Feasibility Assessment of Spectroscopic Methods in Characterising Leachate Dissolved Organic Matter

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ABSTRACT
This research explores the use of UV absorption and fluorescence spectroscopy for rapid monitoring of organic compounds in leachates and performs a systematic comparison of the biodegradation associated evolution of different organic compounds of leachates collected from two UK MSW landfills L1 and L2. Spectroscopic techniques are used to characterize the aromatic compounds and to study the evolution of humic, fulvic and protein like compounds which is compared with the well established organic strength estimation techniques dissolved organic carbon (DOC) and chemical oxygen demand (COD). The biodegradation of different leachates as estimated from the reduction of different organic compounds using spectroscopy show an excellent agreement with the biodegradaibility assessed by the conventional methods DOC and COD indicating that characterization of landfill leachates using spectroscopic methods are reliable. It is also found that leachates collected from treatment plant and phase 4 of landfill L1 (L1 (LTP) and L1 (P4) respectively) and phase 2 of landfill L2 (L2 (P2)) are less biodegradable and contain aromatic ring of more condensed form than those for leachates collected from treatment plant of landfill L2 (L2 (LTP) and L2 (FE)) which indicate a relatively rigorous treatment requirement for L1 (LTP), L1 (P4) and L2 (P2) leachates to meet the effluent standard.

Keywords: aromatic, biodegradation, condensed

INTRODUCTION
Despite recent changes in waste management strategy promoting re-use and recycling, landfill continues to play an important role in solid waste disposal in the UK. One of the potential problems of landfill is the generation of leachates (Tchbanoglous et al., 1993) which is known as a highly contaminated and heterogeneous wastewater containing a continuum of organic compounds of different molecular weight (MW) and structures (He et al., 2006). Leachates are usually treated before being discharged to the receiving water using various physical/chemical and biological processes (Monje-Ramirez and Orta de Velásquez, 2004; Bila et al., 2005; Ntampou et al., 2005). However, the high MW organic compounds in leachate are reluctant to biodegradation (Calace and Petronio, 1997) and often known as recalcitrant organic compounds. A considerable amount of recalcitrant organic compounds can remain after treatment in particular for the biological processes which are the most commonly used methods of leachate treatment in the UK (Robinson and Knox, 2003). An influential component of many recalcitrant organic compounds are also humic substances (Artiola-Fortuny and Fullar, 1982; Christensen et al., 1998) which can significantly affect the accumulation and migration of some priority substances and hence, play an important role in the natural environment (Weis et al., 1989). Therefore, it is essential to understand the evolution and the chemical and structural composition of different organic compounds of leachates. Several studies can be found in the literature that characterized leachates from
different landfills of varying ages to understand the chemical composition of different organic compounds (Kang *et al*., 2002; Nanny and Ratasuk, 2002; Fan *et al*., 2006). Similar studies have also been reported for different UK landfill sites (Knox, 1983; Robinson and Grantham, 1988; Williams *et al*., 2002). However these studies did not provide a chronological and systematic catalogue of the changes in chemical characteristics of organic compounds in course of biodegradation. In particular, in UK a systematic comparison of the biodegradation associated evolution of the organic compounds in different landfill sites has not been done.

Organic contents of leachates are usually characterised by several established chemical methods such as biochemical oxygen demand (BOD), chemical oxygen demand (COD), and total/dissolved organic carbon (TOC/DOC). These methods estimate the organic strength of leachates by oxidizing the constituent organic matter in different ways. While BOD, COD and TOC are used extensively as parameters for leachate characterization, these methods have disadvantages such as lengthy sample preparation, lack of reliability and the difficulty in achieving reproducible results. For an investigation on the chemical and structural composition of different organic compounds of leachates, compositional analysis has also been carried out in the past through the prior separation of sub-compounds using degradation methods and later measurements by spectroscopic methods such as Fourier Transformed Infra-Red (FTIR) and Nuclear Magnetic Resonance (NMR) (Hayes *et al*., 1989; Kang *et al*., 2002; Nanny and Ratasuk, 2002; Fan *et al*., 2006). The degradation methods have disadvantages of lengthy sample preparation, transformations and organic carbon lost (Smith *et al*., 1991). Therefore, these conventional techniques do not provide a method for rapid and effective monitoring of organic compounds in leachates over a time frame that could influence the leachate treatment system.

For a rapid characterisation of organic compounds in leachate, UV absorption and fluorescence spectroscopy could be useful as it can monitor a wide range of constituents such as humic substance, polyaromatic compounds, xenobiotic compounds etc. (Senesi *et al*., 1991). The UV absorption and fluorescence techniques have been widely used in various ecosystems (e.g. marine, Coble, 1996; groundwater, Baker and Lamont-Black, 2001; sewage-impacted rivers, Baker, 2001; wastewater and effluents, Westerhoff *et al*., 2001 and Her *et al*., 2003). These studies suggest that UV absorption and fluorescence techniques have a significant potential in landfill leachate research by fingerprinting various organic compounds as well as analysing compositional characteristic of the different organic compounds in leachates. However, very little work on the characterisation of leachates using these techniques has been carried out (Baker and Curry, 2004; Ham *et al*., 2008; Huo *et al*., 2008).

This article presents an investigation on the several organic compounds in leachates in course of biodegradation and performs a feasibility study on the application of UV absorption and fluorescence spectroscopy for compositional analysis of leachates and/or rapid estimation of biodegradation potential of leachates. A systematic comparison of the biodegradation associated evolution of the organic compounds is carried out for leachates collected from two UK landfills (L1 and L2). These investigations are carried out using combination of potentially new techniques of UV absorption and fluorescence spectroscopy and conventional methods DOC and COD. This provides deep insight into
the characteristics of the organic compounds on the investigated UK landfill sites/phases that could be used to foresee the necessary treatment in different landfill sites. The combined analysis using conventional and spectroscopic methods performs a feasibility study on the use of UV absorption and fluorescence spectroscopy for a rapid and onsite characterisation of organic compounds which might find application if regulatory constraints could be fulfilled.

MATERIALS AND METHODS

Leachate sampling sites
Three untreated and two treated leachate samples were collected from two MSW landfills L1 and L2 in the UK. The characteristics of the leachate samples, and details of the treatment carried out on the treated leachate samples, are presented in Table 1. Both sites have been in operation for over 50 years. The L1 landfill received mainly MSW with commercial, industrial, and non-hazardous liquid wastes. The L2 landfill contains old Phases that accepted MSW and industrial wastes, and more recent Phases containing predominantly MSW and commercial wastes. At these sites, a range of hazardous wastes are co-disposed with municipal solid wastes and there is no dedicated hydraulic isolation between different phases. The collected samples may represent mixture of leachates generated from a diverse range of waste composition and age and hence, merit investigation.

‘Red’ phase leachates indicates leachates collected predominantly from areas of hazardous industrial wastes which contains elevated concentrations of chlorinated aliphatic and aromatic organic compounds than of ‘yellow’ phase leachates.

Aerobic biodegradation
Aerobic biodegradation experiments of the untreated and treated leachate samples were carried out in 1 L batch stirred glass reactors over a period of 30 days. Air was supplied by an aquarium pump (Aquatec, USA) through 5 mm diameter poly-vinyl chloride (PVC) tubing via a 3 cm long airstone at the top of the reactor. The air streams into the reactors were maintained at a flow rate of 100 mL/min. Leachate samples were taken at different days from the reactors, filtered through a 25 mm micro glassfibres filter (MF 200, Fischer, UK), and analyzed for DOC and COD. In addition, their spectroscopic (UV and fluorescence) characteristics were determined at 20°C.
The leachate samples were analysed for pH, BOD\textsubscript{30}, COD, TC (total carbon), TIC (total inorganic carbon), TOC, DOC, TS (total solids), TVS (total volatile solids), TFS (total fixed solids), TDS (total dissolved solids), TSS (total suspended solids), VSS (volatile suspended solids), and anions; Chloride (Cl\textsuperscript{-}) and Nitrates (NO\textsubscript{3}\textsuperscript{-}) and cations; Sodium (Na\textsuperscript{+}), Ammonium (NH\textsubscript{4}\textsuperscript{+}), Potassium (K\textsuperscript{+}), Magnesium (Mg\textsuperscript{2+}) and Calcium (Ca\textsuperscript{2+}) (APHA, 1998).

BOD\textsubscript{30} of the leachate samples was determined by OxiTop control system, WTW, Germany (APHA, 1998). TS, TFS, TVS, TDS, TSS, and VSS analysis were performed according to the standard methods (APHA, 1998). Anions and cations analysis were

### Table 1 - Characteristics of the leachate samples (Information provided by landfill operators).

<table>
<thead>
<tr>
<th>Sample</th>
<th>Label</th>
<th>Nature of waste from which leachate derived</th>
<th>Nature of treatment</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>L1 (LTP)</td>
<td><strong>Landfill L1</strong>&lt;br&gt;• Mixed MSW, commercial, industrial and hazardous wastes, with hazardous liquid wastes until 2002, non hazardous liquid waste thereafter, wastes range in age from 0 to 80 years</td>
<td>Leachate was passed through a treatment plant consisting of aerobic rotating biological contactors</td>
</tr>
<tr>
<td>2</td>
<td>L1 (P4)</td>
<td><strong>Landfill L1, phase 4</strong>&lt;br&gt;• Predominantly MSW waste, with some industrial waste, with liquid non-hazardous wastes, wastes less than 4 years old&lt;br&gt;• The phases are not hydraulically isolated from each other. Large scale leachate recirculation for many years, significant potential of mixing of leachates from different areas.</td>
<td>Untreated</td>
</tr>
<tr>
<td>3</td>
<td>L2 (LTP)</td>
<td><strong>Landfill L2, yellow phase</strong>&lt;br&gt;• Predominantly MSW, some hazardous industrial wastes, over-tipped by recent non hazardous MSW, waste ~30 – 60 years old.&lt;br&gt;• The phases are not hydraulically isolated from each other, less potential of mixing of leachates from different areas.</td>
<td>Untreated</td>
</tr>
<tr>
<td>4</td>
<td>L2 (FE)</td>
<td><strong>Landfill L2</strong>&lt;br&gt;• Sample is effluent from leachate treatment plant, treating “red” and “yellow” phase leachate</td>
<td>Treatment primarily consists of oil separation, air stripping and settlement of iron sludge, followed by activated sludge aerobic treatment</td>
</tr>
<tr>
<td>5</td>
<td>L2(P2)</td>
<td><strong>Landfill L2 phase 2</strong>&lt;br&gt;• Predominantly domestic MSW and non hazardous industrial wastes, waste 0-20 years old.&lt;br&gt;• The phases are not hydraulically isolated from each other, less potential of mixing of leachates from different areas.</td>
<td>Untreated</td>
</tr>
</tbody>
</table>

NB: The terms “LTP” and “FE” relate to Leachate Treatment Plant, Final Effluent after the treatment.

### ANALYTICAL METHODS

The leachate samples were analysed for pH, BOD\textsubscript{30}, COD, TC (total carbon), TIC (total inorganic carbon), TOC, DOC, TS (total solids), TVS (total volatile solids), TFS (total fixed solids), TDS (total dissolved solids), TSS (total suspended solids), VSS (volatile suspended solids), and anions; Chloride (Cl\textsuperscript{-}) and Nitrates (NO\textsubscript{3}\textsuperscript{-}) and cations; Sodium (Na\textsuperscript{+}), Ammonium (NH\textsubscript{4}\textsuperscript{+}), Potassium (K\textsuperscript{+}), Magnesium (Mg\textsuperscript{2+}) and Calcium (Ca\textsuperscript{2+}) (APHA, 1998).
carried out using a Dionex-500 (Dionex, USA) ion chromatograph. Leachate samples were repeatedly analysed in order to validate/evaluate the produced results and they were found within acceptable analytical error (± 4%). All chemicals used for the analytical determinations were of analytical grade.

**Determination of DOC and COD**
TC, TIC, TOC and DOC of leachate samples were analyzed by a high-temperature total organic carbon analyzer (Dohrmann Rosemount DC-190, USA). Before DOC analyses, samples were acidified to pH < 2 using 2N HCl to remove inorganic carbon (IC). COD measurements of the leachate samples taken from the aerobic biodegradation reactor were carried out using the micro-digestion technique (Jirka and Carter, 1975).

**Spectroscopic characterisation of leachates**
5 mL volumes of leachate samples were used for spectroscopic analysis Spectroscopic analysis did not require any sample preparation except for the fact that leachate samples were adjusted to pH 7.0 using 2M NaOH because fluorescence intensity is highly sensitive to pH change.

**UV Absorbance measurements**
UV Absorbance of leachate samples was determined at 254 nm (UV\textsubscript{254}) wavelength on a Cecil Spectrophotometer using a 10 mm quartz cell. Distilled water was used as blank. Leachate samples were diluted until the absorbance value fell below 0.1 cm at 340 nm wavelength to avoid the inner filtering effects (IFE) (Baker, 2005).

**Fluorescence measurements**
The fluorescence spectra of the leachate samples were measured in a standard 10 mm quartz cuvette using a Cary Eclipse fluorescence spectrometer (Varian, USA) at 20°C. Three dimensional (3D) EEMs were generated at excitation and emission slit widths of 5 nm band pass. All samples were scanned at the excitation wavelengths 190 - 800 nm in 10 nm steps and emission wavelengths 200 - 800 nm in 10 nm step intervals. The temperature throughout the study was held constant at 20°C in order to avoid any interference from thermal quenching (Baker, 2005). The spectra of water blank was obtained in the same conditions and was subtracted from the original spectra of leachates to eliminate water Raman scatter peaks. Scan speed was 9600 nm/min. 3D maps were built using Sigma-plot 10 software.

EEMs are illustrated as the elliptical shape of contours. The X and Y-axis represent the emission and excitation wavelength respectively. Contour lines for each EEM spectrum represent the fluorescence intensity. Total fluorescence intensity was calculated by the cumulative integration of the intensity versus emission wavelength data for any given excitation wavelength range corresponding to different types of materials and was corrected by multiplying with the required dilution factor.

Emission spectra were recorded in emission scanning mode over the range 300 - 500 nm at excitation wavelengths 230 - 260 nm and 320 - 370 nm. Fluorescence spectra in emission scanning modes provided important aromatic structural information with the position of the fluorescence peaks of the different compounds. The total intensity was
calculated by adding the intensities from the intensity versus emission wavelength data for every excitation wavelength.

RESULTS AND DISCUSSION
Leachate characterization
Table 2 shows the chemical properties of the untreated and treated leachate samples collected from landfills L1 and L2. The pH of the collected leachates was in the range 7.20 - 8.42. The pH of leachate usually increases with time due to decrease of the concentration of free volatile fatty acids (Chian and Dewalle, 1976; Pohland and Harper, 1985). The reported pH of acidogenic leachates ranges from 5.6 to 6.9 whereas the pH of methanogenic leachates is in the range 6.8 - 8.0 (Lu et al., 1985; McBean et al., 1995; Lo, 1996). The pH values for the untreated samples in this study therefore indicating a methanogenic state although the leachates here may come from a mixture of old and new wastes within the sites.

BOD and COD are used to measure the organic strength in leachates. Table 2 shows that all of the untreated and treated leachate samples had BOD$_{30}$ values in the range of 85 - 452 mg/L and COD values in the range of 850 - 4,500 mg/L. BOD/COD values are correlated with the age of the landfill. Cho et al. (2002), Tatsi et al. (2003), Lopez et al. (2004), Cecen and Aktas (2004) reported that leachates from young landfills are characterised by high BOD and COD concentrations with values ranged from 2,300 to

<table>
<thead>
<tr>
<th>Parameter (mg/L) (except pH)</th>
<th>Sample 1 (treated L1)</th>
<th>Sample 2 (untreated L1)</th>
<th>Sample 3 (untreated L2)</th>
<th>Sample 4 (treated L2)</th>
<th>Sample 5 (untreated L2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>8.42</td>
<td>7.72</td>
<td>7.20</td>
<td>7.60</td>
<td>8.12</td>
</tr>
<tr>
<td>BOD$_{30}$</td>
<td>282</td>
<td>85</td>
<td>113</td>
<td>226</td>
<td>452</td>
</tr>
<tr>
<td>COD</td>
<td>3300</td>
<td>4500</td>
<td>1100</td>
<td>850</td>
<td>3700</td>
</tr>
<tr>
<td>BOD$_{10}$/COD</td>
<td>0.09</td>
<td>0.02</td>
<td>0.10</td>
<td>0.27</td>
<td>0.12</td>
</tr>
<tr>
<td>TC</td>
<td>1026</td>
<td>2728</td>
<td>644</td>
<td>243</td>
<td>2117</td>
</tr>
<tr>
<td>TIC</td>
<td>351</td>
<td>1477</td>
<td>373</td>
<td>104</td>
<td>1422</td>
</tr>
<tr>
<td>TOC</td>
<td>675</td>
<td>1251</td>
<td>271</td>
<td>139</td>
<td>695</td>
</tr>
<tr>
<td>DOC</td>
<td>663</td>
<td>1191</td>
<td>232</td>
<td>125</td>
<td>680</td>
</tr>
<tr>
<td>TS</td>
<td>17190</td>
<td>32890</td>
<td>7170</td>
<td>8200</td>
<td>10870</td>
</tr>
<tr>
<td>TVS</td>
<td>15480</td>
<td>18080</td>
<td>1120</td>
<td>1620</td>
<td>2140</td>
</tr>
<tr>
<td>TFS</td>
<td>1710</td>
<td>14810</td>
<td>6050</td>
<td>6580</td>
<td>8730</td>
</tr>
<tr>
<td>TSS</td>
<td>475</td>
<td>170</td>
<td>167</td>
<td>230</td>
<td>170</td>
</tr>
<tr>
<td>VSS</td>
<td>100</td>
<td>80</td>
<td>125</td>
<td>110</td>
<td>40</td>
</tr>
<tr>
<td>TDS</td>
<td>16713</td>
<td>32710</td>
<td>7000</td>
<td>7830</td>
<td>10490</td>
</tr>
<tr>
<td>Cl$^-$</td>
<td>675</td>
<td>680</td>
<td>701</td>
<td>242</td>
<td>729</td>
</tr>
<tr>
<td>NO$_3^-$</td>
<td>0.63</td>
<td>0</td>
<td>1.40</td>
<td>1.0</td>
<td>4.30</td>
</tr>
<tr>
<td>Na$^+$</td>
<td>382</td>
<td>306</td>
<td>325</td>
<td>307</td>
<td>295</td>
</tr>
<tr>
<td>NH$_4^+$</td>
<td>284</td>
<td>315</td>
<td>343</td>
<td>325</td>
<td>325</td>
</tr>
<tr>
<td>K$^+$</td>
<td>565</td>
<td>461</td>
<td>481</td>
<td>449</td>
<td>456</td>
</tr>
<tr>
<td>Mg$^{2+}$</td>
<td>57</td>
<td>59</td>
<td>17</td>
<td>11</td>
<td>10</td>
</tr>
<tr>
<td>Ca$^{2+}$</td>
<td>696</td>
<td>611</td>
<td>325</td>
<td>254</td>
<td>268</td>
</tr>
</tbody>
</table>
25,000 mg/L and 10,540 to 70,900 mg/L respectively, whereas in old landfill leachates BOD and COD values ranges from 62 to 800 mg/L and 1,409 to 3,460 mg/L respectively. Chian and DeWalle (1976), Chian (1977) and Harmsen (1983) also demonstrated that the leachates generated from old landfills consist mainly of high molecular weight recalcitrant organic compounds, which are correlated with low BOD and COD values. Thus the low BOD and COD values of the collected leachate samples in this study implying significant leaching from the old wastes in the sites and hence, considerable amount of recalcitrant organic compounds should be expected to be present. This can also be verified by the corresponding BOD/COD ratio which is commonly known as a measure of biodegradability (Chen et al., 1996; Lo, 1996). The BOD/COD ratios of the collected leachate samples ranged from 0.02 to 0.30. Studies reported in the literature indicate that leachates containing high molecular weight recalcitrant organic compounds had BOD/COD ratios in the range of 0.01 - 0.40 (Timur and Ozturk, 1999; Cho et al., 2002; Marttinen et al., 2002; Tatsi et al., 2003; Cecen and Aktas, 2004; Lopez et al., 2004).

Table 2 also shows that although L1 (P4) leachate had been collected from the phase where wastes were less than 4 years old (Table 1), it had a high pH and low values of BOD and a low BOD/COD ratio. This may indicate that methanogenic conditions may have been established at an early stage in this phase. The early establishment of methanogenic conditions in this phase may be attributed to a high amount of readily degradable organic waste and the high moisture content (Table 1) allowing fast dissolution of organic compounds and accelerating microbiological decomposition. This may also be due to the fact that older leachates were mixed in with leachates from this phase. The early establishment of methanogenic condition has also been reported in the literature (Lo, 1996; Kulikowska and Klimiuk, 2008). Kulikowska and Klimiuk (2008) showed that in landfills in Poland, methanogenic conditions had been established at an early stage with stable COD values of 610 mg/L after about 4 years. The total carbon content of the untreated leachate L1 (P4) was relatively higher than the untreated leachates collected from L2 implying that organic and inorganic compounds in the L1 landfill was considerably higher than the L2 landfill. However, the treated leachates collected from each of these landfills generally showed lower total carbon content in comparison to the untreated leachates thereby indicating the effect of treatment.

It is found from the Table 2 that with the exception of TFS and VSS of L1 (LTP), the leachates from L1 generally had higher solids content than the leachates from L2. In the L2 leachates the TFS contents were higher than the TVS contents for all of the untreated and treated leachate samples, whereas for the L1 leachates the trend was reversed. This indicates that the leachates from L2 contained higher levels of inorganic solids whereas those from L1 contained higher levels of organic solids. TSS, VSS and TDS contents in all of the untreated and treated leachate samples ranged from 150 to 475 mg/L, 40 to 125 mg/L and 7,000 to 32,710 mg/L respectively, which are significantly higher than the values reported in the literatures (Al-Yaqout and Hamodoa, 2003; Fan et al., 2006). This reflects a high degree of mineralization during active anaerobic decomposition of the waste in L1 and L2 landfills (Al-Yaqout and Hamodoa, 2003).

The concentrations of (Cl⁻), NO₃⁻-nitrogen, NH₄⁺-nitrogen, (Na⁺), (K⁺), (Mg²⁺) and (Ca²⁺) are presented in Table 2. The values of ammoniacal-nitrogen (NH₃-N) observed
in all of the untreated and treated leachate samples were at the high end of the concentration range reported in the literature (Marttinen et al., 2002; Silva et al., 2004). This might be due to the hydrolysis and fermentation of the nitrogenous fraction of biodegradable substrates (Carley and Mavinic, 1991). In comparison to ammonical-nitrogen (NH$_3$-N), low NO$_3$-nitrogen values were found for all of the leachates, indicating that the majority of the nitrogen was in the form of ammonia. The results also show that the values of Na$^+$, K$^+$, and Cl$^-$ observed in all of these leachate samples were in the high concentration range (Chu et al., 1994; Al-Yaqout and Hamooda, 2003; Fan et al., 2006). The high values of these salt contents are correlated with high conductivities and the high TDS values. The Mg$^{2+}$ and Ca$^{2+}$ contents of the L1 leachates were higher than those of L2 leachates. This might be due to higher industrial wastes disposed in L1 landfill than in L2 landfill (Table 1) (Kulikowska and Klimiuk, 2008).

The above results confirm that the chemical composition of leachates may vary significantly from site to site. Differences were found in the concentrations of organic matter, anions and cations and in total and fixed solids contents. Leachates from L1 had higher solids, organic matter, sodium, chloride and magnesium contents than leachates from L2 in all of the untreated and treated samples. Owing to such a variable characteristics of landfill leachates, it is essential to conduct a long term monitoring programme to obtain representative information on leachates and to understand the detailed evolution of the constituent organic matter.

**Aerobic biodegradation of landfill leachates**

The change in the nature of organic compounds in all of the untreated and treated leachate samples during laboratory scale aerobic biological treatment over a period of 30 days was investigated using the conventional characterization methods of DOC and COD. Fig.1 (a) shows the results for DOC and COD as a function of time for all of the untreated and treated leachate samples. The results show a gradual decrease of DOC and COD with time indicating the reduction of organic compounds by biological processes. Fig. 1(a) also shows that DOC and COD concentrations were greatest in the untreated leachates L1 (P4 (phase 4)) and L2 (P2 (phase 2)), indicating that these two leachates contained significant amounts of organic compounds. The treated leachate L1 (LTP; Leachate treatment plant) also had high values of DOC and COD. This suggests that the treatment applied prior to aerobic biodegradation in the laboratory and the subsequent aerobic biodegradation were insufficient to remove all of the organic compounds from this particular leachate. However, aeration of the reactors was observed to reduce DOC and COD for all of the untreated and treated leachates, demonstrating it to be an effective process in further lowering the organic content of the original leachates used in this study. Fig. 1(a) also show that significant quantities of DOC and COD still remained after 30 days, indicating that significant amounts of non-biodegradable or recalcitrant organic material was still present in the leachates after the treatment.

Fig.1 (b) shows the percentage removal of DOC and COD in the laboratory scale aerobic biodegradation experiments as a function of time. The %DOC trend shows that after 30 days aeration the degradation of different leachates are in the order of L2 (LTP) > L2 (FE) > L1 (LTP) > L1 (P4) > L2 (P2) thereby indicating their biodegradability. However, from the %DOC results the leachates can be divided into two groups in terms of their biodegradation after 30 days. The L2 (LTP) and L2 (FE) leachates which have
low concentrations of organic compounds could be classed as easily biodegradable leachates whereas the rest of the leachates which have high concentrations of organic compounds could be classed as not easily biodegradable. The %DOC removal found in different leachates was not the exact replica of the observed %COD removal trend. While the highest %COD removal was observed for L2 (LTP) leachate, the lowest %COD removal was observed for a different leachate, L1 (P4). This could be explained by the difference in the method of estimating non-degraded compounds in these two techniques. Due to the presence of the strong oxidizing agent, some inorganic fractions of leachate get incorporated in COD measurements whereas the DOC measurement mostly estimates the organic fraction of leachate. However, from Fig. 1 (a, b) it can be concluded that the biodegradability of L2 (LTP) leachate is the highest after 30 days of aeration whereas L1 (P4) leachate can be accepted as one of the least biodegradable leachates among the six leachates under consideration.

Fig 2 (a) shows the change of UV$_{254}$ absorbance over time during aerobic biodegradation for all of the leachate samples. The highest initial value of UV$_{254}$ absorbance was observed in the leachate L1 (P4) whereas the lowest value was observed in the L2 (FE) leachate. Intermediate values of UV$_{254}$ absorbance were observed in L2 (P2), L1 (LTP) and L2 (LTP) leachates with decreasing order respectively. This suggests that the L1 (P4) leachate had the highest amount of aromatic organic compounds, with the other leachates having progressively decreasing amount of aromatic compounds. Fig. 2 (a) also shows that in all of these leachates, the UV$_{254}$
absorbance decreased with an increasing number of days of aeration. This suggests the breakdown of the aromatic structures of the constituent organic matter by an aerobic treatment process (Gottschalk et al., 2000).

Fig. 2 (b) shows the percentage reduction of UV\textsubscript{254} absorbance during aerobic biodegradation for all of the untreated and treated leachate samples. A high percentage of UV\textsubscript{254} absorbance reduction was observed for leachates with low UV\textsubscript{254} absorbance values (Fig. 2 (a)). This suggests that leachates containing low aromatic organic compounds had a high percentage reduction of UV\textsubscript{254} absorbance and vice versa. The percentage reduction of UV\textsubscript{254} absorbance showed the degradation of different leachates in the order of L2 (LTP) > L2 (FE) > L1 (LTP) > L2 (P2) > L1 (P4) which was in good agreement with the percentage removal of DOC observed in the different leachates (Fig. 1 (a)). Again from the UV\textsubscript{254} absorbance reduction trend, L2 (LTP) and L2 (FE) leachates can be accepted as easily biodegradable leachates whereas the rest of the leachates can be accepted as not easily biodegradable. However, the percentage reduction of UV\textsubscript{254} absorbance in different leachates was not the exact replica of the observed %COD removal trend. This can be explained again by the fact that some inorganic fractions of leachate get incorporated in COD due to the presence of strong oxidizing agent while the UV\textsubscript{254} absorbance measurable are aromatic organic compounds. Thus, the fairly good agreement on the degradation trend observed in different leachates by UV\textsubscript{254} absorbance and DOC measurements probably indicate that organic compounds contributing DOC in these leachates were mostly aromatic in nature. However, the results of UV spectroscopy and the conventional DOC and COD experiments suggest that leachates containing high aromatic organic compounds usually result in low percentage removal of DOC and COD in the course of a treatment process.

**Fluorescence spectroscopic results**

Fig. 3 shows the Excitation-Emission-Matrix (EEM) maps of the leachate DOM fractions generated before and after laboratory scale aerobic biodegradation for leachates L1 (LTP) and L2 (LTP). Four distinct zones were identified on the EEM maps.
for both of these leachates that were indicative of the presence of different organic substances.

Zone 1 (H-L): Peaks were observed to be present between 230 - 260 nm and 360 - 390 nm excitation and 400 - 460 nm and 460 - 480 nm emission respectively and is widely recognized as a component of the humic-like fractions (H-L) (Coble, 1996; Baker and Curry, 2004; Cumberland and Baker, 2007).

Zone 2 (F-L): A peak, which was present in all of the leachates between 320 - 350 nm excitation and 400 - 440 nm emission, can be attributed to aromatic and aliphatic groups in the DOM fractions, and is commonly labelled as fulvic-like (F-L) (Coble, 1996; Baker and Curry, 2004).

Zone 3 & 4 (Protein-like): Peaks were observed at 230 - 240 nm and 270 - 280 nm excitations and 300 - 320 nm emission, labelled as tyrosine-like (Tyr-L) and at 230 - 240 nm and 270 - 280 nm excitations and 340 - 370 nm emission labelled as tryptophan-like (Trp-L). These peaks are attributed to ‘protein-like’ structures (Coble, 1996; Elliot et al., 2006).

Fig. 3 - Excitation-Emission Matrices (EEM) for landfill leachates L1 (LTP) and L2 (LTP) before and after aeration (Zone 1 H-L; 2 F-L; 3 and 4 protein like) (dilution factor 25) (T = treated and U = untreated).
The intensities of the peaks in different zones thus correspond to the concentrations of different organic compounds and hence, the change of fluorescence peak intensities of these compounds of different untreated and treated leachates from different landfills in the course of treatment may provide the systematic comparison of the biodegradation associated evolution of different organic compounds of the landfill sites.

Figure 4 presents the fluorescence properties for all of the untreated and treated leachate samples over 30 days of period. Leachates L2 (LTP) and L2 (FE) had relatively lower fluorescence intensities in Zones 1 (H-L) and 2 (F-L) and higher intensities in Zone 3 (Tyr-L) and 4 (Trp-L) than leachates L1 (LTP), L1 (P4) and L2 (P2). This suggests that L2 (LTP) and L2 (FE) had relatively lower concentrations of H-L and F-L compounds and higher concentrations of protein-like compounds than leachates L1 (LTP), L1 (P4) and L2 (P2). Figure 4 also show that aerobic biodegradation decreased the intensities of Zone 1 (H-L) and 2 (F-L) materials by about 4 - 64% in all of the untreated and treated leachate samples over 30 days of period. The decrease in intensities could be explained by the decomposition of H-L and F-L fluorophores during aerobic biodegradation.

**Fig. 4 - Integrated fluorescence intensities of H-L, F-L, Tyr-L and Trp-L compounds for all of the untreated and treated leachates during 30 days of aerobic treatment. Total fluorescence intensity was calculated by the cumulative integration of the intensity versus emission wavelength data for any given excitation wavelength range corresponding to different types of materials and was corrected by multiplying by dilution factor 25 (I.R = Intensity reduction).**
(Uyguner and Bekbolet, 2005; Saadi et al., 2006) thereby indicating the degradation potential of humic and fulvic like compounds of different leachates in Fig. 4.

The intensities of Zone 3 and 4 (270 - 280 nm excitation) fluorophores (tyrosine-like and tryptophan-like compounds respectively) was also found to decrease during 30 days of aerobic biodegradation. This reduction can be attributed to the breakdown of proteinous materials by aeration (Zhang et al., 2008). Fig. 4 also shows that the percentage removal of Trp-L compounds was higher than for the H-L and F-L compounds in all leachate samples. This indicates that protein-like compounds were more biodegradable than H-L and F-L compounds and therefore aerobic biodegradation was more effective in removing Trp-L compounds than the H-L and F-L compounds. However, in L2 (LTP) and L2 (FE) leachates, a comparatively high reduction (50 - 64%) of fluorescence intensities in Zone 1 (H-L) and Zone 2 (F-L) materials was observed. This indicates that aerobic biodegradation had significantly broken down the relatively less biodegradable H-L and F-L structures in these two leachates. In the case of L1 (P4) and L2 (P2) leachates, aeration reduced the intensities of Zone 1 (H-L) and 2 (F-L) materials by only about 4 - 13%, indicating that a considerable fraction of high molecular weight organic compounds remained.

A lower reduction of the fluorescence intensities of the humic-like (H-L) and fulvic-like (F-L) compounds in comparison to the protein-like compounds for all leachates is observed in course of the biodegradation. The less biodegradable nature of H-L and F-L compounds suggested that these compounds can be treated as the essential building block of recalcitrant organic compounds. However, among the five leachates under consideration, the L2 (LTP), L2 (FE) leachates exhibited around 60% reduction of the fluorescence intensities of the H-L and F-L compounds after 30 days of aeration which is noticeably higher than for L1 (LTP), L1 (P4) and L2 (P2) leachates (around 4 to 30%). This indicated a relatively high biodegradability of the L2 (LTP), L2 (FE) leachates and can be explained by the presence of lower amount of recalcitrant H-L/F-L compounds than L1 (LTP), L1 (P4) and L2 (P2) leachates.

Fluorescence analyses of humic and fulvic-like compounds in emission scanning mode
Fluorescence spectra in emission scanning modes were recorded to obtain more detailed information about the condensed aromatic structures with peak positions. The spectra of the treated L1 (LTP) and untreated L2 (LTP) leachate samples after days 10, 20 and 30 of aeration are presented in Fig. 5. For L1 (LTP) leachate, Peak II at (320 - 350) nm excitation was the strongest whereas for leachate L2 (LTP), Peak I at (230 - 260) nm excitation was the strongest. Peak II at (360 - 390) nm excitation for leachate L1 (LTP) also had high intensities. As compared with the EEM spectrum (Fig. 3), Peak I at (230 - 260) nm excitation can be assigned as tryptophan-like fluorophores. Peak II at (230 - 260) nm and (360 - 390) nm excitations can be assigned as H-L and at (320 - 350) nm excitations as F-L fluorophores. For leachate L2 (LTP), Peak III with low intensity is also observed at wavelength of (450 - 470) nm which can not be found in the EEM spectra (Fig. 3). This Peak III is probably attributed to ‘red shifted’ high molecular weight H-L fluorophores (Chen et al., 2003).
Kang et al. (2002) reported that the shorter wavelength peaks (360 nm) can be interpreted to be due mainly to the presence of simple aromatic ring in the molecule, whereas the peaks in the longer wavelength (430 nm) are due to the condensed aromatic rings and conjugation of simple aromatic rings. It can be seen from Fig. 5 that leachate L1 (LTP) showed strong intensities at 430 nm (Peak II), suggesting that this leachate was associated with the presence of linearly condensed aromatic rings of H-L and F-L molecules. However, it is also observed that leachate L2 (LTP) showed the highest peaks at 360 nm (Peak I) (Fig. 5). This can be ascribed to the presence of simple aromatic rings. Fig. 5 also shows that aeration reduced the intensities of Peak I and Peak II in these two leachates. This decrease can be attributed to the destruction of aromatic ring structures through aerobic biodegradation. However, aeration also increases the intensities of Peak I for L1 (LTP) leachate. This can be ascribed to the enrichment of the simpler aromatic tryptophan-like structures of L1 (LTP) leachate during aerobic biodegradation.

It was also found that the ratio of intensities of longer to shorter wavelengths for leachate L1 (LTP), L1 (P4) and L2 (P2) were higher than those of leachate L2 (LTP) and L2 (FE). This implies that leachate L1 (LTP), L1 (P4) and L2 (P2) contained aromatic ring of more condensed form than those for leachate L2 (LTP) and L2 (FE) (Kang et al., 2002). This may explain the relatively higher intensity reduction for peak I and II of L2 (LTP) and L2 (FE) leachates in comparison with L1 (LTP), L1 (P4) and L2 (P2) leachates (Figs. for , L1 (P4), L2 (FE) and L2 (P2) leachates are not shown).

The fluorescence spectroscopic results can be correlated with the general trend observed in the UV spectroscopic results and also with the percentage reduction of COD and DOC. Spectral analyses (Fig. 5) indicated that L2 (LTP) and L2 (FE) leachates may have contained simple aromatic rings in the molecules. The amount of aromatic organic compounds was also indicated to be low in these leachates (Fig. 2 (a)). These leachates eventually exhibited high percentage reduction of DOC and COD (Fig.1 (a, b)), UV\textsubscript{254} absorbance (Fig. 2 (b)) and H-L and F-L intensities (Fig. 3) during aerobic treatment. This allows us to conclude that leachates containing low concentration of aromatic organic compounds and simple aromatic structures may be easily degradable.

**Feasibility assessment of spectroscopic methods**

A feasibility assessment of the rapid characterisation of leachates using UV and fluorescence spectroscopy can be made if the biodegradation potential of different leachates obtained by spectroscopic method is compared with the results of well established DOC and COD methods. The biodegradability of different leachates found from %UV\textsubscript{254} and %DOC reduction experiments were in good agreement with each other. Both these methods showed that L2 (LTP) and L2 (FE) leachates were easily biodegradable whereas the rest of the leachates were not so easily biodegradable. The biodegradation study of constituent organic compounds using fluorescence spectroscopy in different leachates was also in agreement with %DOC removal. Fluorescence spectroscopy also indicated that after 30 days of aeration L2 (LTP) and L2 (FE) had high degradability whereas L1 (LTP), L1 (P4) and L2 (P2) showed relatively low degradability.
Although %COD removal results were not an exact replica of %DOC removal and spectroscopic results, in general this can also be accepted as fair agreement, as %COD removal experiment also showed a high degradability for L2 (LTP) leachate and low degradability for L1 (P4) leachate. Mild inconsistency between established COD and
novel methods on a case-by-case basis can be attributed to the difference in the method of estimating non-degraded compounds. As discussed before, due to the presence of a strong oxidizing agent, some inorganic fractions of leachate get incorporated in COD measurements whereas the DOC measurement mostly estimates the organic fraction of leachate. The spectroscopic methods were also organic in nature whereby UV absorption spectroscopy gave a quick estimation on the degradation of aromatic compounds and fluorescence spectroscopy indicated degradation of several different organic compounds.

As a result, the good agreement between spectroscopic method and well established DOC and COD methods point to the fact that a rapid assessment of biodegradation potential of leachates using spectroscopic method was in general reliable. In addition, the UV spectroscopy allowed the study of the possible biodegradation of aromatic compounds whereas fluorescence spectroscopy enabled the study of the proportion of humic and fulvic-like materials and their degradation in leachates. As such, these novel methods provided an insight into the recalcitrant organic compounds in these landfill leachates.

CONCLUSIONS
A feasibility study on the application of UV absorption and fluorescence spectroscopy for rapid monitoring of organic compounds in leachate has been done and a systematic comparison of the biodegradation associated evolution of different organic compounds in leachates has also been undertaken. The leachates were collected from UK MSW landfills (L1 and L2) and analyzed for the first time using a combination of conventional methods DOC and COD and potentially new techniques of UV absorption and fluorescence spectroscopy. The biodegradation of leachates estimated from the reduction of aromatic compounds using UV spectroscopy revealed that L2 (LTP) and L2 (FE) leachates contain lower amount of aromatic organic compounds and more easily biodegradable than the L1 (LTP), L1 (P4) and L2 (P2) leachates. Fluorescence spectroscopic results showed that humic-like (H-L) and fulvic-like (F-L) compounds were less biodegradable and can be treated as the essential building block of recalcitrant organic compounds. Around 60% reduction of the fluorescence intensities of the humic-like (H-L) and fulvic-like (F-L) compounds were found for L2 (LTP) and L2 (FE) leachates after 30 days of aerobic biodegradation which was noticeably higher than for L1 (LTP), L1 (P4) and L2 (P2) leachates (around 4 to 30%) implying a relatively high biodegradability of the L2 (LTP) and L2 (FE) leachates. The biodegradability of different leachates thus estimated from the spectroscopic methods had an excellent agreement with the conventional estimation using %DOC reduction technique implying that the characterisation of the organic components in landfill leachate using spectroscopic methods are reliable and hence, this research shows a viable route for rapid and effective characterization of organic compounds in leachates suitable for onsite monitoring.

REFERENCES


