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## Transformation of dissolved organic matters in swine, cow and chicken manures during composting



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### HIGHLIGHTS

- Difference of DOMs in swine, cow and chicken manure was compared during composting.
- Transformation of DOMs was analyzed by UV, GPC, FTIR, EEM-FL, Biolog and <sup>1</sup>H NMR.
- Pumice was used to avoid the effect of organic bulking agents on manures analysis.
- Specific degradation features of manures impacted their composting process.
- The decline of C–O and carbon chains was faster than olefinic and aromatic carbon.

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### ABSTRACT

The changes of dissolved organic matters (DOMs) extracted from swine, cow and chicken manures were assessed by Fourier transform infrared, ultraviolet, gel permeation chromatography (GPC), excitation–emission-matrix fluorescence (EEM-FL), Biolog Eco and <sup>1</sup>H NMR during 60-day composting. Pumice was adopted to eliminate the disturbing of common organic bulking agents. The results showed chicken manure had the highest DOC, DTN (dissolved total nitrogen) and lowest DOC/DTN among the three manures; cow manure had the highest volatile solids, lowest DTN, slowest DOMs hydrolysis rate and the fastest bio-stabilization rate. <sup>1</sup>H NMR showed the decrease rates of O–C band and saturated carbon chain were distinctly faster than that of olefinic and aromatic structures. The molecular size distribution of DOMs in the three manures was in the range of 1–10 kDa detected by GPC. Microbial carbon utilization capacity decreased in cow manure with composting time, but the contrast was observed in the chicken and swine manures.

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### 1. Introduction

The output of livestock and poultry manure in China had reached approximately 2.2 billion tons per year by 2010, and this number is still continuing to increase (Qiu et al., 2013). Swine, cow and chicken currently have the largest raising population among these livestock and poultry, thus they become the main sources of the animal waste (Erickson et al., 2009; Zhang and He, 2006; Zhu, 2007). The livestock and poultry manures, containing

a large amount of readily biodegradable organics, nutrients and pathogens, are the potential pollution sources to the environment.

Composting is a widely-adopted biological method to achieve organics stabilization, pathogens inactivation and nutrients recycling. The organic compost made from the livestock and poultry manures not only reduces the consumption of chemical fertilizer but also improves soil fertility. However, there are several challenges for current composting process including incubation period shortening, nitrogen loss and odor controlling, phytotoxic compounds transformation, bulking agent and energy consumption reduction (Eftoda and McCartney, 2004; Haug, 1993; Keener et al., 1993; Wang et al., 2013b). Therefore, it is important to develop efficient composting technology to dispose the manures of swine, cow and chicken.

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Evaluating the transformation of dissolved organic matters (DOMs) is essential to understand the composting process of manures (Said-Pullicino et al., 2007). The feces excreted by swine, cow and chicken have different composition and biodegradation characteristics which have great influences on composting operation, including aeration rate, composting period, bulking agent option, odor control and product quality. Hence, the management of composting operation should be optimized according to specific biodegradation properties of these feces. DOMs are the most active fraction in the composting matrix, both biologically and chemically. The chemical composition and structure of the DOMs also have been used to evaluate the quality of composting product (Wang et al., 2013a). The DOMs did not only contain a large amount of biological byproducts but also were the direct nutritional source for the microbes. Because the insoluble organic substrates have to be hydrolyzed to the DOMs before biological utilization, the DOMs greatly impact the microbial community and activity in the composting matrix. Therefore, investigating DOMs transformation is a crucial premise to optimize composting operation separately based on their specific properties of the swine, cow and chicken manures.

A series of spectroscopic techniques is a powerful tool to exhibit chemical composition and structure of mixed organics from different aspects. Fourier transform infrared (FTIR) spectra can provide a qualitative description of the functional groups in a mixture sample (Amir et al., 2010; Carballo et al., 2008). Ultraviolet (UV) spectra have intensive absorption on the aromatic and unsaturated compounds (Albrecht et al., 2011; Domeizel et al., 2004; Li et al., 2010). Gel permeation chromatography (GPC) combined with UV detector is a common method to measure the distribution of molecular weights in the DOMs (Gul et al., 2003; Prudent et al., 1995). Excitation–emission matrix fluorescence (EEM-FL) spectra can determine the organic compounds which have the fluorescent characteristics, such as proteins, humic and fulvic acids (Marhuenda-Egea et al., 2007; Tian et al., 2012). Nuclear magnetic resonance (NMR) is good at quantitatively determining the abundance of functional groups in the mixture (Gigliotti et al., 1997). Therefore, the combination of these spectroscopy methods provides a feasible approach to evaluate the difference of the DOMs among the manures of swine, cow and chicken. Additionally, it also provides more information about the transformation of the DOMs during the manures composting.

Adding organic bulking agents in the composting feedstock would greatly interfere with the chemical and spectroscopic analysis on the manure DOMs. In general, fresh animal feces have relatively high moisture and low porosity. To facilitate oxygen diffusion in the matrix, a large amount of organic bulking agents, such as wood chip, pine bark, sawdust, straw and garden waste, has to be mixed with the feces before the aerobic composting (Yañez et al., 2009). The organic matters in the bulking agents are also biodegraded and produced a large amount of DOMs during the incubation (Barrington et al., 2002). However, the DOMs in animal manure and organic bulking agents have a large difference in chemical composition. Because the manure particles and the bulking agents are spatially separated in the solid composting matrix, the DOMs inside the bulking agent particles commonly cannot be directly utilized by the microbes living inside the manure particles. Therefore, the DOMs released from the bulking agent cannot reflect the biodegradation process of the animal manures. However, the DOMs from the manures and bulking agents were mixed in aqueous extraction process of the composted sample. Therefore, the analysis on the manure DOMs was disturbed by the DOMs released from the organic bulking agents in the previous literature.

In this study, pumice was used as an inorganic bulking agent to avoid the influence of organic bulking agents on the analysis on the transformation of the manure DOMs. Multiple techniques were

adopted to compare the differences of the DOMs extracted from the swine, cow and chicken manures during 60-day composting. The components, chemical structures and molecular weights of these DOMs were evaluated by the methods of FTIR, UV, EEM-FL,  $^1\text{H}$  NMR and GPC, respectively. Microbial carbon-utilization capacity (CUC) and population diversity in three manures were assessed by Biolog Eco method. The degradation properties of the three manures and their effects on composting operation were compared and evaluated.

## 2. Methods

### 2.1. Experimental methodology

Fresh swine, cow, chicken feces were collected from the livestock and poultry farm in Harbin, Northeast China. The characteristics of these fresh feces (Day-0 sample), including dissolved organic carbon (DOC), dissolved total nitrogen (DTN), DOC/DTN ratio, moisture and volatile solids content (VS) and pH are shown in Table 1. The indice of VS was commonly used to reflect the variation of organic content in the solid sample. Pumice, a porous volcanic rock, was used as the bulking agent in the composting of the three feces to avoid the effect of conventional organic bulking agent on the analysis of these animal manures. The chemical and physical properties of the pumice were reported by Wang et al. (2011). 300 g of swine feces, 300 g of cow feces and 300 g of chicken feces separately mixed with 250 g of pumice were composted for 60 days in three cylindrical glass reactors (5 L volume, 20 cm diameter  $\times$  27 cm height), respectively. Three reactors were placed in a constant temperature water bath at 55 °C for the initial 20 days and at 35 °C for the next 40 days. The aeration rates for three runs were at the constant rate of 0.2 L/min during 60-day composting.

### 2.2. Chemistry analysis

The moisture contents of swine, cow and chicken manures at the different composting stages were determined by the weight loss upon drying at 105 °C for 24 h. The pH was determined using pH meter by dissolving 1 g compost sample in 10 mL distilled water. The VS contents of the dry manure samples were measured by the weight loss at 550 °C for 2 h. The dry manure samples were grinded and screened through the mesh size of 200, and 5 g of the residue was extracted with 50 mL DI water 25 °C or 24 h. The values of the DOC and the DTN of the aqueous extract were determined by the TOC analyzer after the filtration through a 0.45  $\mu\text{m}$  membrane. The aqueous extract of the composted manures was adopted to analyze the chemical change of the DOMs by the methods of UV, GPC and EEM-FL according to Wang et al. (2013a). The aqueous extract was freeze-dried to obtain the solid DOMs for the FTIR spectroscopy analysis. Microbial CUC in the composted manures was determined using the Biolog Eco plate according to the Biolog standard methods (Garland and Mills, 1991; Guckert et al., 1996). The Biolog Eco plate contained 31 carbon sources, and each carbon source was measured for three times.

### 2.3. Spectroscopy analysis

The UV–Vis absorption of the aqueous extract from the composted manures was measured by Shimadzu UV-2550 in the spectra range 200–650 nm.  $\text{UVA}_{254}$  and  $\text{UVA}_{280}$  were determined by the specific UV absorbance values at 254 nm and 280 nm. The  $\text{SUVA}_{245}$  and the  $\text{SUVA}_{280}$  of the aqueous extract were calculated as  $(\text{UVA}_{254} \text{ or } \text{UVA}_{280}/\text{DOC}) \times 100$ , respectively. Molecular size distribution of the manures DOMs in the aqueous extract was measured by the

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