for the cow dung substrate. Gel filtration chromatography analysis showed that the molecular weight fraction between 10^3 and 10^6 Da became the main part of WEOM in the final product. ^{1}H nuclear magnetic resonance spectra revealed that the proportion of H moieties in the area of 0.00–3.00 ppm decreased, while increasing at 3.00–4.25 ppm after vermicomposting. Fluorescence spectra indicated that vermicomposting caused the degradation of protein-like groups, and the formation of fulvic and humic acid-like compounds in the WEOM of the substrates. Overall results indicate clearly that vermicomposting promoted the degradation and transformation of liable WEOM into biological stable substances in sewage sludge and cow dung alone, as well as in mixtures of both materials, and testing the WEOM might be an effective way to evaluate the biological maturity and chemical stability of vermicompost.

1. Introduction

Vermicomposting, involving the joint action of earthworms and microorganisms [1–3], considerably improve the decomposition and stabilization of sewage sludge. The end products in the vermicomposting process were found to have higher N and P contents [4,5] and lower human pathogen [6,7], yielding an organic amendment or a soil conditioner. Vermicompost, as a soil organic amendment, could improve the physical, chemical, and microbial properties of the soil, and stimulates plant growth [8–14].

Previous studies on vermicomposting focused on the stabilization of sewage sludge, evaluation of vermicompost as a soil organic amendment or fertilizer, and earthworm population dynamics [15–17]. To date, the influence of vermicomposting on chemical features of the water-extracted organic matter (WEOM) in sewage sludge, and added enrichments such as cow dung, has not been fully studied.

During vermicomposting, microbes are responsible for biochemical degradation of organic matter, while earthworms are the critical drivers of the process, conditioning the substrate and altering the microbiological activity [18]. Since the biochemical transformations of organic matter are a result of microorganisms whose metabolism occurs in the water-soluble phase [19], WEOM represents the most active fraction of sewage sludge, and could directly reflect the biochemical alteration of organic matter. The concentration and chemical changes of WEOM have been found to correlate closely to the stability and maturity of compost during composting [19–22]. Thus, investigating the chemical changes of WEOM during vermicomposting process is highly desirable to better understand the stabilization of sewage sludge and the role played by the WEOM in that process.

The changes in the chemical characteristics of WEOM during composting process have been reported by a number of researchers [19,21–24]. Many analyses, including dissolved organic carbon (DOC), specific ultra-violet absorbance (SUVA), gel permeation chromatography (GPC) and fluorescence excitation–emission matrix spectroscopy (EEM), are used to investigate the properties of WEOM [22]. DOC can serve as a general descriptor of WEOM [21], while SUVA, GPC, ^{1}H NMR and EEM techniques could supply more information on WEOM transformation, e.g., the aromaticity, molecular weight and humification degree of derived compounds [22,24–28].

Volatile fatty acids (VFAs) were regarded as the major malodorous compounds in livestock manure [29] and sludge, and

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could provide useful information about the volatile organic matter. However, information about VFAs changes in WEOM during vermicomposting of sewage sludge is still limited.

The aims of this work were to study the changes in the chemical characteristics of WEOM fractions after the vermicomposting of sewage sludge, and added enrichment such as cow dung, by various analytical approaches.

2. Materials and methods

2.1. Substrates and vermicomposting process

Fresh sewage sludge (FSS) was procured from of the dumping site of a 60 000 $m^3\,d^{-1}$ domestic waste water treatment plant (WWTP) (Quyang WWTP, Shanghai, China). The water content of the FSS approximated 75–85%. Fresh cow dung (FCD) was obtained from a cow farm in a suburb of the Pudong district, Shanghai, China. The FSS and FCD were dried in direct sunlight for two weeks, with periodic turning. Young non-clitellated earthworms *Eisenia fetida* were randomly picked from several stock cultures maintained in the laboratory with cow dung as culturing substrate.

Six circular plastic containers (15 cm diameter × 14 cm depth) were filled with 100 g feed mixture (dry weight) containing different proportion of sewage sludge and cow dung (V1, 100% + 0%; V2, 70% + 30%; V3, 50% + 50%; V4, 30% + 70%; V5, 0% + 100%). 10 g straw (dry weight) was added to the feed mixture as bulking material. These mixtures were manually turned every 24 h for 14 days in order to eliminate volatile toxic substances. After 14 days, 15 non-clitellated earthworms, weighing 200–250 mg live weight, were introduced in to five distinct groups (from V1 to V5), three replicates each. Mixture moisture content was maintained at 70–90% by periodic sprinkling of distilled water. All the containers were kept in the dark at room temperature ($25 \pm 1\,^{\circ}C$). All containers were vermicomposted for 60 days followed by separation of earthworms, cocoons and straw. Vermicomposts were collected from each container for further analyses.

2.2. Extraction of water-extracted organic matter (WEOM)

WEOM was extracted from the initial substrates and vermicomposts with deionized water (solid to water ratio of 1:20) for 24 h on a horizontal shaker at room temperature. The suspensions were then centrifuged at $10^4 \times g$ for 10 min and filtered through a 0.45-μm Whatman® membrane filter [19].

2.3. WEOM analyses

2.3.1. Organic matter contents analysis

Dissolved organic carbon (DOC) and dissolved total nitrogen (DTN) of the filtrates were measured by a TOC-VCPN analyzer (Shimadzu, Japan). Dissolved chemical oxygen demand (DCOD) was measured using a NOVA60 COD meter (Merck, Germany). UV absorption at 254 nm of bulk WEOM samples was measured using a UV 765 spectrophotometer (Shanghai Precision & Scientific Instrument Co., Ltd., Shanghai, China). Before measurement, all solutions were diluted to organic C concentrations <10 $mg\,L^{-1}$ [24]. The measured absorbance was normalized to the concentration of dissolved organic C giving the specific UV absorption ($SUVA_{254}$) [30].

2.3.2. Volatile fatty acids (VFAs) analysis

VFAs of the WEOM from the substrates were measured according to the method [31]. In brief, the filtrate was collected in a 1.5 ml gas chromatography vial and 3% H_3PO_4 was added to adjust the pH to approximately 3.0. A HP5890 Gas Chromatograph (GC, Thermo Finnigan, USA) with flame ionization detector and equipped with a 30 m × 0.32 mm × 0.25 mm CPWAX52CB column was used to analyze the composition of VFAs. N_2 was the carrier gas at a flux of 50 $ml\,min^{-1}$. The injection port and the detector were maintained at 200 and 220 °C, respectively. The oven of the GC was programmed to begin at 110 °C and after 2 min, increase at a rate of 10 $^{\circ}C\,min^{-1}$ to 200 °C, and to hold at 200 °C for 2 min. The sample injection volume was 1.0 μl. Three replicates were measured for each sample.

2.3.3. Gel filtration chromatography (GFC) analysis

The molecular weight of the WEOM was measured by a GFC analyzer. The GFC system consisted of an Lc-10ADVP type gel column (Shimadzu, Japan). The TSKgel G4000PWXL column (Tosoh, Japan) was used, which was suitable for analyzing water-soluble polymers. Polyethylene glycols (PEGs) with molecular weight (M_W) of 1 169 000, 771 000, 128 000, 11 840, 4020, 620, and 194 Da (Merck Corporation, Germany) were used as calibration standards [22].

2.3.4. ^1H nuclear magnetic resonance (^1H NMR) spectra analysis

The WEOM was analyzed for ^1H NMR spectra using a 500 MHz spectrometer (Bruder GmbH, Karlsruhe, Germany) at room temperature. 2 ml of the filtrate was taken and freeze-dried. The freeze-dried fractions were dissolved in 0.5 ml D_2O. The ^1H NMR spectra were measured at a spectrometer frequency of 500.13 MHz, 2 s acquisition time. Chemical shifts were depicted relative to the resonance of tetramethylsilane. MestReNova 8.0 software was used to analyze the ^1H NMR spectral data.

2.3.5. Fluorescence spectra analysis

The WEOM was diluted with 0.1 $mol\,L^{-1}$ phosphate buffer (pH 7.0) and the final DOC was made up to approximately 10 $mg\,L^{-1}$ [22], and analyzed for fluorescence spectra, using F-4600 fluorescence spectrophotometers (Hitachi, Japan). Emission and excitation slits were set at a 10-nm band width, and a scan speed of 500 $nm\,min^{-1}$ was selected for both monochromators. Conventional emission spectra were recorded over the range 380–550 nm at a constant excitation wavelength of 360 nm. Excitation spectra were obtained over a scan range of 300–500 nm by measuring the emission radiation at a fixed wavelength of 520 nm [2]. Emission and excitation slits were set at a 5-nm band width, and a scan speed of 12 000 $nm\,min^{-1}$ was selected for both monochromators. The excitation–emission matrix (EEM) spectra were recorded by scanning the emission wavelength over the 250–600 nm range, while the excitation wavelength was increased sequentially from 200 to 500 nm. The voltage of photomultiplier tube (PMT) was set as 750 mV for low-level light detection. Surfer 8.0 software was used to analyze the data.

2.4. Statistical analysis

One-way ANOVA was used to analyze the differences among treatments.

3. Results and discussion

3.1. Organic matter contents

The organic matter content of WEOM from the initial substrates and vermicomposts is displayed in Table 1. Compared to observations in the FCD, FSS had higher DOC, DCOD and DTN contents, lower $SUVA_{254}$ value and C/N ratio.

After vermicomposting, DOC and DCOD contents and the C/N ratio decreased in all mixtures, ranging from 2.51 to 3.93 $mg\,g^{-1}$, 4.98 to 9.70 $mg\,g^{-1}$ and 0.52 to 0.82 respectively, possibly attributed to the degradation of labile organic matter, particularly carbohydrates, amino sugars and low-molecular weight organic