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Fluorescence excitation–emission matrix spectroscopy with regional integration analysis for characterizing composition and transformation of dissolved organic matter in landfill leachates

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ABSTRACT

Dissolved organic matter (DOM) obtained from landfill leachates was separated into hydrophobic base, hydrophilic matter (HIM), hydrophobic acid (HOA), and hydrophobic neutral fractions. The composition and transformation of the DOM and its fractions were investigated. The results show that the DOM isolated from young, intermediate, and old landfill leachates were mainly composed of tyrosine-, tryptophan-, and humic- and fulvic-like substances, respectively. The primary fractions of the DOM in leachates were HOA and HIM. The HOA and HIM fractions from young leachates predominantly contained tryptophan- and tyrosine-like materials, respectively. The HOA fractions in intermediate and old leachates were mainly composed of humic- and fulvic-like materials, whereas the HIM fractions were dominated by tryptophan-like materials and humic- and fulvic-like substances. The hydrophobic organic fractions and humic- and fulvic-like substances increased with time, whereas the HIM and the tyrosine-like materials decreased during the landfill process, rendering biological processing of leachates ineffective.

1. Introduction

Landfill leachates are composed of a large number of organic substances released from the microbial degradation of municipal solid waste (MSW). These require sufficient treatment before they are discharged into the environment [1]. Dissolved organic matter (DOM) accounts for more than 85% of total organic matter in terms of organic carbon in leachates and is the main component of leachate treatment [2]. In addition, DOM can interact with several inorganic and organic pollutants due to the presence of oxygen-containing and aromatic functional groups in its constituents, which play a significant biochemical and geochemical role in landfill systems [3]. Studies on the compositions of DOM in landfill leachates can guide treatment process selection and establish the groundwork for environmental risk assessment of leachates [4]. As leachate compositions vary significantly with landfill age and may pose additional challenges for leachate treatment techniques [5], investigating changes in leachate DOM during the landfill process is imperative.

DOM in leachates is composed of a heterogeneous mixture of degradation products. Fractionation can reduce DOM complexity, and a number of studies have applied the DOM fractionation method based on compound hydrophobicity [2,6,7]. This method provides relevant data about DOM. Fluorescence excitation–emission matrix (EEM) spectroscopy has been widely used to investigate the composition and biogeochemical cycling of DOM due to its simplicity and sensitivity [8]. Several studies have characterized leachate DOM through EEM spectral analysis: Baker and Curry [9] investigated the EEM spectral characteristics of leachates from three contrasting landfill sites, Huo et al. [10] used EEM spectra to investigate the composition and transformation of the DOM in leachates of different ages, and Lu et al. [11] identified several fluorophores with multiple EEM peaks in leachate DOM by combining size-exclusion chromatography with EEM spectroscopy and parallel factor analysis. However, the analysis of EEM spectra in these previous studies was generally limited to visual identification of peaks or ratios of peak intensities, which cannot ascertain the heterogeneity of DOM samples. Fluorescence regional integration (FRI), a quantitative technique that integrates volumes beneath different excitation–emission regions in EEM spectra, can be used to

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quantitatively analyze EEM spectra and to determine the configuration and heterogeneity of DOM [12–14]. However, data from EEM spectroscopy and FRI analysis used in combination to investigate the composition and transformation of DOM in landfill leachates are limited.

The objectives of the present study were to investigate the structural characteristics of DOM extracted from landfill leachates of different ages and to evaluate the transformation of leachate DOM compositions during the landfill process using EEM spectroscopy in combination with FRI analysis.

2. Materials and methods

2.1. Sample collection and pretreatment

Three leachate samples (L1, L2, and L3) were obtained from different units at the Asuwei Sanitary Landfill in Beijing, China. The landfill site has been operating since 1994, mainly for MSW. The average processing load of the landfill is approximately 2000 t d^{-1}, and the leachate quantity measures approximately 1000 m^3 d^{-1}. Three samples were obtained by pumping from vertical sampling wells. Approximately 2 L of leachates was collected for each sample. Leachate sample L1 was obtained from cells younger than 3 years, L2 was collected from cells ranging in age from 3 to 10 years, and L3 was collected from cells that were more than 10 years old. All three leachate samples were filtered using 0.45 μm Whatman glass fiber filters. The filtrates were stored at 4 °C before analysis or further treatments.

2.2. Fractionation and collection of DOM fractions

DOM from the leachate samples was separated into hydrophobic base (HOB), hydrophilic matter (HIM), hydrophobic acid (HOA), and hydrophobic neutral (HON) fractions based on compound hydrophobicity using a modified procedure originated by Leenheer [15]. The modified procedure was as follows: First, the leachate filtrate was passed through an XAD-8 macroporous resin column (Rohm & Haas Corp., Philadelphia, PN). The effluent from the resin column was then collected and acidified to pH 2. The column was back-flushed with 0.1 mol L^{-1} HCl (the resulting effluent was the HOB fraction). Next, the previously acidified effluent was passed through the XAD-8 resin column again (the effluent was the HIM fraction). The column was then back-flushed with 0.1 mol L^{-1} NaOH (the effluent was the HOA fraction). Finally, the XAD-8 resin was Soxhlet-extracted with anhydrous methanol (the organic matter obtained was the HON fraction) [2,7].

2.3. Fluorescence spectroscopy

Before fluorescence analysis was performed, the dissolved organic carbon (DOC) of all samples was measured using an Analytik Jena Multi N/C 2100 TOC analyzer (Analytik Jena, Jena, Germany). All samples were diluted with 0.1 mol L^{-1} phosphate buffer (pH 7). The final DOC content was set to approximately 8 mg L^{-1}. Fluorescence EEM spectroscopy was performed on each sample using a Perkin Elmer LS50B fluorescence spectrophotometer (Perkin Elmer, New Jersey, USA) at room temperature (∼25 °C). Excitation and emission were simultaneously scanned at wavelengths ranging from 200 to 440 nm and from 300 to 500 nm, respectively, at 5 nm intervals. The slit widths were set at 10 nm for both excitation and emission monochromators, and the scan speed was set at 1200 nm min^{-1}.

Table 1
Composition of landfill leachates of different ages.

	Sample L1	Sample L2	Sample L3
HOA	51.90%	55.86%	61.59%
HON	3.81%	5.86%	5.80%
HOB	2.77%	0.90%	1.45%
HIM	41.52%	37.39%	31.16%

2.4. Data processing

After the scatter in the areas affected by first- and second-order Rayleigh and Raman scattering was regulated using interpolation [16], the FRI technique was adopted for EEM spectral data analysis [12]. Hierarchical cluster analysis (HCA) of the data obtained from the FRI analysis was performed using SPSS 16.0 software (SPSS International, Chicago, USA) and with Ward's method, which uses the squared Euclidean distance as a similarity measure. Finally, Origin 8.0 software (OriginLab, Los Angeles, USA) was used for figure processing.

3. Results and discussion

3.1. Fraction distributions of DOM in leachates

DOM obtained from the landfill leachates was fractionated into four classes according to the hydrophobic/hydrophilic character of the molecules. The fractionation results of the three samples are shown in Table 1. Hydrophobic organic fractions (including HOA, HOB, and HON fractions), which collectively accounted for more than 58.48% of the DOM in terms of DOC, were dominant; these hydrophobic carbon fractions increased with increasing landfill age (from 58.48% to 68.84%). The HOA fraction was the most abundant fraction (>51.90%) and increased with time (from 51.90% to 61.59%), indicating that it constituted much of the organic substance composition in the wastewater. The HOB fraction was the least abundant, constituting less than 2.77% of the DOC, consistent with the findings reported by Zhang et al. [2]. The proportions of HON fractions in all DOM samples were similar (3.81–5.86%), and they were in the intermediate range among the three hydrophobic fractions. The hydrophilic fraction (HIM) constituted more than 31.16% of the DOC in the leachates and had the tendency to decrease as landfill age increased (from 41.52% to 31.16%), indicating that the fraction might have disintegrated or converted into hydrophobic components as landfill age increased. Compared with HIM, hydrophobic materials are not easily used for the energy requirements of microorganisms [3]. Therefore, the increase in hydrophobic matter and the decrease in hydrophilic materials in the leachates stabilize the DOM, rendering the biological process for leachates ineffective.

3.2. Structural characteristics of DOM in landfill leachates

3.2.1. DOM and its fractions in young landfill leachates

The EEM spectra of the DOM and its corresponding fractions from different source ages are shown in Fig. 1. Four protein-like peaks (B1, B2, T1, and T2) were detected in the non-fractionated DOM extracted from the young leachate source (Fig. 1a). Previous studies [9,17,18] have shown that peaks B1 and B2 are associated with tyrosine-like materials as free molecules or bound to amino acids and proteins, whereas peaks T1 and T2 are related to tryptophan-like compounds present as free molecules or bound in proteins, peptides, or humic structures. In addition to protein-like peaks, a humic acid-like peak (peak C) was also observed in the sample; peak C was partly covered by the nearby peak (T1), and its fluorescent center was poorly understood. Previous research