

# Fluorescence characteristic changes of dissolved organic matter during municipal solid waste composting

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**Abstract:** Dissolved organic matter (DOM) of municipal solid waste (MSW) consists of minerals, water, ash and humic substances, and is known to enhance plant growth. In this study, inoculating microbes (ZJ, MS) were used in municipal solid wastes composting, and composting implemented a industrialized technology. During composting, dissolved organic matter was extracted from the compost and purified. The spectral characteristics of dissolved organic matter was determined by fluorescence emission, excitation, and synchronous spectroscopy. Fluorescence emission, excitation, and synchronous spectra characterized by different relative fluorescent intensities and peaks over time. Fluorescence spectra were similar to that of fulvic acid in sewage sludge, indicating the presence of dissolved organic matter with aromatic structures and a high degree of molecular polymerization. Compared with the controls with no microbial inoculation, the microbe-inoculated treatments exhibited the increase of aromatic polycondensation, in the following order: MS + ZJ > ZJ > MS > CK.

**Keywords:** MSW composting; dissolved organic matter (DOM); inoculating microbes; fluorescence spectra

## Introduction

Composting is a traditional, approach to integrated waste management. The raw materials for composting represent a wide spectrum of organic wastes such as municipal solid wastes (MSW), sewage sludge, yard and green wastes, animal manures and others (Chefetz, 1998). Composting is defined as a biological treatment in which aerobic microorganisms utilize organic matter (OM) as a substrate. The final product (compost) consists of stable OM, minerals, water, ash and humic substances (HS). As microorganisms are only active at the solid-liquid inter phase, a study of the liquid fraction is essential to achieve better understanding of the C and N cycles during composting (Lynch, 1993). Moreover, characterization of the composition of dissolved organic matter (DOM), the active OM fraction, has the potential of being a better indicator of the overall transformation of the OM than tests of the solid phase. Compost used as soil amendment is transformed into soil humus after further decomposition. DOM in compost is known to enhance plant growth by repletion of Fe, Mn, Cu, and Zn in solution at sufficient levels. In soils, DOM is related to C and N availability (Gressel, 1995; Zech, 1994), metal complexation, advanced plant growth. Although the transformation of organic matter during composting has been widely studied (Aoyama, 1991; Chefetz, 1996; Chen, 1989; Ciavatta, 1993; Jimenez, 1992), most of the reports have focused on water-insoluble HS.

The determination of DOM composition is difficult since it contains a mixture of low-molecular weight compounds (free amino acids and sugars) and chemically heterogeneous macromolecules (enzymes, amino-sugar complexes, polyphenols, and HS; Chefetz, 1998). Thus, preliminary fractionation was an essential step for better understanding of the variety of different physico-chemical and biological active compounds (Leenheer, 1981). In this paper, inoculating microbes were used in MSW composting. Investigations were conducted in Daqing Meishang MSW Composing Plant in

China. The DOM spectra characteristics were studied during MSW composting by fluorescence spectroscopy. The effect of inoculating microbes on DOM composition characteristics of compost was studied.

## 1 Materials and methods

### 1.1 Materials

MSW consisted of residual compost with metal, plastic and glass removed. The MSW nutrient elements content was: C, 323.24 g/kg; N, 14.88 g/kg; P<sub>2</sub>O<sub>5</sub>, 10.02 g/kg; K<sub>2</sub>O, 12.80 g/kg. Water content was 56%. MS compound microbes (MS) were provided by Daqing Meishang Company of China at a concentration of  $1 \times 10^9$  ml<sup>-1</sup>. ZJ fermentation microbes (ZJ) were provided by Zhongjia Biological Technique Limit Company of China at a concentration of  $1 \times 10^9$  ml<sup>-1</sup>.

### 1.2 Experiment method

The experiment was conducted at the Daqing Meishang MSW compost plant from March 15 to May 18, 2003.

The experiment design included 4 treatments replicated 3 times. The experiment treatments are shown in Table 1.

Table 1 Composting materials and composition

Number	Treatments	MSW, kg	MS, ml	ZJ, ml
1	Control (CK)	5	0	0
2	MS	5	25	0
3	ZJ	5	0	25
4	MS + ZJ	5	12.5	12.5

Each treatment consisted of 5 kg MSW was put into nylon mesh sacks, which were then randomly buried at the same depth into the bar MSW fermentation pile. The bar compost pile was 1.50 m long. The cross section was triangle, 4.5 m in width and 2.2 m height. Compost process implemented two-step fermentation. The main indices are shown in Table 2.

### 1.3 Sampling

When the MSW fermentation piles were turned over, the nylon mesh sacks were removed and ventilated. At the initial

stage of one-step fermentation and final stage of two-step fermentation, a 500 g sub-samples was taken from each sack. A 250 g fresh MSW sample was analyzed for moisture content and water-soluble matter. The rest was air-dried, and ground to pass through a 1-mm sieve. Organic C and humic acid were measured.

**Table 2 Fermentation conditions**

Conditions	One-step fermentation	Two-step fermentation
Water content of input organic matter	60%	50%
Water content of output organic matter	30%	25%—30%
Composting temperature	55 °C ≤ T ≤ 75 °C, lasted more than 5 d	
Fermentation period	28 d	35 d

Notes: Oxygen densities ≤ 10%; fermentation piles were mixed weekly; C/N ≤ 25:1; fermentation piles were 2.2 m high

## 1.4 Analysis methods

### 1.4.1 DOM extraction

Two hundred grams of fresh MSW was added to 2 L of distilled water. The suspension was shaken at 200 r/min for 16 h. The suspension was then centrifuged (10000 g for 30 min) and the supernatant was filtered through a 0.45 μm membrane filter. The filtered supernatant was then freeze-dried.

### 1.4.2 Fluorescence spectroscopy

The scan rates of emission and excitation monochromator were 200 nm/min, with a slit width of 10 nm. Emission spectra were recorded over the range 370—600 nm at the constant excitation wavelength of 360 nm. Excitation spectra were obtained over a scan range of 300—550 nm by measuring the emission radiation at a fixed emission wavelength of 560 nm. Synchronous-scan spectra were measured by scanning simultaneously over the range of 300—600 nm, with optimized wavelength difference:  $\Delta\lambda = \lambda_{em} - \lambda_{ex} = 18$  nm. The DOM concentration was 20 mg/L.

## 2 Results

### 2.1 Emission spectra

DOM fluorescence emission spectra at the excitation wavelength 360 nm are shown in Fig. 1. At the initial stage of composting, the DOM fluorescence emission spectra exhibited a sharp peak at 400 nm and a minor broad shoulder peak centered at 440 nm. At the final stage of composting, the fluorescence peak height of all treatments increased at 400 nm, however, peak shapes broadened, and were similar to shoulder peak. The previously observed shoulder peak became secondary peaks at 440 nm, this approached to the fluorescence characteristic peak of soil fulvic acid at 450—460 nm. However, if compared with the characteristic peaks (470—500 nm) of soil humic acid, the difference was obvious according to the report from Pvoenzano *et al.* (Pvoenzano, 1998).

At fixed excitation wavelengths of 400 nm and 440 nm, a narrow band was observed (Fig. 2a and 2b). DOM fluorescence relative intensity decreased at the final stage of composting compared with the one at initial stage of composting, this indicates an increase of unsaturated compound (aromatic compound) polycondensation in DOM at the final stage of composting (Zhan, 2001). The fluorescence

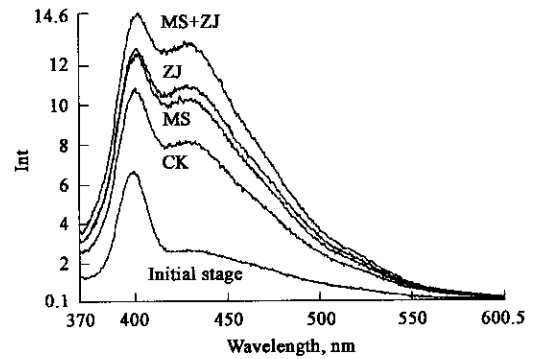


Fig. 1 DOM fluorescence emission spectra in the initial and final stage of MSW composting

emission spectra shapes were very similar among all treatments with the main peaks at similar wavelength. However, the fluorescence relative intensities differed by treatments (Fig. 2c and 2d). The fluorescence relative intensities of inoculating microbes treatments decreased obviously compared with that of CK. According to Miikki (Miikki, 1997), the high degree of multimerization in DOM leads to the reduction of the fluorescence intensity. The results suggested that the degree of aromatization in DOM increased by inoculating microbes in MSW composting, and ordered as follows, MS + ZJ > ZJ > MS > CK.

### 2.2 Excitation spectra

Compared with fluorescence emission spectra, the excitation spectra are generally better to characterized the DOM owing to a number of peaks and shoulders. At the initial stage of composting, the excitation spectra of DOM exhibited a primary peak at 520 nm, two secondary peaks at 390 nm and 460 nm. At the final stage of composting, the main peak at 520 nm disappeared, the secondary peak at 390 nm became minor shoulder peak, and the peak at 460 nm became a primary peak, which was the main peak of soil fulvic acid, and two shoulder peaks formed between 320—350 nm. The fluorescence excitation spectra shape was similar with that of fulvic acid in sewage sludge (Nicola, 1991). This result suggests the DOM molecule structure contains high degree of aromatic polycondensation. Although the fluorescence spectra were similar in shape among different treatments, the relative fluorescence intensities differed, and were ordered as follows, MS + ZJ > ZJ > MS > CK. In addition, the fluorescence spectra of MS + ZJ formed a minor shoulder peak at 490 nm (Fig. 3).

### 2.3 Synchronous-scan spectra

Fig. 4 shows that fluorescence spectra in synchronous-scan mode should allow better peak resolution than obtained by conventional fluorescence modes, i. e., emission or excitation, thus providing a more distinct parameter of differentiation between sample and higher possibility for the identification of the molecular structures responsible for fluorescence in each sample. At initial stage of MSW composting, DOM fluorescence synchronous-scan exhibited a primary peak at 335 nm, two secondary peaks at 385 nm and 453 nm, a minor peak at 475 nm, and a minor shoulder near 500 nm. At the final stage of the composting, peak at 335 nm showed a broad profile, the fluorescence relative intensity of the secondary peak at 453 nm increased, migrated towards the primary peak, and shifted from 453 nm to 458 nm, this

resembles the primary peak of soil fulvic acid. The reason for the red shift was a high degree of polymerization of multiple fluorophores which enhanced the probability of bimolecular processes such as radiative energy transfer and excimer/excimer formation (Komada, 2002; Igor, 2003), and this may be ascribed to a high degree of conjugation and the presence of many aromatic structures. Therefore, the result showed the degree of DOM humification increased at the final stage of MSW composting. In all the treatments, the

fluorescence spectra were similar in shapes at the final stage of MSW composting. Relative fluorescence intensities differed and were ordered as: MS + ZJ > ZJ > MS > CK. Furthermore, the peak wavelength of MS + ZJ at 335 nm shifted to 339 nm, indicating that mixed inoculating of MS and ZJ in MSW composting could increase the degree of polymerization of DOM further compared with that of inoculating MS or ZJ alone.

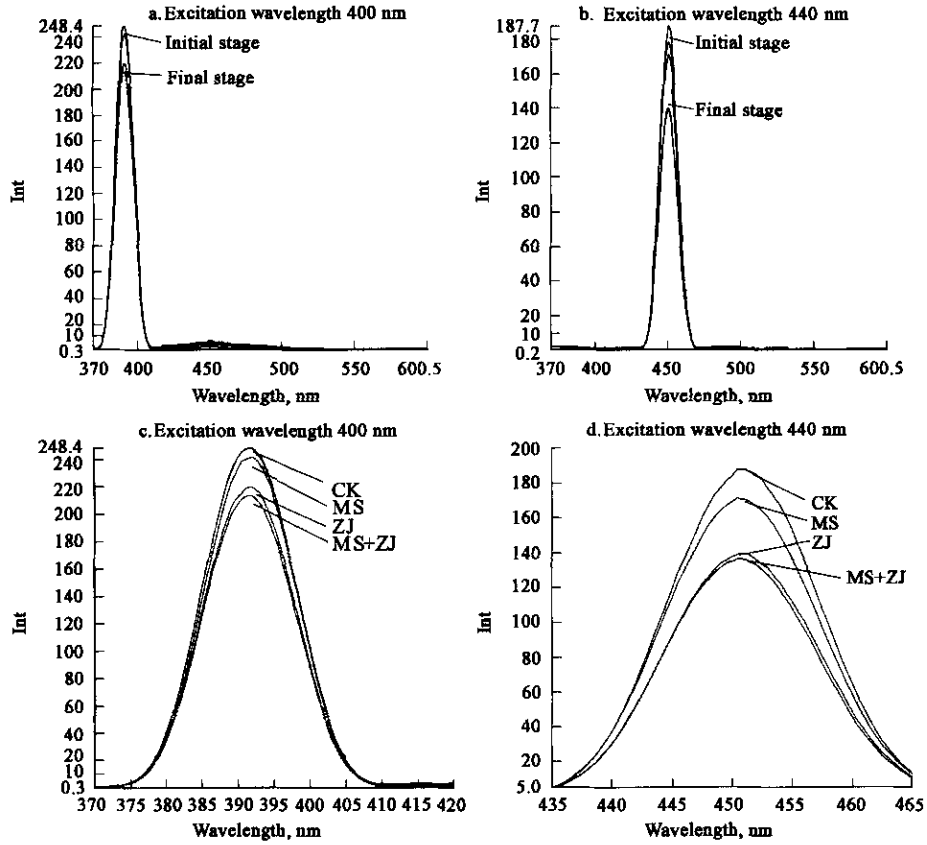


Fig. 2 DOM fluorescence emission spectra in the initial and final stage of MSW composting. C and D were the part of A and B zooms in

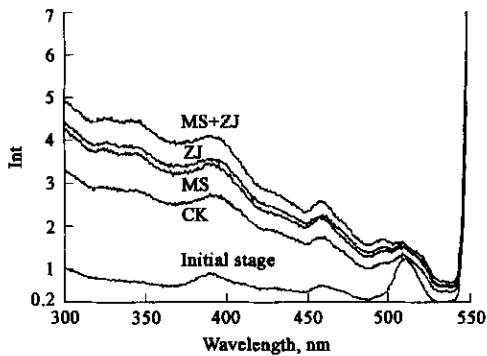


Fig. 3 DOM fluorescence excitation spectra in the initial and final stage of MSW composting

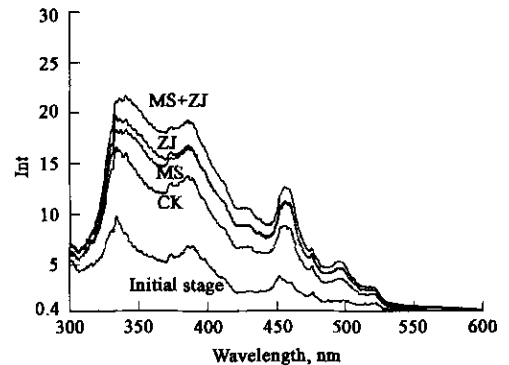


Fig. 4 DOM fluorescence synchronous spectra in the initial and final stage of MSW composting

### 3 Discussions

At present, the fluorescence technique has been preferentially applied to the study of humic substances of aquatic origin, especially the fluorescence spectra of fulvic acid, Application to DOM is relatively limited. The DOM fluorescence spectra from different sources reveals apparent

difference, Identification of the molecular components responsible for DOM fluorescence is still far from being clarified, some reports can be suggested on the DOM activity, such as the relevant fluorescing structures in various humic materials and fulvic acid, which examined on basis of available data and trends of fluorescence properties measured, the paper evaluated the DOM fluorescence

characteristic according to that of humic acid and fulvic acid of other source. In this study, at the final MSW composting, fluorescence emission characteristic peak (440 nm, fixed excitation wavelength 360 nm) of DOM approached to that of soil fulvic acid (Fig. 1), and the peaks of excitation spectra (320–350 nm, 390 nm, 460 nm) were similar to that of fulvic acid of sewage sludge (Fig. 3). These suggested there were abundant levels of fulvic acids in DOM. In addition, according to Liu (Liu, 2004), the peaks of fluorescence synchronous-scan spectra are assigned to functional groups as follows: (1) the peak at 335 nm is bicyclic aromatics; (2) the peak at 350 nm is tricyclic aromatics; (3) the peak at 385 nm is tricyclic aromatics; and (4) that at 450 nm is five-membered ring aromatics. In this study, at the final stage of composting, the tricyclic, four-membered ring as well as the five-membered ring aromatics in DOM composition with inoculating microbes gradually increased comparing with no inoculating microbes (Fig. 4). The increases of relative fluorescence intensities for treatments were in the following order: MS + ZJ > ZJ > MS > CK. These confirmed further that inoculating microbes in MSW composting could increase the content of aromatic compound of DOM, and mixed inoculating of MS and XJ in MSW composting could increase the degree of DOM aromatization further compared with that of inoculating either MS or ZJ alone. Of course, the study was limited, further investigation should associate with information derived from other physico-chemical and spectroscopic techniques such as NMR, IR, GC-MS, and ESR.

#### 4 Conclusions

At the final stage of MSW composting, the degree of DOM aromatic polycondensation increased obviously compared with that at the initial stage of composting. The increases for treatments were in the following order: MS + ZJ > ZJ > MS > CK, and inoculating of MS and ZJ in MSW composting increased the degree of polymerization of DOM further compared with that of inoculating either MS or ZJ alone. The DOM fluorescence characteristic peaks (emission spectra: 440 nm; excitation spectra: 320–350 nm, 390 nm, 460 nm; synchronous spectra: 335 nm, 385 nm, 455 nm, 493 nm) were similar with that of fulvic acid of sewage sludge, this indicated, there were abundant levels of fulvic acid in DOM. Compared to humic acid, fulvic acid is characterized lower molecular weight, simpler structure and lower degree of aromatic polycondensation, therefore, when the composting of MSW amend soil, the DOM of composting would improve physical and chemical properties of soil, and stimulate plant

growth.

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#### References:

- Aoyama M, 1991. Properties of fine and water-soluble fractions of several composts[J]. *Soil Sci Plant Nut*, 37: 629–637.
- Chefetz B, Hadar Y, Chen Y, 1998. Dissolved organic carbon fractions formed during composting of municipal solid waste: properties and significance[J]. *A Hydrochim Hydrobiol*, 26(3): 172–179.
- Chefetz B, Hatcher P G, Hadar Y *et al.*, 1996. Chemical and biological characterization of organic matter during composting of municipal solid waste [J]. *J Environ Qual*, 25: 776–785.
- Chen Y, Inbar Y, Hadar Y *et al.*, 1989. Chemical properties and solid-state CPMAI3C-NMR of composted organic matter[J]. *Sci Total Environ*, 82: 201–208.
- Ciavatta C, Gomi M, Passoti L *et al.*, 1993. Changes in organic matter during stabilization of compost from municipal solid waste[J]. *Bioresource Tech*, 43: 141–145.
- Gressel N, McGrath A E, McColl J G *et al.*, 1995. Spectroscopy of aqueous extracts of forest litter: I. Suitability of methods[J]. *Soil Sci Soc Am J*, 59: 1715–1723.
- Igor A S, Andrei I K, Shin Young A H *et al.*, 2003. Characterization and biological activities of humic substances from mumie[J]. *Agricultural and Food Chemistry*, 51: 5245–5254.
- Jimenez E I, Garcia V P, 1992. Determination of maturity indices for city refuse composts[J]. *Agric Ecosystems Environ*, 38: 331–343.
- Komada T, Schofield O M E, Reimers C E, 2002. Fluorescence characteristics of organic matter released from coastal sediments during resuspension[J]. *Mar Chem*, 79: 81–97.
- Leenheer J A, 1981. Comprehensive approach to preparative isolation and fractionation of dissolved organic carbon from natural waters and wastewaters [J]. *Environ Sci Tech*, 15: 578–587.
- Liu W, Hu B, Yu D Y *et al.*, 2004. Three dimensional fluorescence characters of heavy oil in China and its geological significance[J]. *Geophysical & Geochemical Exploration*, 28(2): 123–129.
- Lynch J M, 1993. Substrate availability in the production of compost[M]. In: *Science and engineering of composting: Design, environmental, microbiological and utilization aspects* (Hoitink H. A. J., Keener H. M. ed.). Worthington, OH: Renaissance Publications. 24–36.
- Mikki V, Senesi N, Hanninen K, 1997. Characterization of humic material formed by composting of domestic and industrial biowastes[J]. *Chemosphere*, 34(8): 1639–1651.
- Nicola S, Teodoro M M, Maria R P *et al.*, 1991. Characterization, differentiation, and classification of humic substances by fluorescence spectroscopy[J]. *Soil Science*, 152(4): 259–271.
- Provenzano M R, Senesi N, Piccone G, 1998. Thermal and spectroscopic characterization of composts from municipal solid wastes[J]. *Compost Science & Utilization*, 6(3): 67–73.
- Zech W, Guggenberger G, Schulten H R, 1994. Budgets and chemistry of dissolved organic carbon in forest soils: Effects of anthropogenic soil acidification[J]. *Sci Total Environ*, 152: 49–62.
- Zhan X H, Zhou L X, Shen Q R *et al.*, 2001. The spectroscopic changes characterizations of dissolved organic matter during composting sludge[J]. *Acta Scientiae Circumstantiae*, 21(4): 470–474.

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