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Tracking changes in fluorescent organic composition in leachates using excitation emission matrix-parallel factor analysis

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ABSTRACT

Landfill and composting are the most important treatment methods for municipal solid waste containing a significant proportion of organic matter. With time the landfill leachate undergoes changes through humification and mineralisation. The influence of landfill age on temporal changes in leachate composition when exposed to different environmental conditions is discussed. The study is based on 3 years monitoring of leachate from a landfill site in Adelaide, Australia and the investigation uses size exclusion chromatography and an excitation emission matrix approach combined with parallel factor analysis. This study showed that the matured leachate contained a broad range of low molecular weight organics with less aromaticity. Fluorescent analysis showed less-matured leachate contained more bio-polymer components. Leachate exposed to ponds showed microbial activity but the biopolymer percentage decreased with increased duration of exposure. The parallel factor analysis revealed four major components (C1–C4) at excitation/emissions of C1: 240/440 nm and 205/440 nm, C2: 225/490 nm and 225/420 nm, C3: 215/390 nm and 215/445 nm, and C4: 250/465 nm. These four components represented humic and fulvic acid-like organics of different molecular compositions. The results demonstrated that environmental variation had a direct effect on the mineralisation and humification of organic matter.

1. Introduction

Industrialisation and demographic expansion have caused an increase in the generation of municipal solid waste (MSW). Global MSW production levels have reached almost 1.3 billion tonnes per year (1.2 kg/person/day) and are expected to double in the next ten years (Hoornweg and Bhada-Tata, 2012). It has been estimated that Australia alone produces about 48.3 million tonnes of MSW annually (Department of Environment, 2014).

Many parts of the world are adopting landfill and compositing for the disposal and treatment of MSW. The landfill sites usually contain a large portion of organic matter that undergoes biological decomposition and alterations through humification and mineralisation processes. Some studies have suggested that the aromaticity and molecular size of leachates increase with increasing landfill age and also suggest that there is wider range of molecular weights in older leachates (Huo et al., 2008; Kang et al., 2002). In addition, their organic composition may vary with the site design

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and climatic conditions (Komilis et al., 1999; Wall and Zeiss, 1995). Landfill leachate typically has a high concentration of refractory organic wastewater with a variety of decomposed organic matter, toxic chemicals and gases (ammonia, carbon-di-oxide, methane) (Christensen and Christensen, 1999). It is considered as one of the main issues related to the long-term environmental impact of MSW including contamination to land, surface and groundwater (Cossu and Raga, 2008; El-Fadel et al., 1997; Huang et al., 2009; Wu et al., 2011). Understanding the leachate composition at various stages may provide crucial information in its management.

It is important to monitor dissolved organic matter (DOM) in landfill leachates because of its role in the binding of many pollutants and cause threat to groundwater and nearby land contamination (Baun and Christensen, 2004; Scott et al., 2005). Leachates generally contain a large number of organic compounds of varied composition and their characterisation can provide useful information on the mineralisation and conversion over time of organic matter of different sizes and molecular weights (Lu et al., 2009). Fluorescence spectroscopy measures the excitation and emission over a wide range of wavelengths simultaneously and produces 3-d spectra called an excitation emission matrix (EEM). Specific photon absorption (excitation) and its release (emission) are the characteristics of particular molecular confirmation (Lakowicz, 2007). EEM is a simple, non-destructive analytical method with high selectivity and sensitivity over a wide range of individual and groups of chemicals (Guo et al., 2010; Yan et al., 2000). EEM has been used in numerous water and wastewater studies to characterise organic matter, its changes with time, space and origin. Since leachate is a complex mixture of a number of refractory organics, a continuum spectral image is observed in the spectra meaning that different chemicals are not distinguishable from one another. Application of multivariate analysis such as parallel factor analysis (PARAFAC) enables EEM spectra to be resolved into a few independent groups. This is achieved by decomposing the EEM spectra into diverse fluorophores that are unique with respect to excitation and emission wavelength (Stedmon and Bro, 2008; Stedmon et al., 2003).

The coupling of molecular size distribution and EEM information can be quite useful to track the behavior of fluorescent organic matter in landfill leachates. This study aimed to examine the changes in the characteristics of organic matter in leachate samples under different environmental conditions with respect to temporal changes using analytical methods. The leachate organic matter characterisation was carried out using fluorescence excitation-emission matrix (EEM) spectroscopy and PARAllel FACtor analysis (PARAFAC). EEM is a simple, sensitive, rapid, cost-effective technique that is widely used to characterise organic matter in water, wastewater and sediments (Aryal et al., 2014a,b; Hong et al., 2012) while PARAFAC modelling decomposes the fluorescence EEMs into diverse fluorescent/chemical components that are unique with respect to their excitation-emission spectra and concentration profiles (Murphy et al., 2013; Stedmon et al., 2003).

2. Materials and methods

2.1. Study area

This study was carried out at Uleybury landfill site which is located in Northern Adelaide, South Australia (34°40′14.9″S 138°43′34.0″E) as shown in Fig. 1. The landfill site is managed by Northern Adelaide Waste Management Authority (NAWMA) who collect waste from approximately 110,000 households and who treat approximately 80,000 tonnes of waste annually, of which 80% is MSW while the remaining 20% is commercial and industrial waste. NAWMA uses an advanced baling technique for waste management (NAWMA, 2015) whereby nearly 1000 kg of waste is tightly packed into a square form.

The Uleybury landfill site commenced operation in 2005. The site consists of two stages based on the time of operation (Fig. 2). Stage I was operated between 2005 and 2010 while the adjacent Stage II has been in operation since late 2010. Leachate is pumped from the base of each landfill stage and discharged into an evaporation pond, called the Top Pond, which has a 2.25 ML capacity. A second pond (Bottom pond), located next to the Top Pond, is designed to hold the overflow from the first pond via a permanent spillway (NAWMA, 2015). Occasionally when neither pond can accommodate leachate, it is sent to the Bolivar municipal wastewater treatment plant (15 km south) for further treatment.

2.2. Sample collection

A total of 16 leachate samples (4 sampling points × four time intervals) were collected manually between 2013 and 2015: (1) Stage I (S1–S4) (Anaerobic-Matured), (2) Stage II S5–S8 (Anoxic), (3) Top Pond – S9–S12 (Aerobic), and (4) Bottom Pond – S13–S16 (Aerobic).

The samples were collected in pre-cleaned 25 mL non-pyrogenic sterile plastic bottles (Sarstedt, Germany) and were immediately stored in an ice cooled portable box (4 °C) for transport to the laboratory. The samples were filtered through a 0.45 μm cellulose acetate membrane filter (Minisart, Supelco) prior to analysis and kept at 4 °C until use. The filtrate was further diluted with Milli-Q water to ensure UV absorbance <0.1. The diluted samples were analysed for dissolved organic carbon (DOC), UV–vis and fluorescence spectra.

2.3. Analysis

2.3.1. Spectral analysis

Fluorescence spectra were recorded using a PerkinElmer LS55 spectrophotometer at wavelengths of 200–600 nm (Excitation – Ex) and 280–600 nm (Emission – Em). Excitation Emission matrix (EEM) spectra are a collection of a series of emission spectra over a range of excitation wavelengths. A xenon lamp was used as the excitation source of energy in the spectrometer and the excitation and emission slits were set to a 7 nm band-pass for both excitation (Ex) and emission (Em). Each EEM spectrum was generated by scanning excitation wavelengths from 200 to 600 nm at 5 nm increment in excitation and 0.5 nm in emission. A 290 nm cutoff filter was used in scanning to limit second-order Raleigh scattering. A spectrum of double distilled water was recorded as a blank and subtracted from samples for blank correction. The X-axis in EEM represents the emission spectra from 280 to 600 nm, whereas the Y-axis represents the excitation wavelength from 200 to 600 nm. Contour lines, as the third dimension, are shown for each EEM spectrum to represent the fluorescence intensity.

Prior to EEM all samples were scanned through UV spectroscopy to ensure the absorbance was less than 0.1 to eliminate the inner filter effect (Murphy et al., 2011). UV scanning was undertaken using a UV spectrophotometer

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