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UNIVERSITY OF SOUTHAMPTON

FACULTY OF ENGINEERING AND THE ENVIRONMENT

**CIVIL, MARITIME AND ENVIRONMENTAL ENGINEERING AND
SCIENCE UNIT**

INFRASTRUCTURE RESEARCH GROUP

**INFLUENCES OF LANDFILL LEACHATE DISSOLVED
ORGANIC CARBON ON THE ATTENUATION OF TOLUENE
AND NAPHTHALENE BY OXFORD CLAY**

By

Clare Fiona Dalton

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ABSTRACT

FACULTY OF ENGINEERING AND THE ENVIRONMENT

Civil, Maritime and Environmental Engineering and Science Unit, Infrastructure Research Group

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**INFLUENCES OF LANDFILL LEACHATE DISSOLVED ORGANIC CARBON ON
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By Clare Fiona Dalton

The uncontrolled release of landfill leachate poses a significant threat to the environment and is prevented in part by the landfill liner. The attenuation of contaminants by the liner material may be crucial in limiting environmental damage should the containment of the landfill fail. While the sorption of hydrophobic organic contaminants (HOCs) to clay materials is well documented in the literature in terms of the organic carbon content of the sorbent in a variety of solution phases, a knowledge gap exists in respect to the influence of landfill leachate dissolved organic carbon (DOC) on the attenuation of HOCs. A laboratory based batch sorption study was undertaken, using leachates with five differing DOC characters and origins, at various dilutions, to establish the influence that DOC present in landfill leachates had on the attenuation of the HOCs toluene and naphthalene by Oxford Clay. The aim of this work was to increase the understanding of attenuation of toluene and naphthalene to Oxford Clay in the presence of leachate DOC and to elucidate the role of DOC chemical composition and concentration in landfill leachates on the sorption of HOCs to the Oxford Clay. The objective of this work was to provide more reliable data for predicting the contribution of attenuation of HOCs by sorption in the risk assessment of landfills and recommending updates to the selection process of K_d values for landfill risk assessment models such as LandSim.

The chemical character of the DOC was found to affect how the DOC interacted with the solid phase and humic substance-like (HSL) DOC was observed to preferentially sorb to the Oxford Clay. The sorption of DOC was reversible, indicating that DOC, and so DOC-HOC complexes, had the potential to desorb from the clay. The addition of DOC to the aqueous phase resulted in deviation from the sorption and desorption isotherms in a DOC free leachate in the case of both toluene and naphthalene. While DOC effects on toluene sorption and desorption behaviour were not clear cut, with both increases and decreases in sorption and desorption observed with the addition of DOC; a uniform decrease in sorption and an increase in desorption relative to the DOC free leachate was observed for naphthalene sorption and desorption behaviour. No desorption was observed for toluene in three of the leachates. In all other DOC containing leachates sorption was reversible and exhibited hysteresis. The alteration in sorption and desorption behaviour of HOCs due to DOC could not be explained solely by the maturity or the concentration of DOC in solution, and was attributed to a complex interaction of both factors. Increasing the hydrophobicity of the HOC resulted in increased sorption (naphthalene > toluene). Recommendations were made for the selection of a K_d value to model HOC attenuation on the basis of a ‘worst case’ scenario. Implications for the post closure monitoring and containment of the landfill and the relevance of commercially available humic acid as a leachate DOC surrogate are also presented.

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Declaration of authorship

I, Clare Fiona Dalton,

declare that this thesis entitled

INFLUENCES OF LANDFILL LEACHATE DISSOLVED ORGANIC CARBON ON THE ATTENUATION OF TOLUENE AND NAPHTHALENE BY OXFORD CLAY

and the work presented in it are my own and has been generated by me as the result of my own original research.

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LIST OF ABBREVIATIONS

| | |
|---------|---|
| AHA | Aldrich Humic Acid |
| AJ | Analytik Jenna |
| AMSW | Aged Municipile Solid Waste |
| AOM | Amorphous Organic Matter |
| A-phase | Acetogenic Phase |
| CCL | Compacted Clay Liner |
| DCB | 1,4-dichlorobenzene |
| DFB | 1,4-difluorobenzene |
| DI | Deionised |
| DIC | Dissolved Inorganic Carbon |
| DOC | Dissolved Organic Carbon |
| DOM | Dissolved Organic Matter |
| EC | Electrical Conductivity |
| EPA | Environmental Protection Agency |
| FA | Fulvic Acid |
| FL | Fulvic-Like |
| FML | Flexible Membrane Liner |
| GC | Gas Chromatography |
| GCL | Geosynthetic Clay Liner |
| GCMS | Gas Chromatography Mass Spectroscopy |
| HA | Humic Acid |
| HASL | Humic Acid Synthetic Leachate |
| HDPE | High Density Polyethylene |
| HI | Hysteresis Index |
| HIX | Humification Index |
| HL | Humic-Like |
| HOC | Hydrophobic Organic Contaminant |
| HR | Humification Ratio |
| HS | Humic Substance |
| HSL | Humic Substance-Like |
| IC | Inorganic Carbon |
| IFE | Inner Filtering Effects |
| IHSS | International Humic Substances Society |
| LDPE | Low Density Polyethylene |
| MBT | Mechanically and Biologically Treated waste |
| M-phase | Methanogenic Phase |
| MS | Mass Spectroscopy |

| | |
|------|---------------------------------|
| MSW | Municipal Solid Waste |
| M:V | Mass to Volume Ratio |
| MW | Molecular Weight |
| NDIR | Non-dispersive Infra-red |
| NOM | Natural Organic Matter |
| OC | Organic Carbon |
| OM | Organic Matter |
| PAH | Polycyclic Aromatic Hydrocarbon |
| PL | Protein-Like |
| PVC | Polyvinyl Chloride |
| TA | Tannic Acid |
| TC | Total Carbon |
| TCD | Thermal Conductivity Detector |
| TCE | Trichloroethylene |
| TdC | Total Dissolved Carbon |
| TIC | Total Inorganic Carbon |
| TN | Total Nitrogen |
| TOC | Total Organic Carbon |
| UHQ | Ultra-High Quality |
| UV | Ultraviolet |

1. Introduction

In 2013 an estimated 21.6 million tonnes of household waste was generated in the UK (DEFRA, 2014). Despite a reduction of 62% in the amount of local authority managed waste being landfilled since 2003/04, and 67% of total household waste being recycled, composted or incinerated by local authorities (DEFRA, 2014), some waste is still landfilled. Landfill remains a necessary method of waste disposal as it incorporates residues from other methods of waste disposal (Calace *et al*, 2001). Although these residues may have further uses such as additives in concrete (Aubert *et al*, 2004) this raises additional environmental issues relating to contaminant leaching (Olsson *et al*, 2006). Since other methods for disposal of non-recyclable waste result in a residue, and under the Landfill Directive (1999) landfilling is still allowable, landfilling will remain necessary. Landfilled waste produces a highly contaminated wastewater, leachate, which changes in composition with time (Kjeldsen *et al*, 2002). The uncontrolled release of landfill leachate poses a threat to the environment due to its contaminant load (Environment Agency, 2003a). Therefore, leachate formed in a landfill must be contained and treated before it can be released into the environment (Zouboulis *et al*, 2003) and strict discharge criteria (Environment Agency, 2003b) are applied to the release of this wastewater. Measures to prevent the uncontrolled release of leachate into the environment must be built into the design of all new landfills (Bagchi, 2004). The inclusion of a low permeability basal liner as a physical barrier to prevent uncontrolled leachate release into the design of a landfill is therefore compulsory (Environment Agency, 2003a).

The containment of leachate also results in an entombing of the waste, resulting in waste degradation times being extended for a period of centuries (Reinhart and Al-Yousfi, 1996; Thornton *et al*, 1993). Since landfill liners are untested over these timescales (Thornton *et al*, 1993), it is important to assess the other contributions of the liner towards leachate attenuation through processes, such as sorption, when producing a risk assessment for future landfill applications (Bright *et al*, 2000; Rebhun *et al*, 1992). In the event of liner failure the sorption of contaminants to the liner material may provide an additional avenue of environmental protection. In order to effectively model the processes taking

place at the liner, an understanding of the sorption behaviour of contaminants to the liner material is therefore essential (Devulapalli and Reddy, 1996).

Landfill liners may be composed of clays which can attenuate contaminants within landfill leachates through sorption processes (Hwang and Cutright, 2002). The organic carbon content of the clay has been shown to affect the sorption of organic contaminants onto clays (Kleineidam *et al*, 1999). Another source of organic carbon in the landfill environment is dissolved organic matter (DOM) or dissolved organic carbon (DOC) (Environment Agency, 2009) which is a major component of landfill leachates. Since DOC may compete for sorption sites on the clay, the DOC content of a leachate may also affect the sorption of contaminants to liners. DOC in leachates is complex and highly variable (Banaitis *et al*, 2006) and has been shown to sorb to clay minerals (Vandenbruwane *et al*, 2007) and act as a sorbent for organic contaminants (Garbarini and Lion, 1986). It is therefore necessary to investigate the effect that leachate DOC constituents have on contaminant attenuation because the chemical nature, as well as the amount of DOC in solution, may have an impact on the sorption behaviour.

1.1 Research Aims and Objectives

The aim of this research is to determine the effect that the presence of DOC in landfill leachate has on the sorption and desorption of the hydrophobic organic contaminants (HOCs) toluene and naphthalene (Section 2.1.7) to Oxford Clay (a landfill liner material from southern England used for compacted clay liners in older landfills and as a base layer of composite liners in new landfill cells, Section 4.2.1).

This work was undertaken with a view to recommending updates to the data input into landfill risk assessment tools such as LandSim (Section 2.1.8) when assessing attenuation of contaminants by sorption. These tools require the input of a K_d value for contaminants in order to predict attenuation (Section 2.2.3.1). Since the K_d values for contaminants can vary depending on the environment and the nature of the DOC in the landfill leachate in which the sorption is taking place; the selection of an appropriate K_d value for the environment is key. The desorption behaviour of the contaminants from Oxford Clay will also contribute to understanding the reversibility of contaminant sorption. If sorption is reversible only under certain conditions, the clay could potentially act as a permanent sink for contaminants sorbing them irreversibly, isolating them from the environment or holding them in place long enough for them to be biodegraded without release into the environment. Alternatively, the clay could act as a secondary pollution source, with sorbed contaminants desorbing back into solution once the concentration of the contaminant in the leachate becomes low enough, or due to readily reversible sorption of the contaminant. If desorption is concentration dependant, this could result in toluene or naphthalene being released back into solution after the landfill is no longer considered to be a hazard to the environment. The release of contaminants from the liner into solution may result in environmentally significant levels of contaminant being present in the leachate again, thus constituting a secondary source of pollution originating from the liner.

This aim will be achieved by the fulfilment of five key objectives:

- 1) To characterise the DOC present in eight leachates including a municipal solid waste (MSW) leachate, a mechanically and biologically treated waste (MBT)

leachate, and an aged MSW waste (AMSW) leachate. In order to ensure that a wide range of DOC values were examined, a synthetic humic acid (HA) leachate was used to provide a fully mature (humified) DOC source. This can also be used to determine whether a synthetic DOC source rather than a real leachate could be used to model contaminant sorption or if it produced different results to real leachates. Diluted versions of the MSW, MBT and HA leachates were used to remove DOC concentration as a factor from the sorption behaviour. This will allow comparison of results from sorption experiments with respect to DOC type, which will be achieved via fluorescence spectroscopy, ultra violet spectroscopy, pH, EC and DOC concentration.

- 2) To quantify the sorption of leachate DOC from a MSW leachate (from a landfill site accepting MSW waste) to the Oxford Clay. The leachate was chosen to contain a range of DOC compounds (Section 3.5) in an effort to elucidate the sorption mechanism of leachate DOC to the clay liner material and to identify any preferential sorption of DOC compounds.
- 3) To quantify the sorption and desorption of the HOCs toluene and naphthalene to the Oxford Clay in the presence of a DOC free synthetic leachate. This will provide a baseline level for HOC sorption and desorption to the liner material when DOC is not present in solution and allow comparison of sorption coefficient values with the literature.
- 4) To measure and account for the effect of the different types of DOC present in the leachates on the sorption and desorption of toluene and naphthalene. Along with results from objectives 2 and 3, this will allow interpretation of interactions between DOC, HOCs and the clay liner material.
- 5) To use the results of objectives 2, 3 and 4 to identify sources of error in, and suggest improvements to, the prediction of contaminant attenuation via sorption using existing landfill risk assessment tools which use literature values of K_d to predict naphthalene and toluene sorption and desorption but do not currently account for leachate DOC effects.

2. Background

2.1 Landfill and Leachate

2.1.1 Overview

Landfills in the UK have evolved from open waste pits or middens, which have been used since prehistory (McOmish, 1996), to the fully lined, contained and monitored waste disposal sites we use today. As our understanding of the pollution potential of waste sites has increased legislation and regulations have been imposed on the disposal of waste in order to ensure that environmental pollution is kept to an absolute minimum. The Control of Pollution Act 1974 (COPA) was an early piece of legislation which outlined (among other things) the regulations for waste disposal on land, the prevention of water pollution by various routes, and permitting regulations for new landfill sites. This was partially superseded by the Environmental Protection Act 1990 which set discharge and emission limits for landfills and provided information on licences for waste disposal, the duty of care, legal responsibilities and penalties for waste disposal sites and operators. In 1999, the EC Landfill Directive was agreed upon. This set out waste management strategies for Europe including the reduction of emissions from landfill (particularly methane) and reducing the amount of waste going to landfill, with a focus on reducing the biodegradable fraction of the waste. The Landfill Directive was brought into force in the UK in 2001 and translated into UK law in 2002.

Waste disposal legislation is constantly updated and improved to make it more robust and reduce the environmental impact of waste disposal. For example, in 2008 the 1990 Environmental Protection Act was used to implement the European Waste framework directive in the UK (excluding Northern Ireland). As such, the UK has a range of different landfill technologies in use, either as an active landfill site or as a closed site. These sites range in technology from unlined waste dumps and clay lined pits to the fully engineered and monitored landfill cells required by today's legislation. As such, the UK

has a legacy of historic landfill sites (Environment Agency Maps, 2015) where remediation of the contaminated land resulting from the landfill is required. Despite this, landfill is a necessary measure for waste disposal, as alternative methods such as incineration and digestion result in a residue which still requires disposal, therefore serving only to reduce the volume of landfilled waste (Abbas *et al*, 2009; Li *et al*, 2009). Whilst landfilling has been a traditional method of waste disposal in the UK, changes in the regulations for the types of waste that can be landfilled (reducing the biodegradable fraction of waste and increasing recycling) (EC Landfill Directive, 1999) alongside landfill taxes (Waste Directive, 2008) have resulted in a reduction of the amount of waste landfilled (DEFRA, 2014). Although some waste reduction residues such as incinerator ash may have value as a product, such as additives in concrete (Aubert *et al*, 2004) landfill is still required. Landfill sites may remain a pollution hazard long after their closure, with the length of polluting potential dependant on the type of management employed (Bagchi, 2004). One of the most significant polluting effluents from a landfill is leachate (Abbas *et al*, 2009; Justin and Zupancic, 2009). This section outlines the different types of landfill design and the benefits and drawbacks of each. The formation process, chemistry and stabilisation behaviour of landfill leachates is then discussed with specific focus on DOC in leachates and potential contaminants. The section concludes with a discussion of the pollution potential of leachates including background information on groundwater legislation in the UK.

2.1.2 Types of Landfill

Historically waste was disposed of on land in open, unlined waste heaps. Concern over the environmental impact of these waste heaps in the 1950s (Bagchi, 2004) led to the formalisation of landfilling practice (COPA 1974). Two types of landfill arose, sanitary landfills (natural attenuation landfills) and engineered landfills (containment landfills).

Natural attenuation is the process of allowing the concentration of contaminants to naturally reduce to environmentally acceptable levels. Natural attenuation landfills rely on the slow release of leachate into the environment and the capacity of underlying strata to attenuate sources of contamination. Contaminants are attenuated via sorption, dilution, microbial degradation and ion exchange mechanisms (Bagchi, 2004), detailed

further in Section 2.2. However, this method of waste disposal was only suitable for small volumes of non-hazardous waste and still resulted in measurable alteration of groundwater quality, even when sites are situated well away from groundwater extraction points (Bagchi, 2004). It was recognised by Bagchi (1983) that natural attenuation alone could not fully eliminate the threat to groundwater from leachate contamination from natural attenuation landfills. The containment landfill is a solution to this issue.

In the UK it is necessary for all new landfill sites to be containment landfills and that they include a basal liner in their design. Containment landfills employ a leachate collection system to allow leachate removal for treatment and are suitable for disposal of both hazardous and non-hazardous wastes, including MSW, which contains a wide variety of materials resulting in variable leachate composition (as discussed in Section 2.1.3). There are four main liner systems for landfills;

- A compacted clay liner (CCL) is a barrier of low hydraulic conductivity clay which is packed onto the base of the landfill cell to prevent leachate escape. A CCL relies on its hydraulic conductivity to contain the leachate. Problems with CCLs include the expense and effort required to pack the clay (often to a depth of 30cm or more) and cracking of the uncovered liner resulting in preferential pathways for the leachate to escape containment.
- A flexible membrane liner (FML), also known as a geomembrane liner, is a plastic membrane, most commonly made of high-density polyethylene (HDPE), linear low-density polyethylene (LLDPE) or polyvinyl chloride (PVC) which should be a minimum of 2 mm thick (Scheirs, 2009). Problems with FMLs include leakage due to defects in the material, seam imperfections, wrinkling due to temperature variation (causing expansion and contraction of the liner before it is covered with waste), piercing and degradation of the liner material itself (Murray *et al*, 1995).
- A geosynthetic clay liner (GCL) uses low hydraulic conductivity clay attached between layers of geomembrane or geotextiles. While GCLs are thinner than CCLs and easier to install, there are still issues with leakage at the seams. The cation exchange capacity of GCLs is also lower than CCLs, and the clays in the GCLs have the potential to swell and move around within the liner, migrating downslope.

- A composite liner is a combination of the liner types outlined above (for example, a compacted clay liner and a synthetic liner used together). Whilst these liners are more expensive to install, composite liners are more effective at preventing leachate leakage than the use of a single liner (Melchior, 1997; Barry *et al*, 2001) as using a combination of liner types at once allows the liner to be tailored to the expected conditions it will have to endure.

Typically a containment landfill will have a composite liner; however, older landfills are likely to have only a CCL (if they are lined). The Oxford Clay is used in the south of England as a CCL or as the base for a composite liner.

Once filled, the containment landfill is sealed with a cap of the same or better containment properties, such as permeability, as the primary liner (Bagchi, 2004). There is still some debate over whether it is best to cap a landfill immediately or leave it open to degrade the waste. This would lead to a faster reduction in the contamination potential of the waste due to increased leaching of soluble contaminants and an increased moisture content promoting biodegradation, but producing greater volumes of leachate. The current approach to MSW in containment landfills is to cap them promptly after filling, so encapsulating the waste. This is largely due to stabilisation of large volumes of waste being unrealistic due to the scale of the landfill cell, build-up of leachate head (Allen, 2001), unknown moisture distribution in the waste (Koerner and Soong, 2000) and uncontrolled release of landfill gasses. Whilst encapsulating the waste initially reduces the amount of leachate and gas produced by the landfill (Allen, 2001) the dry entombment of the waste reduces the degradation and stabilisation of the waste (Allen, 2001). Due to the extended timescale of the polluting potential of the waste the longevity of the liner and leachate collection systems may also be called into question (Bagchi, 2004). Therefore, the landfill may present a perpetual risk to groundwater and the environment, with encapsulation of the waste resulting in the preservation rather than degradation of the waste; which retains the potential to pollute indefinitely, possibly beyond the lifetime of the liner system. The bioreactor landfill provides a potential solution to this problem.

A bioreactor landfill works by adding moisture to the encapsulated waste in order to promote microbial degradation processes within the waste (Pacey *et al*, 1999). The aim

of a bioreactor landfill is to utilise microbial degradation processes to stabilise and decompose organic matter within the waste over a shorter time period, so reducing the long term polluting potential of the waste. The increased stabilisation of the waste does, however, result in the mobilisation of contaminants through degradation and dissolution processes (Abbas *et al*, 2009; Pacey *et al*, 1999). Bioreactor landfills can be managed aerobically, anaerobically or as a hybrid system (Bagchi, 2004; Mertoglu *et al*, 2006; Xu *et al*, 2014). In aerobic management, both air and moisture are introduced into the waste. In anaerobic management only moisture is introduced to the waste and in hybrid systems sequential (up to three months) aerobic and anaerobic management is employed (Bagchi, 2004; Xu *et al*, 2014). Bioreactor landfills reduce the organic constituents in the leachate through biodegradation which is enhanced due to the increase in moisture content which may also aid the leaching of salts and metals from the leachate. However, the increase in moisture content and decomposition also results in an increase in gas generation from the waste if the system is anaerobic. Increased microbial activity may also result in increased clogging of leachate drainage layers and capture systems which may then inhibit leachate capture and level control. An increased leachate head due to clogging within the leachate drainage system can increase the potential for leakage of leachate through the liner (Koerner and Song, 2000) which means that the contaminant attenuation properties of the clay would become more important in preventing the environmental release of contaminants.

Assuming that the additional problems associated with bioreactor landfills are addressed, they result in faster stabilisation and settling of the waste mass, reducing long term risks to the environment. Further detailed information on each of these landfill categories can be found in Bagchi (2004), including discussion on their suitability for different waste disposal situations.

2.1.3 Landfill Leachate

Landfill leachate is a form of environmental pollution originating from landfill sites and may contaminate ground and surface waters if not appropriately contained. Leachate is a highly complex mixture of contaminants that is an inevitable product of landfilling waste (Gálvez *et al*, 2009; Kjeldsen *et al*, 2002; Rivas *et al*, 2003). It is formed when

moisture from the decomposition of waste, infiltration of groundwater, surface water or precipitation percolates through (or is squeezed from) the waste, facilitating the dissolution of soluble compounds and transporting suspended components (Abbas *et al*, 2009; Calace *et al*, 2001; Kjeldsen *et al*, 2002). Because of the variation of waste characteristics and amounts of precipitation leachate composition is highly variable between sites (Calace *et al*, 2001). Leachate composition is also dependent on the age and density of the waste, the management of physical, biological and chemical processes occurring within the site and stabilisation stage of the landfill (Gettinby *et al*, 1996; Kjeldsen *et al*, 2002; Welander *et al*, 1998). Variations in climate and waste compaction may also affect the volume and concentration of the leachate produced (Abbas *et al*, 2009; Kim and Lee, 2009; Linde *et al*, 1995).

Leachate contains four key groups of contaminants: organic matter (OM), inorganic macro components (including ionic compounds, ions in solution and ammonium), heavy metals and xenobiotic organic contaminants (XOCs) (those which do not occur naturally in the ecosystem, such as pesticides and phenols) (Abbas *et al*, 2009; Gettinby *et al*, 1996; Kjeldsen *et al*, 2002; Sun *et al*, 2008; Yusof *et al*, 2009). The DOM and XOC portions of leachate are of importance to this work, more specifically the dissolved organic carbon (DOC) portion of DOM and HOCs such as toluene and naphthalene (which are components of the XOCs present in leachates). This is due to the potential of DOC in leachates to interact with both solid phase organic carbon in the liner materials and HOCs, thus affecting the attenuation of HOCs by landfill liners (Larsen *et al*, 1992; Thornton *et al*, 2000) as discussed in Section 2.2.6. Some values for the typical composition of leachates from landfills accepting MSW waste are shown in Table 1. These values are from a number of landfill sites accepting MSW worldwide; including the UK, China, Brazil and Malaysia. The landfills from which these leachates originated ranged in age, location, management strategy and containment quality. The wide range of values obtained serves to highlight the variability in the composition of leachates derived from the same waste type.

| DOC/TOC* | Concentration (mg/L) | | | pH | Ref. |
|--------------------------|----------------------|-----------------|------------------------------|---------|------|
| | Cl ⁻ | Na ⁺ | NH ₄ ⁺ | | |
| 540 ^d | 2541 | 1882 | 523 | 7.8 | 1 |
| - | - | - | 861 | - | 2 |
| - | 5484 | - | 310 | 8.4 | 3 |
| 709-26600 ^t | 100-3000 | - | 541-2260 | 6.1-8.6 | 4 |
| 70.9-24322 ^t | 569-5500 | 81-2269 | 112-3125 | 3.9-8.9 | 5 |
| 429 ^d | 961 | 595 | 327 | 8.0 | 6 |
| 14000-21000 ^t | 1300-2500 | - | - | 8-9.4 | 7 |
| 59.2-1350 ^t | - | 39.2-1150 | - | 7.0-8.2 | 8 |
| 820-1000 ^t | 4130-5140 | 2700-3200 | 800-750 | 8.2-8.5 | 9 |
| 1430 ^t | 5420 | 3000 | 1040 | 8.2 | 10 |
| 30-29000 ^t | 150-4500 | 70-7700 | 50-2200 | 4.5-9 | 11 |
| 863-18362 ^d | - | - | 892-1896 | 6.6-8.2 | 12 |
| ND-40000 ^t | 2-11375 | 12-6010 | ND-1200 | 3.7-8.9 | 13 |

Table 1: The composition of landfill leachates described in the literature. (1) Environment Agency (2003b) (2) Liyan *et al* (2009) (3) Atmaca (2009) (4) He *et al* (2009) (5) Yusof *et al* (2009) (6) Justin and Zupancic (2009) (7) Li *et al* (2009) (8) Matthews *et al* (2009) (9) Silva *et al* (2004) (10) Amokrane *et al* (1997) (11) Kjeldsen *et al* (2002) (12) Kang *et al* (2002) (13) Bagchi (2004)

ND = not detectable (*)^d DOC (dissolved organic carbon) and ^t TOC (total organic carbon)

2.1.4 Changes to Leachate Chemistry with Landfill Stabilisation

Leachate composition varies throughout the lifetime of the landfill as the waste matures and stabilises (Abbas *et al*, 2009; Kjeldsen *et al*, 2002). The waste passes through five degradation stages, aerobic, anaerobic acid (acetogenic), methanogenic (split into initial and stable phases) and finally the aerobic (humic decomposition) stage as detailed by Foo and Hameed (2009) and Kjeldsen *et al* (2002). Though methanogenic leachates are in contact with the landfill liner for the majority of the landfills operational life (Bright *et al*, 2000) the stabilisation rate of the waste is site dependant and non-uniform. In addition to waste stabilisation and maturation processes, the composition of the waste being deposited and the age of the landfill contribute to the variation of leachate DOC chemistry between sites. Therefore, there is no way to accurately predict the composition of leachate produced by a landfill during its lifetime (Gettinby *et al*, 1996). Despite this, some generalised trends in the composition of leachates as they reach stabilisation are recognisable, as discussed by Kjeldsen *et al* (2002). As this study is focused on the

impact of leachate DOC on the sorption of HOCs, the changes in leachate DOC with stabilisation are described below and summarised in Figure 1.

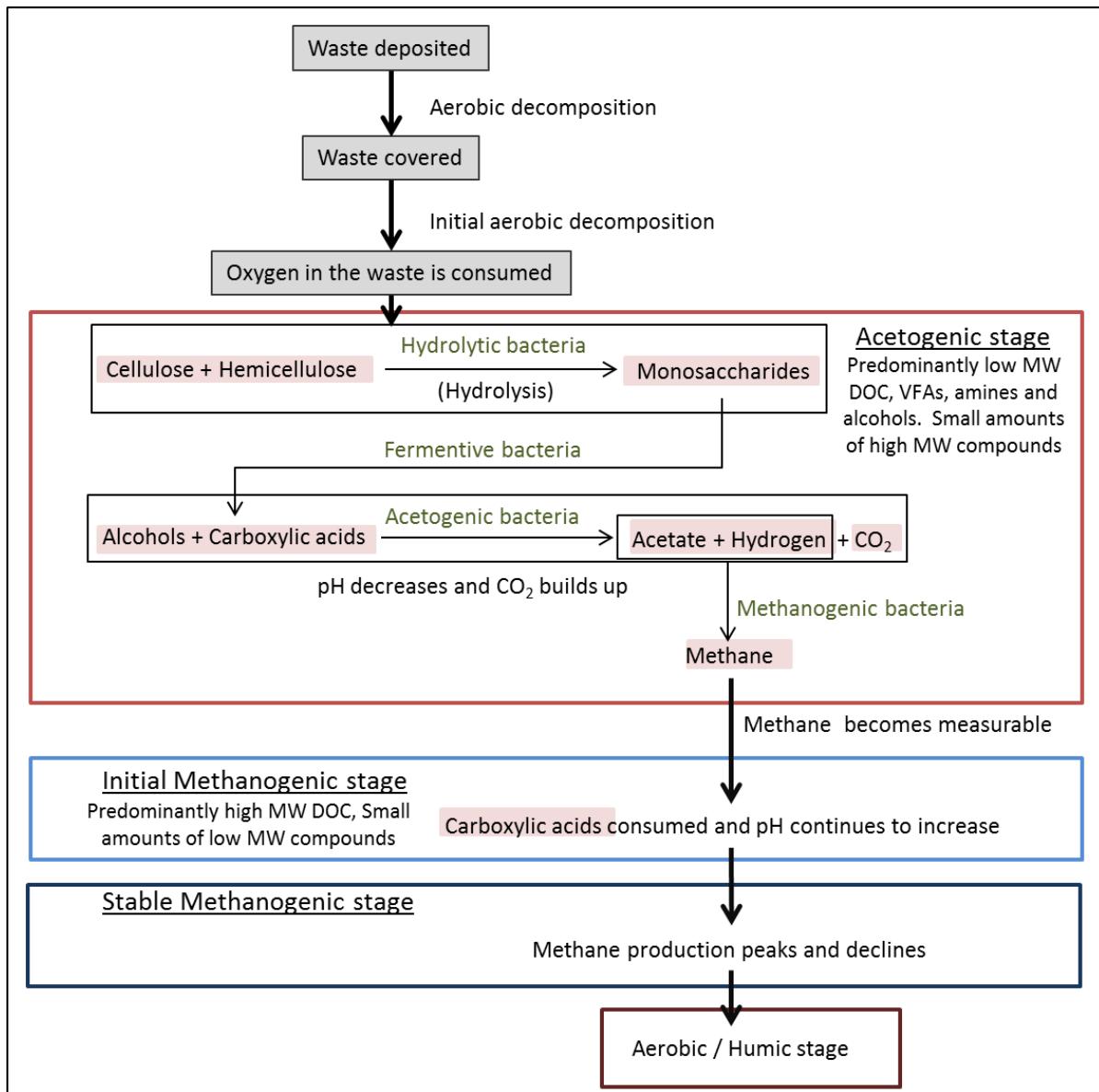


Figure 1: Landfill leachate stabilisation processes, based on Kjeldsen *et al* (2002), Abbas *et al* (2009), Foo and Hameed (2009) and Harmsen (1983).

During the initial aerobic stage of decomposition pockets of oxygen contained in voids in the waste are consumed and carbon dioxide is produced. This is often coupled with an increase in the waste's temperature (Kjeldsen *et al*, 2002). Generally this stage only lasts a few days as once the waste has been covered the oxygen cannot be replenished, as it cannot diffuse through the waste or cap fast enough to maintain aerobic conditions (Kjeldsen *et al*, 2002).

During the anaerobic acid (acetogenic) stage of waste degradation, hemicellulose and cellulose are hydrolysed by hydrolytic bacteria to simple sugars (monosaccharides) which are then converted into carboxylic acids and alcohols by fermentative bacteria (Kjeldsen *et al*, 2002). Acetogenic bacteria then convert the carboxylic acids and alcohols into acetate, hydrogen and carbon dioxide. The acetate and hydrogen are then converted into methane by methanogenic bacteria (Kjeldsen *et al*, 2002).

During the acetogenic stage of decomposition the hydrolytic, fermentative and acetogenic bacterial processes dominate resulting in a build-up in carboxylic acids and a decrease in pH (Reinhart and Al-Yousfi, 1996). Leachates in the acetogenic stage are chemically aggressive due to their acidity which may also increase the solubility of contaminants such as heavy metals (Kjeldsen *et al*, 2002; Reinhart and Al-Yousfi, 1996). Acetogenic leachates also have high concentrations of DOC which consists largely of volatile fatty acids (VFAs) (Gettinby *et al*, 1996; Harmsen, 1983; Yusof *et al*, 2009) with volatile amines, alcohols and a minimal amount (1.3%) of high MW DOC (Harmsen, 1983).

The initial methanogenic stage begins when the pH increases to a point when methanogenic bacteria can begin to establish a population and methane production is measurable. As the carboxylic acids which built up during the anaerobic stage are consumed, the pH of the leachate increases and the stable methanogenic phase begins. During this stage the methane production rate reaches its peak and then declines due to the limiting effects of nutrients and substrates, such as cellulose and hemicellulose, (Kjeldsen *et al*, 2002; Reinhart and Al-Yousfi, 1996). As leachates become methanogenic the DOC concentration in solution decreases and the DOC that is present increases in aromaticity and molecular weight due to the degradation of smaller organic compounds by biological and chemical processes (Calace *et al*, 2001; Harmsen, 1983; Kang *et al*, 2002). The DOC in methanogenic leachates was also found to become more refractory (resistant to degradation) as it matures (He *et al*, 2009; Kulikowska and Klimiuk, 2008; Rivas *et al*, 2003; Welander *et al*, 1998) with a large proportion (32%) of high MW and humic-like (60%) DOC (Harmsen, 1983).

In the aerobic humic stage it is theorised that the rate of microbial processes occurring within the landfill will decrease and the rate at which oxygen can permeate the waste will

become equal to the rate at which it is consumed by the microbes, allowing aerobic conditions to prevail (Kjeldsen *et al*, 2002; Reinhart and Al-Yousfi, 1996).

2.1.5 Dissolved Organic Carbon

DOC present in landfill leachates comprises a highly complex mixture of organic molecules (Foo and Hameed, 2009). In this study, DOC is taken to be the portion of organic matter which can pass through a 0.45 µm filter as this is consistent with the literature (Coble, 1996; Huo *et al*, 2009; Kang *et al*, 2002; Macalady and Walton-Day, 2009). However, scientific understanding of what constitutes dissolved matter has developed significantly since this standard was adopted. An example of this are constituents which may be present in a dissolved form (<1 nm), as individual particles in a solution (1-100 nm) or as aggregates of particles (>100 nm) (Grassion, 2008). Colloidal dispersions are substances that highlight this issue as they are particles that exist within the size range of DOC (1 nm-1 µm in size) which remain suspended in solution and do not settle (Russel *et al*, 1989).

Having a mixture of leachate DOC in the sub 45 µm size range existing in solution complicates the elucidation of DOC effects on contaminants sorption behaviour, as each compound will interact with the clay and contaminants in a differently way due to its chemical characteristics. For example, a dissolved organic biopolymer such as tyrosine may exist in solution alongside a more complex high molecular weight humic substance. Since the two compounds coexist in solution they both have the potential to interact with contaminants in solution and so their sorption behaviour. However, due to their different chemical nature tyrosine will not interact with the system in the same way as a humic substance. Therefore, determining the contribution of specific DOC compounds to contaminant sorption behaviour is a highly complex issue. The International Humic Substances Society (IHSS) is a group with aims which include “*the establishment and maintenance of a collection of standard samples of humic and fulvic acids from lignite, fresh water, a mineral soil, and an organic soil, and the assembling of characterization data.*” (International Humic Substances Society, 2015). The IHSS standard compounds are solutions of humic DOC from multiple sources which have been characterized by the IHSS and extensively studied (Alberts and Taka, 2004). Despite this, the resolution of

the molecular structure of the humic substances in solution is limited to the bulk spectroscopy, elemental composition and identification of functional groups present in the solution (Baigorri *et al*, 2009; Senesi *et al*, 1989).

A common method of distinguishing between DOC compounds in solution is size fractionation. This splits the DOC mixture into different fractions based on their molecular weight. Size fractionation, for example by ultra-filtration, (Guo and Santschi, 1996) also yields a small volume of fractionated sample which may then be further elucidated by functional group determination using techniques such as IR, NMR or FTIR spectroscopy and elemental composition analysis. However, this is time consuming and expensive (Kalbitz *et al*, 2000) and the extraction and purification process for DOC may alter its chemistry (Kjeldsen *et al*, 2002). Fluorescence (Section 2.3.1) has been identified as a quick method for determining the types of DOC compound present in DOC by grouping different compounds based on their generic molecular properties and their fluorescence (Chen *et al*, 2003b; Mobed *et al*, 2008).

Compounds in DOC can be categorised as protein-like (PL) compounds, with the presence of amino acids such as tyrosine and tryptophan, and humic substance-like (HSL) compounds (Hunt and Ohno, 2007; Stedmon *et al*, 2003; Sun *et al*, 2008) (Section 2.3.1.2). Protein-like DOC consists of simply structured low molecular weight compounds which are degradable and are expected to be present in young (acetogenic) leachates. Humic substances are high molecular weight organic macromolecules, >700->10000Da, (Trebouet *et al*, 2001) which are resistant to degradation (refractory) (Qualls *et al*, 2003; Trebouet *et al*, 2001). They are often highly conjugated (Baker, 2002) and contain both aliphatic and aromatic components such as phenolic and carboxylic acid functional groups (Trebouet *et al*, 2001; Zhou *et al*, 2001). Humic substances are formed during the decomposition of organic matter such as the hydrolysis of proteins (Bhatia, 2006; Bottomley, 1915) and may be derived from any organic material (Kang *et al*, 2002). Though humic substances were originally thought to be large polymeric macromolecules Sutton and Sposito (2005) discuss the theory that these substances may be formed by supramolecular association of smaller organic compounds and present evidence such as molecular size change being due to aggregation. In the supramolecular association model groups of molecules with low molecular masses associate and stabilise each other via hydrophobic interaction, forming

micellar structures, as opposed to humic substances forming as large polymers through decomposition reactions.

Humic substances are divided into two further groups based on the solubility of the compounds in acid (Kang *et al*, 2002). In acid conditions ($\text{pH} < 2$) fulvic-like substances are soluble and humic-like substances are insoluble (Kang *et al*, 2002). The IHSS method for separating humic substances into humic acid (HA) and fulvic acid (FA) from aqueous media involves lowering the pH of the aqueous solution to pH 2 and using a resin column such as an XAD column to extract the HA and FA from solution via sorption (Kuwatsuka *et al*, 1992). At pH 2 non HSL material passes through the column so HA and FA can be separated from other compounds remaining in solutions at low pH (IHSS, 2007). The HA and FA are then removed from the resin into basic media and the pH reduced to pH 1 in order to precipitate out the HA (Thurman and Malcom, 1981). Fulvic-like compounds are also smaller in molecular weight than humic-like compounds (500-1000 Da fulvic acids compared to 10,000 Da humic acids) (Trebouet *et al*, 2001). Humic-like and fulvic-like DOC is expected to be predominant in mature (methanogenic) leachates as leachates from more stabilised (mature) wastes have a more refractory DOC character and higher molecular weight (Calace *et al*, 2001; Kang *et al*, 2002; Rivas *et al*, 2003; Welander *et al*, 1998). DOC compounds are, however, diverse in chemical nature and contain many different functional groups (Liu *et al*, 2015; Smidt and Meissl, 2007). This means that DOC has the potential to be a very reactive component in leachate solutions. This is important because if the HOCs interact with DOC then the character of the DOC in the leachates may affect sorption and desorption of HOCs. For example, the presence of an aromatic, higher molecular weight humic substance-like DOC from a methanogenic landfill leachate may increase sorption by binding the HOC more strongly to the sorbent than a less aromatic DOC.

DOC as defined in this work, $<0.45 \mu\text{m}$, is present in leachates at typical concentrations of around 30-29000 mg/L (Table 1). Although the overall carbon concentration of the DOC provides a measure of DOC quantity, it does not take into account the chemical nature of DOM compounds present in the mixture (whether they are aliphatic or aromatic in nature and their molecular weight etc). In this work the term ‘character’ will be used to refer to the chemical nature of the DOC compounds in solution. In order to take into account the character of the DOC, the presence and proportion of the different types of

carbon compound must be taken into account. Fluorescence spectroscopy using an excitation emission matrix method (discussed in Section 2.3.1.2) provides a method for identifying groups of compounds in solution and comparing their proportions and thus can be used as a tool for the assessment of DOC character (Section 2.3.1.4).

2.1.6 Regulation and Polluting Potential of Leachates

The release of some compounds such as pesticides and halogenated compounds is regulated by the Water Framework Directive (2000) and the Groundwater Daughter Directive (2006) due to their potential for harmful impacts on the environment. Within these directives compounds are now defined as either hazardous or non-hazardous. Hazardous substances are “*substances or groups of substances that are toxic, persistent and liable to bio-accumulate, and other substances or groups of substances which give rise to an equivalent level of concern*” (Water Framework Directive, 2000). This definition has replaced the former List I and II substance classifications (Groundwater Directive, 1979; Environment Agency, 2003b). Substances which were formerly classified as List I are now presumed hazardous unless new evidence comes to light, and those formerly List II are assessed on a basis of positive determination using scientific evidence to include or exclude them from hazardous classification (JAGDAG, 2011). Of the compounds assessed so far in the UK, formerly List I substances have been classified as ‘hazardous substances’ and formerly List II substances have been classified as ‘non-hazardous pollutants’ (JAGDAG, 2011). Stringfellow *et al* (2011) however, noted that this may not always be the case since Mecoprop (formerly List I) may be classified as non-hazardous under the new classification scheme.

The nature of leachates is so complex that the identification of all components is difficult (Hasar *et al*, 2009). Bagchi (2004) noted that the presence of putrescible waste increases the difficulty in assessing leachate quality due to increased biodegradation processes. Contaminants that may be present in municipal solid waste (MSW) leachates include polycyclic aromatic hydrocarbons (PAHs), aliphatic and aromatic hydrocarbons, mineral oils, organo-tin compounds, chlorinated organic compounds and pesticides (Environment Agency, 2009) and orthophosphates (Environment Agency, 2003a).

Approximately 2160 million cubic metres of groundwater are abstracted in the UK each year for uses including agriculture, industry and drinking water supply (UK Groundwater Forum, 1998). In the UK groundwater accounts for a third of public water supplies in England and Wales, 3% in Scotland and 6% in Northern Ireland (Environment Agency, 2013; UK Groundwater Forum, 1998). Under the Water Framework Directive (2000) all groundwater bodies in England and Wales have been designated as drinking water protected areas (DrWPAs) which aim “*to manage water resources and to prevent deterioration in water quality that could increase the treatment of water supplied for potable purposes under the Drinking Water Directive (80/83/EEC as amended by Directive 98/83/EC)*” (Environment Agency, 2013). Groundwater is therefore a very valuable resource in the UK which must be protected. Groundwater pollution may occur from either diffuse sources, such as runoff from urban areas and road surfaces and leaching from agricultural sources such as fertilisers on fields or point sources such as chemical spills, leaking sewers and septic tanks and leaching from landfill sites. Therefore, to protect groundwater quality and prevent the release of hazardous substances into the environment, landfills are heavily regulated and highly engineered in order to achieve containment of contaminants (Christensen, 2011; Gettinby *et al*, 1996; Thornton *et al*, 1993). Before a permit for a new landfill is granted, the new site and any future proposed works are evaluated by the authorising body. This includes, but is not limited to, the hydrogeological and geological character of the site, proposed methods of pollution prevention and an operation plan including closure and aftercare plans (Landfill Directive, 1999). A site specific risk assessment (Christensen, 2011; Environment Agency, 2003a; Environment Agency, 2010) can go some way to demonstrating that any contamination risks posed by the landfill site have been considered. A site specific risk assessment includes prediction of the type and duration of the risks associated with the landfill and whether they are acceptable. A range of guidance documents addressing risk assessments and criteria has been published by the Environment Agency for use in England and Wales (Environment Agency, 2010; Environment Agency, 2003a). Risk assessments for landfills are often performed using landfill management tools such as LandSim which takes into account the geological environment, performance of liner systems and the chemistry of the leachate (Golder Associates, 2003).

It is now commonplace for a basal liner to be included in the design of the landfill to provide an impermeable barrier to the leachate (Xie *et al*, 2009). The liner material

chosen for the landfill is predominantly used as a passive barrier to contain leachate (Bright *et al*, 2000; Thornton *et al*, 1993) due to having a permeability no greater than 1×10^{-9} m/s (Raybould *et al*, 1988). However, since clay minerals and organic matter within clays have been shown to contribute to the attenuation of contaminants through sorption (Grathwohl, 1990; Hwang and Cutright, 2002; Rebhun *et al*, 1992) the liner itself may contribute to leachate attenuation.

2.1.7 Contaminants of Interest

While leachate is a highly complex mixture containing a wide range of contaminants (Bagchi, 2004; Kjeldsen *et al*, 2002), in this work only the contaminants toluene and naphthalene will be considered. Toluene and naphthalene were selected for this work as both contaminants are small aromatic hydrocarbons that are commonly found in landfill leachates. They are relatively soluble in an aqueous environment, toxic to aquatic life, and are classified as hazardous substances according to the Groundwater Daughter Directive (2006)

Toluene is a cyclic aromatic hydrocarbon (formula C₇H₈, molecular weight 92.14 g/mol) that occurs as a colourless, highly flammable liquid at room temperature. It is volatile and is irritating to the skin (Sigma Aldrich). Toluene is classified as harmful with possible lung damage, risk of harm to the unborn child and may pose a danger of serious damage to health through prolonged contact. As a BTEX compound (benzene, toluene, ethylbenzene and xylenes) toluene is generally associated with petroleum derivatives and is found in landfill leachates due to waste sources such as paints, adhesives, paint thinners and automotive degreasers (Bagchi, 2004). Though toluene is similar in chemical structure to the carcinogenic benzene it is not classifiable with respect to its carcinogenicity to humans (Sigma Aldrich).

Naphthalene is a bicyclic aromatic hydrocarbon consisting of two conjugated benzene rings and is the smallest of a class of compounds termed the polycyclic aromatic hydrocarbons (PAHs). Naphthalene (formula C₁₀H₈, molecular weight 128.17 g/mol) is a white crystalline solid at room temperature, classified as harmful and may be carcinogenic to humans. It is also very toxic to aquatic life and may cause long term

adverse effects in the aquatic environment, with both acute and chronic aquatic toxicity observed (Sigma Aldrich). Naphthalene is classified as a hazardous substance according to the Groundwater Daughter Directive (2006) and is considered a priority hazardous substance in the UK. As a priority hazardous substance, under article 16 of the Water Framework Directive (2000), water pollution caused by its discharge must be phased out.

Both toluene and naphthalene are HOCs which are typically found in low concentrations in MSW leachates (around 21 µg/L and 0.46 µg/L respectively (Environment Agency, 2009)). This can, however, vary widely between sites, <1-12,300 µg/L for toluene and <1-280 µg/L for naphthalene, (Kjeldsen *et al*, 2002). Naphthalene is more hydrophobic than toluene. This can be demonstrated by comparing their octanol/water partition coefficients (LogK_{ow}) which are 2.54-2.69 for toluene and 3.17-3.36 for naphthalene (Agency for Toxic Substances and Disease Registry, 1994; Bergendahl, 2005; Environment Agency, 2009). Octanol/water partition coefficients give a measure of a compounds affinity for an aqueous or organic phase with higher values indicating greater affinity for the organic phase (and so increasing hydrophobicity of the compound) (Miller *et al*, 1985). It is expected that the HOCs toluene and naphthalene will partition out of the aqueous leachate solution onto the organics present in the clay liner or in solution. A higher organic carbon normalised sorption coefficient (K_{oc}) for naphthalene (38.93 L/g) than toluene (1.72 L/g) (Environment Agency, 2009) indicates the more hydrophobic naphthalene has a higher affinity for the solid phase than toluene. The degree of this partitioning relies on the affinity of the contaminants for either the aqueous solution or the solid matrix (Kalliat, 1988).

While the effect of OM in the solid phase on sorption behaviour is well documented and discussed in Section 2.2.6.1, a change in the character of the DOC in the leachate may also alter the sorption of HOCs to the solid matrix (the liner material) by increasing the hydrophobicity of the aqueous phase (Garoma and Skidmore, 2011). The DOC in the leachate mixture may also act as an alternative hydrophobic surface which may interact with the HOC. In order to carry out an accurate risk assessment of the interaction and attenuation of HOCs within the liner material, the impact of DOC of different quality on the sorption behaviour of HOCs (discussed in more detail in section 2.2.6.2) must be quantified. This will in turn form the basis for suggesting improvements in the

attenuation prediction capability of landfill risk assessment and management tools such as LandSim.

2.1.8 LandSim

In order to get a new landfill site approved in the UK a full risk assessment must first be conducted. The scope of this risk assessment includes modelling of the type of cell that is to be built, the containment systems and the types of waste to be accepted. Estimates then need to be provided detailing the active polluting lifespan of the landfill, including the predicted sorption of contaminants within the leachate to the liner materials as a route for attenuation. LandSim is a programme developed by Golder Associates on behalf of the Environment Agency for use in the risk assessment of landfill sites. The current version of LandSim is version 2.5 which has been updated to include improvements to the output and reporting of results and modelling input features such as the biodegradation of organic components and updates to retardation functionality. LandSim uses visual basic and a probabilistic Monte Carlo extrapolation of parameters inputted by the end user to predict the risks posed to the environment by landfill sites.

As well as features to model the liner, capping, leachate loading and groundwater systems in and around landfill sites the attenuation of contaminants by the liner can be modelled by the input of either K_{oc} values for the contaminant or by K_d and f_{oc} values for the contaminant and sorbent. While it is recommended that the K_d values for the contaminants are site specific and should be determined as such (experimentally) LandSim does incorporate default K_d values for contaminants which are based on literature values for appropriate lithologies (Environment Agency, 2000a). The default K_d values are, however, recognised by the Environment Agency (2000b) as being representative only of the contaminant behaviour under certain conditions and may not be representative of all aqueous phase compositions.

2.2 Natural Attenuation and Sorption

2.2.1 Overview of Natural Attenuation in Landfills

Natural attenuation is the process by which a compounds concentration is reduced with time by microbial degradation, sorption, dilution, precipitation, filtration or ion exchange (Bagchi, 2004; Thornton *et al*, 1993). In landfills natural attenuation will ideally occur to a degree that reduces the contaminant concentration to a safe or environmentally acceptable level (Bagchi, 2004). Baun *et al* (2003) showed that anaerobic conditions, such as those found in a landfill at certain maturation phases (Section 2.1.4) can lead to the natural attenuation of XOCs (including toluene) through dilution, degradation and sorption processes. Sorption is the main method of natural attenuation of interest in this work as sorption K_d values are used to predict the attenuation of contaminants by landfill liners in risk assessment programmes such as LandSim (Section 2.1.8). Alterations in these K_d values, for example due to the presence of leachate DOC, or the selection of a literature value of K_d not obtained under appropriate experimental conditions, may lead to an incorrect estimate of liner attenuation properties such as sorption, desorption and sorption hysteresis (Section 2.2.5) of contaminants. This may affect decisions on contaminant containment strategies and possibly could result in unnecessary environmental pollution due to the overestimation of sorption behaviour. This section introduces natural attenuation processes in the context of landfills with a particular focus on sorption and the isotherms used to model sorption processes. The effect of solid and solution phase DOC and the hydrophobicity of the contaminant on the sorption behaviour of HOCs is then discussed.

2.2.1.1 Dilution

Though dilution does not remove the contaminant from the system it may reduce the concentration of some contaminants to environmentally acceptable discharge levels (Bagchi, 2004). This level will vary for each landfill site depending on the risk of pollution to groundwater posed by the discharge and the background groundwater quality,

but is typically below detection limits for contaminants such as toluene and naphthalene which are classified as hazardous (Environment Agency, 2003a; Groundwater Daughter Directive, 2006). In most cases dilution alone would be inadequate to permit the untreated discharge of leachate.

In containment landfills, assuming that the liner remains intact and functioning, dilution of leachates may occur due to the infiltration of rain and surface water. In the case of bioreactor landfills the deliberate addition of moisture may also dilute leachates. If the concentration of a contaminant in a leachate is limited by its availability in the waste the dilution of leachates will reduce the contaminant loading per volume of leachate. Therefore the direct risk from the leachate due to contaminant concentration is reduced. If the concentration of the contaminant is, however, limited by its solubility dilution will increase the overall amount of contaminant mobilised into solution. Therefore, the concentration in solution would remain the same. In the long term the polluting potential of a waste, where total contaminant concentration of its leachate is limited by its solubility, would be decreased by dilution as more contaminant is mobilised into solution and extracted for treatment. However, over a shorter time period, increased volumes of polluted leachates may increase the potential for treatment methods and physical barriers such as basal liners to be overwhelmed. This may occur by an increased leachate head causing the liner to fail due to the hydraulic pressure on the liner or by the head exceeding the height of the liner material and ‘overflowing’ the containment. Leachate treatment systems may be further overwhelmed by the volume of leachate to be processed as they are designed to only treat a certain volume of leachate at one time and inputting greater volumes of leachate into the system may impact the efficacy of the treatment processes. Regardless of the mechanism of contaminant availability the higher volumes of leachate produced by dilution may cause issues with the containment system in the landfill and will ultimately result in higher volumes of leachate being abstracted and treated. The effect dilution has on leachate pollution potential is, however, limited once the landfill is capped due to the regulations in place to regulate moisture content of the landfill (Environment Agency, 2010) unless it is operated as a bioreactor landfill in which case moisture is deliberately added to the system.

2.2.1.2 Microbial Degradation

Microbial degradation processes which occur during the stabilisation of the waste mass result in a variation in the character of the DOC in leachates of different maturity (Kjeldsen *et al*, 2002) (Section 2.1.4). The microbial degradation of contaminants may also occur within a landfill (Bagchi, 2004; Simoes *et al*, 2005; Stringfellow *et al*, 2011). Baun *et al* (2003) highlighted that, amongst other XOCs, toluene degrades under anaerobic conditions in a landfill forming the degradation product benzyl succinic acid (BSA). The degradation rate of toluene is dependent on the redox conditions of the system, with five other studies showing no degradation at all (Aronsen and Howard, 1997). Simoes *et al* (2011) also found toluene to be recalcitrant to biodegradation over a 3 month time period upon incubation under methanogenic conditions when in contact with MSW leachate and landfill liner material. Recalcitrance of toluene under laboratory conditions similar to this work was reported to be maintained for up to 8 months, with an average lag time of 70 days in lab testing before toluene biodegradation became measurable (Environment Agency, 2009).

While aerobic microbial degradation of naphthalene is widely documented (Atlas, 1981; Aronsen and Howard, 1997) evidence for degradation under methanogenic conditions, in both field and lab environments, is very limited (Aronsen and Howard, 1997). Although anaerobic microbial degradation pathways for naphthalene do exist (Annweiler *et al*, 2002) naphthalene is generally considered to be recalcitrant in methanogenic field environments (Aronsen and Howard, 1997; Nielsen *et al*, 1992; Rugge *et al*, 1999). This is supported by the Environment Agency (2009) where naphthalene was demonstrated to be recalcitrant under methanogenic conditions in a synthetic MSW leachate over an 8 month period when in contact with landfill clay liner materials (London Clay, Oxford Clay and Mercia Mudstone). The recalcitrance of both toluene and naphthalene in methanogenic leachates may therefore result in biodegradation having a limited effect on the concentration of these contaminants in landfills once the methanogenic phase of stabilisation has been reached (Section 2.1.4).

2.2.1.3 Ion Exchange, Precipitation and Filtration

Ion exchange is an isomorphic substitution process in which ions within a material are exchanged for alternatives whilst maintaining the mineral structure of the material (Grim, 1968). This study is focused on HOCs and DOC which can exhibit a negative charge so have the potential to attenuate via anion exchange (Bagchi, 2004). The negative charge on toluene and naphthalene originates from their chemical structure which is aromatic with a conjugated delocalised pi electron system which carries a slight negative charge. As with the HOCs, negative charges on DOC may originate from aromatic components of the molecules which have delocalised electron systems, or from functional groups on the molecules such as carboxyl, carbonyl and reduced sulphur compounds. While Devulapalli and Reddy (1996) showed that the anion or cation exchange capacity of a clay may have affected the sorption of ionic contaminants in landfill leachate, Bagchi (2004) stated that anion exchange only occurs at low pH. As soil-leachate systems converge at an approximately neutral pH (Bagchi, 2004) and the sorption of HOCs generally occurs through a hydrophobic partitioning mechanism (Flores-Cespedes *et al*, 2006; Nzengung *et al*, 1996) significant HOC attenuation through ion exchange mechanisms is not expected.

Precipitation in leachates is reliant on the chemistry of the solution and the solubility of compounds within the leachate (Bagchi, 2004). Undissolved toluene and naphthalene are hydrophobic compounds which exist as an immiscible liquid and a crystalline solid respectively. These HOCs are only sparingly soluble in aqueous solution. However due to toluene being liquid at room temperature precipitation (and therefore filtration) is only relevant to naphthalene. Where a compound exceeds its solubility limit, it will precipitate out of solution and be deposited as a precipitate (Bagchi, 2004). If the volume of leachate in the landfill increases (due to addition of water for example) it is possible that some of the precipitate may dissolve into solution. However, the solubility limit for that compound would remain unchanged. Due to the low concentration of naphthalene in leachates (Section 2.1.7) the removal of naphthalene by precipitation is not expected.

Filtration is the physical trapping of solid phase ‘particulate’ leachate constituents via the pore structure of waste solids or soils which act as a barrier to particulates (Bagchi, 2004). This will largely affect insoluble particulates and is distinct from sorption (mono and multi-layer). However, filtration could occur in the case of HOCs after the precipitation of contaminants out of solution or for un-dissolved organic carbon constituents suspended in the leachate. It is, however, a ‘one time phenomenon’ as once the components are removed from solution they are unlikely to be reintroduced. Therefore, filtration does not result in significant leachate attenuation (Bagchi, 2004).

2.2.1.4 Sorption

Sorption is the term used to describe the partitioning of a compound between a dissolved phase and a solid phase (Environment Agency, 2002; Stumm and Morgan, 1996). In this study sorption is used to describe the collective processes of absorption and adsorption (Bagchi, 2004; Murley and Stevens, 1985). Absorption is the process of diffusion of a compound into the bulk structure of a solid phase (e.g. a soil) (Bagchi, 2004; Environment Agency, 2002). Adsorption is the attachment of molecules to surfaces (Atkins and de Paula, 2006; Heys, 1979). Adsorption may occur by two mechanisms: (1) Chemisorption which is often irreversible and occurs when a chemical bond is formed between the sorbed compound and the sorbent surface, (2) Physisorption which occurs when the physical properties of the compound and sorbent result in interactions such as Van de Waals, dipole and hydrophobic interactions (Atkins and de Paula, 1992 and 2006; Environment Agency, 2002). Due to the hydrophobic nature of HOCs their sorption is expected to be driven by hydrophobic interactions or chemical interactions between DOC, HOCs and the solid phase. The processes involved in this study are therefore likely to be adsorptive in nature. In landfill systems the retardation of organic contaminants (sorption processes) is considered using partition coefficients (K_f and K_d) often in relation to the organic matter content of the solid phase (f_{oc}) which is specific to the solid-solute system being considered (K_{oc}) (Environment Agency, 2006).

2.2.2 Interactions in the Leachate-Liner System

As previously discussed, the leachate system is extremely complex and varied. The level of complexity in a landfill system varies depending on the level of detail at which you model the system. This work only focusses on the interactions in solution between DOC, the HOCs toluene and naphthalene and the Oxford Clay. This simplifies the model to an extremely basic form where the solid phase and dissolved contaminants in the aqueous phase are interacting. The solid phase is modelled as containing both clay minerals and organic matter. The solid phase organic matter is considered to be the functional surface to which sorption can occur. Due to the relatively high OC content of the Oxford Clay in relation to other sediments it was assumed that no sorption occurred at the clay mineral surface, which only acts as a support for the solid phase organic matter. The leachate (aqueous phase) was considered to only contain DOC and the target contaminant (toluene or naphthalene) and these components are considered to be completely dissolved.

However, within the actual landfill system there are many other components such as heavy metals, ionic compounds and other organic contaminants which have the potential to interact with the target compounds and solid phase of this work. In addition to this the pH and ionic strength of the leachate solution affects the behaviour of leachate components. Therefore this section aims to briefly describe the chemical functionality of the system components and their impact on the interactions between components of the system. It should be noted that this is a basic and far from an exhaustive discussion on this topic since the complexity and variability of these interactions is still not fully understood, quantified or characterised by the scientific community. This is largely attributable to the variability and unpredictable nature of leachate composition. Table 2 shows some of the different components of leachates and their possible interactions with other components of the leachate-clay system. These are then discussed in more detail below.

| | Solid phase organic matter | Clay minerals | DOC | HOCs | Heavy Metals | Free ions in solution | Inorganic contaminants |
|----------------------------|----------------------------|---------------|-----|------|--------------|-----------------------|------------------------|
| Solid phase organic matter | X | | X | X | X | | |
| Clay minerals | | X | | | X | X | X |
| DOC | X | X | | X | X | | |
| HOCs | X | | X | | | | |
| Heavy Metals | X | X | X | | | X | X |
| Free ions in solution | | X | | | X | | X |
| Inorganic contaminants | | X | | | X | X | |

Table 2: Possible interactions in a landfill system.

As described earlier (Section 2.2.1.4) there are two main mechanisms for interactions within a leachate system; chemisorption and physisorption. Physisorption involves interactions between compounds that are usually reversible such as electrostatic effects like dipole-dipole or Van der Waals interactions. Chemisorption involves chemical bonding (e.g. covalent bonding) between compounds which may result in the process being irreversible. (Atkins and DePaula, 1992 and 2006).

2.2.2.1 Physisorption

Van der Waals interactions

Van der Waals forces, or interactions, are weak electrostatic associations between two molecules. Van der Walls forces are dependent on the distance between molecules and can be attractive or repulsive (Atkins and DePaula, 2006 and 1992).

Dipole-dipole interactions

Dipole–dipole interactions occur when two functional groups carrying opposite charges, or partial charges, interact. These interactions can be due to a permanent dipole or an induced dipole. Permanent dipoles are found in polar molecules such as heteronuclear dielectric molecules, e.g. HCl and HI. When determining whether a molecule has a dipole, by determining the dipole moment of the molecule, the symmetry of the molecule should be taken into account (Atkins and DePaula, 1992). For example, CO₂ does not have a dipole as it is a linear molecule and therefore has no dipole moment since the partial charges on the atoms are all working in the same direction (Atkins and DePaula, 2006). A dipole-induced dipole interaction will occur when electrons on an otherwise neutral compound change position because of the presence of an ion or polar compound distorting the electron distribution of the neutral compound polarising it. This induces a dipole in the neutral molecule and forms a weak dipole in the molecule that is relatively short lived (Atkins and DePaula, 2006 and 1992).

Hydrogen bonding

Hydrogen bonding is the strongest of the electrostatic interactions which do not form a true bond by the sharing or re-distribution of electrons between atoms. A hydrogen bond is defined as “*The result of a columbic interaction between the partly exposed positive charge at a proton bound to an electron withdrawing atom and the negative charge of a lone pair on a second atom*” (Atkins and DePaula, 1992). Hydrogen bonding is most commonly seen for hydroxyl (-OH) groups and oxygen atoms (O). A well-known example of hydrogen bonding is the case of water, where hydrogen bonding accounts for its high heat capacity and surface tension (Atkins and DePaula, 1992 and 2006).

The hydrophobic effect

The hydrophobic affect is a ‘force’ which is mediated by the solvent properties of the system and can influence the conformation of a macromolecular structure. Hydrophobic compounds are not readily soluble in polar solvents and have been found to require an input of energy when attempting to dissolve them (Atkins and DePaula, 1992). This was identified as being attributable to the formation of a solvent ‘cage’ around the hydrophobic molecule (Atkins and DePaula, 1992). The formation of a solvent cage around the hydrophobic compound isolates it from the polar solvent molecules in much the same way as a solvation sphere would form around a free ion in solution. Since the

clustering of the hydrophobic compounds reduces the energy required to form this solvent cage the hydrophobic effect encourages non-polar compounds to cluster in solution. An example of the hydrophobic effect is the formation of micelles (Atkins and DePaula, 1992 and 2006).

2.2.2.2 Chemisorption

Chemisorption occurs when a chemical bond is formed between two molecules in a system. These chemical bonds can be ionic or covalent. Ionic bonding occurs when electrons from one atom are ‘donated’ to another (Atkins and DePaula, 1992). This results in two ions with opposite charges being produced which then form a bond and interact in order to cancel out the charges present on the two intermediate ions. Covalent bonding occurs when two different molecules share a pair of electrons between atoms (Atkins and DePaula, 1992 and 2006). Where chemisorption occurs the bonding is normally covalent (Atkins and DePaula, 2006).

2.2.2.3 System Components and Functionality

Clay mineral functionality

Clays are fine grained sediments that are composed of tetrahedral silicon oxide and octahedral aluminium oxide sheets. These sheets are assembled in either two or three layers (Figure 2). The two layer assembly consists of one tetrahedral and one octahedral sheet connected together via shared oxygen atoms and the three layer assembly consists of an octahedral sheet sandwiched between two tetrahedral sheets (again connected via shared oxygen atoms) (Bhatia, 2006). These layer assemblies are associated by weak intermolecular forces such as Van der Waals interactions and hydrogen bonds which hold them together (Figure 2). The presence of the electronegative oxygen atoms result in the layers of clays having the potential to absorb water into the spaces between layer assemblies (Ruiswell *et al*, 1980). As there is no chemical bonding between the layer assemblies, this uptake of water into the structure can result in the clays swelling as they absorb more water and the layer assemblies are pushed apart (Figure 2).

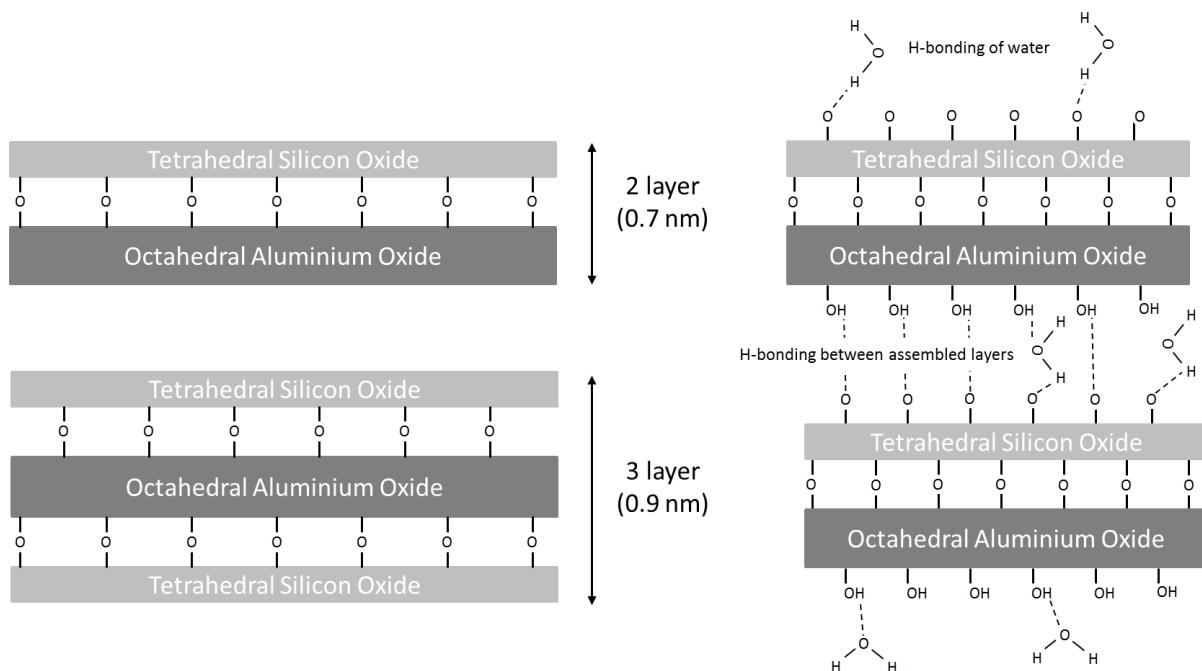


Figure 2: Layered structure of clay particles and the association of assembled layers with each other and with water, which may result in the swelling of clays.

It is also possible for the clay particles to lose aluminium or silicon atoms and replace them with cations which have a lesser charge than aluminium or silicon. This can result in an overall negative charge in the clay particle (Bhatia, 2006). Since the assembly of clay particles doesn't have a fixed size of site into which ions have to fit the clay can uptake cations in order to balance the charge on the clay and return it to neutral. This ability to absorb cations (e.g. Na^+ , K^+ , Ca^{2+} or NH_4^+) is known as the cation exchange capacity (CEC) of a clay (Bhatia, 2006). As well as acting as a sink for cations in the environment clays can release cations if the environment becomes depleted. For example, if a clay absorbs NH_4^+ from a soil after the application of a fertiliser as the crops uptake the fertiliser during their growth, depleting the soil of NH_4^+ , clays can release NH_4^+ in order to maintain equilibrium within the soil system (Ruiswell *et al*, 1980).

In a landfill system clay minerals can therefore absorb ionic constituents of the leachate, for example, ammonia, sodium and potassium (Christensen *et al*, 1998). As there is no restriction of the atomic radius of the cation balancing the charge on the clay, as well as these common ionic components it is possible that the clay could absorb heavy metal ions (M^+) from the leachate. As cation exchange with the clays occurs at equilibrium with the surrounding system it should be noted that clay minerals are unlikely to be a permanent sink for heavy metals. The layers of clay particles are assembled and held

together by electrostatic forces such as hydrogen bonding. In a similar way to water being absorbed into the structure of a clay mineral other molecules with the correct functionality (e.g. a hydrogen bonded to an electron withdrawing atom) may also be incorporated into the structure of the clay (Atkins and DePaula, 1992). This includes DOC compounds containing a hydroxyl or amine group, such as sugars, carbohydrates, humic macromolecules, amino acids and proteins (Atkins and DePaula, 2006 and 1992; Bhatia, 2006).

Organic carbon functionality

The complexity of leachate and solid phase organic carbon compounds mean that they are not well characterised. However, attempts at a fuller characterisation of OC and its functionality have been made (Christensen *et al*, 1998; Harmsen, 1983; Kang *et al*, 2002). These studies used infra-red (IR) spectroscopic techniques such as Fourier transform IR (FTIR) and non-dispersive IR (NDIR) to identify the presence of functional groups present in organic carbon compounds. It should be noted that while the presence of these functional groups was identified, further resolution of the OC structure was not achieved. The literature indicates that the functionality of OC compounds centres around the carbonyl functional group (C=O) and the aromaticity of the compound (Christensen *et al*, 1998; Harmsen, 1983; Kang *et al*, 2002). For example, Christensen *et al* (1998) found that humic acid structure was dominated by aromatic, aliphatic, carboxylic and hydroxyl functional groups. Harmsen (1983) found that the key functional groups in OC were aromatic compounds (including ring structures) and carbonyl (C=O) groups that were present in the form of esters and hydroxyl groups in the form of alcohols. Due to the presence of the electronegative oxygen atom in their structure these groups have the potential to interact with surfaces through Van der Waals forces, dipole-dipole and dipole-induced dipole interactions. The aromaticity of the OC also means that it could behave hydrophobically or remain dissolved due to hydroxyl groups hydrogen bonding with polar solvents. Figure 3 shows some of the different functional groups that may occur in organic carbon compounds, both in solution phase DOC and solid phase OC bound to the clay liner materials.

| Functional group | Abbreviation | Structure |
|------------------|------------------------------------|---|
| Alcohols | R-OH | $\begin{array}{c} R \\ \\ O-H \end{array}$ |
| Carboxylic acids | R-COOH | $\begin{array}{c} O \\ \\ R-C-O-H \end{array}$ |
| Aldehydes | R-CHO | $\begin{array}{c} O \\ \\ R-C-H \end{array}$ |
| Ketones | R ¹ -CO-R ² | $\begin{array}{c} O \\ \\ R-C-R \end{array}$ |
| Esters | R ¹ -COO-R ² | $\begin{array}{c} O \\ \\ R-C-O-R \end{array}$ |
| Ethers | R ¹ -O-R ² | $\begin{array}{c} O \\ \backslash / \\ R-R \end{array}$ |
| Amines | R-NH ₂ | $\begin{array}{c} H \\ \\ R-N-H \end{array}$ |
| Amides | R-CONH ₂ | $\begin{array}{c} O \\ \\ R-C-N(H)-H \end{array}$ |

Figure 3: Functional groups that may potentially be present in dissolved or solid phase organic carbon components of the landfill system (Clayden *et al*, 2003).

The presence of hydroxyl groups in OC allows it to undergo hydrogen bonding. This may occur in the aqueous phase, forming a solvent cage around a DOC compound. Alternatively, since it has been shown that hydrogen bonds can form between clay particles and water, thus incorporating water into the clay structure (Bhatia, 2006; Ruiswell *et al*, 1980) it is also possible that OC compounds may form Hydrogen bonds with the clay and be incorporated into the solid phase.

The aromatic nature of some parts of organic carbon compounds result from the unsaturated bonds and ring systems within their structure. These induce hydrophobic interactions when in an aqueous (polar) solvent system, allowing hydrophobic

interactions between DOC and other hydrophobic components in the system. For example, DOC can interact hydrophobically with hydrophobic contaminants (such as toluene and naphthalene). The complexing of HOCs by DOC was found by Chiou *et al* (1986) to increase the solubility of contaminants due to micelle formation and hydrophobic interaction of organic pollutants and pesticides with the DOC. This was supported by Kopinke *et al* (2001) who found that the transport and fate of HOCs in the environment was affected by the interaction of the HOCs with humic substances in solution. Humic substances are important naturally occurring complexing agents (Bhatia, 2006) which can regulate the concentration of ions, including heavy metal ions, in solution (Nederlof *et al*, 1993). This property is due to the heterogeneous nature of HS complexing sites (Nederlof *et al*, 1993) and the acid-base sorptive and complexation properties of humic substances due to the presence of carboxyl, phenolic and alcoholic hydroxyl and carbonyl groups within the OC compounds (Bhatia, 2006). While not considered in this work, the interaction of organic carbon compounds with heavy metal ions in solution is well documented in the literature. Christensen *et al* (1996) found that DOC in solution complexed M^+ ions such as cadmium (Cd), nickel (Ni) and zinc (Zn), reducing the sorption of M^+ to the solid phase. This was corroborated by Harmsen (1983) who found that M^+ could be complexed by volatile acids in solution, increasing the solubility of M^+ ions such as Zn. The solubility of M^+ during the acetogenic (acid) stage of leachate maturation was also attributed to the complexation of M^+ with volatile acids in the leachate (Harmsen, 1983). The binding of M^+ by HA and FA was found by Shin *et al* (1996) to occur at two different chemical environments on the organic carbon. Both of these sites contained carboxylate functional groups and had either one or two carboxylates. Examples of the complexation sites of heavy metals (M^+) on organic carbon and their interaction are shown in Figure 4.

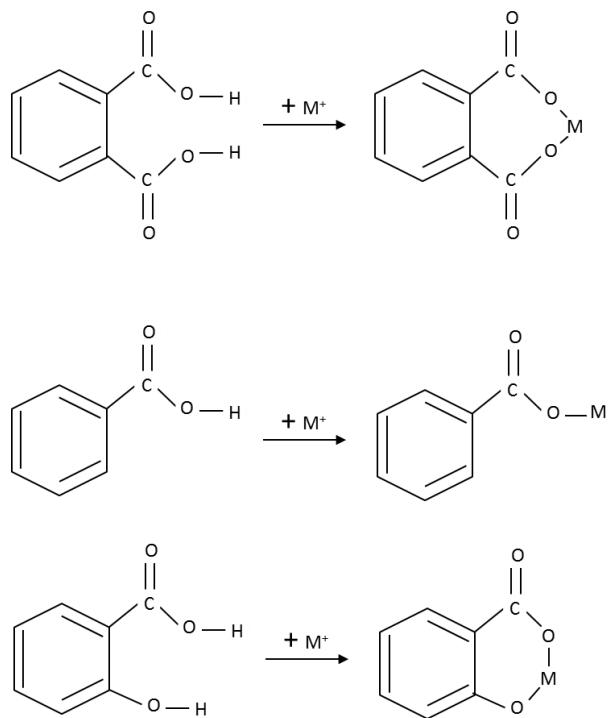


Figure 4: The complexation of heavy metal ions by selected functional groups (Bhatia, 2006; Nederlof *et al*, 1993)

Contaminant functionality

The functionality of toluene and naphthalene is hydrophobic in nature. They both consist of aromatic benzene rings with delocalised Pi systems. The contaminants may, therefore, interact with the other system components either through electrostatic interactions such as Van der Waals forces and induced dipole-dipole interactions, through hydrophobic interactions or through covalent bonding with compounds in the system (organic carbon on the solid phase for example).

2.2.3 Quantifying Sorption

2.2.3.1 Linear Partitioning Model

Partitioning describes the affinity of a compound for either the aqueous or solid phase and is dependent on the chemical and physical properties of a compound. The partition model assumes that the compound of interest partitions between the aqueous solution and the sorbent (e.g. the leachate and the clay or DOC) in the same way as it does between octanol and water, the octanol/water partition coefficient K_{ow} (Miller *et al*, 1985). Karickhoff *et al* (1979) demonstrated that this allowed prediction of sorption properties based on the octanol/water partition coefficient. Sorption and desorption can then be described using a partition coefficient K_d (L/g) as demonstrated by Grathwohl (1990), Equation 1, (Karickhoff, 1984; Rebhun *et al*, 1992).

$$K_d = C_s / C_{aq} \quad [1]$$

Where C_s = concentration of compound per mass sorbent (mg/g)

C_{aq} = equilibrium concentration of aqueous compound. (mg/L)

Some literature values for the partition coefficients of toluene, naphthalene and DOC onto different organic media are shown in Tables 3, 4 and 5.

| Aqueous phase | Solid phase (% organic carbon) | K _d (x10 ³) (L/g) | Ref. |
|-----------------------------|---|---|------|
| Synthetic with tannic acid | Oxford Clay (5.49) | 94 | 1 |
| Water | Humic acid coated Al ₂ O ₃ (0.54) | 400 | 2 |
| | Aldrich humic acid (33.5) | 62500 | |
| | Offhut Soil (0.23) | 440 | |
| | Whiteman soil (0.41) | 320 | |
| Phosphate buffer | Sapsucker woods humic acid | 10.1 | 3 |
| | Sapsucker woods fulvic acid | 2.59 | |
| | Tannic acid | 7.76 | |
| | Lignin | 97.2 | |
| | Zein | 70.3 | |
| | Cellulose | 0.02 | |
| | Aldrich humic acid | 42.4 | |
| Synthetic ground water | Natural aquifer* | 0.37 | 4 |
| Methanogenic-phase leachate | Triassic sandstone West midlands (0.026) | 0.0077 | 5 |
| Acetogenic-phase leachate | Triassic sandstone Nottingham (0.147) | 0.046 | |
| | | 0.018 | |

Table 3: Variation in the partition coefficient of toluene (K_d) within the literature for different aqueous phases and the sorbents. (1) Simoes *et al* (2011) and Environment Agency (2009) (2) Garbarini and Lion (1985) (3) Garbarini and Lion (1986) (4) Schwarzenbach and Westall (1981) (5) Thornton (2000). *From the Glatt Valley, Switzerland, composition not specified.

| Aqueous phase | Solid phase (% organic carbon) | K_d ($\times 10^3$) (L/g) | Ref. |
|--|--|----------------------------------|------|
| Synthetic with tannic acid | Oxford Clay (5.49) | 2140 | 1 |
| Synthetic no tannic acid | | 2330 | |
| Methanogenic-phase leachate | Triassic sandstone West midlands (0.026) | 0.527 | 2 |
| Deionised water | cote st andre cultured soil (1.4) | 4.23 | 3 |
| | cote st andre meadow soil (3.2) | 9.4 | |
| | Pequest (1.4) | 4.8 | |
| | Eurosoil III (3.4) | 14.2 | |
| | Eurosoil IV (1.5) | 5.1 | |
| 0.01 M CaCl_2 | Eustis (0.66) | 3 | 4 |
| | Eustis Rh (0.68) | 5.47 | |
| | Lincoln (0.036) | 0.136 | |
| | Lincoln Rh (0.12) | 9.8 | |
| | Lincoln Rtd (0.063) | 2.3 | |
| 0.005 M CaSO_4 and 0.02% NaN_3 | Columbus aquifer material A (0.027) | 0.11 | 5 |
| | Columbus aquifer material B (0.064) | 0.15 | |
| | Columbus aquifer material C (0.026) | 0.07 | |
| 0.01 M CaCl_2 | Soil 1 (53.4) | 781 | 6 |
| | Soil2 (32.2) | 158 | |
| | Soil 3 (7.38) | 45.4 | |
| | Soil 4 (4.53) | 31.9 | |
| | Soil 5 (2.55) | 13.4 | |
| 0.15 M NaCl , | Baker Soil (1.99) | 23 | 7 |

| | | | |
|---|---|------------|---|
| 0.004 M Na_2HPO_4 and 0.002 M KH_2PO_4 | Baxter Soil (6.06) | 36.8 | 8 |
| | Colwood whole Soil (10.8) | 72 | |
| | Colwood Organic (20.3) | 250 | |
| | Lee Soil (9.82) | 94.3 | |
| | River Sediment (2.96) | 23.8 | |
| | Synthetic sorbents (nd) | 1010-20600 | |
| 0.01 M CaCl_2 | High OC soil (3.2) | 18.2 | |
| | Low OC soil (0.52) | 0.96 | |
| | Hagerstown silt loam (1.94) | 8 | |
| | Berkley silt loam (2.85) | 8.5 | |
| | Tifton sand (0.5) | 2 | |
| 0.01 M CaCl_2 20% by vol. CH_3OH in Deionised water | Hagerstown silt loam (1.94) | 4 | 9 |
| | Berkley silt loam (2.85) | 4.4 | |
| | Tifton sand (0.5) | 1 | |
| 0.01 M CaCl_2 30-50% by vol. CH_3OH in Deionised water | Hagerstown silt loam (1.94) | 0.7-1.8 | |
| | 0.01 M CaCl_2 10-50% by vol. $\text{C}_3\text{H}_6\text{O}$ in Deionised water | 0.5-4.7 | |

Table 4: Variation in the partition coefficient of naphthalene (K_d) within the literature for different aqueous phases and the sorbents. (1) Simoes *et al* (2011) and Environment Agency (2009) (2) Thornton (2000) (3) Bayard *et al* (1998) (4) Bouchard *et al* (1990) (5) Macintyre *et al* (1992) (6) Xing (1997) (7) Guerin and Boyd (1997) (8) Burgos *et al* (1996) (9) Fu and Luthy (1986).

| Aqueous phase | Solid phase (% organic carbon) | K_d ($\times 10^3$) (L/g) | Ref. |
|---|---|----------------------------------|------|
| Rhinebeck soil DOM 103 mg/L | Dark Sand (0.4) | 0.132 | 1 |
| Sinclair inlet porewater NOM 138 mg/L | Sinclair inlet bulk sediment (<0.05%) | 0.12 | 2 |
| Sinclair inlet extracted NOM 175 mg/L | Montmorillonite (N/A) | 0.12 | 3 |
| | Sinclair inlet bulk sediment (<0.05%) | 0.08 | |
| | Montmorillonite (N/A) | 0.33 | |
| Peat Humic Acid | Montmorillonite Na^+ pH 7 | 0.00002-0. 00026 | 3 |
| Peat Humic Acid | Montmorillonite Ca^{2+} pH 7 | 0.00056-0. 00083 | 3 |
| Peat Humic Acid | Kaolinite Na^+ pH 7 | 0.00008-0. 00028 | |
| Peat Humic Acid | Kaolinite Ca^{2+} pH 7 | 0.0009-0.0 019 | |
| Liberty Bay porewater NOM <1000 Da | Na-Montmorillonite | 1.2 | 4 |
| Liberty Bay porewater NOM >1000 Da | Na-Montmorillonite | 1.9 | 4 |
| Liberty Bay extracted NOM <1000 Da | Na-Montmorillonite | 1 | |
| Liberty Bay extracted NOM >1000 Da | Na-Montmorillonite | 1.8 | |
| Artificial Leaf litter | Forest soil E (0.598) (10-19 cm depth) | 0.81 | 5 |

| | | | |
|-------------------|---|------|--|
| leachate 134 mg/L | | | |
| | Forest soil Bh (6.12) (19-22 cm depth) | 3.32 | |
| | Forest soil BS (1.39) (22-32 cm depth) | 8.96 | |
| | Forest soil Bc (0.14) (32-59 cm depth) | 7.77 | |
| | Forest soil C (0.046) (59-/ cm depth) | 4.13 | |

Table 5: Literature values for the partition coefficient (K_d) of toluene. K_d values vary greatly depending on the aqueous phase and the sorbent used. (1) Magee *et al* (1991) (2) Thimsem and Keil (1998) (3) Feng *et al* (2005) (4) Arnarson and Keil (2000) (5) Vandenbruwane *et al* (2007).

The linear partitioning model is, however, only effective over a small concentration range as it assumes a small concentration of contaminant in solution, rapid kinetics and that equilibrium conditions exist (EPA, 1999). It also assumes that an infinite number of sorption sites are available and so a linear relationship between the concentration of contaminants in solution and the amount of contaminant sorbed. Rearrangement of the partition coefficient (Equation 1) gives the linear isotherm (Equation 2, Figure 5). This linear isotherm was used by the Environment Agency (2009) to quantify HOC sorption and desorption over a small concentration range, such as those relevant to HOC concentrations in landfill leachates.

$$C_s = K_d C_{aq} \quad [2]$$

As sorption has been shown to vary with the OC content of the sediment (Section 2.2.6) an organic normalised sorption coefficient (K_{oc}) was defined by Karrickhoff *et al* (1979) (Equation 3). This is a widely accepted method for comparing the sorption coefficients of isotherms between literature sources.

$$K_{oc} = K_d / f_{oc} \quad [3]$$

Where K_d = partition coefficient (L/g)

f_{oc} = fraction of organic carbon present in the sorbent (dimensionless)

Refining the linear partition model to take into account the number of sorption sites that are actually available to the sorbing compound results in the Langmuir isotherm.

2.2.3.2 The Langmuir Isotherm

The Langmuir isotherm (Equation 4, Figure 5) is one of the simplest used in the literature (Environment Agency, 2009; Calace *et al*, 2001; Devulapalli and Reddy, 1996; Sun *et al*, 2008) and assumes a uniform surface containing a finite number of physiochemically equivalent sorption sites. It also assumes that sorption cannot proceed beyond a

monolayer coverage and that the occupation of neighbouring sorption sites has no effect on sorption or desorption (Atkins and de Paula, 2006).

$$S = \alpha\beta C / (1 + \alpha C) \quad [4]$$

Where S = number of occupied sorption sites

α = Langmuir sorption constant

β = number of possible sorption sites

C = Solution concentration

Over a large contaminant concentration range the Langmuir isotherm is non-linear. This is due to factors such as competition between contaminants for a finite number of sorption sites, sorption sites not being physiochemically equivalent and non-uniformity of surfaces (Atkins and de Paula, 2006; Devulapalli and Reddy, 1996; Flores-Cespedes *et al*, 2006; Rebhun *et al*, 1992). These factors are discussed in relation to leachate DOC effects in Section 2.2.6.2. Over a large concentration range the Langmuir isotherm is therefore used to model non-linear behaviour. Over very small ranges of concentration, however, the Langmuir isotherm can be used to model linear sorption and desorption as it may exhibit linear behaviour over a small concentration range.

2.2.3.3 The Freundlich Isotherm

The Freundlich isotherm is largely used in the literature to describe non-linear sorption and desorption (Environment Agency, 2009; Devulapalli and Reddy, 1996; Flores-Cespedes *et al*, 2006; Grathwohl, 1990; Hwang and Cutright, 2002; Kleineidam *et al*, 1999). Unlike the Langmuir isotherm, at low concentrations the Freundlich isotherm does not behave linearly and it does not reach an upper sorption limit (Watson, 1999). The Freundlich isotherm is therefore more appropriate for modelling sorption over a defined range of low contaminant concentration such as those of toluene and naphthalene in leachates, and has been widely applied to heterogeneous systems such as those containing organic compounds (Foo and Hameed, 2010). Equation 5 (Figure 5) demonstrates the Freundlich isotherm which corresponds to a logarithmic change in the sorbed concentration with aqueous concentration. It also attempts to take into account

the effects of substrate-substrate interactions (as outlined in Section 2.2.6.2) on sorption (Atkins and de Paula, 2006).

$$C_s = K_f C_{aq}^n \quad [5]$$

Where C_s = Compound sorbed per mass of sorbent ($\mu\text{g/g}$)

K_f = Freundlich sorption coefficient, an empirical constant ($\mu\text{g}^{1-n} \text{L}^n/\text{g}$)

C_{aq} = Solution phase concentration at equilibrium ($\mu\text{g/L}$)

n = Freundlich exponent, sometimes referred to as “ $1/n$ ”

A plot of C_{aq} vs C_s can be used to determine K_f and n by regression. The Freundlich exponent (n) gives information about the shape of the isotherm. For example, when $n < 1$ the sorption increases with increasing aqueous concentration towards a sorption maxima, with the additional sorption of contaminant becoming less favourable with increasing C_{aq} . When $n > 1$, however, as the aqueous concentration increases the sorption of additional contaminant becomes more favourable leading towards an exponential-type isotherm. In the event that $n=1$, the Freundlich isotherm reverts to the linear isotherm (Equation 2). The linearized form of the Freundlich isotherm (Equation 6) can be determined by plotting $\log(C_{aq})$ vs $\log(C_s)$, where K_f is equal to the intercept and n is the gradient of the plot. It is in this form which data is often reported in the literature.

$$\log(C_s) = \log(K_f) + n \log(C_{aq}) \quad [6]$$

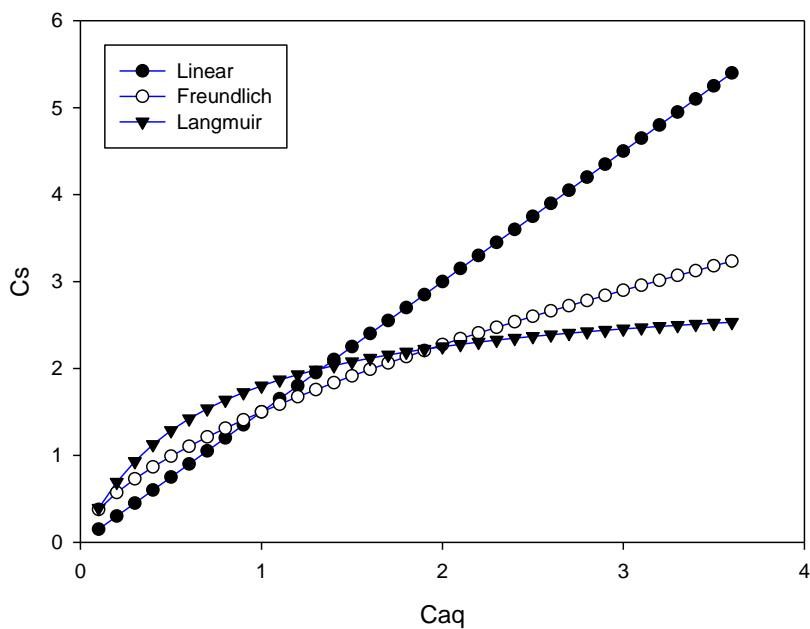


Figure 5: Behaviour of Linear, Langmuir and Freundlich sorption models with varying aqueous concentration of target compound. Data points derived from Equations 2, 4 and 5 using $x=0.1$ to 3.6 , $K_d=1.5$, $K_f=1.5$, $n=0.6$, $\alpha=1.5$ and $\beta=3$.

2.2.3.4 Alternative Isotherms

While the Freundlich or linear isotherms are widely utilised in the literature for modelling sorption and desorption, other isotherms that model sorption and desorption are available, as detailed by Foo and Hameed (2010). Since isotherms are only in agreement with experimental evidence over restricted ranges (Atkins and De Paula, 2006) different isotherms are required to take into account different variables. The exponential adsorption isotherm (Devulapalli and Reddy, 1996) (Equation 7) is one of many alternative isotherms which can be used to model sorption.

$$S = \alpha (1 - e^{-bc}) \quad [7]$$

Where

S = number of occupied sorption sites (sorbed concentration)

α and b = constants

c = concentration in solution

The models examined so far assume that sorption occurs in a monolayer only and that a single layer of sorption sites is available to the contaminants for sorption. However, this is not always the case, as sorbent compounds may have the ability to provide additional sorption sites for the contaminants. The Langmuir and Freundlich isotherms can either be modified in order to account for multi-layer sorption or an alternative isotherm may be used. The Brunauer–Emmett–Teller (BET) isotherm is used to model sorption where the initial adsorbed layer acts as an additional sorption surface for the following layer (Atkins and De Paula, 2006; Foo and Hameed, 2010) (Equation 8).

$$q_e = q_s C_{BET} C_e / (C_s - C_e) [1 + C_{BET} - 1](C_e/C_s) \quad [8]$$

Where

q_e/q_s = Equilibrium sorption capacity (mg/g) / theoretical isotherm saturation concentration (mg/g)

C_e/C_s = Sorbate equilibrium concentration (mg/L) / Monolayer saturation concentration (mg/L)

C_{BET} = BET isotherm (L/mg)

In order to fully model sorption and all the factors which influence it, such as anion and cation exchange, the contributions of chemisorption and physisorption, OM content of the sorbent and DOC content of the solvent; an extremely complex model would be required. It is, therefore, often the case that the availability of data of a sufficient quality and quantity to test the model (for example the exact sorption processes occurring at the sorbent surface) is the limiting factor when modelling sorption (Xie *et al*, 2009) and so by necessity a simpler model is adopted.

2.2.4 Sorption Kinetics

Sorption to a solid phase occurs at different rates which are dependent on the chemical nature of both the solid and solution phase. Sorption tends towards a dynamic equilibrium state where the target compound on the solid phase and in the solution phase is in sorption equilibrium (Gschwend and Wu, 1985). As the time taken to reach true sorption equilibrium may take years it is a parameter that is difficult to gauge accurately when working on a timescale relevant to laboratory testing (Ball and Roberts, 1991). Sorption equilibrium was defined by the US Environmental Protection Agency (EPA) as a rate of change of aqueous phase concentration of less than 5% over 24 hours, and by Oman and Spannar (1999) as less than 10% over 6 hours. For example the Environment Agency (2009) found that seven days was an adequate contact time to achieve sorption equilibrium of toluene to the Oxford Clay, whereas 72 hours was sufficient for perchloroethene (PCE) sorption to unlithified clay rich sediments (Allen-King *et al*, 1995).

The contact time with the clay also affects sorption (Oman and Spannar, 1999). Farrell and Reinhard (1994) found that sorption and desorption are two stage processes, with an initial fast stage followed by a longer slow stage. This was supported by work done for the Environment Agency (2009), which found sorption of toluene to be a biphasic process with an initial fast stage of sorption (24 to 48 hours) followed by slower sorption towards equilibrium for the remaining 30 days of the kinetic testing. Therefore, the optimum contact time for each HOC should be determined before testing is initiated and while it may not be practical to allow full sorption of the contaminant, it should ensure that the bulk of sorption has taken place.

The rate of desorption is also an important factor in the attenuation of HOCs in landfill liners as it determines the residence time of the HOC on the liner material and slow desorption rates could be mistaken for irreversibility of sorption. The desorption behaviour of a target compound from the solid phase may vary significantly from the sorption behaviour of the same compound. Therefore, the sorption and desorption rates of a compound may be different (Weber *et al*, 1998). Despite this, both desorption and sorption kinetics remain dependent on the character of the solution, the sorbent, the

sorbate and the nature of the interactions between them. For example, Bergendahl (2005) found that in an aqueous solution phase the desorption rate constant of naphthalene was two orders of magnitude larger than that of phenanthrene (7.75×10^{-3} hr⁻¹ and 5.87×10^{-5} hr⁻¹ respectively). This was attributed to the hydrophobicity of the contaminant, with naphthalene being less hydrophobic than phenanthrene (\log_{10} octanol/water partition coefficients of 3.17-3.36 and 4.57 respectively) and so having a lower affinity for hydrophobic sorption sites.

2.2.5 Sorption Hysteresis

Many sorption and desorption isotherms exhibit only partly reversible behaviour (Di Torro and Horzempa, 1982). Sorption hysteresis occurs when there is a discrepancy between the sorption and desorption isotherms. While it has been theorised that hysteresis may be caused by experimental artefacts as identified by Huang *et al* (1998) as: (1) sorption or desorption not reaching equilibrium, (2) third phase (solids) effects, (3) loss of contaminant to the reactor components. It was, however, noted by Di Torro and Horzempa (1982) that hysteresis persists despite making alterations to the experimental methods in an attempt to eliminate it. Examples of experimental alterations include allowing long equilibration times (Farrell and Reinhard, 1994). Due to these findings, and as discussed by Kan *et al* (1994) and Flanagan *et al* (1987) ‘true’ hysteresis can therefore be accepted to exist.

The literature is in general agreement that true hysteresis occurs due to three main reasons as outlined by Weber *et al* (1998): (1) irreversible sorption, (2) slow desorption rates (Pignatello, 1990; Kan *et al*, 1994), e.g. due to non-uniform distribution of contaminants on the sorbent (Belyaev and Yushmanov, 2008) and (3) entrapment of sorbed molecules, e.g. by alteration of the sorbing environment by the initial sorption (Farrell and Reinhard, 1994; Schwab *et al*, 2014). Irreversible sorption may be caused by the compound being strongly bound to the sorbent (Mikutta *et al*, 2007). This may occur via chemisorption which due to its strong, usually covalent, bonding nature can result in the chemical alteration or destruction of the target compound upon sorption (Atkins and de Paula, 1992).

Huang *et al* (1998) and Weber *et al* (1998) described the reasons behind hysteresis in greater detail and Huang *et al* (1998) proposed a hysteresis index (HI) (Equation 9). The HI indicates the level of hysteresis occurring within a system by comparing the sorbed contaminant concentrations for sorption and desorption at the same aqueous contaminant concentration. Since direct measurement of C_s values is unrealistic in an experimental situation Huang *et al* (1998) suggested the calculation of sorption coefficient (K_d) values for sorption and desorption isotherms at the same aqueous contaminant concentration extrapolated from the isotherm best fits (Equation 10). This allows the calculation of a hysteresis index in the case of both linear and non-linear isotherms.

$$HI = C_s^D - C_s^S / C_{aq}^S \quad |_{T, C_{aq}} \quad [9]$$

$$HI = K_d^D - K_d^S \quad |_{T, C_{aq}} \quad [10]$$

Where C_s^D = Sorbed contaminant concentration (desorption)

C_s^S = Sorbed contaminant concentration (sorption)

C_{aq}^S = Aqueous contaminant concentration (sorption)

K_d^D = Sorption coefficient (desorption)

K_d^S = Sorption coefficient (sorption)

$|_{T, C_{aq}}$ indicates that the temperature and C_{aq} should remain constant in the application of this equation.

2.2.6 Solid Phase Organic Carbon, DOC and Their Effect on the Sorption of HOCs

2.2.6.1 The Effect of Solid Phase Organic Carbon on Sorption Behaviour

HOCs in the leachate may sorb either permanently or reversibly to the liner material. The extent of this sorption is often dependant on the OC content of the liner material. The OC content of the sorbent can impact the sorption of contaminants as it can alter the chemical characteristics of the solid phase. Karickhoff *et al* (1979) demonstrated that

the sorption coefficients of HOCs were directly related to the OC content of the solid phase to which they were sorbing and Allen-King *et al* (1997) found that greater sorption of trichloroethylene (TCE) occurred to liner materials with higher OC contents. This has been repeatedly tested and it is now widely accepted that an increase in the OC content of a solid phase will result in an increase in the sorption of HOCs (Bright *et al*, 2000; Cox *et al*, 2000; Devulapalli and Reddy, 1996). The nature of the organic carbon in a solid phase is also important to the sorption of contaminants. Grathwohl (1990) found that geologically older carbon sources in solid phases (sandstones, mudrocks, shales, silts and soil samples) resulted in higher sorption coefficients. Therefore, it is predicted that solid phases rich in kerogen, a geologically mature form of organic carbon found in sediments, (Taylor *et al*, 1998) will sorb HOCs to a greater extent than sediments with little or no kerogen.

2.2.6.2 The Effect of DOC on Sorption Behaviour

In addition to solid phase OC, the DOC in solution may also affect the sorption of contaminants since it may also undergo sorption to the solid phase. It has been demonstrated by Larsen *et al* (1992) that HOCs partition onto DOC in leachates. Huo *et al* (2009) found that the degree of sorption of DOC to a solid phase (sediment) was dependent on the chemical nature of the DOC and that increased sorption of DOC to the sediment was observed with increasing molecular weight and humification of the DOC. The Environment Agency (2009) observed a decrease in the sorption of the HOCs toluene and naphthalene ($\log K_{ow}$ 2.54-2.69 and 3.17-3.36 respectively) to the Oxford Clay upon the addition of tannic acid to the solution. Hwang and Cutright (2002) suggest three different scenarios to describe the effect of DOC on HOC sorption by liner materials: (1) DOC has no effect on HOC sorption, (2) DOC and HOCs undergo co-sorption and (3) HOCs undergo cumulative sorption to the solid phase with DOC.

In co-sorption the HOC sorbs to a secondary molecule in solution (DOC). The DOC-HOC complex then sorbs to the liner material (Figure 6). Where sorption of the HOC alone was less favourable this may result in a net increase in HOC sorption to the clay. The sorption of HOCs to the DOC may, however, reduce sorption by allowing the HOC to remain in solution bound to the DOC (Figure 7).

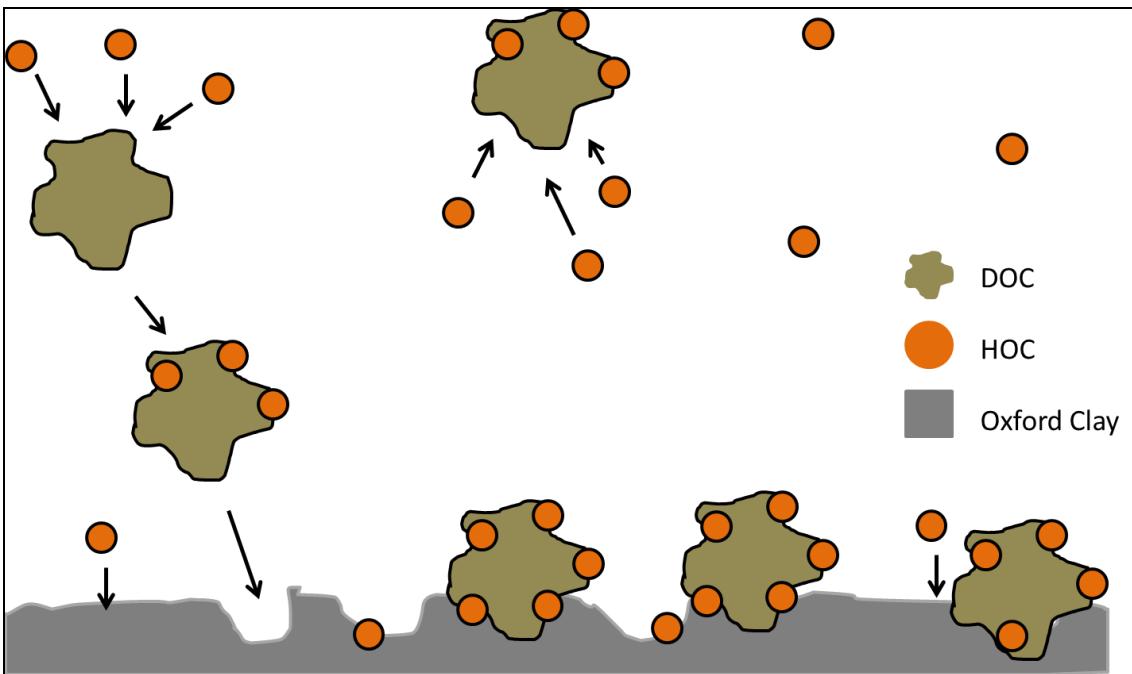


Figure 6: HOC co-sorption with DOC to the Oxford Clay. If the HOCs partition onto the DOC and the DOC sorbs to the Oxford Clay, then the HOC can co-sorb to the Oxford Clay, resulting in an increase in sorption to the clay. Direct sorption of the HOC may still occur.

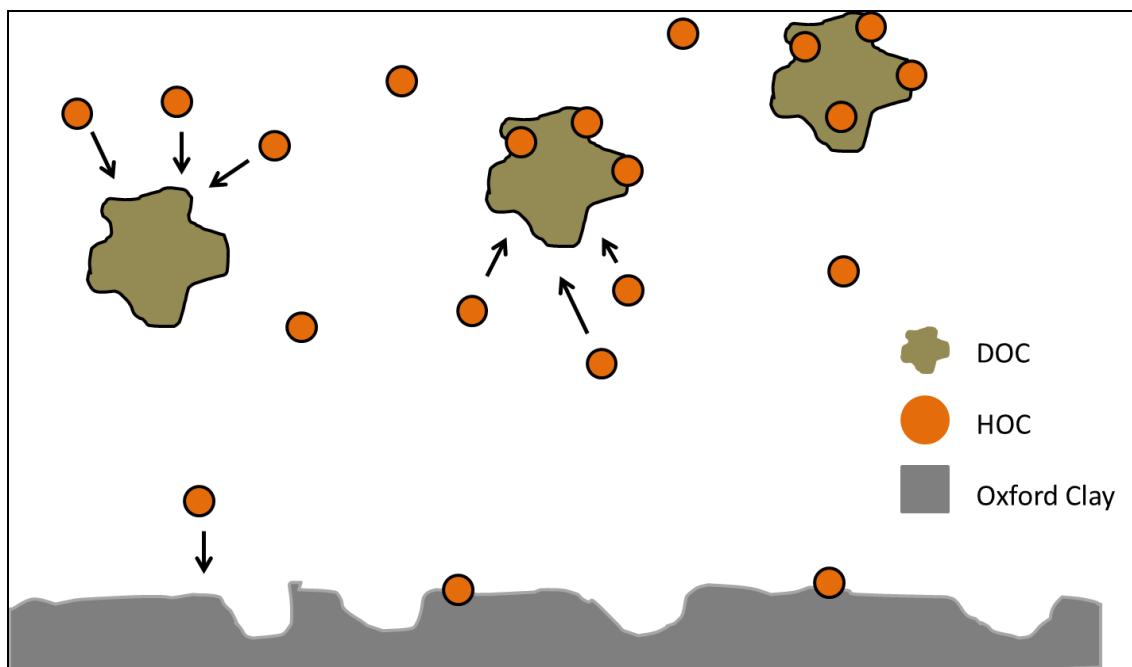


Figure 7: Sorption of HOC to DOC that remains in the aqueous phase. If the HOCs partition onto the DOC and the DOC remains in solution then the HOC can remain in solution rather than sorb to the Oxford Clay, resulting in a decrease in sorption to the clay.

In cumulative sorption a secondary molecule in the solution (DOC) sorbs to the liner material. The HOC then sorbs to the DOC coating on the liner (Figure 8). This may occur due to the DOC increasing the OC content of the sorbent, so increasing available sorption sites or creating sites that are more favourable for HOC sorption.

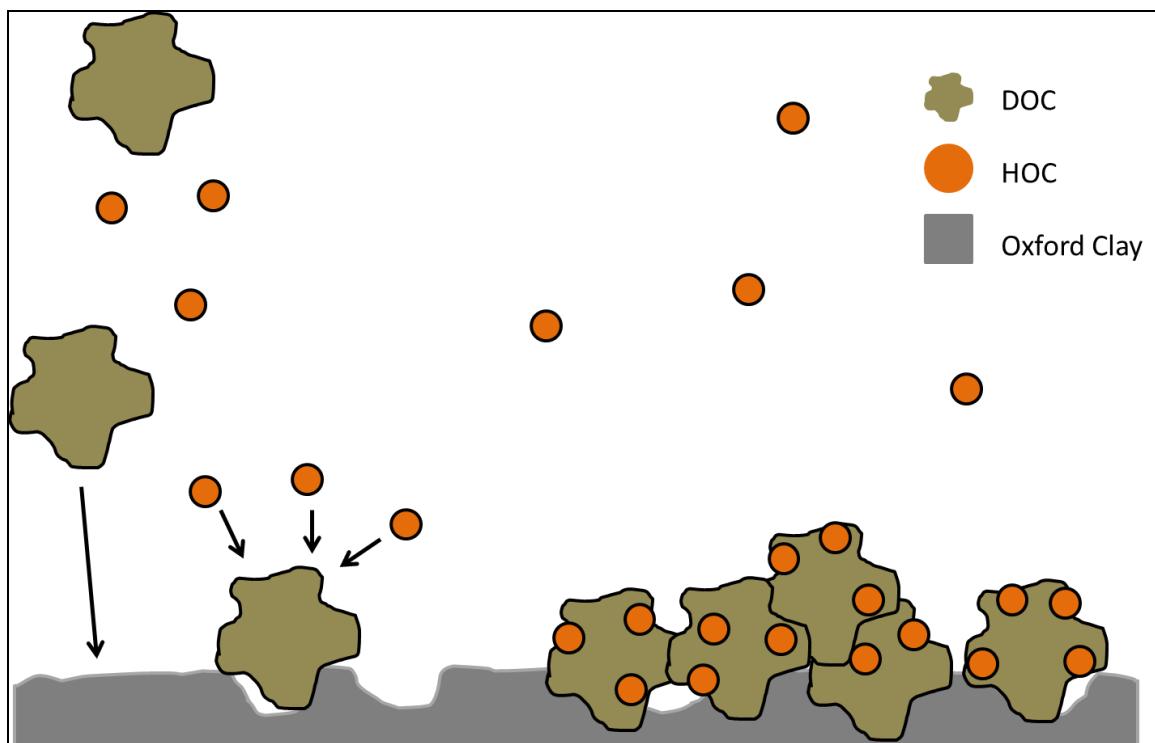


Figure 8: Cumulative sorption of DOC and HOC to the Oxford Clay. If the DOC partitions onto the Oxford Clay, it may increase the organic carbon content of the Oxford Clay making the surface of the clay more hydrophobic, and/or creating additional sorption sites on the solid phase for the HOC. This would result in an increase in sorption to the clay. Direct sorption of the HOC may still occur.

The sorption of DOC to the clay may also be a competitive process with the HOC competing with the DOC for sorption sites, either blocking or changing the conformation of the sorption sites on the clay, thus reducing HOC sorption (Figure 9).

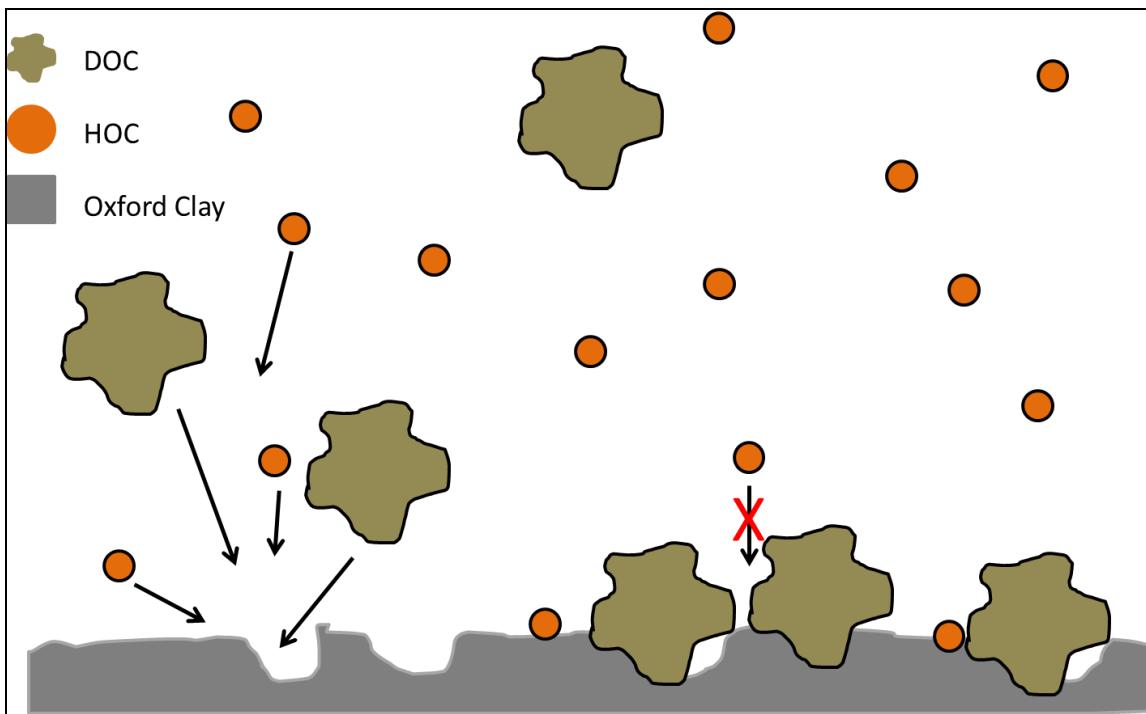


Figure 9: Competitive sorption of DOC with HOC for sorption to the Oxford Clay. The HOCs compete with the DOC for sorption sites on the Oxford Clay. This may occur by direct competition for individual sorption sites, by the larger DOC molecules blocking free sorption sites due to their size (steric inhibition) or by the DOC binding to more than one site, thereby blocking them. Competitive sorption results in a decrease in the sorption of HOCs to the Oxford Clay.

It should be noted that the processes detailed in Figures 6-9 are not necessarily mutually exclusive and may occur simultaneously. The promotion or prevention of HOC sorption by competitive, cumulative and co-sorptive processes is supported by Larsen *et al* (1992) who found that the presence of DOC in solution could either increase or decrease the transport of organic micropollutants in an aquifer material. Thornton *et al* (2000) further demonstrated that age of the DOC in leachates affected the transport of XOCs in leachate impacted groundwater through an aquifer. Thornton *et al* (2000) found that whilst acetogenic leachate decreased sorption of XOCs to aquifer materials by 70-90%, the presence of methanogenic leachates increased XOC sorption by 40-500%. Both Larsen *et al* (1992) and Thornton *et al* (2000) noted that the prediction of the effect of a leachate on a given aquifer material is challenging due to complex leachate-aquifer interactions.

Since the sorption of HOCs to aquifer material is dependent on the hydrophobicity of the carrier solution as well as the solid phase (Larsen *et al*, 1992) it follows that the degree of hydrophobicity of the DOC in solution will affect the sorption behaviour of HOCs. From the findings of Thornton *et al* (2000), the sorption of the target contaminants

toluene and naphthalene to the liner material could either be increased or decreased by DOC in solution depending on the type of DOC present. Since methanogenic leachates were shown to increase the sorption of organic contaminants (Thornton *et al*, 2000) and methanogenic leachates contain high proportions of humic substance-like DOC (outlined in Section 2.1.4) it follows that leachates containing humic-like substances may increase the sorption of HOCs to clay liner materials. This may be because the more conjugated structures of humic-like and fulvic-like DOC, coupled with their surface functionality, mean that they have the potential to form complexes with HOCs more effectively and provide a more organic (hydrophobic) phase than DOC fractions which have less aromaticity and functionality (Zhang *et al*, 2012; Wang *et al*, 1997).

Cox *et al* (2000) studied the effect of four organic soil additives on the sorption of the HOC simazine to soils. Three of the compounds were largely humic in character and contained numerous carboxylic acid functional groups. The organic amendments with humic-like character were shown to increase the sorption of simazine to the soil. However, the fourth, consisting of smaller non-humified molecules, resulted in a decrease in sorption to the soil. The results of Cox *et al* (2000) are comparable to those of Thornton *et al* (2000). It has been suggested that this is due to competition between HOCs and non-humic DOC molecules for sorption sites on the sediment (Cox *et al*, 2000) as in Figure 9.

2.2.6.3 The Effect of Hydrophobicity of the Contaminant on Sorption

As well as the presence of DOC in solution or solid phase, Flores-Cespedes *et al* (2006) showed that adding DOC amendments such as natural organic matter (NOM) and tannic acid (TA) to soils increased the sorption coefficient of the hydrophobic contaminants 3,4-dichloroaniline (3,4-DCA) and 4-bromoaniline (4-BA) from 1.12 and 0.57 L/kg respectively to 1.57 and 6.75 L/kg in NOM and 26.58 and 2103 L/kg in TA ($\log K_{ow}$ 2.26 and 2.69 respectively). However, the sorption coefficient of imadacloprid (an insecticide) which had a lower hydrophobicity ($\log K_{ow}$ 0.57) decreased from 0.45 L/kg to 0.39 L/kg in NOM and 0.36 L/kg in TA. This was attributed to DOC competing with the contaminant for sorption sites. Flores-Cespedes *et al* (2006) therefore demonstrated

that the hydrophobicity of the contaminant plays a role in the sorption behaviour observed. It was observed that the addition of NOM and TA (DOC) to a soil reduced the sorption of imadacloprid (which had a lower $\log K_{ow}$) through competition between the DOC and imadacloprid for sorption sites on the soil. The addition of NOM and TA to soils was also observed to increase the sorption of 3,4-DCA and 4-BA (with a higher $\log K_{ow}$) to the soil by the DOC increasing the sorption capacity of the soil and, therefore, increasing sorption.

The addition of tannic acid to a synthetic leachate was however, found to decrease the sorption of naphthalene ($\log K_{ow}$ 3.17-3.36) from $K_d=2330$ to $K_d=2140$ (Environment Agency, 2009) despite the $\log K_{ow}$ values being similar to the 4-BA and 3,4-DCA used by Flores-Cespedes *et al* (2006). This difference in behaviour may originate in the properties of the sediment used in sorption tests as Flores-Cespedes *et al* (2006) used a low OC (0.27%) soil whereas the Environment Agency (2009) study uses the Oxford Clay which had a higher OC (5.49%) content.

2.2.6.4 Natural Attenuation and Sorption Summary

As with the OC present in the sediment the nature of the DOC present in solution is significant. The sorption behaviour of both the HOCs and solid phase OM have been found to vary depending on the chemical character of the DOC in solution (Cox *et al*, 2000; Flores-Cespedes *et al*, 2006; Thornton *et al*, 2000). Since the DOC character of leachates is variable and complex (as discussed in Section 2.1.3) it may be beneficial to conduct sorption experiments on both the bulk leachate solution and isolated types of DOC present in the mixture, such as humic-like substances and protein-like substances. This may be achieved using real leachates which have been size-fractionated using techniques such as ultrafiltration (Ogura, 1974) or cross flow filtration (Buesseler *et al*, 1996). Alternatively, since real leachate composition is difficult to predict, using a commercially available DOC substitute such as humic acid or a IHSS standard may be an effective alternative to using real leachates for risk assessment purposes. It is not clear, however, if a synthetic leachate is an appropriate substitute for real leachate DOC as the chemical character of the DOC in synthetic leachates. For example, a commercially available DOC compound such as tannic acid or humic acid may not interact with the

sediment or contaminants in the same way as ‘natural’ leachate DOC (Environment Agency, 2009). Landfill leachate composition has been shown to vary greatly between landfills and is dependent on the type of waste deposited, its construction and its management (Section 2.1.4). The complexity and variability of leachate composition and leachate DOC will therefore be a major obstacle to the determination of its effect on the sorption of HOCs.

2.3 DOC Characterisation Techniques in Wastewaters

In the wastewater industry fluorescence and ultraviolet spectroscopy measurements are routinely used to monitor wastewater quality (Baker, 2001 and 2002c; Baker and Curry, 2004; Henderson *et al*, 2009; Huo *et al*, 2009; Lu *et al*, 2009; Saadi *et al*, 2006; Sun, 2008). These analytical techniques can be used to distinguish between the types of carbon present in a sample. This section discusses these techniques in greater detail and describes their application to the proposed research. Particular attention is paid to the use of fluorescence excitation-emission matrices within the wastewater industry and their potential for use in landfill leachate characterisation.

2.3.1 Fluorescence

2.3.1.1 Overview

Fluorescence is a highly sensitive, rapid and experimentally simple technique (Cumberland and Baker, 2007; Henderson *et al*, 2009; Hunt and Ohno, 2007; Mostofa *et al*, 2005). Baker and Curry (2004), Coble (1996) and Fu *et al* (2007) have all demonstrated the use of fluorescence in the identification of pollution sources in the wastewater industry. Baker (2002c) showed that the tracing of water from different origins is possible as fluorescence allows discrimination between different sources of DOC that absorb at similar wavelengths. This makes fluorescence up to 1000 times more sensitive than UV spectroscopy as a method of DOC discrimination (Coble, 1996; Henderson *et al*, 2009). Baker and Curry (2004) noted that much of the DOC present in landfill leachate is fluorescent, allowing the characterisation and fingerprinting of leachate DOC by fluorescence. Information about leachate DOC obtained from fluorescence fingerprinting may be used to refine and monitor leachate treatment processes, as well as detecting and tracing leachate plumes from specific landfill sites (Huo *et al*, 2009; Sun *et al*, 2008). Therefore, fluorescence fingerprinting of leachates may also be specific enough for use in characterising the DOC in different leachates and monitoring its sorption.

2.3.1.2 Excitation Emission Matrices (EEM) and the Characterisation of Organic Matter

Usually fluorescence is measured using a synchronous scan method which uses a single excitation wavelength and measures the intensity at a range of emission wavelengths. While this is a good option for determining the fluorescence of a single compound, DOC is a complex mixture in solution with compounds that may have identical absorption or emission wavelengths. In this case a synchronous scan method cannot fully elucidate the individual DOC compounds and, therefore, the DOC character of leachates and changes in it. An excitation emission matrix (EEM) method has been shown to be a more appropriate method for monitoring the chemical character of DOC mixtures in a solution (Baker and Curry, 2004; Fu *et al*, 2007; Henderson *et al*, 2009; Hunt and Ohno, 2007). The EEM method produces a three dimensional plot of peak intensity at a range of excitation and emission wavelengths and is a quick way of characterising the overall fluorescence of a mixture of compounds in solution. As it records emission across a range of excitation wavelengths, the EEM consists of a large amount of data and is able to be analysed as excitation or emission spectra, a synchronous scan or a contour plot (Fu *et al*, 2007; Henderson *et al*, 2009). This results in a technique which has a large degree of flexibility during analysis.

The EEM contour plot produces a 3D landscape where each peak corresponds to a different type of compound within the DOC mixture. However, as highlighted by Seredynska-Sobecka *et al* (2007) the precise nature of the compounds in the mixture is difficult to determine due to the complex heterogeneous nature of DOC. Fu *et al* (2007) determined that the relationship of DOC with fluorescence is complex as “*the exact relationship between fluorescence properties and biogeochemical structure of DOM remains unknown*”. Therefore, DOC is categorised into groups of compounds with similar properties such as humic substance-like (HSL) and protein-like (PL) DOC which are identifiable as different groups as they fluoresce at different wavelengths due to their molecular structure. Hunt and Ohno (2007) detailed the limitations posed by the complex interactions of the sample mixture such as the unknown interactions of non-fluorescing DOC with the fluorophores. Despite this, Baker and Curry (2004)

demonstrated that fluorescence is an effective technique for DOC characterisation in leachates due to fingerprinting, since fingerprinting of DOC in landfill leachates allows rapid qualitative determination of the type of OC present in the leachate of interest.

Since the character of the DOC in a solution has the potential to affect the sorption of HOCs to liner materials (Section 2.2.6.2) a technique for characterisation of the nature of the DOC in the leachate is required. The simplicity and non-destructive nature of fluorescence combined with the large amount of information that can be gathered in a short timescale during an EEM scan make fluorescence an ideal method for the characterisation of DOC in leachates being used for contaminant sorption experiments.

2.3.1.3 Excitation Emission Matrix (EEM) Peaks of Interest

DOC fluorescence has been found to be present in a wide variety of aqueous environments. Table 6 outlines literature values for fluorescence peaks present in a variety of aqueous systems including landfill leachates. The fluorescence peaks are labelled A-F and illustrated in detail in Figure 10 for clarity.

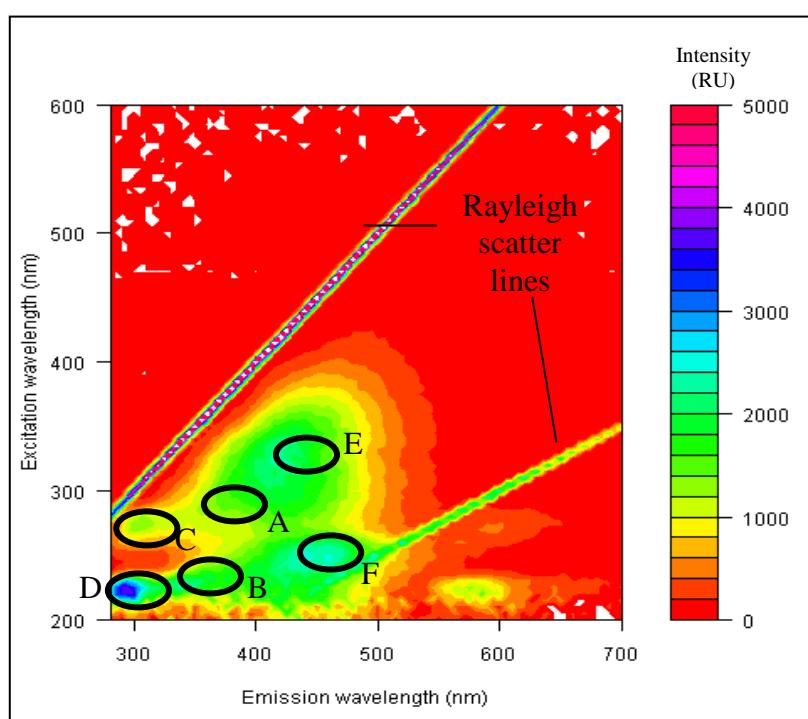


Figure 10: An EEM spectrum of a MSW leachate (1:100 dilution). Emission is represented on the x axis and excitation on the y axis. Intensity is given in Raman units. Peaks A-F selected for analysis are shown. A and B = tryptophan-like, C and D = tyrosine-like, E = fulvic-like (FL), F= humic-like (HL).

The Rayleigh scattering lines present in EEM spectra are also labelled in Figure 10. These are an artefact of the technique rather than being of diagnostic significance.

Coble (1996) compared the fluorescence of humic-like and fulvic-like DOC in seawater and freshwater and found that seawater humics exhibited fluorescence at lower wavelengths than freshwater humics. This was attributed to the chemical character of the DOC in solution since the ionic composition of the solution affects the conformation of the DOC. Work by Coble (1996) has been used by other researchers (Baker and Curry, 2004; Huo *et al*, 2009; Lu *et al*, 2009; Sun *et al*, 2008) as the basis for assigning the humic-like peak region in leachate fluorescence. Baker (2001) and Baker *et al* (2004) identified protein-like compounds in non-leachate wastewaters. Baker and Curry (2004) then used this data to identify protein-like peaks in leachate fluorescence. Henderson *et al* (2009) examined sewage sludge effluent contamination in water systems and identified two further peaks which are attributable to protein-like DOC (denoted B and D). Landfill leachates were found to exhibit peaks in all of the regions identified by the literature.

Overall six peaks were identified from the literature (summarised in Table 6) as being relevant to this work. Of these two peaks correspond to HSL compounds (Huo *et al*, 2004; Baker and Curry, 2004; Coble, 1996) and four correspond to PL compounds (Henderson *et al*, 2009; Yunus *et al*, 2008; Banaitis *et al*, 2006). Of the four PL compounds two are attributed to tyrosine-like DOC (Henderson *et al*, 2009) and two are attributed to tryptophan-like DOC (Baker and Curry, 2004). The two HSL peaks are split into one humic-like and one fulvic-like peak (Huo *et al*, 2009). All six of these peaks have been observed in landfill leachates (Yunus *et al*, 2008; Baker and Curry, 2004). Therefore, EEM regions which had previously been identified in the literature as containing the excitation and emission wavelength ranges for the DOC peaks of landfill leachate were used in this work.

Literature values of fluorescence for optical brighteners and XOC are summarised in Table 7. Baker and Curry (2004), Lu *et al* (2009) and Yunus *et al* (2008) noted that the fluorescence of peaks B and D overlap the fluorescence peak attributed to XOC compounds such as naphthalene in studies focusing on leachate fluorescence. Toluene is also fluorescent (Table 7) however in this work the concentration of both toluene and

naphthalene was controlled in leachates (Section 4.2.4.1) as all the leachates were screened for the presence of toluene and naphthalene before use in further experiments. Therefore, the leachates were unlikely to contain peaks attributable to either toluene or naphthalene.

| Identified Peak for use in this work (excitation/ emission) (nm) | Literature Value (excitation/ emission) (nm) | Reference | Context | nm Tyrosine-like | | | sewage contamination |
|---|---|-------------------------------|--|--|----------------------|---------------------------------------|---|
| Peak A 275-280/ 340-380 nm Tryptophan-like | 275-280/350-360 | Baker and Curry, 2004 | Landfill leachates | Peak E 300-370/ 400-500 nm Fulvic-like | 300-370/400-500 | Yunus <i>et al</i> , 2008 | Landfill leachates |
| | 270-280/340-380 | Huo <i>et al</i> , 2009 | Landfill leachates | | 320-340/400-440 | Baker and Curry, 2004 | Landfill leachates |
| | 270-280/340-380 | Yunus <i>et al</i> , 2008 | Landfill leachates | | 300-350/400-460 | Cumberland and Baker, 2007 | Relating DOM in freshwater to TOC |
| | 220-280/340 | Du <i>et al</i> , 1998 | Photochemical Reference value | | 339-392/424-482 | Mostofa <i>et al</i> , 2005 | Lake watershed runoff (taken from Table 1) |
| | | Mostofa <i>et al</i> , 2005 | Lake watershed runoff | | 310-340/420-440 | Huo <i>et al</i> , 2009 | Landfill leachates |
| | 275/340 | Henderson <i>et al</i> , 2009 | Monitoring recycled water systems for sewage contamination | Peak E labelled as 'humic-like' due to labelling entire humic/fulvic-like region as containing 2 humic-like peaks. | A 220-250/400-460 | Seredynska-Sobcka <i>et al</i> , 2007 | Characterising colloidal and particulate organic matter in freshwater |
| Peak B <255/ 340-380 nm Tryptophan-like | 220/350 | Pitts <i>et al</i> , 2001 | Protein fluorescence | | B 300-340/400-460 | | |
| | <250/350 | Banaitis <i>et al</i> , 2006 | Sorption driven fractionation of DOM | | A 260/400-500 | Coble, 1996 | Marine and terrestrial DOM in seawater |
| | 225-237/340-381 | Henderson <i>et al</i> , 2009 | Monitoring recycled water systems for sewage contamination | | B 370/400-500 | | |
| | 220-240/340-370 | Yunus <i>et al</i> , 2008 | Landfill leachates – representing naphthalene | | 260-330/445 | Mounier <i>et al</i> , 1999 | DOC in the Amazon basin (abstract only) |
| | 220-230/340-370 | Baker and Curry, 2004 | Landfill leachates – representing naphthalene | | 220-260/400-500 | Yunus <i>et al</i> , 2008 | Landfill leachates |
| | | | | | 230-250/400/440 | Baker and Curry, 2004 | Landfill leachates |
| Peak C 275-280/ 305-312 nm Tyrosine- like | 270-280/305-312 | Yunus <i>et al</i> , 2008 | Landfill leachates | Peak F 220-300/ 400-500 nm Humic-like | 220-240/420-440 | Huo <i>et al</i> , 2009 | Landfill leachates |
| | 220-275/300-305 | Coble, 1996 | Marine and terrestrial DOM in seawater | | 230-320/420 | Lu <i>et al</i> , 2009 | Landfill leachates |
| | 275-310 | Banaitis <i>et al</i> , 2006 | Sorption driven fractionation of DOM | | 245/436 | Fu <i>et al</i> , 2007 | DOM complexation with Hg in rivers |
| | 275/310 | Henderson <i>et al</i> , 2009 | Monitoring recycled water systems for sewage contamination | | 237-260/400-500 | Henderson <i>et al</i> , 2009 | Monitoring recycled water systems for sewage contamination |
| Peak D <240/ 309-321 | 225-237/309-321 | Henderson <i>et al</i> , 2009 | Monitoring recycled water systems for | | | | |

Table 6: Summary of fluorescence excitation emission (EEM) peaks selected for use in this work alongside literature values for the regions representing the peaks. Peaks used in this work were selected using the existing literature values for fluorescence peaks in leachates alongside a fluorescence EEM of a MSW leachate used in this work.

| Compound | Excitation wavelength (nm) | Emission Wavelength (nm) | Reference |
|----------------------|----------------------------|--------------------------|-----------|
| Optical Brighteners | 375, 350, 330 | 410-450 | 1 |
| XOC e.g. naphthalene | 220-230 | 340-370 | 2 |
| | 220-240 | 340-370 | 3 |
| Toluene | 242 | --- | 4 |

Table 7: Wavelength regions for characterisation of other compounds in a fluorescence spectroscopy excitation emission matrix: (1) He *et al* (2009) (2) Baker and Curry (2004) (3) Yunus *et al* (2008) (4) PhotochemCAD.

2.3.1.4 Interpretation of the EEM

Whilst it has been demonstrated to be a valuable tool for the identification of the type of DOC in solution; Baker (2002), Baker and Curry (2004) and Yunus *et al* (2008) remind us that fluorescence is primarily a qualitative technique which shows changes in the character and structure of substances being studied. Therefore, fluorescence peak intensity cannot be used to compare concentrations of fluorophores in samples directly, without first performing a calibration. The complex interactions which take place between the DOC and associated fluorophores such as inner filtering effects (IFE), detailed in Section 4.3.1.2, (Hunt and Ohno, 2007) quenching and inter-molecular interactions need to be taken into account when extrapolating concentration information from intensity data (Baker, 2002; Banaitis *et al*, 2006). Fluorescence peaks indicating different groups of compounds can be shifted by atoms with lone pairs of electrons or substituent groups containing double bonds, such as carbonyls and carboxyls, as these contain electrons which can resonate within the molecules. Resonance within molecular structures has been shown to cause an increase (red shifting) in the excitation and emission wavelengths of compounds (Baker, 2002; Coble, 1996). Structural changes within the molecule may also result in red or blue shifting of the fluorescence signal due to changes in the energy difference between the ground and excited molecular states (Coble, 1996). This may mean that as a leachate matures and the DOC in that leachate becomes more refractory (as discussed in Section 2.1.5) a change in the position of a peak may be observable. Due to the complex nature and the unknown and variable chemical character of landfill leachates a direct comparison between the peak intensity of samples cannot be used to quantitatively describe the character of each leachate.

Hunt and Ohno (2007) identified peak picking as a simple way of comparing the change in peak intensity of a sample. Whilst peak picking can be undertaken manually, programmes such as R (Lapworth and Kinniburgh, 2008) or principle component analysis (PCA) (Stedmon *et al*, 2003) using Matlab (PARAFAC script) (Henderson *et al*, 2009; Hunt and Ohno, 2007; Stedmon *et al*, 2003) are quicker and less subjective methods of analysis than manual peak picking (Stedmon *et al*, 2003). Despite the use of picked peak intensity to monitor the change in peak intensity of a single sample, fluorescence peak intensity is still a qualitative assessment. In order to make it quantitative and be able to compare samples directly in terms of concentration a calibration standard curve would still have to be produced. In the case of landfill leachate DOC this is not feasible as the exact concentrations, relative proportions and chemical makeup of the DOC in leachates is unknown. Therefore, comparison of DOC character between samples must be achieved via the comparison of the ratios of the peaks. Cox *et al* (2000) used a humification index (HIX) to achieve this. As its name suggests a HIX provides a measure of the humification, the ratio of humic-like substances in relation to the ratio of protein-like substances, in the mixture (Equation 11). Example literature values for humification indices are presented in Table 8. These are diverse and demonstrate the large variation possible in DOC from within the same environment as well as from different environments. The use of 254 nm as the excitation wavelength is within the range of light absorption by humic substances and so makes the HIX sensitive to the aromaticity of DOM in the solution (Banaitis *et al*, 2006; Hunt and Ohno, 2007; Ohno, 2002). Cox *et al* (2000) used a HIX to determine the humification of organic amendments to soils and thus were able to relate the degree of humification of an organic soil amendment to the sorption properties of the soils. Similarly Banaitis *et al* (2006) showed that DOC with a lower HIX underwent less sorption of humic substances to the clay than DOC with a high HIX value. The HIX was also recognised by Hunt and Ohno (2007) as a measurable property in the characterisation of DOC. The HIX increases with increasing humification of the source DOM (Ohno, 2002) and with increasing DOM molecular weight (Hunt and Ohno, 2007). As shown in Equation 11, the HIX is a ratio of two regions of the fluorescence spectra both with excitation wavelength 254 nm and emission wavelength ranges 435-480 nm and 300-345 nm respectively.

$$\text{HIX} = (\Sigma I_{(435/480)}) / (\Sigma I_{(300/345)}) \quad [11]$$

Where I is the intensity at each emission wavelength using an excitation wavelength of 254 nm

The two regions in the HIX ratio correspond to the humic-like and protein-like peaks on a leachate EEM (equivalent to the peak ratio F:B from this work). Therefore, as shown in the literature, an increase in humic substance like character or molecular weight will result in an increase in the ratio.

Fluorescence ratios have also been used by Chen *et al* (2003a and 2003b) to successfully differentiate between trace NOM and sewage OM in rivers and estuaries and by Sheng and Yu (2006) to indicate alterations in the chemical structure of extra cellular polymeric substances in biological wastewater treatment processes. The monitoring of OC character during landfill leachate treatment processes can also be achieved by use of fluorescence ratios (Sun *et al*, 2008) demonstrating the potential use of fluorescence ratios and HIX values for the quantitative monitoring of DOC in landfill leachates.

| HIX value | Context | Ref. |
|-----------|---|------|
| 0.77 | Grapmere (by-product from winemaking), untreated | 1 |
| 0.19 | Grapmere (by-product from winemaking), anaerobically digested | |
| 0.45-2.75 | Sea water (upper range) | 2 |
| 0.61 | Sea water | 3 |
| 0.78 | Freshwater | |
| 0.47 | Rainwater | 4 |
| 2.12-7.04 | Water level fluctuation zone | 5 |
| 2-18 | Hydrodynamic Mediterranean lagoon system | 6 |
| 0.37-2.41 | Lake sediment cores | |
| 8.14 | Agricultural land (abandoned farmland) | 7 |
| 9.43 | Agricultural land (corn) | |
| 0.33 | Cropped corn field | 8 |
| 0.25 | Grass land | |
| 0.57 | Aqueous corn extract | |
| 0.84 | Aqueous soil extract | 9 |
| 0.94 | Soil FA | |
| 0.76-0.89 | HA and Dom from farm soils | 10 |
| 0.77-0.96 | Alaskan forest soil pore water | 11 |
| 4.47-4.95 | Sediment HS in a polluted natural water system | 12 |

Table 8: Literature values for HIXs in various environments. (1) Brunetti *et al* (2012) (2) Bai *et al* (2013) (3) Chen *et al* (2011) (4) Salve *et al* (2012) (5) Fang *et al* (2011) (6) Catalan *et al* (2014) (7) Guo *et al* (2012) (8) Saviozzi *et al* (1994) (9) Ohno (2002) (10) Traversa *et al* (2014) (11) Wickland *et al* (2007) (12) Yeh *et al* (2014).

2.3.2 Ultra Violet Spectroscopy

2.3.2.1 Overview

Thomas *et al* (1999) describes ultra violet (UV) spectroscopy as a fast and simple analytical method which can be used either qualitatively or quantitatively (following appropriate calibration). In UV spectroscopy incident radiation is absorbed by unsaturated molecular functional groups, chromophores, resulting in a lower intensity transmitted radiation. However, UV spectroscopy is less sensitive than fluorescence and, unlike fluorescence, UV spectroscopy cannot distinguish between different sources of DOC that absorb light at similar wavelengths (Henderson *et al*, 2009; McKnight *et al*, 2001). Therefore UV spectroscopy is often used in parallel with fluorescence measurements (Henderson *et al*, 2009; Kang *et al*, 2002; Yunus *et al*, 2008). Baker and Curry (2004) and Macalady and Walton-Day (2009) found that combining the two techniques gave more information than when they were used independently. For example, some compounds may be optically active under both techniques or only in a single technique so more information can be gathered about the sample.

2.3.2.2 UV and DOM

UV spectroscopy is frequently used to measure DOC concentration (Hunt and Ohno, 2007; Yunus *et al*, 2008) with a linear relationship existing between DOC concentration and UV absorbance at 254 nm (Zouboulis *et al*, 2003). The absorbance at wavelengths below 280 nm is also widely accepted to relate to the degree of aromaticity present in the sample (Domeizel *et al*, 2004; Ghabbour *et al*, 1998; Kang *et al*, 2002). However the wavelength most commonly used to define aromatic character is 254 nm (Banaitis *et al*, 2006; Cox *et al*, 2000; Sun *et al*, 2008; Zouboulis *et al*, 2003). Therefore change in the absorbance at 254 nm will be used in this work to give a measure of the aromatic character of the DOC in leachates. This can be extrapolated to indicate humification and thus the maturity of DOC since DOC increases in aromaticity as it becomes more mature and humified. In a similar method to the use of a HIX in fluorescence spectroscopy; the

peak ratios of humic acid and fulvic acid DOC in a solution were used by Domeizel *et al* (2004) to measure the extent of humification in composts. This may be applied to support data on the aromaticity of compounds gathered by the absorbance at 254 nm.

Domeizel *et al* (2004) also found that the shoulders on the UV emission peaks at excitation wavelength of 254 nm related to unsaturated functional groups such as C=C, C=O and C=N. This was supported by Thomas *et al* (1999) who showed that UV spectra vary in shape between 200 and 350 nm for different types of organic matter at the same OC concentration. A method for elucidation of the structure of the DOC in solution may be possible; consistent with the work of both Hunt and Ohno (2007) and Kang *et al* (2002), who found that the molecular weight of DOC compounds was inversely proportional to the ratio of absorbance at 254:365 nm (Hunt and Ohno, 2007) and 405:665 nm (Kang *et al*, 2002). Therefore UV spectroscopy has the potential to provide information about the structure of DOC compounds as well as their concentration, which cannot be achieved by carbon measurement alone (Domeizel *et al*, 2004). This would be particularly applicable to this work should isolated forms of DOC be extracted from leachates in order to assess their individual contribution to the bulk leachate DOC effects on HOC sorption.

The use of UV spectroscopy in monitoring wastewater quality has been well established in the literature. Rivas *et al* (2003) demonstrated that UV absorbance at 254 nm (unsaturated or aromatic chromophores) and 410 nm (colour removal) could be used to monitor landfill leachate treatment processes. UV monitoring may be used alongside determination of TOC concentration of a wastewater as discussed by Thomas *et al* (1999) to monitor the quality of the OC as well as its concentration. Thomas *et al* (1999) found that the shape of UV absorbance spectra provides an indication of the composition of the organic compounds in solution and so is complimentary to TOC analysis. Yunus *et al* (2008) noted that aerobic treatment of leachates resulted in a decrease in UV absorbance at 254 nm indicating a decrease in aromatic character. However, during the treatment of landfill leachates by biological processes, Sun *et al* (2008) found that an increase in aromatic nature was indicated by an increase in UV absorbance at 254 nm. Sun *et al* (2008) observed an increase in absorbance after a biological treatment step in the leachate treatment processes which may be due to biological alteration of simple carbon compounds toward more complex humic-like substances which are more aromatic. This

process may be similar to biodegradation processes in landfills, as detailed in Section 2.1.4, and so could potentially be used to indicate the onset of biological degradation stages in landfills via monitoring the leachate quality. The decrease in absorbance observed by Yunus *et al* (2008) occurs after an aerobic treatment process. The breakdown of unsaturated molecular bonds, and so aromatic structure, has been suggested as the mechanism for decreased aromaticity (Lguirati *et al*, 2005). The UV absorbance at 254 nm may be used to assess and monitor changes in the humic character of leachate DOC, as an increase in aromaticity is an indication of an increase in the degree of humification of the OM in solution. This application was demonstrated by Kang *et al* (2002) who found that the aromaticity of humic substances in leachates increased with landfilling age.

2.4 Background Chapter Summary

- Sorption and biodegradation have been identified as mechanisms for hydrophobic organic contaminant attenuation in landfills; with the sorption of HOCs being driven by hydrophobic interactions such as partitioning.
- Sorption and desorption kinetics for HOCs are two stage processes, with an initial fast sorption stage which can last hours to days followed by a slower sorption stage which can last for months or years.
- The sorption of HOCs to the solid phase is widely accepted to increase with increasing OC content of the solid phase.
- DOC in solution may increase sorption by co-sorption or cumulative sorption. It may also decrease sorption by competing with the HOC for sorption sites on the sediment or by the HOC sorbing to the DOC in the aqueous phase allowing the HOC to remain in solution.
- In an EEM, fluorescence peak ratios normalise the measurements of fluorescence peak intensity, allowing direct comparison between samples using the proportion of a type of DOC present in solution rather than its concentration.
- The intensity of fluorescence peaks in EEMs cannot be used quantitatively in the case of DOC due to its heterogeneous nature. Therefore a humification index (HIX) may be used to monitor the humic character of DOC compounds present in leachate.

In landfill risk assessment tools, such as LandSim, the attenuation of contaminants is modelled using K_d values either obtained experimentally or from the literature with a similar lithology. While the OC content (f_{oc}) of the sediment can be accounted for unless K_d is obtained in a DOC containing environment, interactions between the leachate and contaminants in solution and the effect of these interactions on sorption to the solid

phase is neglected. The poor understanding of these interactions (Guyonnet *et al*, 2005) highlights a knowledge gap in the modelling of contaminant retardation and attenuation within the landfill liner material and its impact on contaminant transport. This research aims to reduce this knowledge gap by examining the effect that different leachate DOC chemical character has on the attenuation of the HOCs toluene and naphthalene for Oxford Clay.

3. Research Strategy and Method Justification

This work follows from research by the Environment Agency (2009) which examined the sorption and desorption behaviour of a range of contaminants to three landfill liner materials used in the UK. The Environment Agency (2009) used a synthetic leachate as the aqueous phase (both with and without tannic acid in solution acting as a commercially available DOC surrogate). The findings, however, did not include the behaviour of the contaminants in solutions containing a variety of DOC types, and recommendations were made that this was an area worthy of further study.

The overall aim of this work was to determine the impact that DOC in solution had on the sorption and desorption of toluene and naphthalene to and from the Oxford Clay, in order to recommend improvements to procedures for estimating the contribution of contaminant sorption in the landfill risk assessment process. Four main experimental tasks and objectives were identified as necessary in order to effectively complete this research:

- (1) To obtain or produce leachates and characterise their DOC content in order to select leachates for sorption and desorption testing.
- (2) To quantify the amount of DOC sorption and desorption to and from the Oxford Clay with no HOC present, in order to gain an understanding of the behaviour of DOC sorption.
- (3) To quantify the amount of toluene sorption and desorption to and from the Oxford Clay both without DOC being present in the aqueous phase and with different types of DOC (using the DOC free leachate as a control). This will allow the determination of the effect of DOC on the sorption and desorption behaviour of toluene.
- (4) To quantify the amount of naphthalene sorption and desorption to and from the Oxford Clay both with and without DOC being present in the aqueous phase (using different types of DOC). Again this will use DOC free leachate as a control against which the effect of DOC on the sorption and desorption behaviour of naphthalene can be determined.

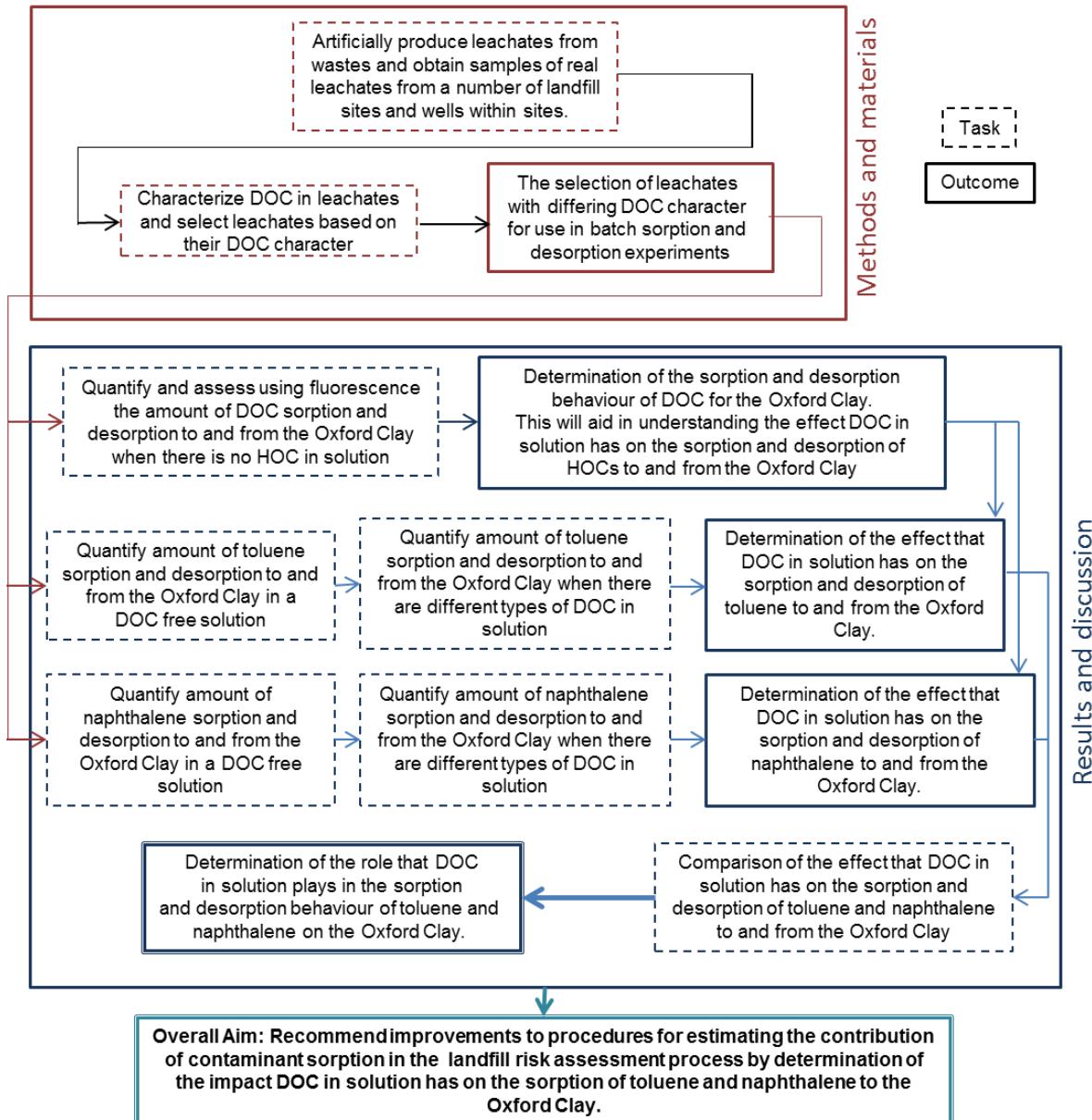


Figure 11: Overview of chapter 3, 4, 5 and 6 experimental tasks and outcomes. A dashed border denotes a task and a solid border denotes an outcome.

3.1 Solid Phase Selection

The Oxford Clay outcrops in the south of England and is used as a liner material. It was used alongside the Kimmeridge Clay and the Mercia Mudstone as a solid phase by the Environment Agency (2009) for the determination of sorption of contaminants to liner materials. Of these three solid phases Oxford Clay was selected for study as its high OC content means that the sorption behaviour of HOCs to the clay will be likely to be dominated by the OC rather than the mineral portion of the clay (Karickhoff *et al*, 1979).

The Oxford clay has also been shown to be capable of attenuating leachate components, such as ionic sodium and potassium (Batchelder *et al*, 1998) and organic contaminants (Stringfellow *et al*, 2011; Environment Agency, 2009). As HOC sorption is dominated by hydrophobic interactions (Piwoni and Banerjee, 1989) the high organic content of the clay will result in a more hydrophobic phase for the HOC to sorb to. As landfill leachates have a large range of DOC concentration (Section 2.1.3) a clay with high OC content will also facilitate HOC partitioning between the hydrophobic DOC in solution and the solid phase (Section 2.2.5.1).

3.2 Contaminant Selection

As with the composition of the DOC in leachate solutions, the contaminant composition in landfill leachates is also complex and highly variable. HOCs are a group of contaminants commonly found in UK leachates which are harmful to the environment and their release into the environment is controlled. Polycyclic aromatic hydrocarbons (PAHs) were selected for study as their structure is relatively simple, consisting of only benzene rings conjoined in different combinations. As PAHs increase in size more benzene rings are added to the structure. The building block for PAHs, and therefore the smallest unit of the sequence, is the single ringed benzene. Benzene is a BTEX compound, which are recognised as environmentally important contaminants in leachate systems (Environment Agency 2009). Due to the toxicity, volatility and carcinogenic potential of benzene, however, the decision was made that an alternative compound would be preferable for study. Therefore toluene was selected as an alternative compound as it is structurally similar to benzene, with only a hydrogen substituted for a methyl group, and it is present in the majority of leachates in the UK. Naphthalene is the smallest PAH, containing only two benzene rings, and is also present in most UK landfill leachates. Naphthalene was therefore chosen as the second contaminant for study. Toluene and naphthalene were also used by the Environment Agency (2009) and so were obvious candidates for use in this work. Before the complexity of this research problem was fully determined, phenanthrene was also identified as a suitable third contaminant since it contains three benzene rings. These three contaminants in sequence were intended to determine the contribution of contaminant hydrophobicity to the effect of leachate DOC on contaminant sorption and desorption. This could be followed by the

extrapolation of any trends up to larger PAHs, such as tetracene and pentacene and ring-form PAHs such as corannulene or ovalene. However, as the complexity of the experimental leachate system became clear it was decided to focus only on toluene and naphthalene.

3.3 Interface Modelling and Experimental Method Selection

In an actual landfill we model sorption at the clay-leachate interface as sorption to a single surface (Figure 12). If the whole landfill was being considered then contaminant diffusion toward the clay would be used to model the movement of contaminants to the interface. However, since sorption to the liner material only occurs directly at the liner-leachate interface, the transport of contaminants in solution should be considered over a smaller scale. As shown in Figure 12, initially the system starts with all contaminants residing in the leachate (A). As compounds sorb to the clay, the concentration of contaminants near the surface reduces (B). This sets up a concentration gradient in the leachate solution which causes more contaminant to diffuse toward the solid phase (C) and so move toward the interface (mass transport). Mass transport assumes that this concentration change is only occurring in a small part of the system near its boundaries, the solid-liquid phase interface, (Cussler, 2009). The amount of sorption to the interface and the contaminant concentration in the bulk leachate solution will determine the rate of mass transport.

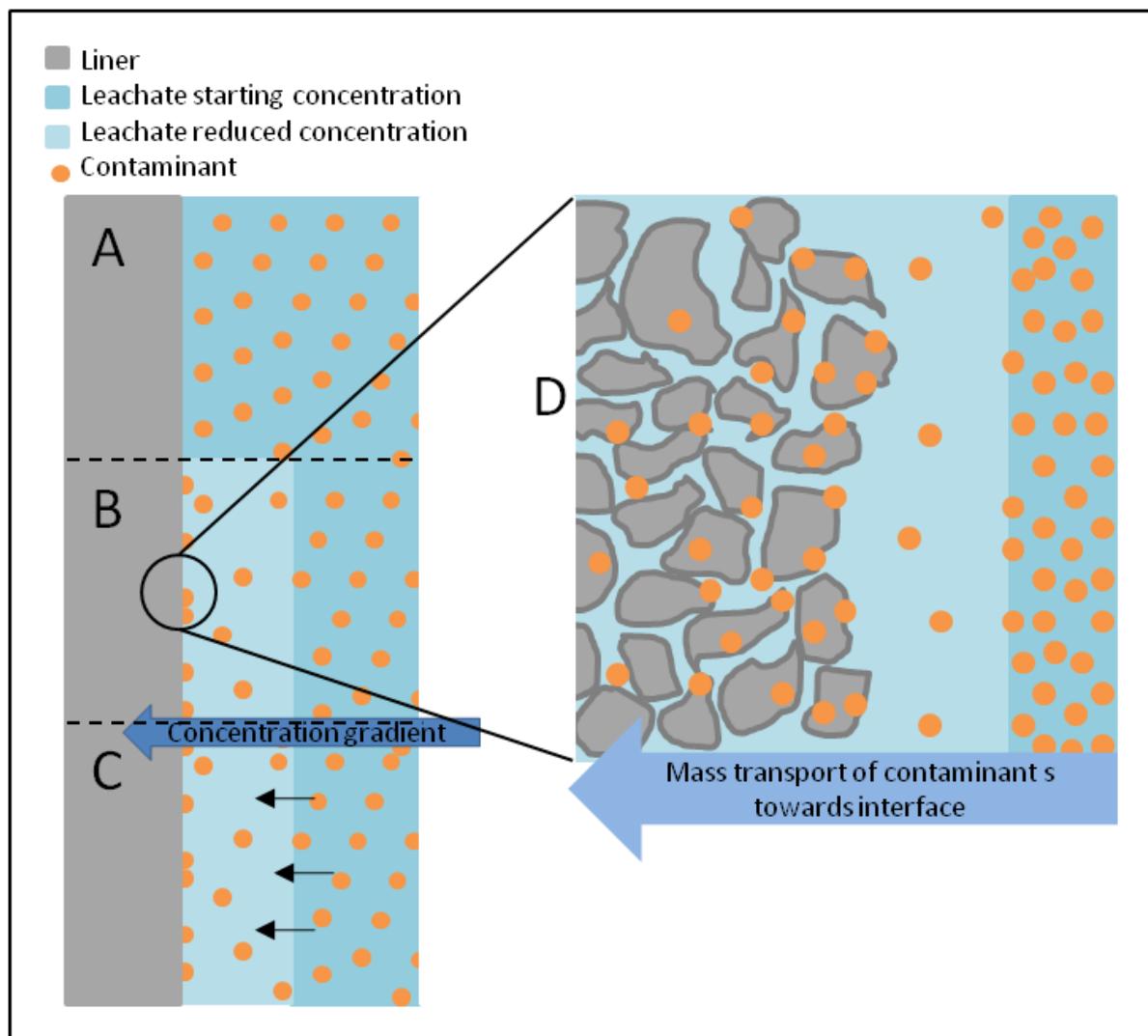


Figure 12: Mass transport at the interface and expanded view demonstrating the particulate nature of clay materials

However, in reality the surface of the liner is not a single ‘sheet’ containing sorption sites. It is a mass of compacted particles with interstitial sites into which the leachate can penetrate (D). Each of these particles contains clay minerals and organic compounds which provide sorption sites for both DOC and HOCs. In the case of the Oxford Clay these clay minerals are smectite, illite, kaolinite and chlorite, 32%, 15%, 9% and 0.5% respectively, and are present alongside 5.49% OC by mass (Environment Agency, 2009). Due to the high organic carbon content of the Oxford Clay, the contribution of the mineral component to sorption behaviour can be ignored (Karickhoff *et al*, 1979; Karickhoff, 1981) meaning that the solid phase OC is the primary site for the sorption of aqueous phase HOCs and DOC to the liner material.

A column test is an experimental way to observe sorption at this interface. In column testing an aqueous phase is passed through a core of the solid phase material under pressure and the difference between the original aqueous contaminant concentration and the post-sorption concentration is measured. Thus the amount of sorption per unit volume of clay can be calculated by mass balance (MacIntyre *et al*, 1992). However, the surface of the column test (representing the clay-leachate interface in a landfill) is unlikely to exactly mirror that of a landfill liner material which has been excavated and compacted during insertion into a landfill cell. There are two options for sample preparation for column tests, either using an intact core of sediment taken directly from an in-situ sediment bed or liner, or homogenisation and compaction of the sampled sediment. Of the two methods homogenisation is preferable to coring as it reduces variability in the solid between samples by eliminating preferential flow pathways through the column which may form due to cracking of the sediment when taking the core and around the edge of the core where it meets the column. Sample storage may also be an issue with column testing as the in-situ moisture content of the sediment should be maintained. The flow of leachate through the column also requires the system to be pressurised and a flow rate maintained. However, the low hydraulic conductivity of clays make them less suited to testing via column methods due to the potentially long breakthrough times for liquids passing through the sediment.

Batch testing eliminates variation in the solid phase of repeated samples due to differences in core structure or column packing and sediment compaction. Batch testing uses a ground homogenised air dried clay sample which is weighed into sorption bottles. The sediment is then agitated with the aqueous phase and the difference in the concentration before and after the contact stage is measured and mass balance used to determine sorption to the solid phase. While batch testing does not model the true interface between the clay and the leachate as well as column tests do (since the ground clay exposes a greater surface area of clay to the fresh leachate than a packed column core) it does allow higher throughput of samples with very little variation in the contact between the solid and aqueous phase. Batch testing will also allow the sorption conditions to be reproduced over multiple test repeats. Batch testing is also recommended by the Environment Agency (2000a and 2000b) for the examination of sorption of contaminants to wastes and the quantification of contaminant desorption from wastes producing leachates; as well as being widely used in the literature including

Environment Agency (2009) from which this work follows. Therefore batch testing was selected for this study as it offers a greater throughput of tests, better reproducibility and direct comparison with a key literature influence on this work.

3.4 DOC Characterisation Techniques

Fluorescence spectroscopy was selected for the determination of DOC character in leachates as it is fast, relatively cheap and non-destructive. Alternative methods of determining DOC compounds in leachates include GCMS, GC, LCMS, LC, size fractionation, IR and NMR. All of these techniques are either destructive or expensive in nature. The highly complex nature of DOC in leachates (especially humic substances) also means that IR or NMR spectra are difficult and time consuming to resolve. For example, although FTIR was found to be a useful technique for monitoring the treatment of leachates (Smidt and Meissl, 2007), it could not be used to identify individual compounds in solution. While fluorescence spectroscopy also cannot be used to identify the individual compounds in the leachate mixture, fluorescence EEM results can be used to quickly produce a clear visual representation of the overall structural types of DOC in solution.

While GCMS has been utilised for the characterisation of volatile acids and amines in leachates (Harmsen, 1983) organic compounds such as HSL and PL DOC tend to be non-volatile. This makes the measurement of DOC compounds (e.g. amino acids) by GC/GCMS more challenging. For example, the DOC compounds may need to be derivatised before analysis and then measured against an internal standard. While pre-bought kits do exist for derivatisation, they are expensive and the process is time consuming, for example, the Phenomenex Easy Faast kit (Phenomenex.com, 2015). LC techniques may overcome the requirements for compound derivatisation, however, the highly complex mixture of DOC present in leachates would require a large amount of method development in order to achieve adequate compound separation. This is because both LC and GC methods require some advance knowledge of the compounds present in the DOC and an internal standard for each compound in order to quantitatively determine the amount of each DOC compound in solution.

Size fractionation of DOC compounds could be achieved by ultrafiltration, where solutions can be separated into fractions based on their molecular size, as detailed by Cheryan (1998). This would, however, only allow a range of sizes to be extracted and then the percentage of the DOC falling into that size fraction to be measured. Whilst this separates out compounds based on ranges of molecular size, it does not provide any further information on the exact composition of the DOC. Size fractionation could be used in parallel with another technique (e.g. LCMS) however, compound identification would still prove challenging since the initial composition of leachates remains unknown. Fluorescence spectroscopy excitation emission matrices (EEM) were therefore selected for the characterisation of DOC compounds, since although it only identifies groups of compounds it has been widely used in the literature for waste water characterisation, including use on landfill leachate. In addition to this it is cost effective, non-destructive, fast and outputs an easily compared visual representation of the results. Selection of the EEM method rather than synchronous scan method, and its implementation are detailed in Sections 2.3.1 and 4.3.1.

The concentration of the target contaminants toluene and naphthalene in solution was determined using GCMS. Whilst both contaminants are detectable by spectrophotometry, the complex DOC nature of the leachates would interfere with their detection and identification, since other leachate components are excited or emit at similar wavelengths (Baker and Curry, 2004; Yunus *et al*, 2008; PhotochemCAD). Liquid chromatography methods were also deemed not suitable for the detection of toluene and naphthalene in leachates due to the complex mixture of compounds in leachate solutions. This would produce a large number of eluting peaks, complex spectra and could limit the life of the column. As toluene and naphthalene are hydrophobic organic contaminants, and can be volatilised from an aqueous solution, headspace GCMS analysis provided a straightforward method to directly measure contaminant concentration whilst generating relatively clean spectra, since non-volatile DOC compounds do not get introduced to the column.

3.5 MSW Leachate Selection

The DOC character of a number of leachates was determined and is discussed in Section 4.2.5. Characterisation was based on DOC concentration and the fluorescence peak ratios of the DOC which corresponded to different types of OC in solution (Section 4.3.1.3). This allowed the selection of leachates for experimental work which contained a range of differing OC character. Having leachates with a range of OC character in the experimental work enabled an overview of how the different structural types of carbon in solution affected the sorption and desorption behaviour of the HOCs toluene and naphthalene to and from Oxford Clay. From the real leachates studied in Section 4.2.5.1 the MSW leachate was chosen because:

- 1) It was the only leachate obtained which contained all of the different types of DOC. This enabled an overview of DOC sorption and desorption behaviour whilst highlighting any preferential sorption of different OC compound types. This was important because if HOCs partition onto DOC then the preferential sorption of particular DOC types could result in alteration of HOC sorption and desorption behaviour depending on the type of DOC to which they are bound. For example, if HOCs partition into HSL DOC and HSL DOC is preferentially sorbed to the Oxford Clay then an increase in HOC sorption would also be expected due to co-sorption of the HOC along with the DOC.
- 2) The effect of dilution of leachates on the OC character could be assessed due to the MSW leachate having the highest OC concentration of all the leachates. Therefore it could be used at a greater range of dilutions when examining DOC sorption to the Oxford Clay in the absence of toluene and naphthalene.

3.6 The Complexity of the Leachate System

Leachates are a highly complex aqueous system containing numerous different compounds and varying widely both between landfill sites and within the same landfill cell, Sections 2.1.3 and 4.2.5.1. Compounds present in leachates include DOC, ionic components, heavy metals, organic and inorganic contaminants, all of which have the potential to interact with the DOC, HOCs and solid phase being studied in this work.

This interaction will vary depending on the pH, EC, DOC and chemical compositions of the leachates. These interactions are partially described in Section 2.2.2, however, the interactions between them are so complex and varied that their full elucidation, and the examination of these interactions under every possible solution condition and combination, is impossible to determine. This issue is further compounded by the variation between leachates from different sites.

3.7 Experimental Rationale

Table 9 summarises the sorption and desorption batch testing experiments undertaken in this work. The sorbent used was exclusively Oxford Clay (Section 4.2.1). Three different sorbates were used; MSW leachate DOC (Section 4.2.5.2) and the two contaminants of interest, toluene and naphthalene (Sections 3.2 and 4.2.2). The solutions in which sorption and desorption were measured were the leachates detailed in Section 4.2.3. In each case the desorption solution was the same as the sorption solution but omitted the sorbate being examined. All desorption solutions were agitated with the same mass to volume ratio of Oxford Clay as in the sorption experimental step in order to eliminate third phase (solids) effects (Huang *et al*, 1998). A brief description of the DOC character in solution and the rationale behind its inclusion into experimental work is included.

The sorption and desorption behaviour of leachate DOC to Oxford Clay was examined in an effort to identify possible sorption mechanisms by monitoring the amount of sorption taking place and the type of DOC being sorbed. This was achieved using the change in both the DOC concentration and the fluorescence spectra of the aqueous phase. This will give information about the types and quantities of DOC that sorb to the solid phase. If one type (e.g. PL or HSL, Section 2.1.5) is preferentially sorbed to the Oxford Clay and HOCs sorb to the DOC, the type of DOC present in the solution may directly affect the amount of HOC sorbed to the solid phase by processes such as competition, steric inhibition, co-sorption and cumulative sorption. MSW leachate at a range of concentrations was selected as the aqueous phase for this experiment as it was shown to display a high DOC concentration (the highest of the eight leachates that were used in experimental work) and contained all of the DOC types (HSL and PL) that were present

in the eight leachates (Section 4.2.5). Therefore the level of partitioning of each type of DOC at a range of aqueous concentrations can be ascertained.

| Sorbent (Solid phase) | Sorbate (Contaminant) | Solution (Aqueous phase) | Rationale/DOC representation |
|--------------------------|---------------------------------------|-----------------------------|--|
| Oxford Clay | DOC from MSW leachate (1.8-2268 mg/L) | DOC free synthetic leachate | Information on the sorption and desorption of all DOC compounds present in landfill leachates at a range of concentrations in the absence of the target contaminants toluene and naphthalene. With the aim of clarifying DOC sorption and desorption behaviour at differing concentration in solution. |
| Oxford Clay | Toluene | DOC free synthetic leachate | Providing a background level for the sorption of the contaminant to Oxford Clay in the absence of DOC to which sorption in the presence of DOC can be compared. |
| | | MSW leachate | Leachate DOC from a young, unstabilised waste, representing a 'natural' leachate DOC composition. |
| | | AMSW leachate | Waste derived DOC from an aged, stabilised (mature) waste representing leachate from an older, leached and stabilised landfill. |
| | | MBT leachate | Waste derived DOC from an artificially stabilised (pre-treated) waste. |
| | | HA leachate | Entirely humic like DOC representing a possible synthetic surrogate for a leachate from a stabilised landfill where the OC is well degraded. |
| | | Diluted MSW leachate | MSW leachate at comparable concentration to AMSW and diluted HA leachates. Allowing comparison between sorption and desorption in different types of solution DOC independent of concentration and between the same type of DOC at differing concentrations |
| | | Diluted HA leachate | Diluted HA leachate at comparable concentration to AMSW, diluted MSW and diluted MBT leachates. Allowing comparison between sorption and desorption in different types of solution DOC independent of concentration and between the same type of DOC at differing concentrations |
| Oxford Clay | Naphthalene | DOC free synthetic leachate | Providing a background level for the sorption of the contaminant to Oxford Clay in the absence of DOC to which sorption in the presence of DOC can be compared. |
| | | MSW leachate | Leachate DOC from a young, unstabilised |

| | | | |
|--|----------------------|--|--|
| | | | waste, representing a 'natural' leachate DOC composition. |
| | AMSW Leachate | | Waste derived DOC from an aged, stabilised (mature) waste representing leachate from an older, leached and stabilised landfill. |
| | MBT leachate | | Waste derived DOC from an artificially stabilised (pre-treated) waste. |
| | HA leachate | | Entirely humic like DOC representing a possible synthetic surrogate for a leachate from a stabilised landfill where the OC is well degraded. |
| | Diluted MSW leachate | | MSW leachate at comparable concentration to AMSW, diluted HA and diluted MBT leachates. Allowing comparison between sorption and desorption in different types of solution DOC independent of concentration and between the same type of DOC at differing concentrations |
| | Diluted HA leachate | | Diluted HA leachate at comparable concentration to AMSW, diluted MSW and diluted MBT leachates. Allowing comparison between sorption and desorption in different types of solution DOC independent of concentration and between the same type of DOC at differing concentrations |
| | Diluted MBT leachate | | MSW leachate at comparable concentration to AMSW, diluted MSW and diluted HA leachates. Allowing comparison between sorption and desorption in different types of solution DOC independent of concentration and between the same type of DOC at differing concentrations |

Table 9: Overview of the sorption and desorption batch testing experiments undertaken in this work.

Elucidation of the sorption and desorption behaviour of DOC for Oxford Clay will allow an increased understanding of how the DOC will impact on toluene and naphthalene sorption and desorption. This may be achieved by comparing the observed sorption and desorption behaviours of DOC, such as any preferential sorption of particular types of DOC, in the different leachates used in the contaminant sorption and desorption batch tests. These observations can then be considered alongside the toluene and naphthalene sorption and desorption behavioural trends in the different leachates in order to determine the probable impact of DOC on HOC sorption behaviour. For example, if an increase in HOC sorption is observed in a leachate containing only HSL DOC, and DOC sorption tests indicate that predominantly HSL DOC is sorbed to the clay, it is reasonable to conclude that the HOCs are co-sorbing with the DOC to the clay or undergoing cumulative sorption as discussed in Section 2.2.6.2. Similarly, this principle could be used to explain why HOC sorption in a high DOC strength, but low DOC maturity, leachate may differ to HOC sorption in a low DOC strength high DOC maturity leachate. Therefore, the results of DOC sorption and desorption behaviour will allow possible mechanisms to be suggested for alterations in HOC sorption and desorption behaviour due to the presence of DOC in solution, such as those outlined in Section 2.2.6.2.

Sorption and desorption isotherms for toluene and naphthalene to Oxford Clay were initially established in a DOC free leachate. This allowed determination of a baseline level of toluene sorption and desorption for the Oxford Clay without any influence of DOC in solution. This can be used as a standard against which the sorption and desorption of toluene to and from the Oxford Clay in leachates containing DOC can be compared. The toluene and naphthalene sorption and desorption isotherms were then examined using four leachates which displayed a variety of DOC character. This allowed both a comparison between the DOC free leachate baseline and leachates with a range of DOC character and the results of toluene with those of naphthalene. The four leachates used were MSW, AMSW, MBT and HA which comprised:

- A mixed DOC (MSW) leachate.
- Predominantly HSL DOC leachates
 - Aged waste derived (AMSW)
 - Stabilised waste derived (MBT)

- Fully synthetic (HA)

From fluorescence spectroscopy analysis the MSW leachate DOC contained all the different types of DOC that were observed in leachates and was sourced from a real landfill. The AMSW, MBT and HA leachates all had predominantly HSL DOC character, however, they had differing origins, Section 4.2.3:

- The AMSW DOC originated from aged MSW waste from the landfill which produced the MSW leachate.
- The MBT leachate DOC originated from an artificially stabilised MSW waste.
- The HA leachate DOC originated from a commercially available ‘synthetic’ laboratory chemical supplier.

Differences between sorption and desorption behaviour of the contaminants in the leachates containing and omitting DOC may indicate how different types of DOC in leachates, with differing origins, affect toluene and naphthalene sorption and desorption to Oxford Clay.

In an effort to eliminate the effects of concentration on the sorption and desorption behaviour, the MSW and HA leachates were diluted to a concentration analogous to that of the AMSW leachate. These experiments allowed a direct comparison between toluene and naphthalene sorption and desorption behaviour in a mixed DOC (MSW leachate) and predominantly HSL DOC leachates, both derived from an aged waste (AMSW) and fully synthetic source (HA), independent of concentration effects. For naphthalene, in addition to MSW and HA leachates, the MBT leachate was also diluted to a concentration analogous to that of the AMSW leachate in order to facilitate further comparison. The additional diluted leachate (MBT) was added in order to allow a better comparison between naphthalene sorption and desorption behaviour in leachates of analogous concentration and differing DOC character. This is important because the dependency of toluene and naphthalene sorption and desorption behaviour on leachate DOC concentration and character will determine how predictable variation in the sorption parameters are for the purpose of landfill modelling and risk assessment. If the sorption and desorption behaviour of toluene and naphthalene varies with DOC concentration

alone, the effect of DOC in solution on toluene and naphthalene sorption and desorption will be more easily predictable for landfill modelling and risk assessment purposes as it is dependent on a single parameter. If, however, the sorption and desorption behaviour varies with DOC character (either independently or alongside DOC concentration) then the effect of DOC on the system becomes more complex and harder to predict, due to the highly variable nature of DOC in landfill leachates.

Should the sorption and desorption of toluene and naphthalene be dependent on the character of the DOC in solution then implications for determination of sorption coefficients for landfill risk assessment include:

- Re-evaluation of the use of literature values for K_d to determine sorption coefficients.
- Re-examining the relevance of using values of K_d obtained in laboratory testing using surrogate leachates to determine the sorption coefficient.
- Consideration of variation in the sorption coefficient of contaminants due to changes in leachate DOC character as the landfill stabilises.

The isotherm results for both toluene and naphthalene sorption and desorption behaviour for Oxford Clay in DOC free and DOC containing leachates were compared in order to provide an indication of the effect of contaminant hydrophobicity on sorption behaviour in different aqueous DOC environments. Differences in contaminant hydrophobicity may impact on contaminant interaction with the DOC in solution. It is expected that if the contaminants are sorbing to the DOC then an increase in contaminant hydrophobicity would result in increased sorption of the contaminant to the DOC and, therefore, either increased co-sorption with the DOC to the solid phase if the DOC sorbs to the clay or reduced sorption to the solid phase if the DOC remains in solution. However, if the contaminants are not sorbing to the DOC, then the more hydrophobic HOCs may not be able to remain in solution to the extent that a less hydrophobic compound could. Therefore a more hydrophobic contaminant would exhibit greater sorption to the solid phase. The effect of hydrophobicity of the contaminant on the sorption behaviour of contaminants in DOC containing leachates may, therefore, allow further elucidation of the mechanism by which the DOC in solution affects the sorption behaviour of contaminants. This may give an indication of how DOC dependant sorption behaviour

varies with contaminant hydrophobicity. This is important due to the wide range of different contaminants which may be present in landfill leachate and the need to identify trends within contaminant groups rather than individual compounds since the final leachate composition in a landfill is almost impossible to accurately predict. This work covers small HOCs with a narrow range of hydrophobicities ($\log K_{ow}$ 2.54-2.69 and 3.17-3.36, MW 92.14 g/mol and 128.17 g/mol for toluene and naphthalene respectively, Section 2.1.7. Should the results show significant variations in sorption behaviour within this range, then the impact of contaminant hydrophobicity on the prediction and modelling of sorption in landfill leachate environments with a range of DOC character is likely to be very significant. This could result in alteration in the ways that sorption coefficients are selected for landfill risk assessment modelling, with a more experimental approach required. It could also impact on the management strategies and monitoring timescales for landfills with differing contaminant profiles, with the level of sorption occurring being dependant on not only the contaminant partitioning properties, but on the DOC characters of the leachates.

Based on the alteration in sorption and desorption behaviour of toluene and naphthalene, due to the presence of DOC in solution, the variation in K_d values and the effect of using sorption and desorption coefficients obtained in different leachates on the prediction of contaminant sorption and desorption to and from the Oxford Clay when using landfill risk assessment tools such as LandSim is discussed. Recommendations could then be made for the best approach in selecting a sorption or desorption coefficient value in order to ensure environmental protection. Additionally recommendations for more accurately prediction of the extent of contaminant sorption and desorption to and from Oxford Clay in the event of direct leachate contact with a compacted clay liner could be made, for example in the event of a synthetic liner failure or in an older landfill (Bagchi, 2004).

4. Methods and Materials

Batch sorption and desorption tests were used to determine the role of leachate DOC in the sorption of the HOCs toluene and naphthalene to Oxford Clay, Section 2.1.7, 3.2 and 4.2.2.

Initially the sorption and desorption behaviour of leachate DOC to the Oxford Clay was established using a MSW leachate diluted to a range of DOC concentrations whilst maintaining the electrical conductivity of the leachate solutions. The sorption of different types of DOC (Section 2.1.5) to the clay was monitored using DOC concentration and fluorescence spectroscopy. The sorption and desorption behaviour of toluene and naphthalene to Oxford Clay in a DOC free leachate solution was established as a baseline, Section 5.2 and 5.3. Leachates with differing DOC character were then used as the aqueous phase in sorption tests to identify the effect of DOC character on the sorption and desorption behaviour of toluene and naphthalene to the Oxford Clay, Section 5.2 and 5.3. Leachate characteristics including DOC character were determined via fluorescence spectroscopy, DOC concentration, UV spectroscopy, pH and EC measurements.

4.1 Batch Testing

4.1.1 Introduction

This study employs batch testing as a means of determining the sorption and desorption behaviour of contaminants to Oxford Clay. Batch testing also allows the use of a milled solid phase which ensures complete saturation and homogenisation of the clay material. This offers the maximum solid phase surface area for sorption processes to take place as well as simplifying the preparation of the solid phase as reconstitution, which would be required in column testing, is not necessary. Batch testing is also recommended by the Environment Agency (2000b) and was used in preference to column testing for generating K_d data due to its simplicity and potential for generating a large amount of data. K_d values from batch testing can then be inputted into landfill modelling programs such as LandSim (Section 2.1.8) (Environment Agency, 2000). Batch testing is usually performed using synthetic or surrogate leachates that broadly reflect the anticipated chemical character of leachates (Environment Agency, 2003a; 2009; 2000b). However, it is recognised that synthetic leachates may not interact with contaminants in the same way as real leachates, so testing with real leachates would be beneficial (Environment Agency, 2009). While batch testing is recommended over column testing (Environment Agency 2000b) realistically the way in which the leachate and contaminant contact the clay in batch testing is not analogous to a real landfill liner-leachate interface. This is largely due to the surface area of the clay particles presented to the sorbate. In a real landfill situation, the clay liner is compacted, presenting a solid surface to the leachate (as in column testing). However, in batch testing the clay is finely divided and forms a mull which is suspended in solution by agitation of the reaction vessel. As identified in Section 3.3, however, the liner-leachate interface for CCLs is not, in reality a completely solid surface, but consists of compacted clay particles. Due to the low hydraulic conductivity of clays it is reasonable to assume that the penetration of leachates into the liner is limited and so that sorption occurs only in a saturated surface layer. Therefore, the fully saturated clay-leachate system in batch testing could be taken to represent this surface layer of the clay liner. This, however, is a limitation of batch testing method when considering the sorption behaviour in the liner over a larger scale, for example, over

the entire liner depth.

Batch testing, as described by Lobenstein (1962) and the Environment Agency (2000 and 2009) is a technique which allows a solid-phase and contaminant containing aqueous phase to reach sorption equilibrium. Sorption equilibrium is defined by the US Environmental Protection Agency (EPA) as a rate of change in the solution concentration of less than 5% over 24 hours or 10% over six hours (Oman and Spannar, 1999). The sorption process for toluene and naphthalene was found by Environment Agency (2009) to be biphasic, with an initial fast sorption stage lasting 24-48 hours followed by a slower ‘non equilibrium’ sorption stage characterised by slower sorption of the contaminant towards equilibrium. While the time taken to reach a true equilibrium state may be months or years (Environment Agency, 2009) sorption equilibrium was achieved after seven days for both toluene and naphthalene (Environment Agency, 2009). Despite significant sorption of toluene and naphthalene being achieved in the first 24-48 hours (Environment Agency, 2009), this study uses a contact time of seven days (168 hours). This contact time is to allow the sorption equilibrium of both toluene and naphthalene to be reached and was used by Environment Agency (2009) to achieve 50-65% sorption of contaminant to the clay liner material (Oxford Clay). Optimising the sorption to 50-60% of the total contaminant concentration reduces errors in the measurement of the sorption.

Third phase effects occur when a portion of the sediment, in this case clay, is suspended into solution (Huang *et al*, 1998; Weber *et al*, 1998). Larger particulates are removed from suspension by the centrifugation process which separates the clay from the supernatant phase in batch testing. However, some colloidal material may remain in solution constituting a third phase. Therefore, in order to replace HOC the contaminated leachate solution ‘like for like’ with a non-contaminated solution during the desorption step, it is important that the fresh leachate also contains this third phase. This was achieved by agitating the contaminant free leachates with the same mass to volume ratio of clay as in the sorptionbatch tests before exchanging the leachates for the desorption step. Figure 13 provides an overview of the sorption and desorption batch testing processes used in this work.

Sorption

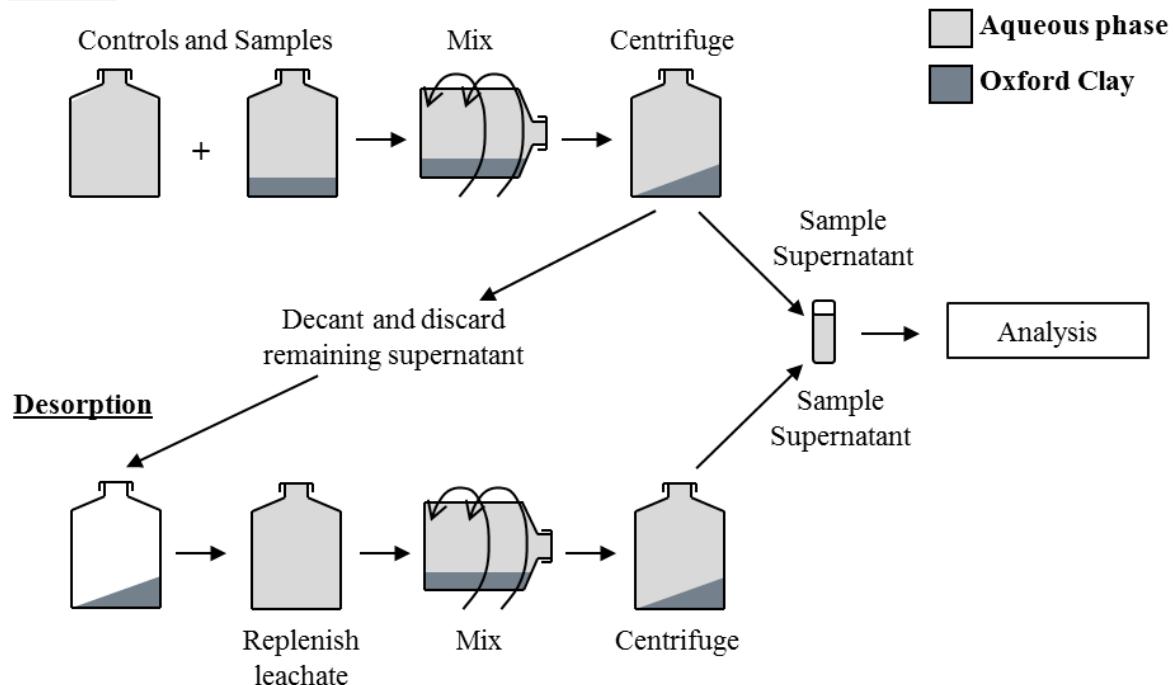


Figure 13: A graphical representation of the batch testing process used in this work for sorption and desorption.

4.1.2 DOC Sorption and Desorption

4.1.2.1 Sorption

To assess the sorption of DOC to Oxford Clay tests were performed with MSW leachate at a range of dilutions. The MSW leachate was selected as it contained both PL and HSL DOC compounds (from the presence of fluorescence peaks B, D, E and F). It also had the highest DOC concentration, therefore allowing a wider range of concentrations to be examined. The EC of the diluted leachate was adjusted to that of the original leachate value using the salt mixture for the DOC free synthetic leachate in order to prevent changes to the DOC character due to a change in ionic strength (Oman and Spannar, 1999). Sorption and desorption of the DOC was monitored by both DOC concentration and fluorescence ratios, Sections 4.3.4 and 4.3.1.3. Leachate dilutions used ranged from 1:1 to 1:1000. Clay (0.16 g/mL) was added to pre-weighed acid washed bottles of average internal volume 120 mL. Samples of each leachate dilution were prepared in duplicate. The bottles were partially filled with leachate, loosely capped and left to stand for two hours in an anaerobic cabinet (5% carbon dioxide, 5% hydrogen

and 90% nitrogen) allowing the clay to saturate with leachate to eliminate air bubbles trapped within the clay. This was particularly crucial in the case of the DOC sorption and desorption tests where a large mass of clay (40 g) was used due to the high DOC concentration in solution, in order to ensure that more than 20% of the DOC in the MSW leachate with the highest DOC concentration (2268 mg/L) was achieved (Delle Site, 2001). The bottles were then filled with leachate and sealed using pre-weighed PTFE septa and aluminium seals taking care to keep the headspace to a minimum. Two control bottles per DOC concentration, each containing no clay, were used to assess the extent of sorption to the bottle, septa and cap. One of these control bottles was sacrificially sampled immediately after starting the experiment in order to give an accurate reading of the initial DOC concentration within the bottle. The samples were agitated on a roller mixer stirrer for seven days at 20°C and then centrifuged at 1200 rpm for 40 minutes to separate the leachate from the clay. Duplicate samples (10 mL) were taken from the supernatant for DOC and fluorescence analysis, Section 4.3.1.1. Comparison of initial to final DOC concentration gave the amount of DOC sorbed by the clay liner material, which was then corrected for sorption to the bottle (mass balance method) detailed in Section 4.4.3.1. No biological inhibitors were used due to the recalcitrance of leachate DOC over a 7 day timescale (Simoes, 2005).

4.1.2.2 Desorption

After sampling for sorption testing the supernatant was decanted, retaining the clay, in preparation for desorption testing. The bottles containing the wet clay were weighed and refilled with DOC free leachate (with the same EC as the leachates used in the sorption step, pH was not controlled). The leachate used for desorption was pre-rolled with the same mass:volume ratio of clay as used in the sorption step in order to eliminate third phase affects (Huang *et al*, 1998). The bottles were then resealed using the original septa and new pre-weighed aluminium caps. The samples were agitated on a roller mixer stirrer for seven further days at 20°C. The bottles were then centrifuged at 1200 rpm for 40 minutes to separate the supernatant leachate from the clay. Samples (10 mL) were again taken in duplicate from the supernatant for DOC and fluorescence analysis.

4.1.3 Contaminant Sorption and Desorption Tests

4.1.3.1 Sorption

Mass:volume (m:v) ratios of 0.013 g/mL for toluene and 0.0004 g/mL for naphthalene were chosen. Different amounts of clay for each contaminant were chosen in order to optimise the observed sorption of the contaminant to the clay. This allowed for better assessment of sorption behaviour since these m:v ratios have been previously shown to achieve 50-60% sorption of the contaminants (Environment Agency, 2009). This was well within the ideal range of 20-80% sorption advised by Dell Site (2001) outside of which measurement errors become dominant. Clay (0.013 g/mL for toluene and 0.0004 g/mL for naphthalene) was added to pre-weighed acid washed bottles of average internal volume 120 mL. The bottles under test were partially filled with leachate, loosely capped and left to stand for two hours in the anaerobic cabinet allowing the clay to saturate with leachate in order to eliminate air bubbles trapped within the clay. This was particularly crucial in the case of toluene sorption tests where bottles may contain a mass of clay in excess of 1g. The bottles were then capped and moved to a fume cupboard where they were spiked with contaminant, filled with leachate and sealed using pre-weighed PTFE septa and aluminium seals whilst taking care to keep the headspace to a minimum. Each contaminant spiked sample was prepared in duplicate. As with the DOC sorption tests, two control bottles per spike concentration containing no clay were used to assess the extent of sorption to the bottle, septa and cap. One of these control bottles was sacrificially sampled immediately after spiking in order to give an accurate reading of the initial contaminant concentration within the bottle. The samples were then agitated on a roller mixer stirrer for seven days at 20°C and then centrifuged at 1200 rpm for 40 minutes to separate the leachate from the clay. Duplicate samples (10 mL) were taken from the supernatant for GCMS analysis (Figure 13). Comparison of initial contaminant concentration to the final concentration gave the amount of contaminant sorbed by the clay liner material, which was then corrected for contaminant sorbed by the bottle (mass balance method). This is detailed in Section 4.4.3.1.

4.1.3.2 Desorption

After sampling for sorption testing the supernatant was decanted, retaining the clay in preparation for desorption testing. The bottles containing the wet clay were weighed and refilled with contaminant free leachate (the same as used in the sorption step) which had been pre-rolled with the same m:v ratio of clay as in the sorption step in order to eliminate third phase affects (Huang *et al*, 1998). The bottles were then resealed using the original septa and new pre-weighed aluminium caps. The samples were agitated on a roller mixer stirrer for seven further days at 20°C. The bottles were then centrifuged at 1200 rpm for 40 minutes to separate the supernatant leachate from the clay. Samples (10 mL) were again taken in duplicate from the supernatant for GCMS analysis, Section 4.3.6. Contaminant spikes and leachates used in sorption and desorption testing are detailed in Sections 4.2.2 and 4.2.3.

4.2 Materials

4.2.1 The Oxford Clay

The clay used in this work was a sample of the Peterborough member of the Oxford Clay which outcrops in central and southern England (Bright *et al*, 2000). This unweathered clay is used throughout the UK to form a landfill liner with hydraulic conductivity $<1 \times 10^{-9}$ m/s (Batchelder *et al*, 1998). The clay was collected from a waste disposal site in Bletchley, UK (Environment Agency, 2009). The clay sample had previously been air dried and ground into 3 mm granules using a soil grinder and was determined to have an OC content of 5.49% (Environment Agency, 2009). The clay is described in detail by Environment Agency (2009) and was found to have a residual moisture content, after air-drying, of 4.35%. Table 10 shows the characteristics of the Oxford Clay (Environment Agency, 2009).

| Parameter | Oxford Clay |
|---|-------------------|
| Total Carbon (%) | 7.22 ^a |
| Organic Carbon (%) ^b | 5.49 |
| Cation Exchange Capacity (meq/100 g) | 30.63 |
| Specific Surface Area (m ² /g) | 55.5 / 50.2 |
| Total Fe ₂ O ₃ | 4.5 |
| Extractable Fe | 1.4 |
| Clay Minerals (%) | |
| -Smectite | 32 |
| -Illite | 15 |
| -Kaolinite | 9 |
| -Chlorite | 0.5 |
| Major Non-clay Minerals (%) | |
| -Quartz | 18 |
| -Dolomite | 0 |
| -Calcite | 9 |

Table 10: The characteristics of the Oxford Clay as given in Table 6.2 of Environment Agency (2009). (^a) average, (^b) calculated from difference between total carbon and inorganic carbon. Further details of the techniques used to produce these values are available from the original table (Environment Agency, 2009).

4.2.2 Sorption Reagents and Standards

The contaminants of interest in this work are the HOCs toluene and naphthalene, discussed in Section 2.1.7. Though their concentrations can vary significantly between individual landfill sites (<1-12,300 µg/L for toluene and <1-280 µg/L for naphthalene) (Kjeldsen *et al*, 2002) toluene and naphthalene are typically found in low concentrations in MSW leachates (21 µg/L and 0.46 µg/L respectively) (Environment Agency, 2009; 2000; 2003d). In brief, toluene and naphthalene were selected for this work as both contaminants are small aromatic hydrocarbons that are commonly found in landfill leachates. They are relatively soluble in an aqueous environment and are classified as hazardous substances according to the Groundwater Daughter Directive (2006). In addition to this, naphthalene is considered a priority hazardous substance in the UK. Under Article 16 of the Water Framework Directive (2000) water pollution caused by its discharge must be phased out and ceased, Section 2.1.6.

A 400 mg/L toluene stock solution was made by diluting toluene (Sigma Aldrich) first in methanol (Fisher Scientific) and then in UHQ DI water. This was used to spike leachates with concentrations of toluene ranging from 10-300 µg/L. A 1000 µg/L naphthalene stock solution was prepared from the pre-prepared 5000 µg/mL standard solution (Supelco Analytical). This was then used to spike leachates with concentrations of naphthalene ranging from 1-50 µg/L. The stock solutions used for contaminant spiking were made up fresh whenever a batch sorption test was started, stored in amber glass 40 mL borosilicate glass Volatile Organic Analysis (VOA or EPA) vials, with PTFE septa to limit sorption, below 5°C to limit volatile loss before use. Stock spike solutions were then discarded within 24 hours.

4.2.3 Leachates

The objective of this work was to determine the effect of DOC type on the sorption and desorption of toluene and naphthalene to the Oxford Clay. Leachates were specifically selected to have varying DOC maturity represented by fluorescence peak intensity ratios, HIX values (discussed in Sections 2.3.1.4 and 4.3.1.3) and a range of DOC concentration.

Leachates were sourced from landfill sites, artificially produced or synthesised from common laboratory chemicals.

- A single leachate was selected from a MSW landfill site as being representative of a MSW leachate, Section 4.2.5.2. The leachate originated from a landfill site in Essex that currently accepts MSW but had previously accepted assorted waste types.
- Artificially produced leachates were made by leaching waste sourced from landfill or waste processing plants, Section 4.2.5.3. Leachates were artificially produced from a MBT waste and an aged, well leached sample of waste from the landfill site which provided the MSW leachate (AMSW).
- Two synthetic leachates were used.
 - The first contained no DOC and was used to establish a baseline for the sorption and desorption behaviour of the contaminants to Oxford Clay.
 - The second contained a solution of Sigma Aldrich humic acid (AHA), in order to represent a highly stabilised leachate with a high degree of humification (Section 4.2.5.4) which contained only HL DOC.

Since the portion of the total organic matter in a landfill increases in HS content as composting of MSW occurs (Fourti, 2010) a purely HA containing leachate represents an extreme case of landfill stabilisation. The HA leachate also offers a comparison between a ‘natural’ mature leachate DOC (AMSW) and a fully synthetic version (humic acid synthetic leachate (HASL)). If the results from sorption tests using the synthetic version proved analogous to the results from the mature AMSW leachate, HASL may

offer an appropriate surrogate for batch testing predicting contaminant sorption in a mature MSW leachate.

4.2.4 Leachate Preparation

4.2.4.1 Real Leachates

A total of seventeen leachates from eleven different landfill sites in the UK were analysed in order to facilitate the selection of a real leachate for use in experimental work. The leachates were assigned labels a-k denoting individual landfill sites and the numbers 1-5 representing leachates from different wells within the same landfill site. The leachate samples were stored in the dark under nitrogen in sealed containers at 5°C until required.

The toluene and naphthalene concentrations of the MSW leachate selected for experimental work were high enough to have a significant effect on the contaminant spikes used in sorption experiments, discussed further in Section 4.2.2. Therefore, the leachate was purged of volatiles, including toluene and naphthalene, by bubbling nitrogen through the leachate. Due to the inert, anoxic, nature of the gas, this process removed the toluene and naphthalene from the solution without further interacting with the solution whilst maintaining an anoxic environment. Fluorescence, DOC concentration, pH and EC measurements were taken before and after bubbling with nitrogen. Bubbling with nitrogen was found to have a limited effect on these characteristics of the leachate. The MSW, MBT and HA leachates were used both as undiluted and diluted versions (diluted 1:20, 1:10 and 1:2 with UHQ DI water to 116 mg/L, 111 mg/L and 122 mg/L respectively). This brought the leachates into the same concentration range as the AMSW leachate and therefore allowed a direct comparison of leachates with different DOC character to be made during sorption testing, independent of concentration. Although the dilution of the leachates resulted in a reduction in EC, which may affect the conformation of the DOC, fluorescence ratios indicated that the DOC types in solution did not undergo much alteration and the pH did not alter significantly. Comparing the diluted leachates will aid in removing DOC concentration as a factor in determining the effect of DOC character on toluene and naphthalene sorption to the Oxford Clay.

4.2.4.2 Artificially Produced Leachates

Two leachates were produced artificially. One originated from a well leached aged MSW waste (AMSW) and the other from a MBT waste from a waste treatment plant. The wastes used are discussed in greater detail below. The AMSW waste was sourced from the same landfill site that produced the MSW leachate (leachate k), Section 4.2.5.1. It was excavated from the MSW landfillsite and estimated to be in excess of 10 years old and, therefore, expected to be fairly well stabilised. The waste was not shredded before use due to its decomposed nature. Waste composition for the excavated sample is detailed in Table 11, though this may not be entirely representative of the smaller sub-sample used in the experimental work. This is due to the data in Table 11 representing the composition of a very large sample size of MSW waste. The waste used to produce the AMSW leachate was a very small subsample (13.4 kg) of that used in the original waste characterisation (Velkushanova, 2011).

The MBT waste was from a processing plant in Dorset, Southern England where MSW waste was treated via mechanical and biological processes to create an MBT waste. The waste underwent mechanical separation to extract metals and plastics for recycling followed by shredding, screening and a further ferrous metal recover step (Siddiqui *et al*, 2012). This was followed by an aerobic composting stage lasting six weeks with regular aeration, wetting and turning to stabilise any remaining organics (New-Earth-Solutions, 2013; Siddiqui, 2011; Siddiqui *et al*, 2012). The waste was then screened again to remove any remaining dry recyclables resulting in a particle size of approximately 20 mm (Siddiqui *et al*, 2012). The MBT waste composition was determined after a further screening in the laboratory (Velkushanova, 2011) and is detailed in Table 11 alongside the composition of the waste used to produce the AMSW leachate. While the two wastes contain a similar percentage mass of glass (22.8% and 22.8% for the MBT and AMSW respectively) 58.1% of the MBT waste was unidentified in comparison with only 1.87% in the AMSW waste. This may be because a higher portion of OM was left in the MBT waste due to the initial mechanical treatment process to separate out recoverable materials.

| Material | MBT (% mass) | AMSW waste (% mass) |
|------------------|---------------------|----------------------------|
| Bones | 0.25 | 0.3 8.92 ^a |
| Ceramics | 2.29 | |
| Stones | 1.73 | |
| Flexible plastic | 4.57 | 3.48 |
| Glass | 22.77 | 22.83 |
| Metal | 0.49 | 3.04 |
| Unidentified | 58.10 | 1.87 |
| Paper | 0.43 | 5.68 |
| Rigid plastic | 6.27 | 7.25 |
| Rubber | 0.18 | N/A |
| Soil-like | N/A | 35.86 |
| Textiles | 1.33 | 0.89 |
| Wood | 1.57 | 9.88 |
| TOTAL | 100 | 100 |

Table 11: Compositional breakdown by material of MBT (<20mm particle size) and AMSW waste from the Essex landfill site (Velkushanova, 2011). ^acombined value

AMSW and MBT were loaded into airtight 30 L reaction vessels (Figure 14). The waste was covered to approximately 2/3 of the vessel depth with a 2% solution of sewage sludge in de-aired rainwater which acted as an anaerobic decomposition bacterial seed in order to ensure the occurrence of microbial breakdown of the waste OM. M:v ratios of dry waste to the seed solution were 0.176 and 0.166 g/mL respectively for AMSW and MBT wastes. Fluorescence, UV, pH and EC of the leachate (Appendix B) were measured via 20 mL samples to monitor the evolution and stabilisation of the leachate produced. Samples were initially taken every working day, reducing to once a week after 140 days as the observable changes in the leachate characteristics decreased over time. This totalled 93 samples for AMSW and 124 samples for MBT, equating to 1.86 L and 2.48 L respectively. After each sample was taken, the volume of liquid removed was replaced with de-aired rainwater. Due to the volume of leachate removed and replaced by rainwater analytical results were corrected for the dilution effects due to sampling procedure via a correction factor, which was applied retrospectively using Matlab (code written by Galloway (2011)) before correcting for the background. The correction factor assumed that the volume of liquid in the vessel is constant (no loss through evaporation). The dilution effect was small (sample size is <0.15% of total liquid volume) and the vessel was considered well mixed, so dilution by the rainwater was the only significant process to be considered in the correction.

Adequate mixing within the vessel was ensured by draining the leachate and returning it

to the vessel. This was initially done on a weekly basis, decreasing to monthly as sampling frequency was reduced. Gas bags (Tedlar) were attached so that the composition of any gas produced by the waste could be monitored by GC to confirm that the leachate had become methanogenic, Sections 2.1.4 and 4.3.5. Leachates were considered mature and ready to use in sorption experiments once their pH, fluorescence and UV signatures had stabilised and gas production had ceased. Details on the maturation of the leachate can be found in Appendix B.

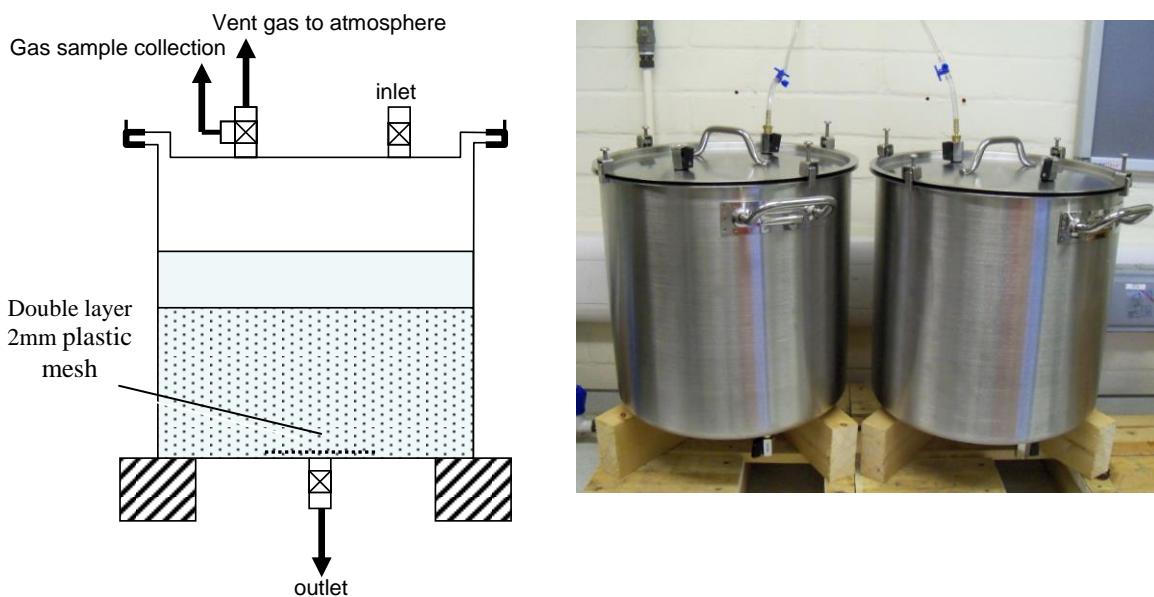


Figure 14: Schematic and photograph of 30 L reaction vessels for artificial leachate production.

The MBT leachate was used at full strength and diluted (1:10 with UHQ DI water to 111 mg/L) to more closely match the DOC concentration of the AMSW leachate (136 mg/L). This was in order to provide a concentration equivalent comparison between the DOC character of an aged (mature) MSW leachate and a MBT leachate (which aims to produce a waste with lower biodegradability which has already passed through acetogenic leachate decomposition and will produce minimal gas) (Praagh *et al*, 2009; Robinson *et al*, 2005; Siddiqui *et al*, 2012).

4.2.4.3 Synthetic Leachates

Two synthetic leachates were used in the experimental work; DOC free synthetic leachate and humic acid synthetic leachate (HASL). All reagents used to produce the synthetic leachates were of analytical reagent grade or higher and were sourced from either Sigma Aldrich Ltd or Fisher Scientific Ltd. UHQ deionised (DI) water refers to water of measured resistivity 18.2 Ω. The DOC free synthetic leachate was based on the recipe for synthetic MSW leachate (Environment Agency, 2009) and contained ammonium chloride (2 g/L), sodium chloride (2 g/L) and sodium bicarbonate (4 g/L), but no DOC source.

An initial humic acid synthetic leachate (HASL) was produced by stirring 0.1 g/L humic acid purchased from Sigma Aldrich Ltd (AHA) in DOC free synthetic leachate for 12 hours. AHA has been found to be of high maturity due to its molecular size and highly aromatic and condensed nature (Kang, 2002). This is supported by its low humification index (HIX) and the presence of predominantly HL and FL peaks in fluorescence spectroscopy, indicating that it has largely humic character. The resulting solution was then filtered through a 0.45 µm cellulose nitrate filter (Whatman). However, this yielded a low humic acid concentration in solution (30 mg/L). Therefore a method by Lozano (2011) was adopted whereby 6.67 g of humic acid was stirred in 2 L UHQ DI water for 3 days and then filtered sequentially through a pre-washed 11 µm GF/F filter (Whatman) and 0.45 µm cellulose nitrate filter (Whatman). This yielded a solution of 238.1 mg/L DOC.

The HASL was used at both the original concentration and as a diluted version (diluted 1:2 with UHQ DI water to 122 g/L) to match the DOC concentration of the AMSW leachate, and therefore to represent an entirely HL DOC composition at this concentration.

4.2.5 Leachate Properties

4.2.5.1 Real Leachates

The seventeen leachate samples from landfill sites were analysed for their DOC character using DOC concentration, fluorescence and ultraviolet spectroscopic techniques. EEM spectra for all leachates are shown in Appendix C, Figure C1. Figures 15 and 16 illustrate the differences in DOC fluorescence between leachates from the different sites (a-k), and between different wells on the same landfill site (a1-5 and b1-3). These differences demonstrate the high variability of leachate DOC composition within landfill sites. It is noted that the six fluorescence peaks identified as being present in leachates (Section 2.3.1.3) are not all obvious in the majority of the leachates. This is most notable in the case of leachates a3 and f which lack the HSL peaks E and F (Figure 15) and in leachates c, d, f, h, and i (Figure 15) which lack the tyrosine-like peaks C and D.

Table 12 displays the DOC properties for the 17 leachates studied. It summarises fluorescence intensity ratios (represented graphically in Figure 16), HIX values (F:B ratio), DOC concentrations and UV absorption at 254 nm. Leachate DOC concentration was observed to range over two orders of magnitude, with DOC concentrations of between 12 mg/L (leachate f) and 4728 mg/L (leachate b3). All of the leachates displayed a B:D ratio greater than one, indicating that the PL DOC in solution was dominated by tryptophan-like compounds. The E:F ratios of the majority of the leachates (excepting d, e, h and k) were lower than the literature limit for mature composts. Therefore, the HSL DOC was more mature, where humic maturity is a measure of the proportion of HSL that is humic acid-like or fulvic acid-like, than the literature value for defining a compost as humically mature (0.62 and less; derived from literature value for F:E peak of 1.6 and higher as E:F=1/F:E (Fourti, 2010). Leachates d, e, h and k had E:F ratio values which were higher than 0.62, indicating that they were less humically mature than the other leachates. Leachate d displayed the least humic maturity of all of the leachates, with a E:F ratio of 1.31, which is less humically mature

than literature values for soil OM (1.15-1.22, derived from literature value for F:E peak of 0.82-0.87 as E:F=1/F:E) (Chung *et al*, 2012). The leachate HIX range (Section 2.3.1.4) was 0.73-2.05 and eight of the leachates had a HIX value lower than one indicating more PL DOC present in solution than HSL DOC. Nine of the leachates had HIX values greater than one indicating a more humified leachate containing more HSL DOC than PL DOC.

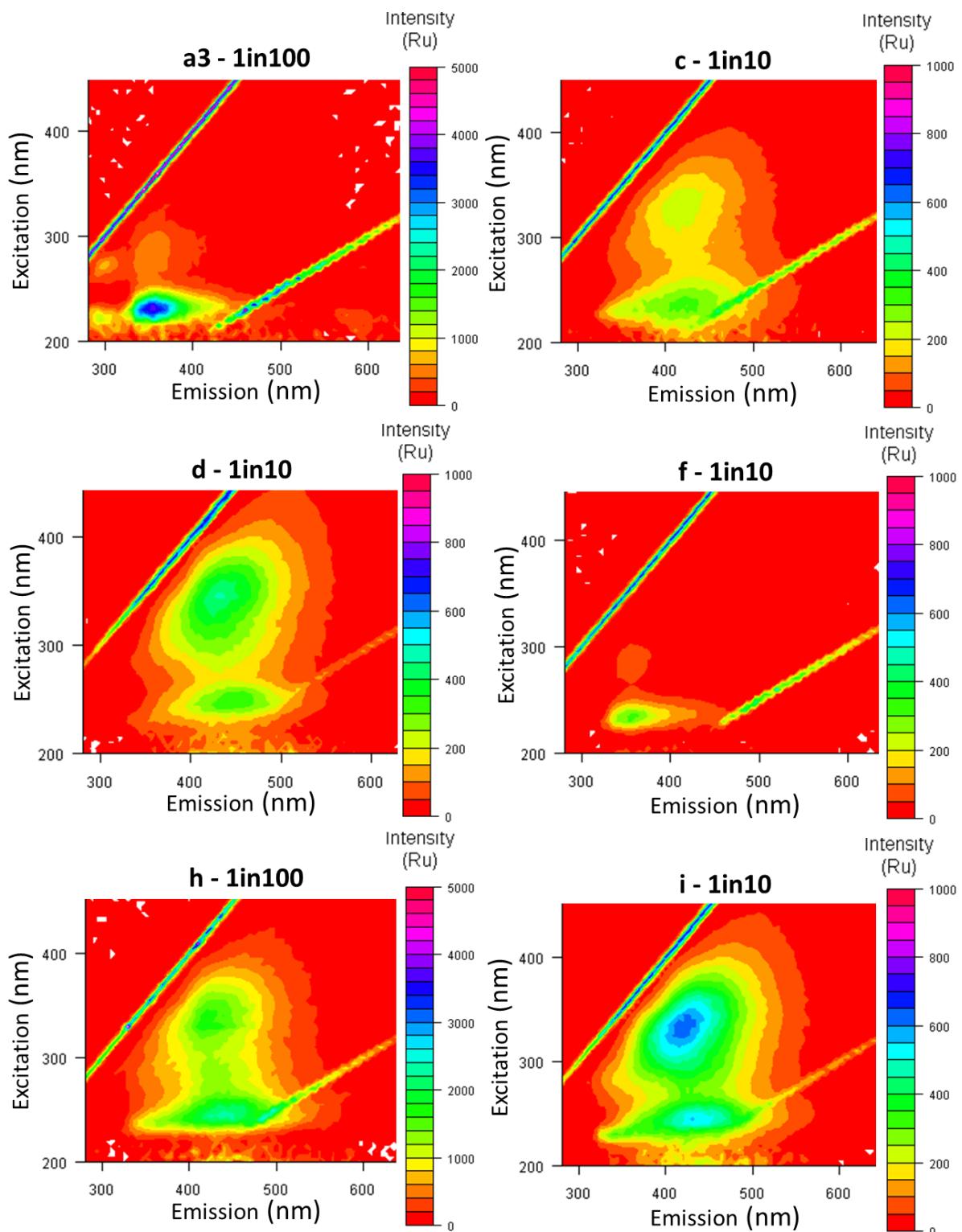


Figure 15: EEM spectra of leachates a3, c, d, f, h and i showing the variation in DOC observed in different leachates.

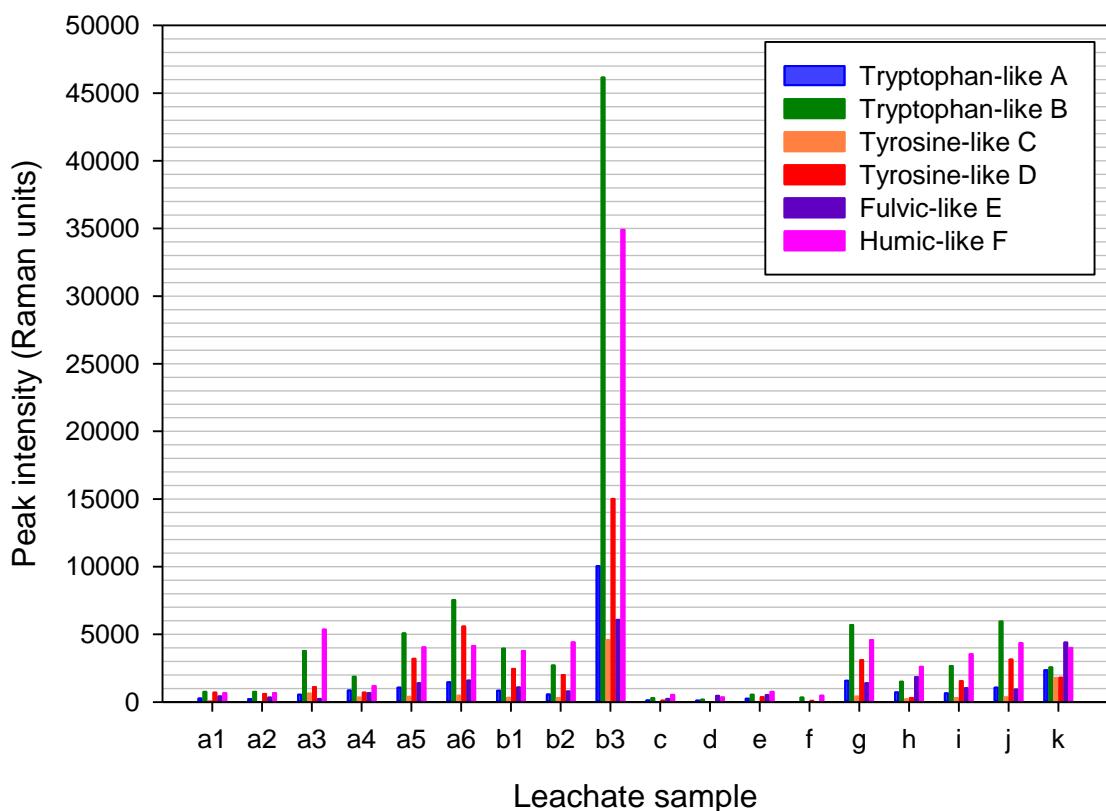


Figure 16: Graphical representation of the fluorescence peak intensities of the 17 leachates studied illustrating the ratio of the intensities.

| Sample | [DOC] (mg/L) | E:F | B:E | B:F | D:E | D:F | B:D | UV (254 nm) | HIX |
|--------|--------------|------|-------|------|------|------|------|-------------|------|
| a1 | 217 | 0.63 | 1.83 | 1.15 | 1.72 | 1.08 | 1.07 | 3.6 | 0.87 |
| a2 | 166 | 0.50 | 2.25 | 1.13 | 1.77 | 0.90 | 1.27 | 1.8 | 0.88 |
| a3 | 396 | 0.04 | 16.60 | 0.71 | 4.85 | 0.21 | 3.42 | --- | 1.42 |
| a4 | 344 | 0.55 | 2.87 | 1.59 | 1.07 | 0.59 | 2.68 | 4 | 0.63 |
| a5 | 411 | 0.34 | 3.67 | 1.26 | 2.31 | 0.79 | 1.59 | 3 | 0.80 |
| b1 | 404 | 0.29 | 3.64 | 1.04 | 2.26 | 0.65 | 1.61 | 1 | 0.96 |
| b2 | 388 | 0.18 | 3.47 | 0.61 | 2.56 | 0.45 | 1.36 | --- | 1.63 |
| b3 | 4728 | 0.17 | 7.60 | 1.32 | 2.47 | 0.43 | 3.07 | 90 | 0.76 |
| c | 133 | 0.45 | 1.20 | 0.54 | 0.45 | 0.20 | 2.67 | --- | 1.85 |
| d | 519 | 1.31 | 0.37 | 0.49 | 0.09 | 0.12 | 3.92 | 10 | 2.05 |
| e | 286 | 0.69 | 1.05 | 0.73 | 0.69 | 0.48 | 1.52 | 1 | 1.37 |
| f | 12 | 0.08 | 8.75 | 0.71 | 2.27 | 0.18 | 3.85 | --- | 1.40 |
| g | 369 | 0.30 | 4.10 | 1.24 | 2.23 | 0.68 | 1.84 | 7 | 0.80 |
| h | 459 | 0.71 | 0.82 | 0.58 | 0.17 | 0.12 | 4.94 | --- | 1.73 |
| i | 344 | 0.29 | 2.58 | 0.75 | 1.51 | 0.44 | 1.72 | 3 | 1.33 |
| j | 296 | 0.21 | 6.40 | 1.36 | 3.39 | 0.72 | 1.89 | 7 | 0.73 |
| k | 2268 | 0.7 | 1.03 | 0.72 | 0.82 | 0.58 | 1.25 | 61 | 1.38 |

Table 12: Summary of the properties of leachate DOC from eleven different landfill sites (a-k) and wells within those sites (1-5).

HIX values from the literature are summarised in Table 8, Section 2.3.1.4. HIX values for all leachates were in agreement with literature values of the HIX for untreated grape marc (a wine making by-product) (0.77) (Brunetti *et al*, 2012), the upper range for seawater (0.45-2.75) (Bai *et al*, 2013), freshwater (0.78) (Chen *et al*, 2011) and soil extracts (0.77-0.96, 0.76-0.88, 0.84, and 0.94) (Ohno, 2002; Traversa *et al*, 2014; Wickland *et al*, 2007). This indicated that landfill leachates have similar DOC humification to these sources. Leachate DOC did, however, exhibit HIX values that were higher than rainwater (0.47) (Salve *et al*, 2012), grassland soils (0.25) (Saviozzi *et al*, 1994), water soluble corn extract (0.57) (Ohno, 2002) and the lower HIX range for seawater (0.61 and 0.45-2.75) (Bai *et al*, 2013; Chen *et al*, 2011). This indicated that leachate DOC was more humified than these sources. Whilst leachate DOC HIX values are within the overall range of literature HIX values for seawater, a large variation in seawater HIX values was noted. This is unlikely to be due to seasonality since the samples (Bai *et al*, 2013; Chen *et al*, 2011) were collected within a 22 day period. Variation in sampling depth, the position of water currents and discharge from terrestrial sources is a more likely reason for the large variation in range of seawater HIX (Bai *et al*, 2013). Leachate HIX values were lower, indicating less humification, than the HIX of water level fluctuation zones (2.12-7.04) (Fang *et al*, 2011), agricultural land (8.14-9.43) (Guo *et al*, 2012), polluted (4.47-4.95) and highly dynamic (2-18) natural water systems (Yeh *et al*, 2014; Catalan *et al*, 2014). Therefore, based on HIX values, the DOC humification in landfill leachates was found to be of a similar level to that of soil extracts, un-polluted freshwater and seawater. This may indicate that DOC sources from these environments are of similar maturity, and therefore may potentially be suitable for use as DOC surrogates in synthetic leachates. It also indicates that the sorption of toluene and naphthalene may be affected by leachate DOC in the same way as it is affected by these DOC sources and that DOC derived from wastes degrades to become similar to that found in natural environments.

4.2.5.2 Real Leachate Selection

From the 17 leachate samples, a single leachate was selected for experimental work. Since this work focuses on the effect that DOC in leachates has on the sorption of HOCs a leachate with a high DOC concentration was desirable. On this basis, the 5 leachates with highest DOC concentration (a5, b3, d, h and k) were selected for further consideration. They are summarised in Table 13 for ease of comparison.

| Sample | Concentration of DOC (mg/L) | E:F | B:E | B:F | D:E | D:F | B:D | UV 254 nm | HIX |
|--------|-----------------------------|------|------|------|------|------|------|-----------|------|
| a5 | 411 | 0.34 | 3.67 | 1.26 | 2.31 | 0.79 | 1.59 | 3 | 0.80 |
| b3 | 4728 | 0.17 | 7.60 | 1.32 | 2.47 | 0.43 | 3.07 | 90 | 0.76 |
| d | 519 | 1.31 | 0.37 | 0.49 | 0.09 | 0.12 | 3.92 | 10 | 2.05 |
| h | 459 | 0.71 | 0.82 | 0.58 | 0.17 | 0.12 | 4.94 | --- | 1.73 |
| k | 2268 | 0.7 | 1.03 | 0.72 | 0.82 | 0.58 | 1.25 | 61 | 1.38 |

Table 13: Summary DOC parameters for the 5 leachates selected for further consideration due to their high DOC concentration.

As landfill leachates display such high variation in DOC character between different landfill sites (Figures 15 and 16 and Table 12) and since this DOC character evolves during the decomposition and stabilisation of the waste (Kang *et al*, 2002; Kjeldsen *et al*, 2002) ideally the selected leachate should exhibit fluorescence peaks for all DOC compound types identified as being present in leachate, Section 2.3.1.3. Since HSL DOC increases and PL DOC decreases as leachates mature (He *et al*, 2011), this would likely relate to a moderately stabilised, acetogenic or early stage methanogenic leachate (Kjeldsen *et al*, 2002). A leachate from a very young waste is, therefore, expected to contain predominantly PL DOC and very little HSL DOC and an old, mature, leachate is expected to contain predominantly HSL DOC with very little PL DOC. Fluorescence peak ratios and HIX values identified leachates d and h as mature, with much lower PL:HSL ratios than the other leachates, which indicated a lack of PL DOC character. Similarly, leachate b3 was identified as immature and largely consisting of PL DOC, with a lack of HSL DOC, as indicated by high B:E, D:E and D:F peaks. Leachates b3, d and h were therefore excluded, leaving leachate a5 and k for consideration.

Of the two leachates, leachate k was selected for continuing experimental work as the distribution of the HSL peaks between HL and FL (E:F ratio) and the PL peaks between tyrosine-like and tryptophan-like (B:D ratio) were closer to one, indicating that their

fluorescence intensities, and therefore proportions, were more evenly distributed in solution. With the exception of the D:F ratio, the PL:HSL fluorescence intensity ratios for leachate k were also closer to one than leachate a5, indicating a more even distribution of DOC character within leachate k. From this point onward, leachate k is referred to as ‘MSW leachate’. Figure 17 and Table 14 show the fluorescence EEM and a summary of the properties of the MSW leachate for both the full strength solution and a diluted version of the leachate.

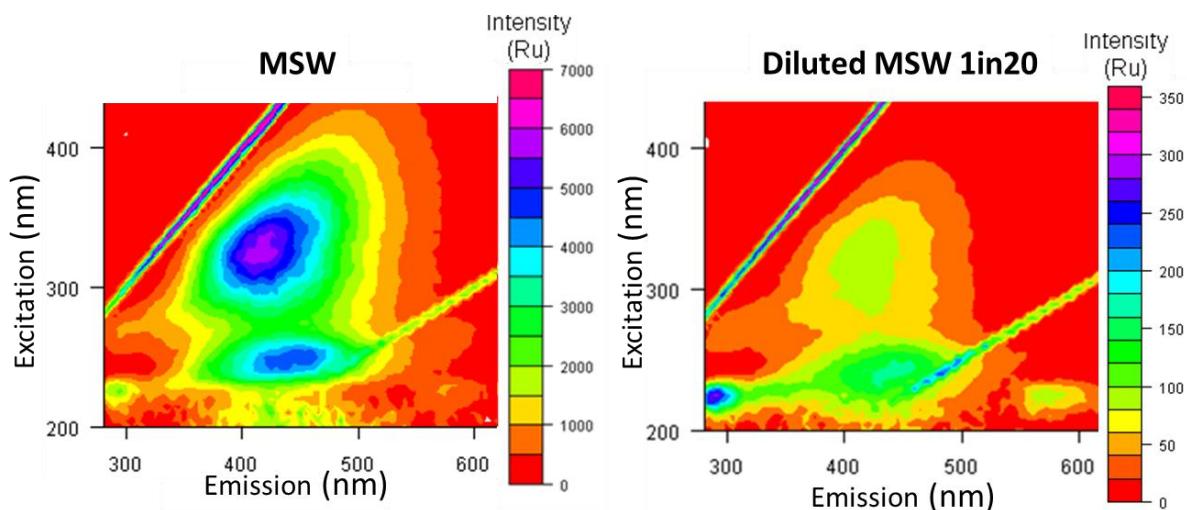


Figure 17: Fluorescence EEM of MSW leachate (k) (undiluted and 1:20 dilution). Intensity is given in Raman units.

| | [DOC] (mg/L) | E:F | B:E | B:F | D:E | D:F | B:D | [TOL] ($\mu\text{g}/\text{L}$) | [NAPH] ($\mu\text{g}/\text{L}$) | EC (mS/m) | pH | HIX |
|-------------|--------------|------|------|------|------|------|------|----------------------------------|-----------------------------------|-----------|------|------|
| MSW | 2268 | 0.70 | 1.03 | 0.72 | 0.82 | 0.58 | 1.25 | 0.04 | 0.03 | 42.9 | 8.87 | 1.38 |
| Diluted MSW | 116 | 0.65 | 1.09 | 0.71 | 0.98 | 0.64 | 1.11 | n/o | n/o | 25.2 | 8.85 | 1.42 |

Table 14: A summary of the fluorescence ratios, DOC concentration, toluene and naphthalene concentration in the neat and diluted MSW leachate. (n/o) none observed.

The MSW leachate had the lowest HSL maturity of all the leachates used in the experimental work. This was demonstrated by the relatively high values of the PL:HSL DOC fluorescence intensity ratios B:E, B:F, D:E and D:F and by it having the lowest HIX of all the leachates used in experimental work. The HIX values for MSW leachate (1.4) (both diluted and undiluted) were higher than the majority of the literature values for soil and sediment DOC (Brunetti *et al*, 2012; Chen *et al*, 2011; Ohno, 2002; Saviozzi *et al*, 1994). This indicated that the MSW leachate DOC is more mature than the

environmentally derived DOC studied in the literature. The HIX of the MSW leachate was, however comparable to the range given for highly biodegraded soil derived DOM (Kalbitz *et al*, 1999).

4.2.5.3 Artificially Produced Leachates

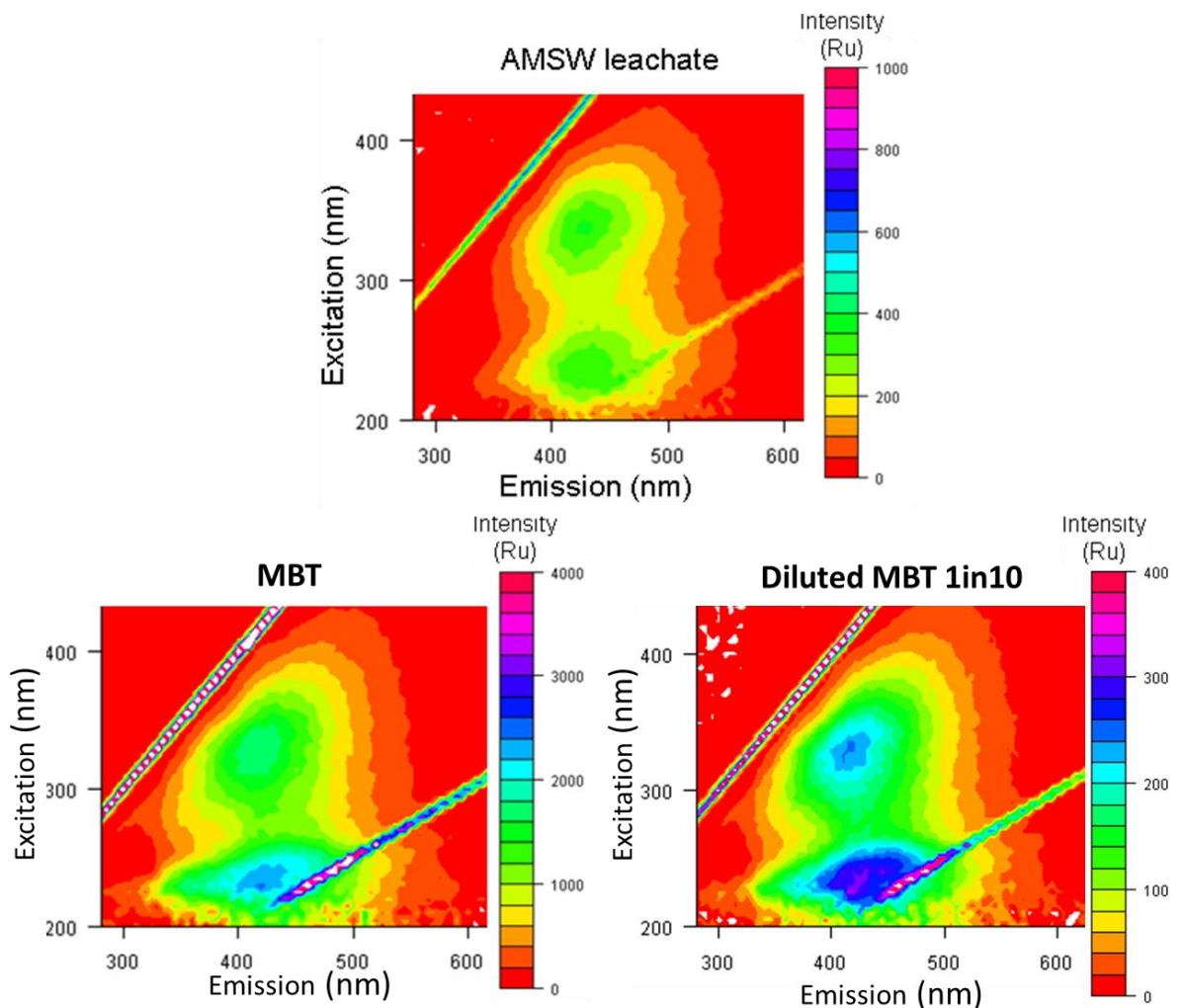


Figure 18 : Fluorescence EEM of AMSW and MBT artificial leachates. Intensity is given in Raman units. Note the difference in intensity scale. Therefore ratios of the peaks must be used to directly compare the two fluorescence spectra.

| | [DOC] (mg/L) | E:F | B:E | B:F | D:E | D:F | B:D | [TOL] (µg/L) | [NAPH] (µg/L) | EC (mS/m) | pH | HIX |
|-------------|--------------|------|------|------|------|------|------|--------------|---------------|-----------|------|------|
| MBT | 1052 | 0.79 | 0.74 | 0.58 | 0.18 | 0.14 | 4.05 | 0.021 | 0.027 | 7.7 | 7.29 | 1.71 |
| Diluted MBT | 111 | 0.79 | 0.74 | 0.59 | 0.18 | 0.14 | 4.14 | n/o | n/o | 3.4 | 7.52 | 1.71 |
| AMSW | 137 | 1.00 | 0.34 | 0.34 | 0.07 | 0.07 | 5.00 | 0.008 | 0.005 | 2.9 | 7.21 | 2.94 |

Table 15: A summary of the fluorescence ratios and DOC concentration of the artificially produced leachates used in the experimental work.

The MBT, diluted MBT and AMSW leachates were found to be more mature (humified) than the neat and diluted MSW leachates as demonstrated by their higher HIX values (1.71, 1.71 and 2.94 compared to 1.38 and 1.42 respectively). The peak intensity ratio E:F is, however, higher in MBT and AMSW leachates than MSW (0.79-1 compared to 0.65-0.7) indicating a more humified HSL DOC fraction in the MSW, with the MBT and AMSW leachates having a higher proportion of FL DOC (peak E) than the MSW. The E:F ratio of 1.00 observed for the AMSW leachate indicates that equal proportions of HL and FL DOC were present in solution. In comparison to the literature, all the leachates exhibited a maturity lower than that for compost (less than 0.62) (Fourti *et al*, 2010) but higher than that of whole soils (1.15-1.22) (Chung *et al*, 2012). The lower values of HIX for MBT leachate (1.71) indicates that overall its DOC is less humified than the AMSW (2.94). However, the higher values of ratio E:F in AMSW compared to MBT indicated that the HSL AMSW DOC FL proportion is greater than in MBT. The concentration of DOC in the MBT leachate was an order of magnitude higher than the AMSW leachate but was still half the concentration of the real MSW leachate used. The diluted MBT and diluted MSW leachates are of a comparable DOC concentration to the AMSW leachate (1.11, 1.16 and 1.37 mg/L respectively). The MBT, diluted MBT and MSW leachates had a B:D ratio much greater than one (4.05, 4.14 and 5 respectively) indicating that tryptophan-like DOC is more dominant in these leachates than tyrosine-like DOC. This differs from the PL DOC peak intensities of diluted MSW and MSW leachates, which had values close to one (1.11 and 1.25 respectively) indicating that while tryptophan-like DOC is still slightly more dominant in the MSW leachates than tyrosine-like DOC, the proportions present are more equal than in the MBT and AMSW leachates.

4.2.5.4 Synthetic Leachates

DOC free

The DOC free synthetic leachate had no fluorescence or UV signal as it consisted entirely of inorganic salts which were not fluorescent or UV active. pH and EC character are detailed in Table 16 for comparison.

Humic acid

DOC and leachate properties of the HASL are shown below (Figure 19 and Table 16).

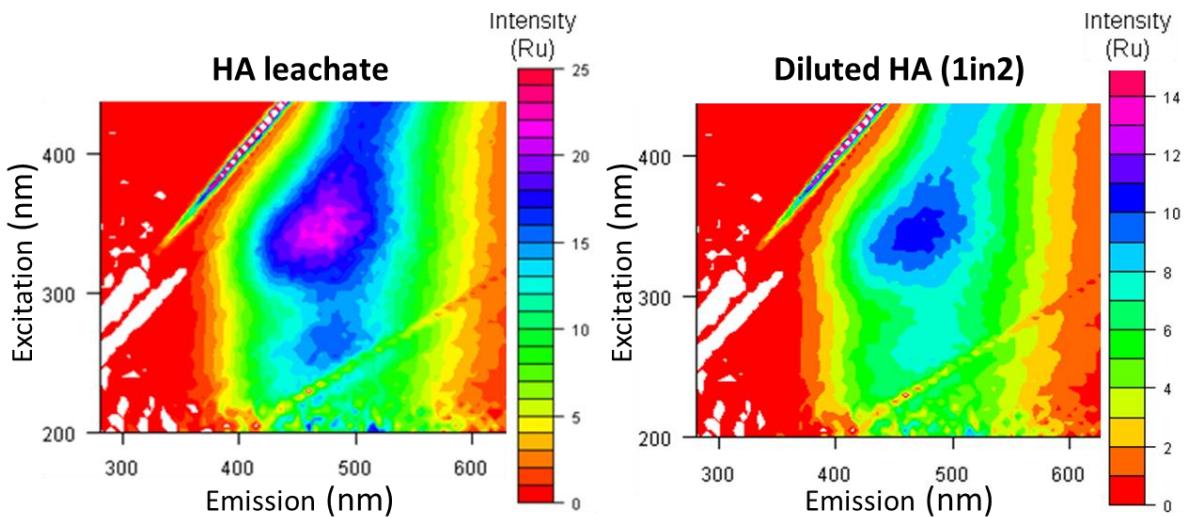


Figure 19: Fluorescence EEM of humic acid synthetic leachate. Intensity is given in Raman units.

| | [DOC] (mg/L) | E:F | B:E | B:F | D:E | D:F | B:D | EC (mS/m) | pH |
|------------|--------------|-------|-------|-------|-------|-------|-------|-----------|-----|
| DOC free | N/A | N/A | N/A | N/A | N/A | N/A | N/A | 158.5 | 8.8 |
| HA | 238 | 1.357 | 0.065 | 0.088 | 0.001 | 0.001 | 61.85 | 8.2 | 7.2 |
| Diluted HA | 122.2 | 1.356 | 0.068 | 0.092 | 0.001 | 0.001 | 65.35 | 4.4 | 7.2 |

Table 16: A summary of the fluorescence ratios and DOC concentration of the synthetic leachates used in the experimental work. There was no toluene or naphthalene present in the synthetic leachates.

The Fluorescence ratios for HASL indicate that it has largely humic character. The very low PL:HSL DOC ratios B:E, B:F, D:E and D:F (0.001-0.092) indicate that PL DOC in the HA and diluted HA leachates was negligible. The high value of B:D ratio seen in HASL (61.85) was due to the detection of a negligible amount of tryptophan-like DOC in comparison with the other leachates alongside an almost zero tyrosine-like DOC. HASL (both diluted and undiluted) had the highest HIX of all the leachates used in experimental work (10.8 and 11.4 respectively). This was higher than HIX values in the literature for the majority of soil and sediment extracts from a range of different environments (Fang *et al*, 2011; Ohno, 2002; Saviozzi *et al*, 1994; Traversa *et al*, 2014; Wickland *et al*, 2007; Yeh *et al*, 2014) and aqueous environments (Bai *et al*, 2013; Salve *et al*, 2012; Chen *et al*, 2011). The HIX values for HASL were, however, within the range observed by Catalan *et al* (2014) for a dynamic, vegetated Mediterranean lagoon environment, which had a seasonally dependant HIX range of 2-18.

4.2.5.5 Leachate Properties Summary

Table 17 summarises the properties of all the leachates selected for experimental work. Of the leachates selected, MSW, diluted MSW, MBT, diluted MBT and AMSW were derived from wastes and DOC free, HA and diluted HA were entirely synthetic. Of the waste derived leachates, MBT and AMSW were produced from the waste in a laboratory setting (artificial) and MSW was obtained from a landfill site. The diluted leachates were diluted from the original full strength leachates in the laboratory. The maturity of the leachate DOC was measured by the HIX and increased in the order:

HSL maturity (HIX - F:B ratio):

$$\text{HA} \approx \text{diluted HA} > \text{AMSW} > \text{MBT} \approx \text{diluted MBT} > \text{MSW} \approx \text{diluted MSW}$$

| | | | | | | |
|--------|--------|-------|-------|-------|-------|-------|
| (11.4) | (10.8) | (2.9) | (1.7) | (1.7) | (1.4) | (1.4) |
|--------|--------|-------|-------|-------|-------|-------|

The DOC concentration of the leachates was measured using an AJ Multi N/C 3100 and decreased in the order:

DOC concentration (mg/L):

$$\text{MSW} > \text{MBT} > \text{HA} > \text{AMSW} \approx \text{diluted HA} \approx \text{diluted MSW} \approx \text{diluted MBT} > \text{DOC free}$$

| | | | | | | |
|--------|--------|-------|-------|-------|-------|-------|
| (2268) | (1051) | (238) | (136) | (122) | (116) | (111) |
| (0) | | | | | | |

| | [DOC] (mg/L) | E:F | B:E | B:F | D:E | D:F | B:D | [TOL] (µg/L) | [NAPHI] (µg/L) | EC (mS/m) | pH | HIX |
|-------------|--------------|------|------|------|-------|-------|-------|--------------|----------------|-----------|-----|------|
| MSW | 2268 | 0.70 | 1.03 | 0.72 | 0.82 | 0.58 | 1.25 | 0.04 | 0.03 | 42.9 | 8.9 | 1.38 |
| Diluted MSW | 116 | 0.65 | 1.09 | 0.71 | 0.98 | 0.64 | 1.11 | --- | --- | 25.2 | 8.9 | 1.42 |
| MBT | 1052 | 0.79 | 0.74 | 0.58 | 0.18 | 0.14 | 4.05 | 0.021 | 0.027 | 7.7 | 7.3 | 1.71 |
| Diluted MBT | 111 | 0.79 | 0.74 | 0.59 | 0.18 | 0.14 | 4.14 | --- | --- | 11.4 | 7.5 | 1.71 |
| AMSW | 137 | 1.00 | 0.34 | 0.34 | 0.07 | 0.07 | 5.00 | 0.008 | 0.005 | 2.9 | 7.2 | 2.94 |
| DOC free | --- | --- | --- | --- | --- | --- | --- | --- | --- | 158 | 8.8 | --- |
| HA | 238 | 1.36 | 0.07 | 0.09 | 0.001 | 0.001 | 61.85 | --- | --- | 8.2 | 7.2 | 11.4 |
| Diluted HA | 122 | 1.36 | 0.07 | 0.09 | 0.001 | 0.001 | 65.35 | --- | --- | 4.4 | 7.2 | 10.8 |

Table 17: Attributes of leachates selected for the experimental work.

4.3 Analytical Methods

4.3.1 Fluorescence

Fluorescence was measured using a Varian Cary Eclipse fluorescence spectrophotometer equipped with a Peltier cooler (20°C). This was used to generate EEMs. The wavelengths used were excitation 200-700 nm and emission 280-700 nm with a 5 nm interval and 24,000 nm/m scan rate.

4.3.1.1 Fluorescence Sample Analysis

Leachate samples of volume 20 mL were collected in clean high-density linear polyethylene (HDLP) sample bottles. Once collected the samples were stored untreated in the dark at 5°C and analysed as soon as possible.

Cellulose nitrate filters (0.45 µm, Whatman) were used to filter the samples prior to analysis where appropriate. Background fluorescence from the filter paper was negated by pre-washing the filter with ultra high quality (UHQ) deionised water. Dilution of the sample by residual moisture on the filter paper was negligible. The contribution of the new, clean, HDLP bottles to fluorescence and TOC/DOC was also found to be minimal, so they were not acid prewashed.

Fluorescence samples were typically diluted between 1:10 to 1:1000 for the leachates (described in Section 4.2.3). Dilutions were 1:1000 for MSW leachate, 1:100 for artificially produced MBT leachate and 1:10 for the artificially produced AMSW leachate in order to optimise the fluorescence readings for the samples. All dilutions were performed with a pH 7 phosphate buffer (0.06 M Na₂HPO₄•12H₂O and 0.04 M NaH₂PO₄•2H₂O) to eliminate any effects of pH on fluorescence and also to allow comparison of the samples which varied in pH. All results were corrected for concentration, buffer and background fluorescence arising from the 2% sewage sludge in rainwater seed solution where appropriate. The spectra were then normalised to the averaged Raman peak of water at excitation wavelength 348 nm (Mostofa *et al*, 2005).

Contour plots of the EEM were created from the fully corrected and Raman normalised data using ‘R’ (Lapworth and Kinniburgh, 2008) and Sigma Plot. Figure 10 (page 64) shows a contour plot for the MSW leachate, Section 2.3.1.3. Six peaks (labelled A-F) were identified from the literature (discussed in Section 2.3.1.3) for analysis and extracted using the programme ‘R’ (Lapworth and Kinniburgh, 2008).

4.3.1.2 Inner Filtering Effects

Inner filtering effects (IFE) occur during fluorescence when incident or emitted photons are absorbed by the solution. Primary IFE occurs when the incident radiation is absorbed by other components of the solution before it can interact with the fluorescing compound. This will result in a lower than expected emission fluorescence intensity. Secondary inner filtering effects occur where the photon emitted during the fluorescence of an initial compound (M1) is at the excitation wavelength of a secondary compound (M2) which then fluoresces. This results in an overall red shifting of the fluorescence and is illustrated in Figure 20.

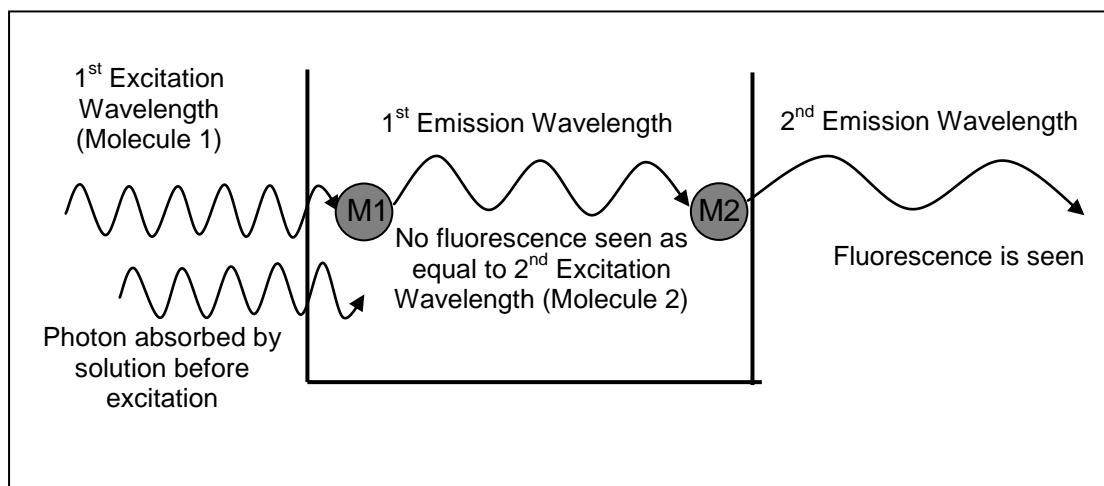


Figure 20: A simplified schematic representing inner filtering effects (IFE). M1 is the initial fluorescing compound and M2 represents a secondary fluorescing compound (based on Lakowicz (1999)).

Humic substances (such as dissolved humic material) are very susceptible to IFE (Henderson *et al*, 2009) resulting in a red-shifting of the peaks. Therefore, it is

important that IFE are corrected to allow better peak definition of the EEMs (Mobed *et al*, 1996; Stedmon *et al*, 2003).

IFE correction can be achieved by a number of methods such as: dilution of the sample (Baker and Curry, 2004; Cox *et al*, 2000), comparison to absorbance spectra (McKnight *et al*, 2001; Mobed *et al*, 1996; Ohno, 2002) or by using Raman scattering of water (Larsson *et al*, 2007). Correction using Raman scattering or UV absorbance is often complex due to the large amount of data collected in an EEM and so is generally performed using a program such as Matlab (McKnight *et al*, 2001; Mobed *et al*, 1996). Dilution of samples to an UV spectroscopy absorbance of <0.1 as suggested by Ohno (2002) was considered as an alternative to mathematical correction of IFE for UV spectra in this work. In order to achieve this, dilution of at least an order of magnitude greater than used in fluorescence measurements (between 1:100 and 1:10000 for UV as opposed to between 1:10 and 1:1000 for fluorescence) was necessary. However, at dilutions suitable for elimination of IFE the fluorescence spectra observed from leachate samples was frequently too weak to be usefully interpreted. This was also observed in the literature where studies of the fluorescence of leachates typically involve dilutions which are often less than required to bring the UV absorbance to below 0.1 absorbance units (Baker and Curry, 2004). Since IFE results in red-shifting of the emission peaks (Mobed *et al*, 1996) and there is no apparent red-shifting in the positions of the fluorescence peaks, it is reasonable to assume that there will be no significant impact on results due to IFE (Yunus *et al*, 2008). Therefore, this work will use dilution of the samples to a level which optimises the resolution of the fluorescence peaks without any significant peak loss (Figure 21) thereby reducing IFE to a point where they have no significant impact on fluorescence results. The position of the peaks was also monitored in order to detect red shifting, as used by Yunus *et al* (2008) as an indicator of the extent of IFE removal. Though it is recognised that dilution may not completely negate the effects of inner filtering on fluorescence, it will reduce the impact of IFE on results.

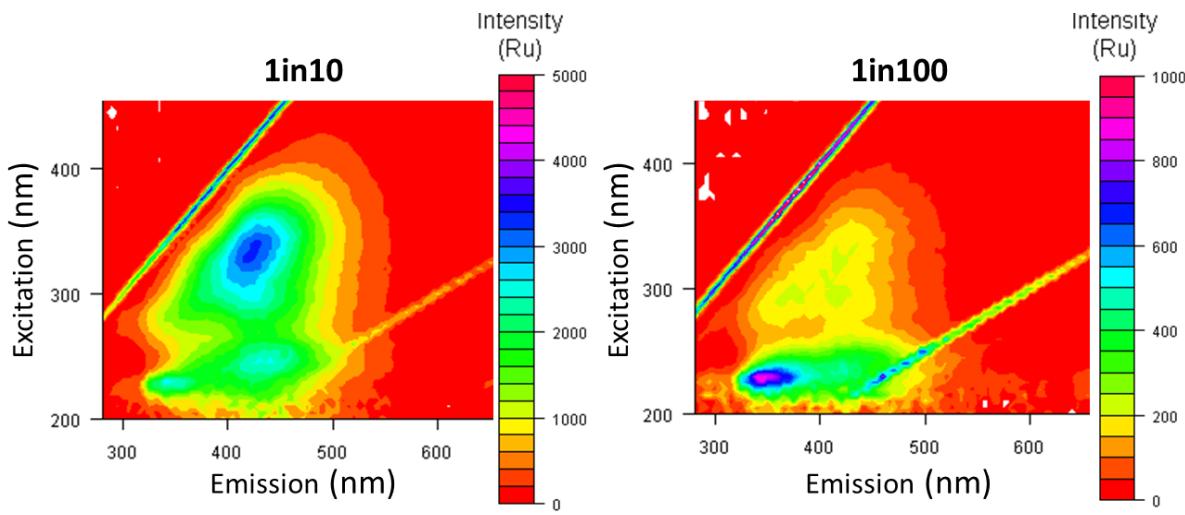


Figure 21: Dilution of fluorescence samples showing a greater peak resolution with dilution due to reduction of IFE.

4.3.1.3 Fluorescence Ratios

In simple solutions of OM where only a single fluorescence active compound is present, or in mixtures where the contribution of different compounds to the overall fluorescence is well characterised, a quantitative relationship between fluorescence peak intensity and the amount of a compound in solution can be established. This would be achieved by calibration of the fluorescence intensity using standards of known composition. However, in landfill leachates the complexity of the DOC is such that quantitative calibration is not feasible. This is due to the highly variable composition of leachate DOC. Therefore, the fluorescence of leachate DOC remains a qualitative technique, meaning that the intensities of the fluorescence peaks cannot be used directly to quantitatively compare OC character in samples.

In order to allow direct comparison of leachate samples using fluorescence ratios of their peak intensities were taken (Section 2.3.1.4). As these ratios give a measure of the proportions of different types of DOC in solution relative to each other they can be used to draw direct comparisons between different samples. For example, Baker (2002) used the ratio of fluorescence peak intensities for tryptophan-like to fulvic-like DOC to distinguish between types of agricultural slurry. This relationship was then used to trace them in river waters via their fluorescence fingerprint. Fluorescence ratios have been used in the literature largely to trace and fingerprint anthropogenic DOM pollution, from

agriculture or sewage treatment, in river waters (Baker, 2002; Henderson *et al*, 2009). Chen (2003) also demonstrated that ratios of fluorescence peak intensity could be used to track changes in natural organic matter (NOM) in a natural water system. Baker (2001) and Henderson (2009) demonstrated that fluorescence ratios could be used to trace sewage in water bodies. Baker (2001) noted that the tryptophan-like to fulvic-like peak intensity ratio was approximately one in treated sewage, thus allowing the tracing of water bodies (e.g. sewer outfalls) via DOM. The ratios used in this work are discussed as follows.

Of the six peaks identified in leachates (Figure 10) peaks B and D were selected for ratio comparison of tyrosine-like and tryptophan-like peaks. Peaks A and C were discounted for ratio comparison as they showed greater distortion due to the presence of the HSL peaks. Humic-like (HL) and fulvic-like (FL) peaks (F and E) were also selected for ratio comparison as more mature leachates have greater HSL character (Kang *et al*, 2002) and the ratio of HL:FL can be used as an indicator of the maturity of the HSL DOC (Catalan *et al*, 2014; Chung *et al*, 2012; Fourti *et al*, 2010). As the F:E peak ratio decreases the proportion of humic-like DOC present in solution increases in proportion with respect to fulvic-like DOC in solution. The fluorescence ratio F:E therefore is indicative of the degree of humification of the HSL leachate DOC (Hernandez, 1988). Table 18 shows some literature values for the F:E humification ratio (HR).

| System being studied | HR | Ref. |
|---|----------------|------|
| Mediterranean Lagoon with seasonal freshwater ingress | 1.46-3.69 | 1 |
| Subtropical forest soil | 1.27-1.30 | 2 |
| Co-composting MSW and sewage sludge | (Waste 1) 23.6 | 3 |
| | (Waste 2) 32.2 | |
| Mature compost value | >1.3 | 3 |
| Immature compost value | <1 | |
| Composting pig manure initial value | 0.2 | 4 |
| Composting pig manure final value | 0.9 | |

Table 18: Literature values for the humification ratio (HR) of organic carbon in different systems. The HR compares the ratio of HL to FL DOC and is equivalent to the fluorescence peak ratio F:E. (1) Catalan *et al* (2014) (2) Chung *et al* (2012) (3) Fourti *et al* (2010) (4) Hsu and Lo (1999)

The fluorescence ratios B:E, B:F, D:E and D:F compare the proportions of protein-like (PL) DOC to HSL DOC present in the leachates. An increase in these ratios indicates

more PL DOC character in relation to HSL character. This is indicative of a younger, less mature, leachate (Kang *et al*, 2002; Rivas *et al*, 2003) since during landfill OM stabilisation a decrease in tyrosine-like (PL) fluorescence and an increase in HSL fluorescence occurs (He, 2011). It has already been established (Section 2.3.1.4) that the ratio F:B corresponds to the humification index (HIX) as described by Zsolnay (1999) and Ohno (2002). A decrease in the ratio of PL to HSL DOC will result in an increase in the HIX value, indicating more humified character of the leachate.

4.3.2 UV Spectroscopy

Ultra Violet measurements were made using a Shimadzu UV-1800 measuring absorbance between 200 and 700 nm in 0.2nm intervals. UV samples were diluted with phosphate buffer (Section 4.3.1.2) until the maximum absorbance values were <0.1 in order to reduce the potential of results being affected by IFE (Baker and Curry, 2004; Banaitis *et al*, 2006; Ohno, 2002). This dilution was typically 1:1000 to 1:10,000 for both MBT and MSW leachates and 1:100 for AMSW. All results were corrected for concentration, buffer and against background signal (initial sewage sludge seed (Section 4.2.4.2) and rainwater) where appropriate.

4.3.3 pH and EC

All samples were analysed for pH and electrical conductivity (EC) using a Mettler Toledo Fe20/EL20 pH probe and HANNA HI99301 EC/TDS/Temperature probe.

4.3.4 Dissolved Organic Carbon Determination

The DOC concentration in solution was determined using an AnalytikJena multi N/C 3100 using thermocatalytic oxidation in the presence of a CeO₂ catalyst in a combustion tube. Following condensation and halogen removal steps detection was via a non-dispersive infra-red (NDIR) detector alongside a reference detector (for TC/DOC measurement). For inorganic carbon (IC) measurement phosphoric acid (20%) was added to the sample and the CO₂ produced was detected via the NDIR detector. Oxygen

was used as the carrier gas at a pressure of 4-6 bar and instrument control and sample evaluation was achieved using MultiWin software. Sampling was automatic via an attached APG64 auto sampler.

The analytical method used consisted of three to five repeat sample analyses (sample volume 100 µL) with a UHQ DI water reverse rinse between samples. Rinses with the sample were also performed before analysis (500 µL) and repeat sample analyses were averaged to obtain the final result. The combustion tube furnace was set to 850°C.

The TOC concentration in solution was determined by a differential method, whereby the TC and IC in the solution were directly measured and TOC was calculated (TOC = TC-IC). Check-standards containing 150 ppm TC, 50 ppm IC and 100 ppm TOC were run alongside samples in order to monitor instrument response. Leachate samples were diluted between 1:10 and 1:1000 based on their expected carbon content in order to ensure that sample concentrations did not exceed 500 ppm to avoid overloading the column and causing excessive reduction in column life. Samples were filtered on a cellulose nitrate filter (0.45 µm) (Whatman) before dilution in order to ensure that the DOC content of the sample was determined rather than the TOC content. This was achieved by drawing up approximately 5 ml of the sample in a syringe and pushing the sample through a pre-washed (UHQ DI) filter paper using a syringe mounted support. The initial portion of the filtered leachate was discarded in order to eliminate any effect of dilution on the sample.

Before initial sample analysis, and subsequently at regular intervals, a multipoint calibration with constant sample volume was performed for the TOC method. This calibration was linked directly to the method. Calibration standards (Table 19) were made up from a standard stock standard solution of 1500 ppm TC (0.22 g sodium carbonate, 0.18 g sodium hydrogen carbonate and 0.31 g glycine in 100 ml UHQ DI).

| TC (mg/L) | IC (mg/L) | TOC (mg/L) |
|------------------|------------------|-------------------|
| 1500 | 500 | 1000 |
| 750 | 250 | 500 |
| 375 | 125 | 250 |
| 300 | 100 | 200 |
| 187.5 | 62.5 | 125 |
| 150 | 50 | 100 |
| 75 | 25 | 50 |
| 37.5 | 12.5 | 25 |
| 15 | 5 | 10 |
| 7.5 | 2.5 | 5 |
| 3 | 1 | 2 |
| 1.5 | 0.5 | 1 |
| 0.75 | 0.25 | 0.5 |

Table 19: Calibration standard concentrations for calibration of the AnalytikJena C/N 3100 using the TOC method.

4.3.5 Gas Chromatography (GC)

During the stabilisation of artificially produced leachates (Appendix B) gas chromatography (GC) was used to determine the carbon dioxide and methane content of gases produced by the waste in order to monitor the maturation of the waste up to and throughout the methanogenic stages of decomposition. Gas was collected from the reaction vessel using Tedlar gas bags (Setek) and samples drawn from the bags for analysis using a 10 mL syringe fitted with a three way valve. The syringe was flushed with the gas from the bag three times with the total volume of the syringe discarded before sampling on the third draw in order to eliminate any residual gasses from the system.

Samples were analysed immediately using a Varian Star 3400CX at 50°C incorporating a 13X, 60-80 mesh molecular sieve (1.5 mm × 4 mm i.d.) and Porapak Q 80-100 mesh 1/8" packed (1.5 m) column. The columns were operated in back-flush mode with a thermal conductivity detector (TCD) at 150°C and filament temperature of 200°C. The sample was injected using a 250 µL injection loop at an injection temperature of 80°C. The carrier gas used was argon at a flow rate of 6 mL/min. Before sample analysis a calibration using a gas standard of known composition (34.88% carbon dioxide and 65.12% methane) was performed. The first sample injection of each sample analysis

was discarded and sample analysis was repeated until three consecutive results that were in agreement with each other were obtained.

4.3.6 Gas Chromatograph - Mass Spectroscopy (GCMS)

Toluene and naphthalene concentrations for contaminant batch tests were determined using headspace gas chromatography mass spectroscopy (GCMS) analysis. This was performed using a Thermo Finnigan Trace GC Ultra attached to a Thermo Finnigan Polaris Q with a 30 meter, 0.25 mm ID, 1 µm Rtx-5MS column (Crossbond 5% diphenyl / 95% dimethyl polysiloxane) (Restek, UK) and a CombiPal auto sampler. The GC method used a gas flow of 1 mL/min with oven temperature increases as shown in Table 20. The mass spectroscopy (MS) method used an ion source temperature of 200°C and maximum ion time of 25 ms. A mass range of 50-650 m/z was detected with a total scan time of 0.58 seconds. Table 21 details the characteristic ions and the retention times for toluene, naphthalene and the internal standards used.

| Initial temp (°C) | Ramp (°C/min) | Target temp (°C) | Hold for (min) |
|-------------------|---------------|------------------|----------------|
| 45 | n/a | 45 | 5 |
| 45 | 8 | 190 | 2 |
| 190 | 15 | 260 | 1 |

Table 20: GC oven temperature increments.

| Contaminant | Characteristic ion (m/z) | Retention time (min) | Internal standard | Characteristic ion (m/z) | Retention time (min) |
|-------------|--------------------------|----------------------|-------------------|--------------------------|----------------------|
| Toluene | 91 | 9.0 | DFB | 114 | 6.1 |
| Naphthalene | 128 | 19.5 | DCB | 146 | 15.6 |

Table 21: GCMS characteristic ions and retention times. NIST MS Search, version 2.0 (Stein *et al*, 2002). 1,4-dichlorobenzene (DCB) and 1,4-difluorobenzene (DFB) were used as internal standards.

GCMS analysis was performed on two 10 mL sub-samples from each sorption or desorption bottle. The samples were agitated at 80°C for ten minutes to volatilise contaminants before a headspace gas sample was taken and injected via the CombiPal auto sampler. Calibration standards ranging from 5-400 µg/L toluene and 0.5-25 µg/L naphthalene (Table 22) were run at the start of each sample set which consisted of six samples in duplicate separated by blanks, and ending with a check standard and blanks.

Each sample was also spiked with an internal standard (100 µg/L 1,4-dichlorobenzene (DCB) or 1,4-difluorobenzene (DFB)) in order to determine the concentration of contaminant present in solution. Concentrated standards (Supelco analytical) of 5000 µg/mL toluene, 5000 µg/mL naphthalene, 5000 µg/mL 1,4-dichlorobenzene and 2000 µg/mL 1,4-difluorobenzene, once decanted from the hypo-vials were stored in 2 mL vials sealed with PTFE septa in the dark at less than 5°C to limit loss of volatiles, sorption to the vial and UV degradation. The calibration standards, internal standards and naphthalene spike solutions were made up from the concentrated standards when required, used immediately and then discarded.

| Toluene (µg/L) | Internal standard (DFB) (µg/L) | Naphthalene (µg/L) | Internal standard (DCB) (µg/L) |
|-------------------|-----------------------------------|-----------------------|-----------------------------------|
| 400 | 100 | 25 | 100 |
| 300 | 100 | 10 | 100 |
| 200 | 100 | 5 | 100 |
| 100 | 100 | 2.5 | 100 |
| 50 | 100 | 1 | 100 |
| 20 | 100 | 0.5 | 100 |

Table 22: Calibration standards for toluene and naphthalene.

4.4 Data Handling and Statistical Methods

This section briefly describes the quantitative analysis of results in this work. These have been grouped by analytical technique or method in order to make them easier to distinguish

4.4.1 Fluorescence and UV-Visible Data

The fluorescence EEM data extracted from the instrument was inputted into Excel and was arranged into a format suitable for R, Sigma Plot and Matlab using Excel macros. The data was then corrected for dilution and a Raman correction applied using Matlab (program written by Galloway (2011)). The corrected data was then inputted into ‘R’ (Lapworth and Kinniburgh, 2008) which was used to apply a baseline correction to the data and pick the fluorescence peaks. Peak picking was achieved by averaging the fluorescence intensities across the peak maxima using R. Contour plots of the EEM were then created from the fully corrected and Raman normalised data using Sigma Plot. The ratios of the peaks were then taken for comparison of the DOC type in different leachates. The UV-Visible spectroscopy data was corrected for dilution only. A baseline correction was automatically applied to the data by the instrument by a UV-visible measurement from a reference cell.

4.4.2 DOC Concentration Data

The concentration of DOC in solution was determined by calculation of the difference between the directly measured total carbon (TC) and total inorganic carbon (TIC). The TC and TIC were observed by averaging between 3 and 5 repeat direct measurements. The number of repeats was automatically determined by the software depending on the variation in the results, with fewer repeats if there was less variation in the repeated results. The averaged values were then used by the software to calculate total organic carbon (TOC). As the samples were pre-filtered before analysis TC, TIC and TOC were actually total dissolved carbon (TdC), dissolved inorganic carbon (DIC) and dissolved organic carbon (DOC). DOC concentration was then either used directly in leachate

comparisons or used in mass balance calculations for the determination of sorption and desorption .

4.4.3 HOC Concentration Data

Batch tests for each different contaminant concentration were performed in duplicate. Samples from each different batch test were also taken in duplicate (Figure 22). These samples were analysed using GCMS. The results were then reprocessed and integrated by hand using the ‘Quan’ software of the instrument and extracted into Excel where a calibration curve was produced and fitted using linear regression. The results were then converted from signals to concentrations using the calibration curve and the duplicate samples for each batch test averaged. This resulted in one data point for each batch test (so two points for every concentration tested) which were used in mass balance calculations for determining sorption and desorption.

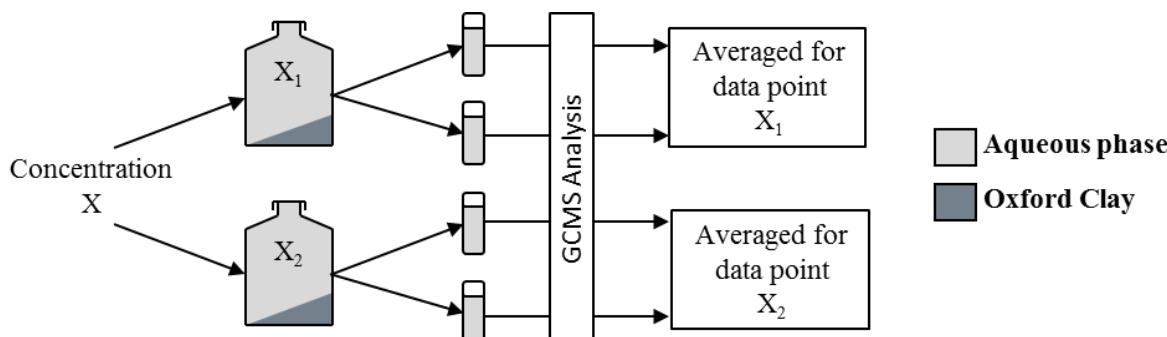


Figure 22: Sampling from sorption batch tests at concentration ‘X’ and subsequent data points obtained for further analysis.

4.4.3.1 Mass Balance Calculations for Sorption and Desorption Batch Testing

Sorption and desorption was determined via a mass balance method using concentration data from either the DOC or HOC sorption and desorption tests. When calculating the sorption and desorption of contaminants, it was assumed that the amount of the compound which is sorbed to the solid phase is equal to that removed from solution. Therefore, by comparing the aqueous concentrations before and after sorption, the mass

balance of the compounds can be used to determine the amount of the compound remaining sorbed to the solid phase (Equation 12).

$$C_s = (C_{aq\ initial} - C_{aq\ final}) \times V/M \quad [12]$$

Where $C_{aq\ initial}$ = the aqueous concentration of the target compound in the starting (pre-sorption) solution ($\mu\text{g/L}$)

$C_{aq\ final}$ = the aqueous concentration of the target compound in the final (post-sorption) solution ($\mu\text{g/L}$)

V = the volume of leachate used (L)

M = the mass of solid phase used (g)

C_s = the amount of compound sorbed to the solid phase ($\mu\text{g/g}$)

$C_{aq\ initial}$ must be corrected in order to account for any sorption of the compound by the container or loss by volatilisation. This was done using a blank control sample which contained no solid phase.

When considering the mass balance for the desorption isotherm it is assumed that the amount desorbed from the solid phase is equal to the amount that is measurable in the aqueous phase post desorption step. However, some of the original (post sorption step) aqueous phase is retained by the solid phase after centrifugation. This retained aqueous phase is impossible to remove from system without impacting the measurement of C_s through loss of contaminant by desorption, volatilisation or loss of solids. Therefore the target compound in the retained aqueous phase must be accounted for. This can be done by calculating the volume of aqueous phase remaining in the system through differences in mass, expressed as a fraction of the leachate in the bottle (r) (Equation 13 and Figure 23), and applying the measured $C_{aq\ final}$ from the sorption step

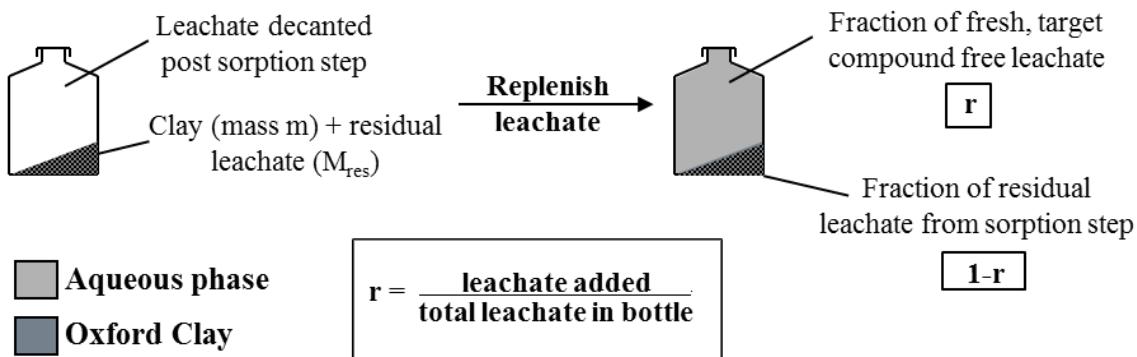


Figure 23: A graphical summary of the origin of the value ‘r’ for use in calculation of the contribution of target compounds in the residual leachate (from the sorption step) to the overall aqueous target compound concentration in order to eliminate it from desorption mass balance calculations.

$$r = \text{leachate added} / \text{total leachate in bottle}$$

[13]

Where:

$$\begin{aligned} \text{Total leachate in bottle} &= (M_{\text{des test}}) - M_{\text{clay}} - M_{\text{bottle}} - M_{\text{cap}} \\ \text{Leachate added} &= (M_{\text{des test}}) - M_{\text{bottle}} - M_{\text{cap}} - (M_{\text{clay}} + M_{\text{res}}) \end{aligned}$$

$M_{\text{des test}}$ is the total weight of the desorption test bottle after refilling and sealing ($M_{\text{bottle}} + M_{\text{cap}} + M_{\text{clay}} + \text{total leachate in bottle}$) (g), M_{clay} is the dry mass of the clay (g), M_{bottle} is the mass of the sorption bottle (g), M_{res} is the residual leachate in the bottle post centrifuge and decant (g), and M_{cap} is the mass of the cap and septa used to seal the test bottle (g).

The fraction ‘r’ is the amount of leachate added, so the fraction ‘1-r’ is equal to the residual leachate in the centrifuged solid phase. Applying the aqueous concentration of the target compound in the final (post-sorption) solution and incorporating it into the desorption mass balance (Mass desorbed = Mass in aqueous phase (post desorption) – Residual mass (post sorption)) results in Equation 14.

$$C_{s \text{ pd}} = (C_{aq \text{ pd}} - C_{aq \text{ final}} (1-r)) \times V/M$$

Where:

$C_{aq \text{ pd}}$ = the aqueous concentration of the target compound in the starting (post-desorption) solution ($\mu\text{g/L}$)

$C_{aq \text{ final}}$ = the aqueous concentration of the target compound in the final (post-sorption) solution ($\mu\text{g/L}$)

V = the volume of leachate used (L)

M = the mass of solid phase used (g)

$C_{s \text{ pd}}$ = the amount of compound sorbed to the solid phase post desorption ($\mu\text{g/g}$)

4.4.4 Sorption Isotherms

Isotherms of C_{aq} vs C_s were plotted for DOC and HOC sorption and desorption tests using Sigma plot. As detailed above (Figure 22), each testing concentration had two data points associated with it which were the average of duplicate samples. The isotherms were fitted with both linear and Freundlich regressions using least squares method, where the overall solution minimises the sum of the squared errors (residuals) across all data points (Gardiner, 1997). This was performed automatically by the Sigma plot software. The R^2 values of the regressions, Equation 15 (Gardiner, 1997) were calculated automatically by Sigma plot and used to determine which model the data was better fitted to (a higher R^2 value indicated a better fit).

$$R^2 = \frac{\text{Variation due to regression model fitted}}{\text{Residual variation}} \quad [15]$$

95% confidence limits for the regressions were calculated using Sigma Plot, allowing the comparison of the isotherms. The 95% confidence limits denote the range of values within which 95% of the experimental data will lie (for the given experimental effect). They are constructed in an additive manner (Equation 16, as detailed by Gardiner (1997)). The isotherms were deemed significantly different when their 95% confidence limits were independent of each other. The value of p was calculated by Sigma Plot software upon generation of the 95% confidence interval of data fitted to an isotherm. p values indicated the fit of the data to the 95% confidence interval of a particular regression and the likelihood of the data fulfilling the null hypothesis. A p value of <0.05 disagrees with the null hypothesis and indicated that the data fits the isotherm and the result is unlikely to be due to random variation in the system.

[16]

$$\text{Confidence limit} = \text{estimate} \pm \text{critical value} * \text{function of critical value}$$

A two-tailed t-test (Gardiner, 1997; Miller and Miller, 2010) was then performed on the isotherms. A two tailed approach was selected since the isotherms being compared had

the potential to have values either higher or lower than the target for comparison, rather than operating in one direction only.

As the comparison of one isotherm against another was required, a regression was compared against a specific target (Gardiner, 1997); Equation 17.

$$t = (b_1 - b_2) / S_{b1} \quad [17]$$

Where: b_1 = the slope of the reference isotherm

b_2 = the slope of the target isotherm

S_{b1} = the standard error in the reference slope

However, as our target is another regression which has an error itself, Equation 17 is not ideal for this situation. Therefore we have to account for the error in the target slope as well as in the reference slope, which results in Equation 18.

$$t = (b_1 - b_2) / \sqrt{(S_{b1}^2 + S_{b2}^2)} \quad [18]$$

Where b_1 , b_2 and S_{b1} are the same as defined above and S_{b2} is the standard error in the target slope.

Calculated t- values were obtained using Equation 18. Values for t critical were obtained from statistical tables (Gardiner, 1997). Where calculated t values were greater than the critical t values the difference between the two isotherms was significant ($T > 0$).

It should be noted that using t values to determine significance of the isotherm is a numerical application of the more visual 95% confidence limits. This is because t critical is determined at a p value of <0.05 ($\alpha = 0.05$), which is equivalent to a 95% confidence interval.

5. Results

5.1 DOC Sorption and Desorption to the Oxford Clay

Isotherms for MSW leachate sorption and desorption to the Oxford Clay are shown in Figure 24 and the sorption and desorption parameters are summarised in Table 23.

| | | Linear | | Freundlich | | | |
|-------------------------|------------|-------------------------|----------------|--------------------------|--|------|----------------|
| | | K _d (L/g) | R ² | K _{oc} (L/g) | K _f (mg ¹⁻ⁿ L ⁿ /g) | n | R ² |
| Full data set | Sorption | 0.0014 | 0.96 | 0.026 | 0.0039 | 0.86 | 0.97 |
| | Desorption | 0.016 | 0.70 | | 0.0026 | 1.42 | 0.74 |
| Omitting highest points | Sorption | 0.0014 | 0.96 | | 0.0039 | 0.86 | 0.97 |
| | Desorption | 0.016 | 0.70 | | 0.0026 | 1.42 | 0.74 |

Table 23: Sorption and desorption parameters for MSW leachate DOC sorption and desorption to and from Oxford Clay.

The sorption of MSW leachate DOC to Oxford Clay was equally well fitted both by linear and Freundlich isotherms (Equations 2 and 5). When fitted to a Freundlich isotherm, the K_f and n values for sorption were 0.0039 mg¹⁻ⁿ Lⁿ/g and 0.86 respectively indicating that the sorption of DOC increased with increasing solution concentration but that sorption became less favourable as the aqueous concentration increased toward a sorption maximum (though the sorption maximum was not reached in this work). When fitted to the linear model, the K_d value for DOC sorption was 0.0014 L/g indicating an increase in sorption of DOC with increasing aqueous concentration. The difference in fit between linear and non-linear isotherms was, however, negligible (R² 0.96 and 0.97 respectively). The R² values were not skewed by the highest point on the isotherm as its removal resulted in no alteration to the isotherm parameters or fit of the isotherm as shown in Figure 25 and Table 23 (accurate to two significant figures).

The desorption of MSW leachate DOC from Oxford Clay into DOC free synthetic leachate was better fitted by a non-linear; Freundlich isotherm (Table 23) than a linear

isotherm (R^2 values 0.70 and 0.74 for linear and Freundlich isotherms respectively). As with DOC sorption, the removal of the highest points had no effect on the isotherm parameters, indicating that the isotherm was not skewed toward non-linearity by the highest points alone (Table 23; Figure 25).

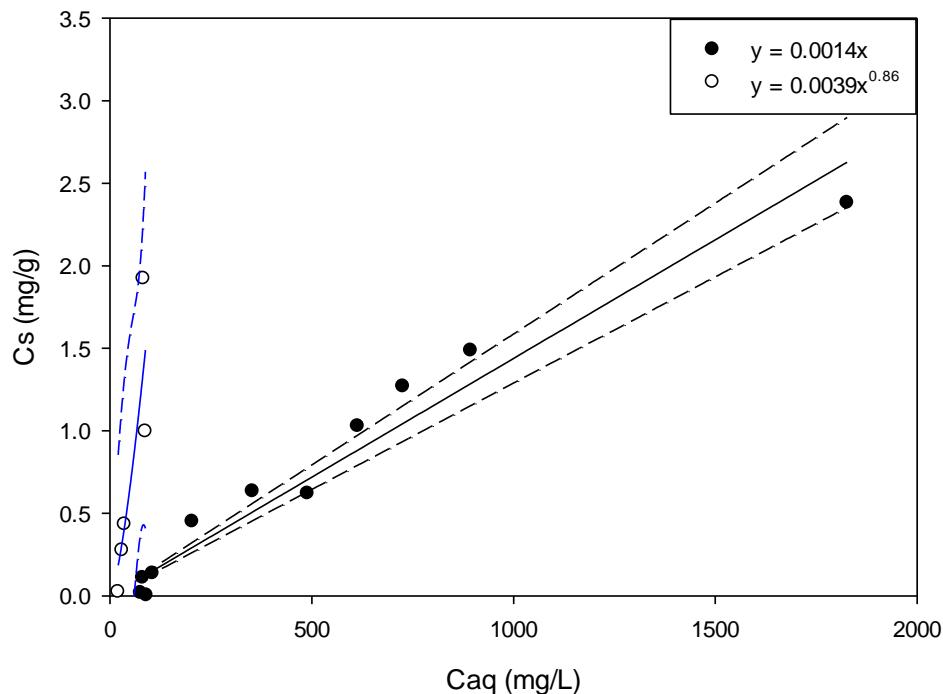


Figure 24: Sorption and desorption isotherms of MSW leachate DOC to Oxford Clay. The 95% confidence limits of the regressions are indicated by dashed lines and the isotherms by solid lines. Filled data points indicate sorption data and open points represent desorption data.

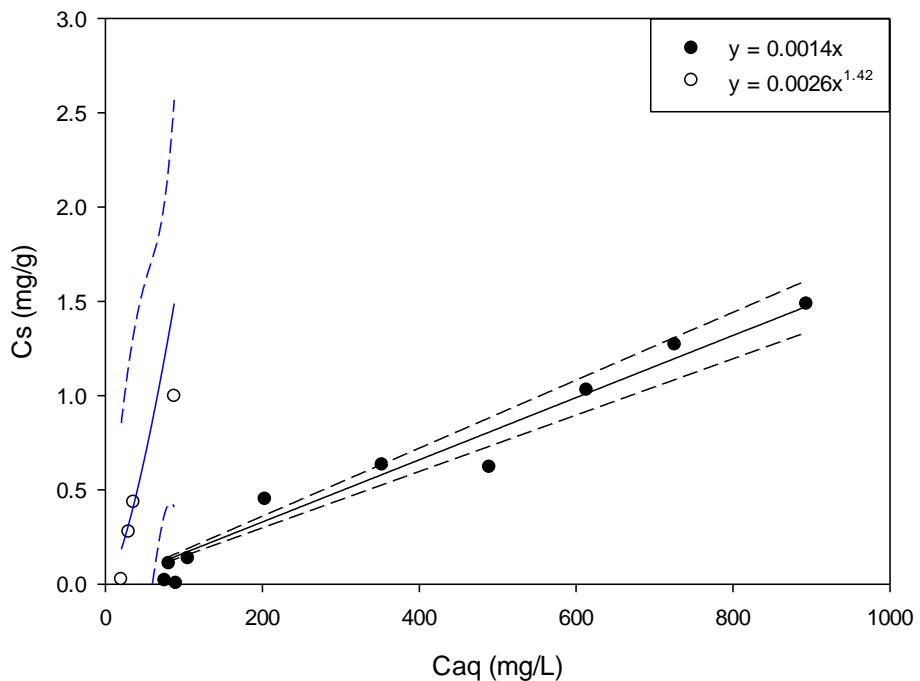


Figure 25: DOC sorption and desorption isotherms to the Oxford Clay omitting the highest data point in each case.

Fluorescence ratios from EEM spectra of the leachates were used to identify the types of DOC present in solution and to determine whether any types of DOC were preferentially sorbed to the Oxford Clay. Tables 24 and 25 show the differences in fluorescence ratios of the aqueous phase before and after the sorption and desorption steps at the different leachate dilutions.

| % leachate in solution | [DOC] (mg/L) | EC (mS/m) | Sorption to bottle only (baseline) | | | | | | After Sorption to clay | | | | | |
|------------------------|--------------|-----------|------------------------------------|------|------|------|------|------|------------------------|------|------|------|------|------|
| | | | B:D | B:E | B:F | D:E | D:F | E:F | B:D | B:E | B:F | D:E | D:F | E:F |
| 100 | 2348 | 42.9 | 1.10 | 0.96 | 0.69 | 0.87 | 0.63 | 0.73 | 1.01 | 0.73 | 0.65 | 0.72 | 0.64 | 0.89 |
| 20 | 423 | 42.9 | 1.40 | 0.65 | 0.59 | 0.47 | 0.42 | 0.90 | 1.05 | 0.77 | 0.62 | 0.73 | 0.59 | 0.80 |
| 10 | 205 | 42.7 | 1.11 | 0.94 | 0.69 | 0.85 | 0.62 | 0.73 | 0.89 | 1.00 | 0.67 | 1.12 | 0.76 | 0.68 |
| 2 | 42 | 42.9 | 0.88 | 1.57 | 0.78 | 1.79 | 0.89 | 0.50 | 1.10 | 0.70 | 0.57 | 0.63 | 0.52 | 0.82 |
| 1 | 7.2 | 42.8 | 1.56 | 0.66 | 0.57 | 0.42 | 0.37 | 0.87 | 2.27 | 0.30 | 0.40 | 0.13 | 0.17 | 1.31 |
| 0.2 | 3.4 | 42.8 | 1.19 | 1.10 | 0.65 | 0.93 | 0.55 | 0.59 | 3.09 | 0.33 | 0.39 | 0.11 | 0.13 | 1.18 |
| 0.1 | 1.8 | 43.1 | 1.10 | 1.14 | 0.63 | 1.03 | 0.57 | 0.55 | 2.72 | 0.30 | 0.38 | 0.11 | 0.14 | 1.27 |

Table 24: MSW leachate fluorescence ratios before and after the sorption step at different dilutions. Starting fluorescence was taken from control bottles containing no clay in order to account for sorption to the inside of the bottle and the septa. An increase in fluorescence ratio is indicated by red shading and a decrease in ratio is indicated by blue shading.

| % leachate in solution | [DOC] (mg/L) | EC (mS/m) | Desorption from bottle | | | | | | Desorption from clay | | | | | |
|------------------------|--------------|-----------|------------------------|------|------|------|------|------|----------------------|------|------|------|------|------|
| | | | B:D | B:E | B:F | D:E | D:F | E:F | B:D | B:E | B:F | D:E | D:F | E:F |
| 100 | 2348 | 42.9 | 0.87 | 1.5 | 0.85 | 1.65 | 0.97 | 0.59 | 1.40 | 0.68 | 0.61 | 0.48 | 0.43 | 0.89 |
| 20 | 423 | 42.9 | 0.69 | 2.1 | 0.95 | 3.10 | 1.37 | 0.44 | 1.08 | 1.33 | 0.80 | 1.22 | 0.74 | 0.60 |
| 10 | 205 | 42.7 | 1.06 | 4.2 | 1.53 | 3.98 | 1.45 | 0.36 | 1.33 | 0.97 | 0.77 | 0.73 | 0.58 | 0.79 |
| 2 | 42 | 42.9 | 1.69 | 11.2 | 2.60 | 6.63 | 1.54 | 0.23 | 2.45 | 0.68 | 0.63 | 0.28 | 0.26 | 0.93 |
| 0.2 | 3.4 | 42.8 | 2.23 | 17.9 | 3.18 | 7.99 | 1.42 | 0.18 | 2.92 | 0.71 | 0.60 | 0.24 | 0.21 | 0.85 |
| 0.1 | 1.8 | 43.1 | 0.89 | 12.1 | 2.13 | 13.6 | 2.40 | 0.18 | 2.94 | 0.65 | 0.56 | 0.22 | 0.19 | 0.87 |

Table 25: Difference in fluorescence ratios observed in the leachate after DOC desorption from the solid phase into DOC free synthetic leachate. Starting fluorescence was taken from control bottles containing no clay in order to account for sorption and desorption to the inside of the bottle and the septa. An increase in fluorescence ratio is indicated by red shading and a decrease in ratio is indicated by blue shading. Each row refers to different leachate dilutions. Details for the 1% leachate solution are omitted as the bottles containing the samples failed during testing.

For the sorption step leachate concentrations in solution of less than two percent by volume showed a clear trend in the differences between fluorescence ratios of DOC sorption to the bottle alone and to the bottle and the clay together (Table 24). An increase in the B:D ratio (tryptophan-like to tyrosine-like, from 0.88-1.56 to 1.10-3.09) and E:F ratio (fulvic-like to humic-like, from 0.50-0.87 to 0.82-1.31) was observed. The changes in B:D ratio indicated either a decrease in tyrosine-like DOC or increase in tryptophan-like DOC. The change in E:F ratio indicated either a decrease in HL or an increase in FL DOC between DOC sorption to the bottle alone and sorption to the bottle and clay. A decrease was also observed in the B:E, B:F, D:E and D:F ratios; from 0.66-1.57 to 0.3-0.70, from 0.57-0.78 to 0.38-0.57, from 0.49-1.79 to 0.11-0.63 and from 0.37-0.89 to 0.13-0.52 respectively. This indicated an increase in the proportion of HSL DOC (peaks E and F) in solution relative to PL DOC (peaks B and D).

Therefore, the change in ratios may indicate either an increase in HSL DOC or a decrease in PL DOC in solution. At low DOC concentrations an increase in HSL DOC may originate from desorption of DOC from the solid phase (Kaiser *et al*, 1996). Preliminary work on the desorption of DOC from the Oxford Clay into a DOC free synthetic leachate (detailed in Appendix A) carried out at the same m:v ratio as this sorption test (Table 26) determined that this was likely to be the case.

| M:V (g/mL) | DOC (mg/L) | % OC desorbed | B:D | B:E | B:F | D:E | D:F | E:F |
|---------------|---------------|------------------|------|------|------|------|------|------|
| 0.17 | 33.4 | 3.00 | 4.14 | 0.50 | 0.50 | 0.12 | 0.12 | 1.00 |

Table 26: Preliminary work fluorescence data for the desorption of DOC from Oxford clay into a DOC free synthetic leachate, part of Figure A1. Fluorescence ratios are detailed in Section 4.3.1.3.

The ratios of the fluorescence peak intensities from the preliminary work indicated that while the desorption of both PL and HSL DOC from the Oxford Clay into the DOC free leachate occurred, the proportion of DOC desorbed with HSL character was greater than that with PL character. This was indicated by the fluorescence ratios for B:E, B:F, D:E and D:F having a value of less than one, and was further supported by the fluorescence intensity of the humic-like peak F, which increased with increasing m:v ratio, whereas the other peaks stabilised (Appendix A, Figure A1).

Examining the PL DOC desorbed from the clay, the high value for B:D ratio (4.14) alongside D:E and D:F ratios that were lower than the B:E and B:F ratios (0.12 compared to 0.50) indicated that of the DOC desorbed from the clay, tryptophan-like rather than tyrosine-like DOC dominated. The concentration of the DOC desorbed from the clay was 33.4 (+/- 2.01) mg/L; which was greater than the concentration of DOC present in 0.1-1% MSW leachate solutions (1.8-7.2 mg/L); and close to the DOC concentration in the 2% MSW leachate solution (42 mg/L). The increase in HSL DOC in solution relative to the PL DOC observed in the sorption step at low DOC concentrations was therefore attributed to the desorption of HSL DOC from the Oxford Clay.

During the sorption step, at leachate concentrations above 2% (>42 mg/L DOC), although the trends in leachate fluorescence peak ratios are less clear, preferential sorption of HSL DOC to the clay was observed. This was demonstrated by the increase in the PL:HSL DOC fluorescence peak ratios which relate to either an increase in PL DOC in solution or a decrease in HSL DOC in solution. As an increase would be due to the desorption of PL DOC from the clay, which was shown by preliminary work to be predominantly HSL like, this could not account for an increase in solution phase PL DOC. Therefore, a decrease in HSL DOC through preferential sorption of HSL DOC to Oxford Clay is indicated.

Compared to the desorption of DOC from the bottle alone (post sorption step), desorption of DOC from the bottle and clay into a DOC free leachate showed a decrease in the PL:HSL fluorescence peak ratios at all concentrations studied; B:E (7.85-1.45 to 1.33-0.65); B:F (3.18-0.85 to 0.80-0.56); D:E (13.64-1.65 to 1.22-0.22); and D:F (2.40-0.97 to 0.74-0.19). This indicated a drop in PL DOC in solution in relation to HSL DOC, which is likely to be due to preferential desorption of HSL DOC from the clay increasing the proportion of HSL DOC in solution. This was supported by the desorption of HSL DOC from the Oxford Clay into solutions with a low DOC concentration (two percent leachate or less by volume) as identified during the sorption step.

Preferential desorption of HSL DOC from the clay was also observed at greater than 42 mg/L DOC in solution. This was attributed to fractionation of the DOC onto the clay at the sorption stage resulting in DOC available for desorption from the clay which was largely HSL in nature (Kaiser *et al*, 2000). This was also in agreement with Mikutta *et al* (2007) who observed that the affinity of compounds for the clay affected their desorption behaviour, and may also be an explanation for hysteresis effects.

DOC sorption was reversible, and at low DOC concentration in solution, HSL DOC occurring both naturally within and sorbed to the clay may desorb from the solid phase into solution. This may result in increased desorption of HOCs from the clay at low aqueous DOC concentrations due to desorption of HOCs bound to HSL DOC. This may result in an additional source of pollution from the landfill when leachate DOC levels fall below 42 mg/L^(a). This may occur after the landfill has been closed and the post-closure monitoring period of the landfill has finished. Longer term monitoring of the landfill and the surrounding environment may therefore be required should the desorption of HOCs from the clay be significant.

(^a) The DOC concentration at which DOC desorption from the Oxford Clay and preferential HSL DOC sorption to the Oxford Clay intersect is unlikely to be precisely at the 2% leachate in solution (42mg/L) point, but rather between 10% and 2% leachate in solution (205-42 mg/L) range. The alteration of behaviour at 2% leachate is due to the dilutions selected for study and further work would be required to further refine the point at which behaviour alters.

5.1.1 DOC Sorption and Desorption to the Oxford Clay Summary and Implications for HOC Attenuation

- Sorption of leachate DOC to Oxford Clay was linear at the DOC concentrations tested.
- At low aqueous DOC concentrations in solution (<= 42 mg/L)^(a), desorption of DOC from Oxford Clay into solution was observed, but at higher concentrations HSL DOC was preferentially sorbed to Oxford Clay relative to PL DOC.
- DOC sorption to Oxford Clay was reversible, with desorption of DOC observed from Oxford Clay.
- HSL DOC was observed to preferentially desorb from Oxford Clay into solution.

The sorption of HOCs to the Oxford Clay may therefore be increased due to complex formation with HSL leachate (co-sorption), or via cumulative sorption. DOC was preferentially sorbed to Oxford Clay and HSL DOC sorbing to Oxford Clay may increase the OC content solid phase, enhancing the sorption of HOCs to clays (Thornton *et al*, 2000). Sorption of HOCs to Oxford Clay may, however, be decreased due to the competitive sorption of HSL DOC. Desorption of HOCs from Oxford clay may be increased if they have bound to, and therefore desorb alongside HSL DOC into solution. Desorption of HOCs may also be increased by HSL DOC desorption resulting in a more hydrophobic aqueous phase, making HOC desorption more favourable.

DOC concentrations low enough for DOC desorption from Oxford Clay are not likely to be realistically achieved during the active lifetime of a landfill. There may be a point during the post closure lifetime of a landfill at which the DOC concentration in the leachate falls sufficiently to allow DOC or HOC-DOC complexes to be released from the solid phase into solution. This process may be accelerated in landfills where flushing of the waste is used to speed up removal of soluble contaminants (Section 2.2.1.1). However, if this does occur, the timescales involved are likely to be in the order of many decades or centuries as current closed landfills may contain DOC at concentrations in the order of g/L decades after closure (Christensen *et al*, 1998).

There is the potential for the release of DOC or DOC-HOC complexes from the solid phase at low leachate DOC concentrations to result in the liner becoming a secondary contamination source; releasing HOCs into solution after the polluting potential of the landfill has been deemed negligible. However, the timescales involved for this to occur are likely to be such that biological degradation processes may reduce the concentrations of the contaminants bound to the clay (Guerin and Boyd, 1997). The post-closure monitoring period of the landfill may therefore need to be extended in order to accommodate this scenario.

5.2 Sorption and Desorption of Toluene to the Oxford Clay

Isotherms for toluene sorption and desorption for Oxford Clay in aqueous phases (leachates) with differing DOC compositions (described in Section 4.2.3) are shown in Figures 26 and 27. The linear and Freundlich isotherm parameters for sorption and desorption are shown in Table 27. Those isotherms which were better fitted by a Freundlich isotherm than a linear isotherm were linearized via log-linearization of the Freundlich isotherm (Figure 27). MSW and HA leachates were used at their original concentrations and additionally at dilutions of 1:20 and 1:2 respectively in order to normalise DOC concentration and so examine the effect of DOC type on sorption and desorption behaviour.

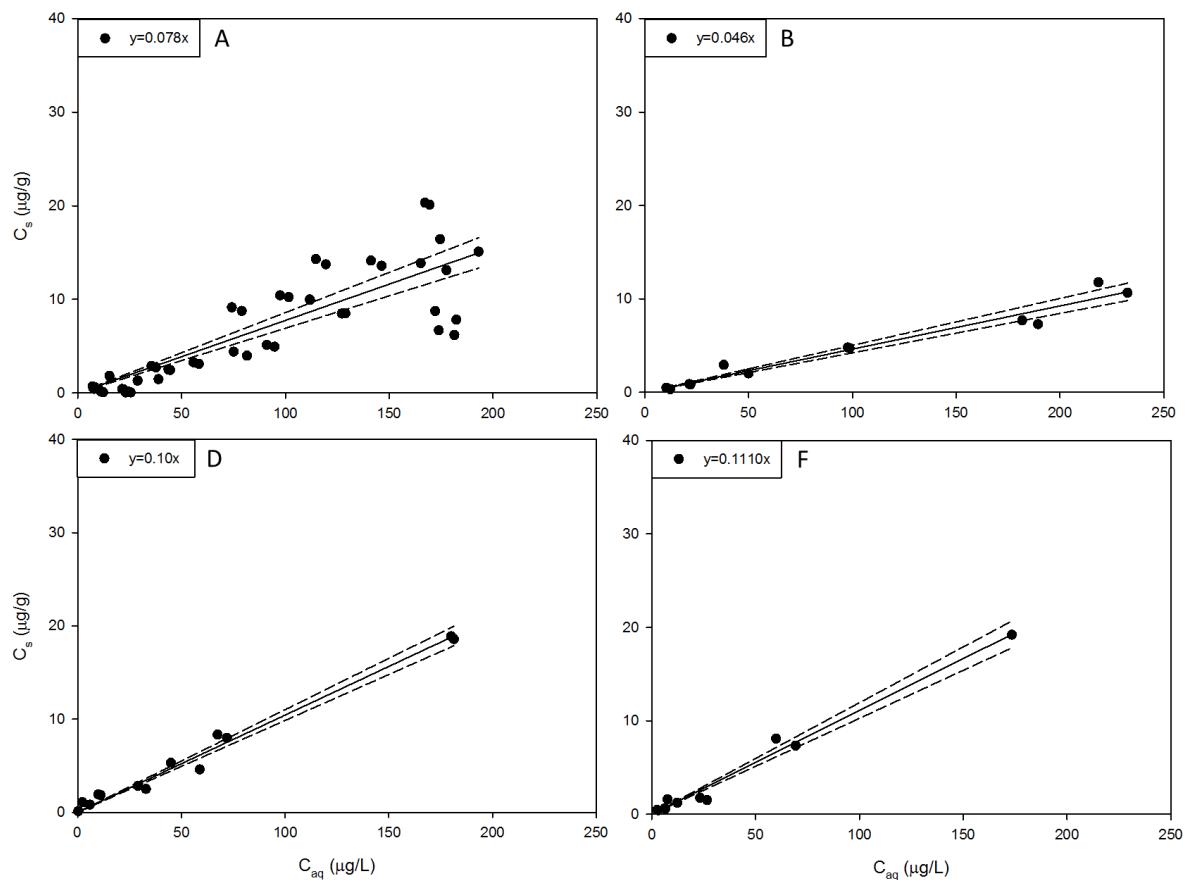


Figure 26: Linear toluene sorption and desorption isotherms for Oxford Clay using different leachates as the aqueous phase; A (DOC free), B (MSW), D (MBT) and F (Diluted MSW). Solid points indicate sorption data and open points indicate desorption data. Dashed lines indicate the 95% confidence interval of the isotherm.

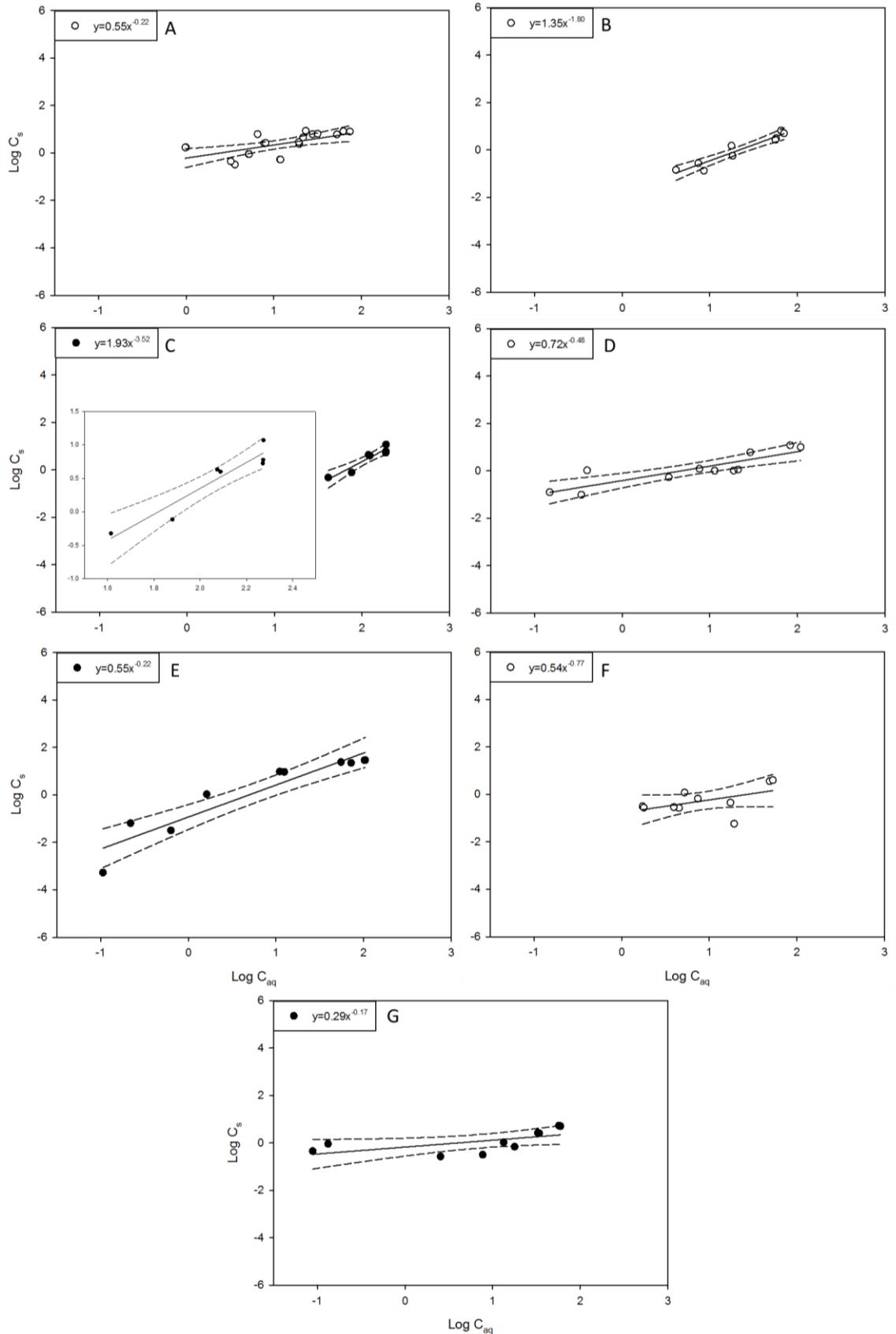


Figure 27: Linearized Freundlich isotherms (Section 2.2.3.3) for sorption and desorption of toluene for Oxford Clay in different leachates. Solid data points indicate sorption data and open data points indicate desorption data. Dashed lines denote the 95% confidence limits of the isotherm.

| Leachate | Stage | Linear | | Freundlich | | |
|----------|-------------|----------------------|----------------|--|-------------------|--|
| | | K _d (L/g) | R ² | K _f ($\mu\text{g}^{1-n}\text{L}^n/\text{g}$) | n | R ² (C _s =K _f C _{aq} ⁿ form) |
| DOC free | Sorption | 0.078 | 0.73 | 0.081 | 0.99 | 0.73 |
| | Desorption* | 0.14 | 0.45 | 0.80 ^a | 0.55 ^a | 0.62 |
| MSW | Sorption | 0.046 | 0.96 | 0.047 | 1.00 | 0.96 |
| | Desorption* | 0.070 | 0.83 | 0.16 ^a | 1.35 ^a | 0.86 |
| AMSW | Sorption* | 0.038 | 0.63 | 0.03 ^a | 1.93 ^a | 0.70 |
| | Desorption | --- | --- | --- | --- | --- |
| MBT | Sorption* | 0.10 | 0.98 | 0.62 ^a | 0.72 ^a | 0.99 |
| | Desorption* | 0.11 | 0.54 | 0.66 ^a | 0.61 ^a | 0.88 |
| HA | Sorption* | 0.31 | 0.91 | 0.39 ^a | 1.35 ^a | 0.98 |
| | Desorption | --- | --- | --- | --- | --- |
| MSW 1:20 | Sorption | 0.11 | 0.98 | 0.10 | 1.02 | 0.98 |
| | Desorption* | 0.068 | 0.84 | 0.46 ^a | 0.54 ^a | 0.88 |
| HA 1:2 | Sorption* | 0.085 | 0.93 | 0.84 ^a | 0.29 ^a | 0.96 |
| | Desorption | --- | --- | --- | --- | --- |

Table 27: Isotherm parameters for toluene sorption and desorption to Oxford Clay. The data was fitted to linear ($C_s=K_d C_{aq}$) and Freundlich ($C_s=K_f C_{aq}^n$) models. Where the isotherm was better fitted by a non-linear isotherm (*) K_f and n are derived from the log linearization of the Freundlich isotherms ^(a); Section 2.2.3.3)

5.2.1 Sorption

As shown in Table 27, sorption isotherms for DOC free, MSW, MBT and diluted MSW leachates (Figure 26) fitted equally well to linear and non-linear isotherms with near identical R² values. For simplicity these were modelled as linear with the sorption of toluene seen to increase as the aqueous concentration of toluene increased. Sorption isotherms for AMSW, HA and diluted HA leachates (Figure 27) were better fitted to Freundlich isotherms by their R² values (Table 27). The n values for the sorption of AMSW and HA leachates were greater than one indicating that as the aqueous concentration of toluene increased, sorption of additional toluene to the clay became more favourable. The n-value for the sorption of diluted HA leachate was less than one indicating that toluene sorption increased with increasing concentration in solution towards a sorption maximum. As the sorbent used in the batch sorption tests was identical, this difference in sorption behaviour of toluene between leachates of differing DOC concentration is likely to be due to the aqueous phase. This may be due to the higher concentration of DOC in the AMSW and HA leachates creating additional sorption

sites for toluene on the Oxford Clay by multi-layer sorption, whereas the lower DOC concentration of the diluted HA leachate is not saturating the system and sorbing to surface binding sites only. Alternatively, the higher concentration of DOC in the diluted HA and AMSW leachates may be aiding the sorption of toluene via cumulative or co-sorption processes to a greater extent than the diluted HA.

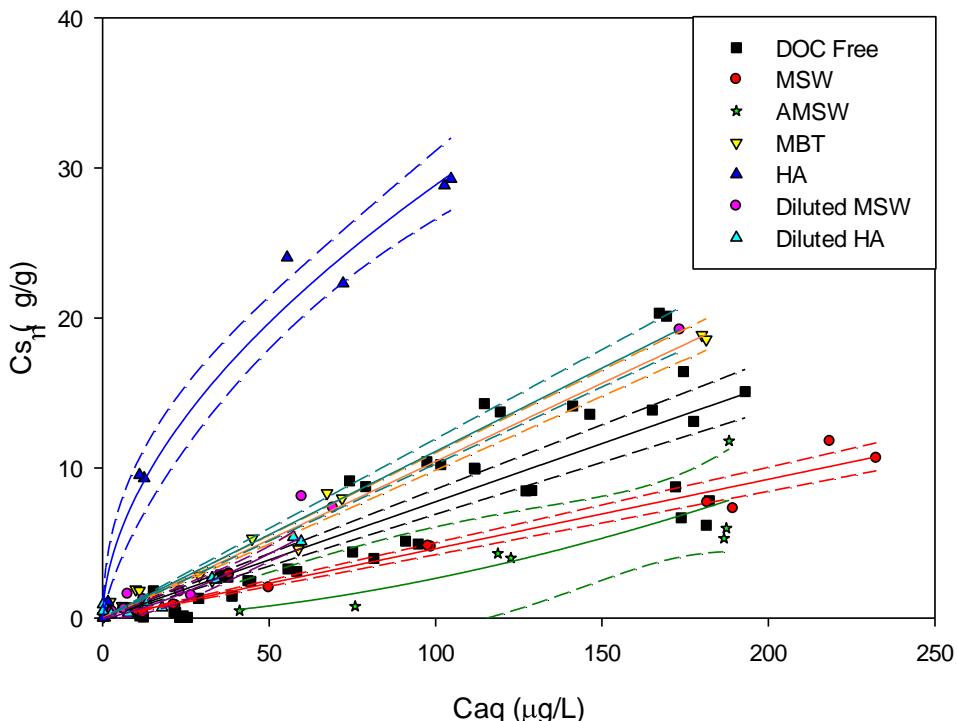


Figure 28: Isotherms for toluene sorption to Oxford Clay in different aqueous phases.

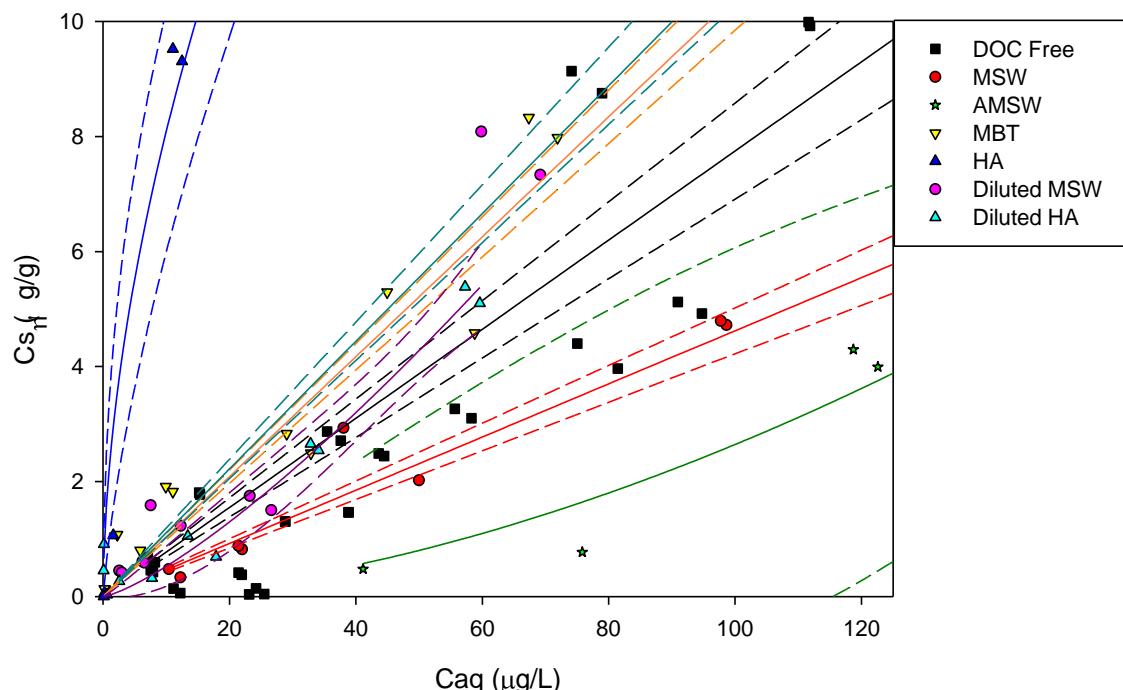


Figure 29: Expanded view of isotherms for toluene sorption to Oxford Clay in different aqueous phases.

The sorption of toluene to Oxford Clay varied with type of leachate solution in a specific order as shown below and illustrated in Figures 28 and 29 HSL maturity (indicated by HIX values) (Section 2.3.1.4) and DOC concentration of the leachates are also shown for comparison.

Sorption (K_d ; L/g):

| | | | | | | | | | | | | |
|------|---|-------------|-----------|------|---|------------|-----------|----------|---|-------|---|-------|
| HA | > | Diluted MSW | \approx | MBT | > | Diluted HA | \approx | DOC free | > | MSW | > | AMSW |
| 0.31 | | 0.11 | | 0.10 | | 0.085 | | 0.078 | | 0.046 | | 0.038 |

HSL maturity (HIX; F:B ratio, Section 2.3.1.4):

| | | | | | | | | | | |
|------|-----------|------------|---|------|---|-----|---|-----|-----------|-------------|
| HA | \approx | Diluted HA | > | AMSW | > | MBT | > | MSW | \approx | Diluted MSW |
| 11.4 | | 10.8 | | 2.9 | | 1.7 | | 1.4 | | 1.4 |

DOC concentration (mg/L):

| | | | | | | | | | | | | |
|------|---|------|---|-----|---|------|-----------|------------|-----------|-------------|---|----------|
| MSW | > | MBT | > | HA | > | AMSW | \approx | Diluted HA | \approx | Diluted MSW | > | DOC free |
| 2268 | | 1051 | | 238 | | 136 | | 122 | | 116 | | 0 |

The difference in sorption between diluted MSW and MBT leachates was not statistically significant as they were within each other's 95% confidence limits ($t=-0.50$). This was also the case with the diluted HA and MBT leachates; and DOC free and AMSW leachates as they were also within each other's 95% confidence limits ($t=-1.78$ and -0.68 respectively; indicating that these isotherms were similar) (Figure 28, Section 4.4.4). The AMSW leachate was also statistically similar to sorption in the DOC free and MSW leachates ($t=-0.79$ and -1.71 respectively).

Compared to toluene sorption in DOC free leachate (K_d 0.078 L/g); more sorption of toluene was observed in MBT, HA and diluted MSW leachates (K_d 0.10, 0.31, and 0.11 L/g, respectively). Less sorption was observed in MSW leachate (K_d 0.046 L/g) than in DOC free leachate. Figure 30 compares the K_d to the DOC concentration and demonstrated that the concentration of DOC in solution was not directly related to the amount of toluene sorption with a p value of 0.66 indicating no significant trend (in agreement with the null hypothesis), Section 4.4.4. This was supported by the diluted HA leachate having a K_d value lower than that of neat HA leachate but the diluted MSW leachate having a K_d higher than that of the neat MSW leachate. The diluted HA and AMSW (low concentration, high maturity DOC) isotherms were not statistically different

($t=-0.68$), but the diluted MSW leachate had a K_d higher than the K_d of AMSW leachate; indicating that the type of DOC in solution may be playing a role in sorption behaviour as well as DOC concentration.

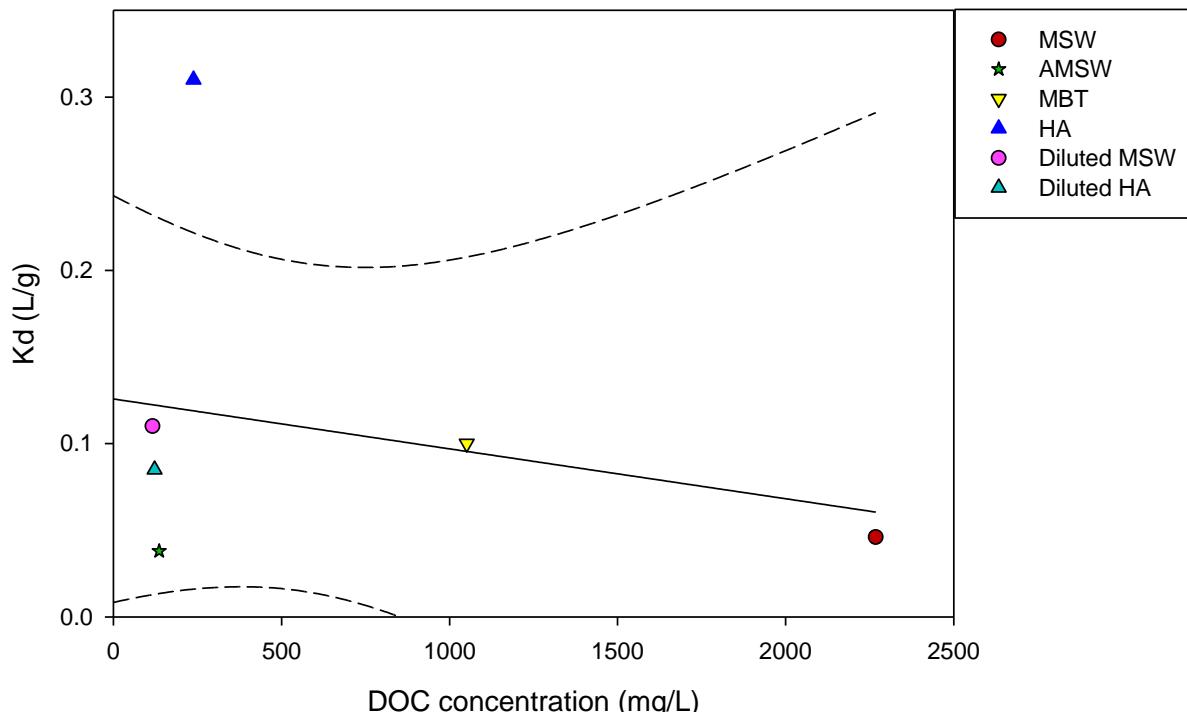


Figure 30: DOC concentration of leachates plotted against the linear sorption coefficients (K_d) of toluene sorption isotherms.

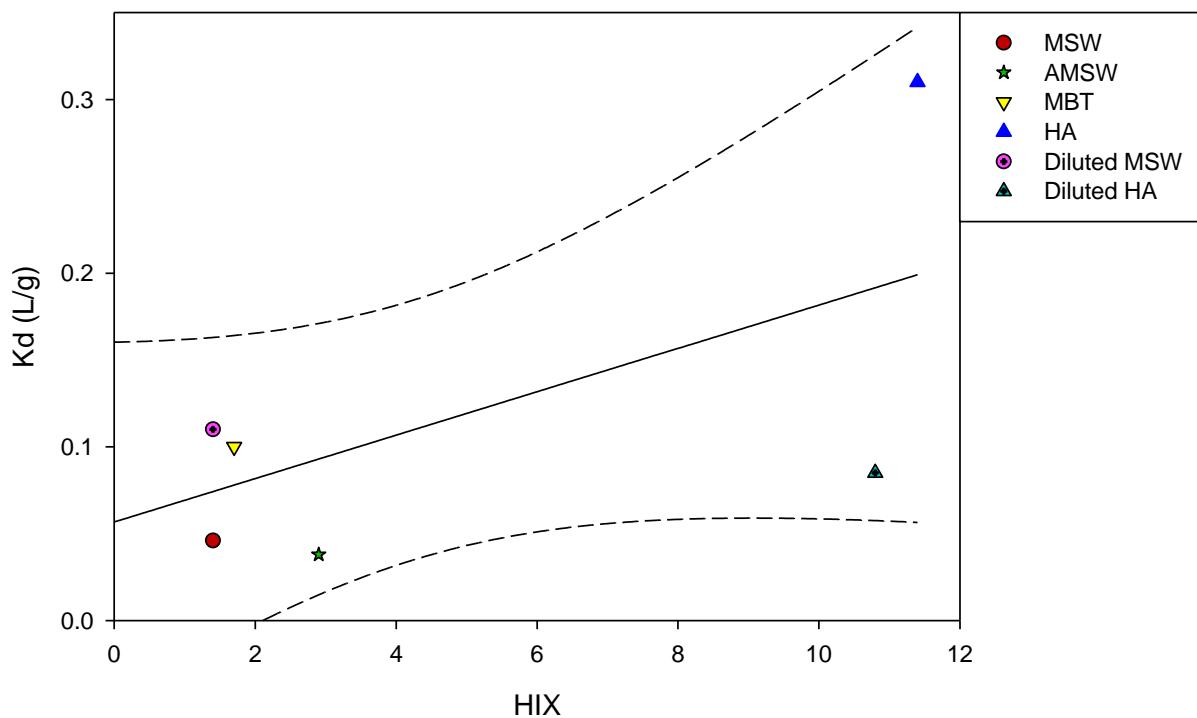


Figure 31: HSL maturity of leachates (inferred from the fluorescence ratio, Section 2.3.1.4) plotted against the sorption coefficient K_d .

Figure 31 shows the K_d values of toluene sorption isotherms plotted against the HSL maturity of the leachate, as indicated by the HIX (detailed in Section 2.3.1.4). Overall, toluene sorption to the Oxford Clay appeared to increase with DOC maturity. The isotherm had a p value of <0.001, indicating that the observed trend was not due to random variation in the data, Section 4.4.4.

Toluene sorption and desorption tests were performed with MSW and HA leachates diluted to DOC concentrations comparable to the AMSW leachate (136 mg/L) in order to eliminate DOC concentration effects from the sorption and desorption processes and therefore clarify the effect of the type of DOC on sorption behaviour independently of DOC concentration. Comparison of the original leachate with its diluted counterpart also indicated how DOC concentration (independent of HSL maturity) affected toluene sorption and desorption. Both leachates were diluted using UHQ deionised water (MSW leachate diluted 1:20 and HA leachate diluted 1:2) and leachate parameters are given in Section 4.2.5.5. The diluted versions of the leachates all displayed similar HSL maturity compared to their undiluted counterparts (HIX 1.38 and 11.4 neat and 1.42 and 10.81 diluted for MSW and HA leachates, respectively). This indicated that the change in EC resulting from the dilution of the leachates using deionised water (from 42.9 to 25.6 mS/m for MSW and from 8.2 to 4.4 mS/m for HA) had very little effect on the nature of the DOC in the leachates, as supported by the similarity observed in the fluorescence ratios between the neat and diluted leachates (Table 28). The differences between sorption isotherms in diluted and undiluted leachates were statistically significant from their 95% confidence intervals and t values of 9.35 for MSW and diluted MSW; and 4.68 for HA and diluted HA (Figure 28)

| | EC (mS/m) | [DOC] | E:F | B:E | B:F | D:E | D:F | B:D | HIX |
|-------------|----------------------|--------------|------------|------------|------------|------------|------------|------------|------------|
| MSW | 42.9 | 2268 | 0.70 | 1.03 | 0.72 | 0.82 | 0.58 | 1.25 | 1.38 |
| Diluted MSW | 25.2 | 116 | 0.65 | 1.09 | 0.71 | 0.98 | 0.64 | 1.11 | 1.42 |
| HA | 8.2 | 238 | 1.36 | 0.065 | 0.089 | 0.001 | 0.001 | 61.85 | 11.4 |
| Diluted HA | 4.4 | 122 | 1.36 | 0.068 | 0.092 | 0.001 | 0.001 | 65.35 | 10.8 |

Table 28: Leachate characterisation parameter values for neat and diluted MSW and HA leachates.

The K_d value for toluene sorption in MSW was approximately half that of the diluted MSW leachate, with less sorption observed in the undiluted leachate than the diluted leachate (0.046 L/g and 0.11 L/g respectively). This may be attributable either to the high aqueous DOC concentration in the undiluted MSW leachate allowing greater sorption of toluene to solution phase DOC than in the diluted MSW leachate. Alternatively, it may also be due to DOC and toluene competitively sorbing to the solid phase, resulting in reduced toluene sorption in environments with a high DOC concentration.

Unlike the MSW and diluted MSW leachates, toluene sorption was greater in the neat HA leachate than in the diluted HA leachate ($K_d = 0.31$ L/g neat and 0.085 L/g diluted). This may be due to the higher humic maturity of the HA and diluted HA leachates (HIX 11.42 and 10.81) facilitating sorption of toluene to Oxford Clay via cumulative or co-sorption processes in comparison to the less mature (HIX 1.42 and 1.38) MSW and diluted MSW DOC which may compete with the toluene for sorption sites. Toluene sorption data in HA and diluted HA leachates were best fitted to non-linear isotherms. However, their isotherms were statistically different ($t=4.68$), with the undiluted HA leachate ($n=0.29$) showing sorption increasing but becoming less favourable as the aqueous contaminant concentration increases toward a sorption maximum and the diluted HA leachate ($n=1.35$) which showed sorption increasing and becoming more favourable as the aqueous contaminant concentration increased. This difference in the sorption isotherms may be due to the DOC concentration of the leachate solutions, with increased DOC concentration facilitating sorption of a greater proportion of the toluene than the diluted leachate, so resulting in differing sorption behaviours; or the higher DOC concentration of the neat HA leachate facilitating multilayer sorption.

The diluted HA leachate isotherm was not statistically different from the AMSW leachate isotherm ($t=-0.68$). Greater toluene sorption was, however, observed in the presence of diluted MSW leachate than in the AMSW leachate. As these leachates have similar DOC concentrations and were examined using the same solid phase, it is likely that this is due to the type of DOC in solution. The diluted HA leachate and the AMSW leachate had greater HSL maturity (HIX 10.81 and 2.94) than the diluted MSW leachate (HIX 1.42). Less sorption was observed in the more mature AMSW and diluted HA leachates than in the diluted MSW leachate. This may be explained by the PL DOC in the diluted

MSW leachate co-sorbing with the toluene or altering the sorption capacity of the clay (Flores-Cespedes *et al*, 2006). This is, however, contrary to the theory that the PL nature of the DOC in MSW leachates may mean competitive sorption with toluene to Oxford Clay occurs rather than co-sorption or cumulative sorption as with the HA leachate, so resulting in reduced sorption in the neat MSW leachate in comparison to the HA leachate despite their concentration difference. It may therefore be the case that the behaviour of the PL DOC is dependent on the concentration in solution and so competitive sorption of the DOC only becomes a factor at high DOC concentrations. This would indicate a concentration dependant process where at low concentration a less mature mixture of DOC (with lower HIX values) enhanced toluene sorption relative to HSL DOC alone. This may be due to the steric differences between PL and HSL DOC. HSL DOC is sterically large and high MW, whereas PL DOC is sterically smaller. Therefore, the PL DOC may enhance the OC content, and so the sorption capacity, of the clay by binding to sorption sites that the HSL DOC sterically cannot (Lion *et al*, 1990; Sykes, 1986). Alternatively, PL DOC at lower concentrations may co-sorb with toluene to the solid phase. Conversely, at high DOC concentrations, the sorption of the less mature PL DOC to the clay may become competitive, with the high concentration of DOC in solution effectively inhibiting toluene sorption (Magee *et al*, 1991). This accounts for both the reduction in toluene sorption in the MSW leachate in comparison to the diluted MSW leachate and the increased sorption of toluene in the less mature diluted MSW in comparison with the more mature diluted HA and AMSW leachates.

A decrease in sorption in comparison to DOC free leachate may, therefore, be explained by less mature PL DOC competing with toluene for sorption sites (in the case of MSW leachate) or low concentration mature (high HIX) DOC allowing the toluene to remain in solution by providing a hydrophobic phase on which the HOC can reside (in the case of AMSW and diluted HA leachates). An increase in sorption in comparison to DOC free leachate may also be explained by DOC sorbing to the solid phase increasing the sorption sites available. This could be either through increasing the OC content of the sorbent in the case of low maturity PL DOC or by multilayer sorption. Alternatively it may be due to toluene co-sorbing with the DOC to the sorption sites. For example, HOC-(HSL)DOC complexes sorbing to the clay preferentially to HOC-(PL)DOC complexes due to the preferential sorption of HSL DOC to the solid phase, Section 5.1.

This would result in the ‘active’ transport of the HOC onto the sorbent alongside the HSL DOC.

5.2.2 Desorption

Desorption isotherms for toluene in all leachates were better fitted by non-linear, Freundlich, isotherms than linear isotherms (as shown in Table 27). These isotherms were linearized using Log linearization ($\text{Log}(C_s) = \text{Log}(K_f) + n \text{ Log}(C_{aq})$); where $\text{Log}(K_f)$ is the y-intercept and n is the gradient, with K_f calculated from the value of $\log K_f$. R^2 values indicated good fit to the linearized form, so supporting the non-linear nature of the original isotherms. No desorption of toluene was observed from the Oxford Clay in AMSW, HA and diluted HA leachates. The MSW leachate isotherm had a value of n of greater than one ($n=1.35$) indicating that desorption became less favourable as the aqueous toluene concentration increased. Desorption isotherms for DOC free, MBT and diluted MSW had n values less than one (0.55, 0.61 and 0.54 respectively) indicating that sorption increased as the aqueous concentration of toluene increased, moving towards a desorption maximum. No desorption was observed in AMSW, HA and diluted HA leachates. This may be due to either irreversible sorption or very slow desorption kinetics when more mature DOC was present in solution.

Figure 32 shows the desorption of toluene in different leachate solutions. The observed values for desorption K_d , HSL maturity (HIX), DOC concentration and HI of the leachates are shown below for comparison.

Desorption (K_d ; L/g):

| | | | | | | | | |
|-------|---|-------------|---|------|---|----------|---|---------------------------|
| MSW | > | Diluted MSW | > | MBT | > | DOC free | > | (AMSW, HA and Diluted HA) |
| 0.070 | | 0.0680 | | 0.11 | | 0.14 | | (not detected) |

HSL maturity (HIX; F:B ratio, Section 2.3.1.4):

| | | | | | | | | | | |
|------|-----------|------------|---|------|---|-----|---|-----|-----------|-------------|
| HA | \approx | Diluted HA | > | AMSW | > | MBT | > | MSW | \approx | Diluted MSW |
| 11.4 | | 10.8 | | 2.9 | | 1.7 | | 1.4 | | 1.4 |

DOC concentration (mg/L):

| | | | | | | | | | | | | |
|------|---|------|---|-----|---|------|-----------|------------|-----------|-------------|---|----------|
| MSW | > | MBT | > | HA | > | AMSW | \approx | Diluted HA | \approx | Diluted MSW | > | DOC free |
| 2268 | | 1051 | | 238 | | 136 | | 122 | | 116 | | 0 |

Hysteresis Index (HI) (L/g):

| | | | | | | |
|-------------|---|----------|---|-------|---|---------|
| Diluted MSW | > | DOC free | > | MBT | > | MSW |
| 0.29 | | 0.074 | | 0.069 | | -0.0013 |

The difference in desorption between the DOC free and MBT leachates and the MSW and diluted MSW leachates was not statistically significant as their 95% confidence intervals were shown to overlap and their t values were -1.96, -1.10 and -0.62 respectively), Section 4.4.4.

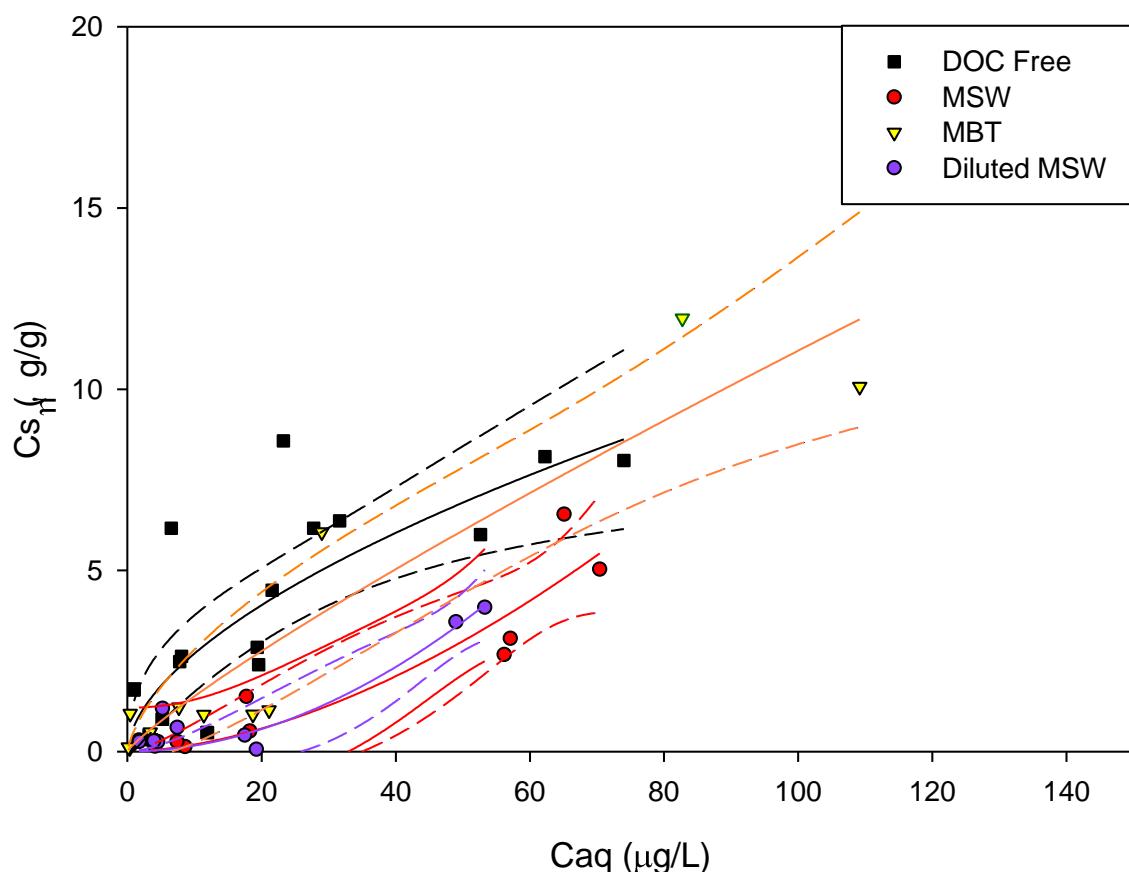


Figure 32: Desorption isotherms for toluene from Oxford Clay in leachates of differing DOC character.

The only two desorption isotherms that were statistically different from each other were toluene desorption in MBT and diluted MSW leachates ($t= 0.09$). Based on two tailed t-testing, no statistically significant difference was observed between toluene desorption in the DOC free leachate and any leachate containing DOC. Therefore no further

conclusions can be drawn from this. No desorption of toluene was observed in the presence of HA, AMSW and diluted HA leachates, which displayed the highest HSL maturities (highest HIX). This may indicate that leachates containing more mature DOC (greater HSL nature) may impact the sorption behaviour of toluene to the solid phase, resulting in inhibition of desorption (Murphy *et al*, 1992; Murphy and Zachara, 1995). The MBT and diluted MSW leachates were different, however, so they can be discussed further. This may indicate that the sorption of toluene in the presence of higher HSL maturity DOC leachates results in the stronger binding of toluene to Oxford Clay, for example via chemisorptive processes (Section 2.2.2.2) than in the less mature HSL leachates. This is supported by the more humically mature MBT leachate having a higher K_d (0.11 L/g), and so exhibiting less desorption, than the less mature diluted MSW leachate which had a lower K_d and so exhibited more desorption (K_d 0.068 L/g). This is because the mechanism by which the sorption of a compound occurs can dictate how readily it can be desorbed. For example; molecules may be sorbed to surfaces by non-destructive interactions such as electrostatic forces, allowing desorption, or they may be sorbed by more permanent interactions such as covalent bonding which can result in irreversible sorption either due to the energy required to break the bond and release the molecule back into solution, or as the process of binding to the surface may result in the solute being broken apart (Atkins and DePaula, 1992). A hysteresis index (HI) (Section 2.2.5) was calculated for toluene sorption and desorption from the Oxford Clay (Table 29). The HIs indicate that hysteresis was observed for toluene desorption from the DOC free, MSW and MBT leachates ($HI > 1$), but not in the Diluted MSW leachate ($HI < 1$). The observation of hysteresis in the DOC free leachate is in agreement with the Environment Agency (2009) where hysteresis was also observed.

| Leachate | K_d^s | K_d^d | HI |
|-----------------|---------------------------|---------------------------|-----------|
| DOC free | 0.078 | 0.15 | 0.074 |
| MSW | 0.046 | 0.33 | 0.29 |
| AMSW | 0.044 | --- | --- |
| MBT | 0.1 | 0.17 | 0.069 |
| HA | 1.1 | --- | --- |
| Diluted MSW | 0.11 | 0.11 | -0.0013 |
| Diluted HA | 0.059 | --- | --- |

Table 29: Hysteresis index values for toluene desorption from the Oxford Clay at a set aqueous concentration (50 µg/L). Hysteresis was apparent when HI was positive ($K_d^d > K_d^s$), where K_d^d and K_d^s are the sorption coefficients derived from toluene sorption and desorption isotherm parameters assuming a constant aqueous phase concentration of 50 µg/L toluene (Section 2.2.5, Equation 10).

5.3 Sorption and Desorption of Naphthalene to the Oxford Clay

Isotherms are shown for the sorption and desorption of naphthalene to Oxford Clay in leachates of differing DOC character (Figure 33 and 34). Sorption and desorption parameters from experimental work are summarised in Table 30.

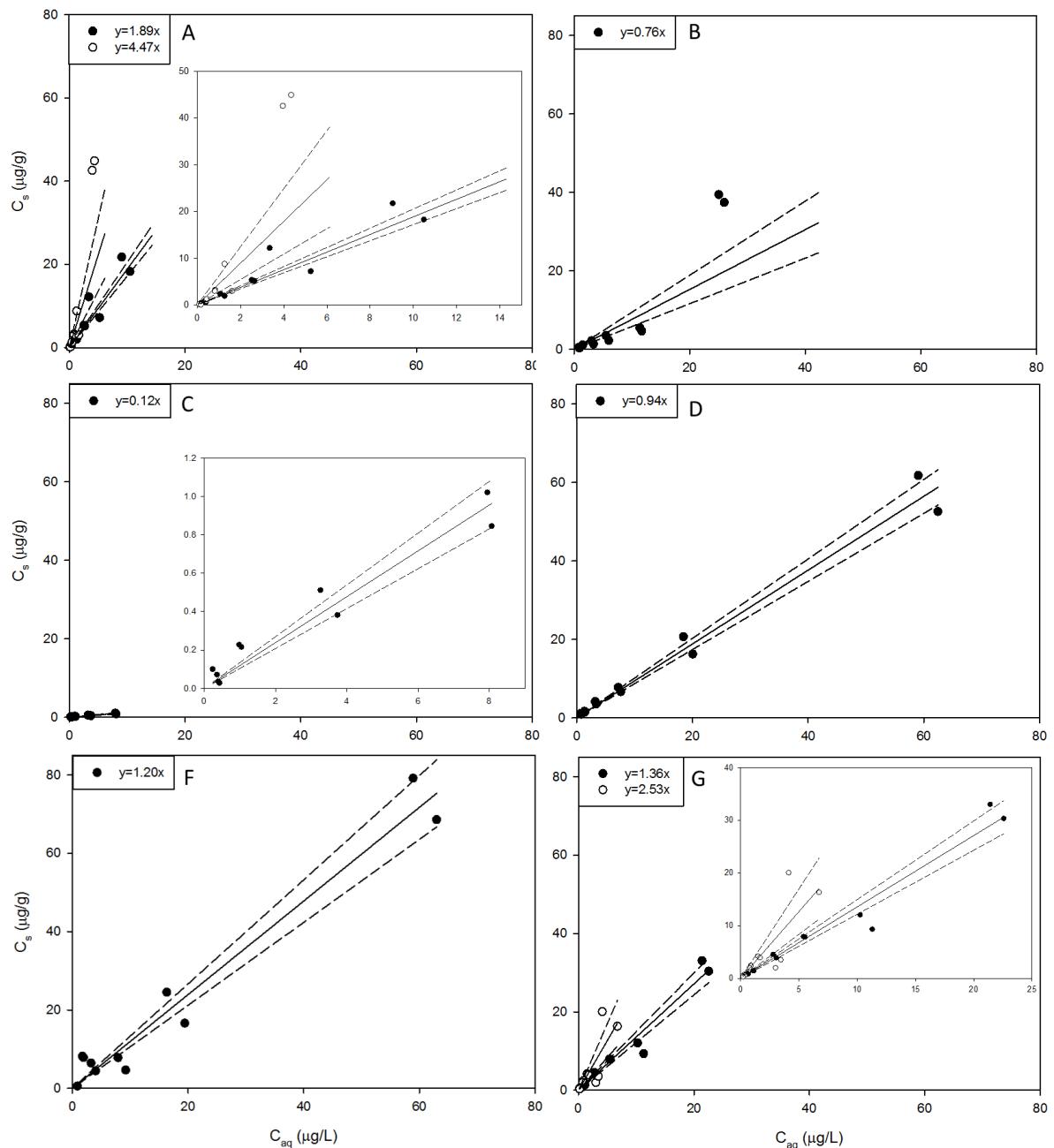


Figure 33: Linear isotherms for naphthalene sorption and desorption for Oxford Clay in different leachates. Solid data points denote sorption data and open points denote desorption data. Dashed lines indicate the 95% confidence intervals.

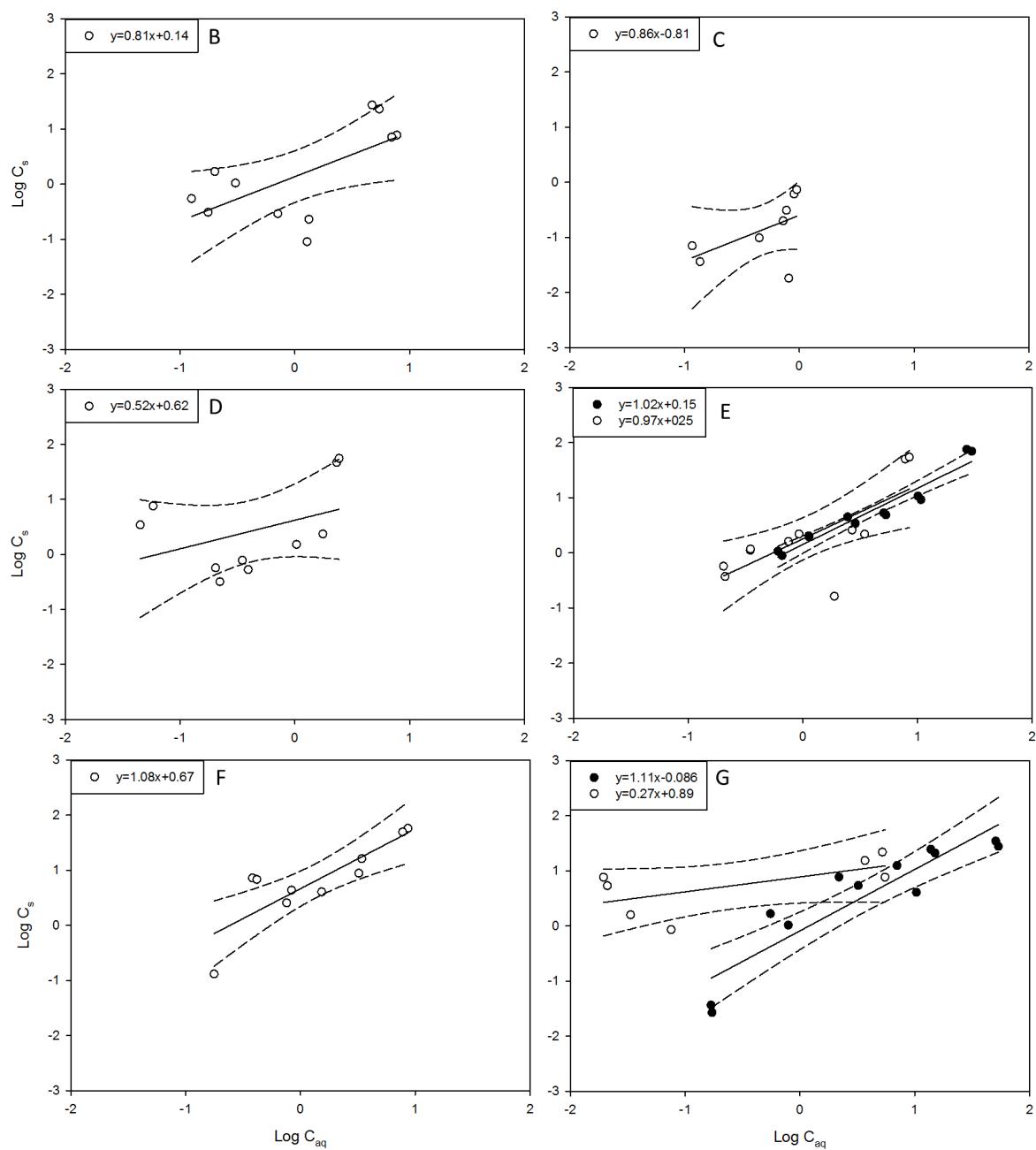


Figure 34: Log linearized Freundlich isotherms for naphthalene sorption and desorption to Oxford Clay in different leachates. Solid data points indicate sorption data and open data points indicate desorption data. Dashed lines indicate the 95% confidence limits of the regression.

| Leachate | Stage | Linear | | Non-linear | | |
|----------|-------------|----------------------|----------------|--|-------------------|--|
| | | K _d (L/g) | R ² | K _f ($\mu\text{g}^{1-n}\text{L}^n/\text{g}$) | n | R ² (C _s =K _f C _{aq} ⁿ form) |
| DOC free | Sorption | 1.89 | 0.93 | 1.36 ^a | 0.99 ^a | 0.94 |
| | Desorption | 4.47 | 0.44 | 5.55 | 0.85 | 0.44 |
| MSW | Sorption | 0.76 | 0.68 | 0.68 | 1.03 | 0.68 |
| | Desorption* | 2.21 | 0.39 | 1.15 ^a | 0.81 ^a | 0.43 |
| AMSW | Sorption* | 0.12 | 0.94 | 0.44 ^a | 0.86 ^a | 0.96 |
| | Desorption* | 0.46 | 0.46 | 0.55 ^a | 0.82 ^a | 0.81 |
| MBT | Sorption | 0.94 | 0.98 | 1.10 | 0.96 | 0.98 |
| | Desorption* | 15.88 | 0.65 | 1.86 ^a | 0.52 ^a | 0.97 |
| HA | Sorption* | 2.31 | 0.91 | 1.16 ^a | 1.02 ^a | 0.97 |
| | Desorption* | 5.56 | 0.84 | 1.29 ^a | 0.97 ^a | 0.99 |
| MSW 1:20 | Sorption | 1.20 | 0.96 | 1.07 | 1.03 | 0.96 |
| | Desorption* | 5.99 | 0.91 | 1.95 ^a | 1.08 ^a | 0.95 |
| HA 1:2 | Sorption* | 0.68 | 0.67 | 1.14 ^a | 0.98 ^a | 0.85 |
| | Desorption* | 3.07 | 0.35 | 1.36 ^a | 1.00 ^a | 0.56 |
| MBT 1:10 | Sorption | 1.36 | 0.96 | 0.92 ^a | 1.11 ^a | 0.97 |
| | Desorption | 2.53 | 0.67 | 2.44 ^a | 0.27 ^a | 0.68 |

Table 30: Parameters for naphthalene sorption and desorption to Oxford Clay in different leachates. Where the isotherm was best fitted by a non-linear isotherm (*) the values of K_f and n are derived from the log linearization of the Freundlich isotherms (^a); Section 2.2.3.3.

5.3.1 Sorption

As shown in Table 30 sorption isotherms of naphthalene for the Oxford Clay in DOC free, MSW, AMSW, MBT, diluted MSW and diluted MBT leachates fitted equally well to linear and non-linear isotherms. They were therefore modelled using linear isotherms for simplicity; with an increase in the sorption of naphthalene observed with increasing aqueous naphthalene concentration. Naphthalene sorption isotherms in HA and diluted HA were better fitted by non-linear, Freundlich, isotherms than linear isotherms. The non-linear nature of the sorption may be due to the high DOC maturity of the HA and diluted HA leachates (as indicated by their high HIX values; 11.4 and 10.8 respectively). The n values for naphthalene sorption to the Oxford Clay of the non-linear (HA and diluted HA) sorption isotherms were, however, close to one, indicating that the isotherm was close to linear, with sorption increasing as the naphthalene concentration in solution increased.

Naphthalene sorption was shown to vary with the type of leachate solution in the following order based on K_d values (illustrated in Figure 35). The maturity of the DOC, as indicated by HIX values, and the DOC concentration of the leachates is also shown for comparison.

Sorption (K_d ; L/g):

| HA | DOC free | Diluted MBT | Diluted MSW | MBT | MSW | Diluted HA | AMSW |
|------|----------|-------------|-------------|------|------|------------|------|
| 2.31 | 1.89 | 1.36 | 1.2 | 0.94 | 0.76 | 0.68 | 0.12 |

HSL maturity (HIX; F:B ratio, Section 2.3.1.4):

| HA | Diluted HA | AMSW | MBT | Diluted MBT | MSW | Diluted MSW |
|------|------------|------|-----|-------------|-----|-------------|
| 11.4 | 10.8 | 2.9 | 1.7 | 1.7 | 1.4 | 1.4 |

DOC concentration (mg/L):

| MSW | MBT | HA | AMSW | Diluted HA | Diluted MSW | Diluted MBT | DOC free |
|------|------|-----|------|------------|-------------|-------------|----------|
| 2268 | 1051 | 238 | 136 | 122 | 116 | 111 | 0 |

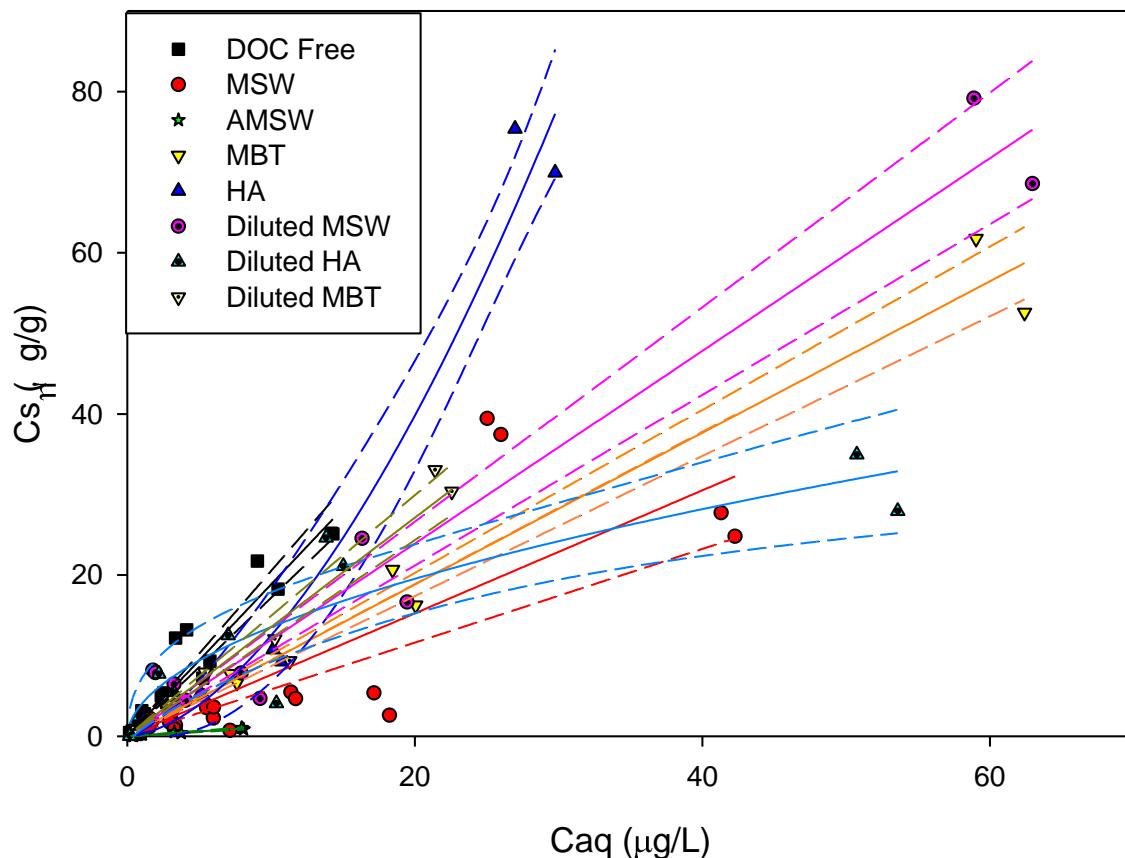


Figure 35: All naphthalene sorption isotherms to Oxford Clay in leachates of differing DOC character.

All isotherms were statistically different to the isotherm in DOC free leachate, as determined by their t values, Section 4.4.4. In comparison to naphthalene sorption in DOC free leachate (K_d 1.88 L/g), naphthalene sorption to the Oxford Clay decreased when DOC was present in solution (K_d 0.12-1.36 L/g) in all but the HA leachate. This may be due to DOC allowing naphthalene to remain in solution by providing a hydrophobic media in the aqueous phase for the naphthalene to sorb to. Naphthalene sorption in the presence of the HA leachate, however, was greater than it was in the presence of a DOC free leachate as the isotherm for DOC free leachate and HA leachate were statistically separate ($t=1.10$). This indicates that the commercially available HA DOC behaves differently in solution than a waste derived leachate DOC.

Based on their t-values, the diluted MBT and diluted MSW ($t=-3.90$); MBT and MSW ($t=-0.96$); and MSW and diluted HA ($t=-0.68$) are statistically similar. Therefore, the order of sorption resolves into;

HA > DOC Free > (Diluted MBT≈Diluted MSW) > (MBT≈[MSW]≈diluted HA] > AMSW

As with toluene sorption and desorption tests (Section 5.2), naphthalene sorption and desorption tests were performed with diluted leachates at comparable DOC concentrations to the AMSW leachate (136 mg/L) in order to eliminate DOC concentration effects from sorption and desorption trends. The MSW leachate was diluted 1:20 to 116 mg/L and the HA leachate was diluted 1:2 to 122 mg/L. In addition to diluted MSW and diluted HA leachates used in toluene sorption and desorption tests MBT leachate was also diluted (1:10 to 111 mg/L) in order to provide an additional DOC maturity for comparison. The MBT leachate was diluted with UHQ deionised water and, as with the MSW and HA leachates and their diluted counterparts, the MBT and diluted MBT leachates displayed similar maturities (HIX 1.7 for both), indicating that the dilution had a minimal effect on the DOC character of the leachate.

The sorption isotherms of naphthalene in MSW, MBT, diluted MSW, and diluted MBT leachates were all linear. More sorption was observed in the diluted leachates than the neat leachates (K_d 0.76 and 0.94 undiluted compared to 1.20 and 1.36 neat for MSW and

MBT leachates respectively). This may be attributable to the higher concentration of DOC in the neat MSW and MBT leachates competing with naphthalene for sorption sites on the clay, or allowing naphthalene to remain in solution by creating a more hydrophobic aqueous phase than the diluted leachates, making it more favourable for the naphthalene to remain in solution.

In comparison with naphthalene sorption in AMSW leachate (K_d 0.12 L/g), sorption was increased in diluted MSW, diluted HA and diluted MBT leachates (K_d 1.2, 0.69 and 1.36 L/g respectively). The 95% confidence limits for the leachate isotherms indicate that AMSW was distinct from the diluted leachates. Diluted MBT and diluted MSW leachate isotherms were, however, within each other's 95% confidence limits ($t = -3.90$) and were therefore not statistically different. The overall the sorption of naphthalene to the Oxford Clay in leachates of analogous DOC concentration therefore decreased in the order;

$$(\text{Diluted MSW} \approx \text{diluted MBT}) > \text{diluted HA} > \text{AMSW}$$

This may be due to the increased maturity of the leachates (HIX values 1.4, 1.7, 10.8 and 2.9 respectively) as more sorption was observed for the lower maturity diluted MSW and diluted MBT leachates than the higher maturity diluted HA and AMSW leachates. This could be explained by the higher maturity DOC inhibiting sorption by competing with naphthalene for sorption sites on the Oxford Clay to a greater extent than the less mature DOC or creating a more hydrophobic aqueous phase, allowing naphthalene to remain in solution. Alternatively, naphthalene may sorb to the more mature DOC, then being prevented from co-sorbing to the clay due to the molecular size of the DOC (e.g. sterics, (Sykes, 1986)).

However, there was not a clear trend between sorption and the maturity of the DOC, as less sorption was observed in the AMSW leachate (K_f 0.11 $\mu\text{g}^{1-n} \text{L}^n/\text{g}$) than in the diluted HA leachate (K_f 0.89 $\mu\text{g}^{1-n} \text{L}^n/\text{g}$), despite the diluted HA leachate having a greater maturity than the AMSW leachate (HIX value 10.8 compared to 2.9). This may indicate that the origin of the DOC has an impact on sorption behaviour, as the diluted HA

leachate is derived from a commercially available DOC source, whereas the other leachates were derived from wastes.

Naphthalene sorption in neat HA leachate was, however, greater than that observed in diluted HA leachate. This indicates that the behaviour of naphthalene sorption in HA and diluted HA leachates may be different than that of the other leachates. This could either be due to the higher maturity of the HA and diluted HA leachates than the other leachates (HIX 11.4 and 10.8 respectively) or due to the origin of the DOC since HA is a commercially available mixture whereas the other leachates have DOC originating from wastes.

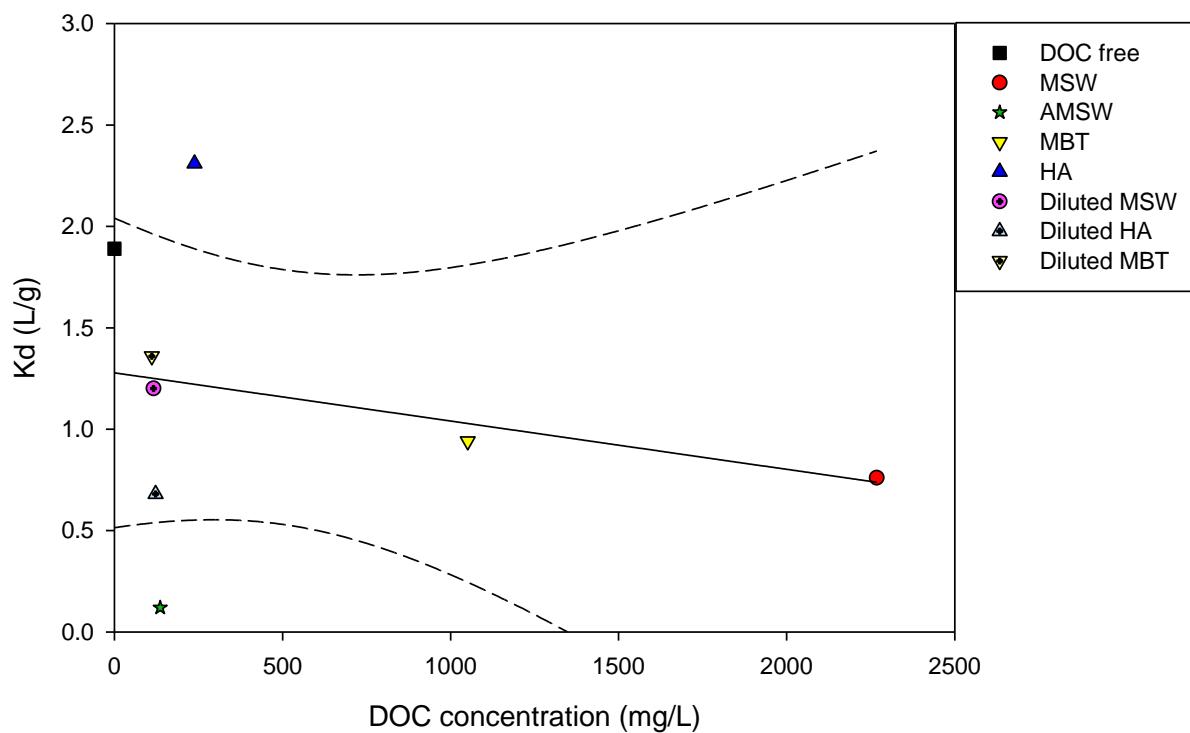


Figure 36: DOC concentration of the different leachates plotted against sorption coefficient K_d for naphthalene sorption to the Oxford Clay.

Excluding the higher maturity HA (HIX 11.4; 236 mg/L), diluted HA (HIX 10.8; 122 mg/L) and AMSW (HIX 2.9; 136 mg/L) leachates, naphthalene sorption to Oxford Clay decreased with increasing DOC concentration (Figure 36). However, when considering all data, there was no trend, with a p value of 0.52 indicating no significant difference from the null hypothesis, Section 4.4.4. The DOC concentration cannot, however, be the only factor determining the sorption behaviour of naphthalene since AMSW and diluted HA leachates (DOC concentration 136 mg/L and 122 mg/L respectively)

exhibited less sorption than MSW which would be expected to have lowest the sorption, if the sorption behaviour was based solely on the DOC concentration (as the MSW leachate DOC concentration was 2268 mg/L).

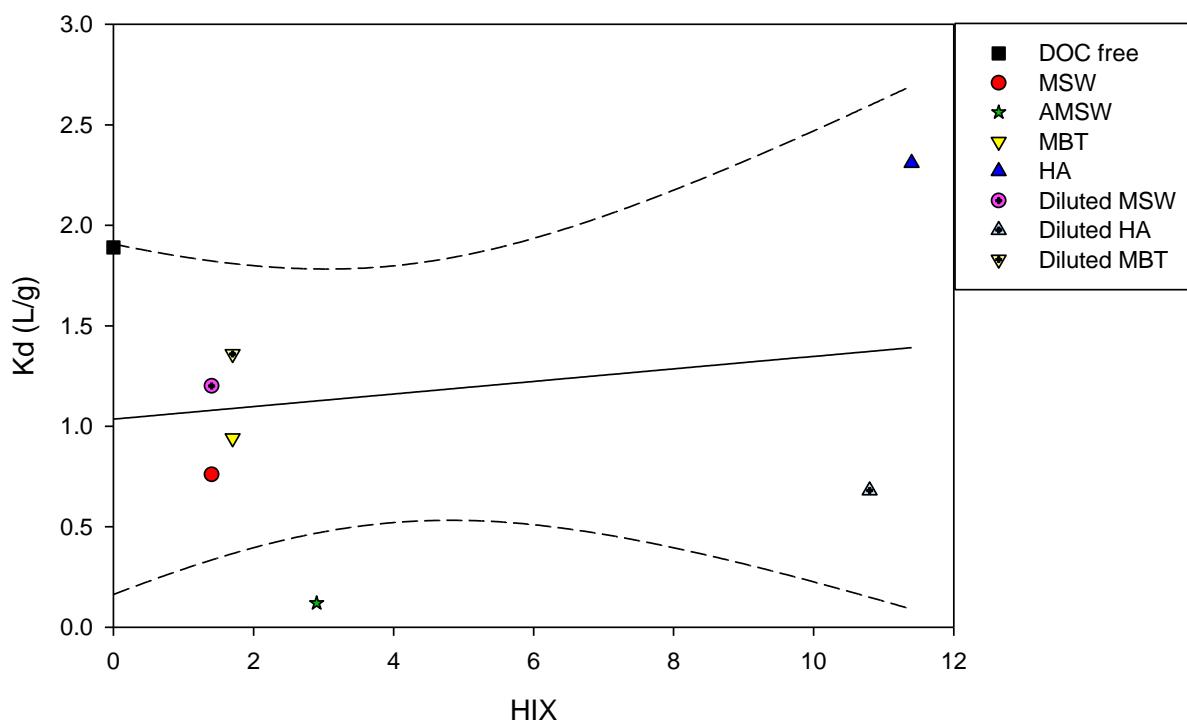


Figure 37: HSL maturity of leachates (HIX) plotted against sorption coefficient K_d .

Figure 37 shows the maturity of the DOC in the leachates (determined by their HIX values) plotted against the naphthalene sorption coefficients for the Oxford Clay. It is apparent that there was no significant trend between the maturity of the DOC in solution and the amount of naphthalene sorption to the Oxford Clay ($p= 0.63$), Section 4.4.4. More sorption was observed for the more mature HA leachate than in the lower maturity leachates (K_d 2.31 compared to 1.89-0.12). However, the diluted HA leachate and AMSW leachates (HIX 10.8 and 2.9 respectively) which are the next two most mature leachates after HA leachate had the lowest K_d of all the other leachate samples which does not fit with an increase in DOC maturity resulting in increased naphthalene sorption.

Despite their comparable DOC concentrations alongside differing DOC maturities, the isotherm for naphthalene sorption in diluted MBT and diluted MSW were statistically similar, and therefore indistinguishable from each other ($t=-3.90$). This supported the

lack of a direct relationship between DOC maturity in the leachate and naphthalene sorption behaviour (Figure 37).

It is therefore likely that both the concentration and maturity of the DOC combine to affect the sorption of naphthalene to Oxford Clay, with low naphthalene sorption observed in the high maturity (diluted HA and AMSW) or high concentration (MSW) leachates because the DOC creates a more hydrophobic aqueous phase and/or the DOC is competitively sorbing to the clay preventing naphthalene sorption. The high sorption of naphthalene observed with HA leachate (K_d 2.31) didn't fit with the results of the other leachates when K_d was compared to either DOC concentration or maturity. This may indicate that HSL synthetic leachates may be behaving differently to waste derived leachates. For example it may be sorbing via a multilayer sorption process.

5.3.2 Desorption

Desorption isotherms for DOC free and diluted MBT leachates were equally well fitted by linear and Freundlich isotherms. For simplicity they were therefore modelled as linear. All other desorption results were better fitted by non-linear, Freundlich, isotherms, as demonstrated by their R^2 values (Table 30). Unlike the toluene desorption tests, desorption of naphthalene was observed in the presence of all leachates indicating that naphthalene sorption was reversible. The n values for desorption of naphthalene in HA, diluted MSW and diluted HA leachates were close to one, indicating that they were close to linear. The n values for the desorption of naphthalene in all the other leachates were less than one, which indicated that the isotherm tends towards a maximum limit, however, this does not discount the possibility of an irreversibly bound portion. Linearized isotherms showed good fit, and so conformity with the Freundlich isotherm.

Naphthalene desorption in both MSW and diluted MSW leachates and HA and diluted HA leachates was best fitted by non-linear isotherms. Naphthalene desorption in MBT leachate was also better fitted by a Freundlich isotherm, however, diluted MBT leachate was equally well fitted to linear and Freundlich isotherms and therefore was modelled as linear. Desorption of naphthalene was greater in the neat MSW leachate than the diluted MSW leachate (K_d 2.21 and 5.99 L/g respectively). However, greater desorption was

observed for the diluted MBT and diluted HA leachates than their neat counterparts (K_d 15.88 and 5.56 respectively for neat leachates and K_d 2.55 and 3.07 L/g respectively for diluted leachates). This difference may be due to the maturity of the leachates, as more mature leachates may allow the naphthalene to bind more tightly to the solid phase at higher concentrations in solution resulting in less desorption. Alternatively, more mature DOC may result in further DOC sorption to the solid phase, creating a second sorbed DOC layer and entrapping the sorbed naphthalene. This would result in less desorption being observed in the more mature leachates at higher concentrations. The desorption of naphthalene was shown to vary with type of leachate solution in the following order, based on K_d values; illustrated in Figure 38. The maturity and concentration of the DOC in the leachates are also shown for comparison.

Desorption (K_d ; L/g):

| AMSW | > | MSW | > | Diluted MBT | > | Diluted HA | > | DOC free | > | HA | > | Diluted MSW | > | MBT |
|------|---|------|---|----------------|---|---------------|---|-------------|---|------|---|----------------|---|-------|
| 0.46 | | 2.21 | | 2.53 | | 3.07 | | 4.47 | | 5.56 | | 5.99 | | 15.88 |

HSL maturity (HIX; F:B ratio, Section 2.3.1.4):

| HA | \approx | Diluted HA | > | AMSW | > | MBT | \approx | Diluted MBT | > | MSW | \approx | Diluted MSW |
|------|-----------|---------------|---|------|---|-----|-----------|----------------|---|-----|-----------|----------------|
| 11.4 | | 10.8 | | 2.9 | | 1.7 | | 1.7 | | 1.4 | | 1.4 |

DOC concentration (mg/L):

| MSW | > | MBT | > | HA | > | AMSW | \approx | Diluted HA | \approx | Diluted MSW | \approx | Diluted MBT | > | DOC free |
|------|---|------|---|-----|---|------|-----------|---------------|-----------|----------------|-----------|----------------|---|-------------|
| 2268 | | 1051 | | 238 | | 136 | | 122 | | 116 | | 111 | | 0 |

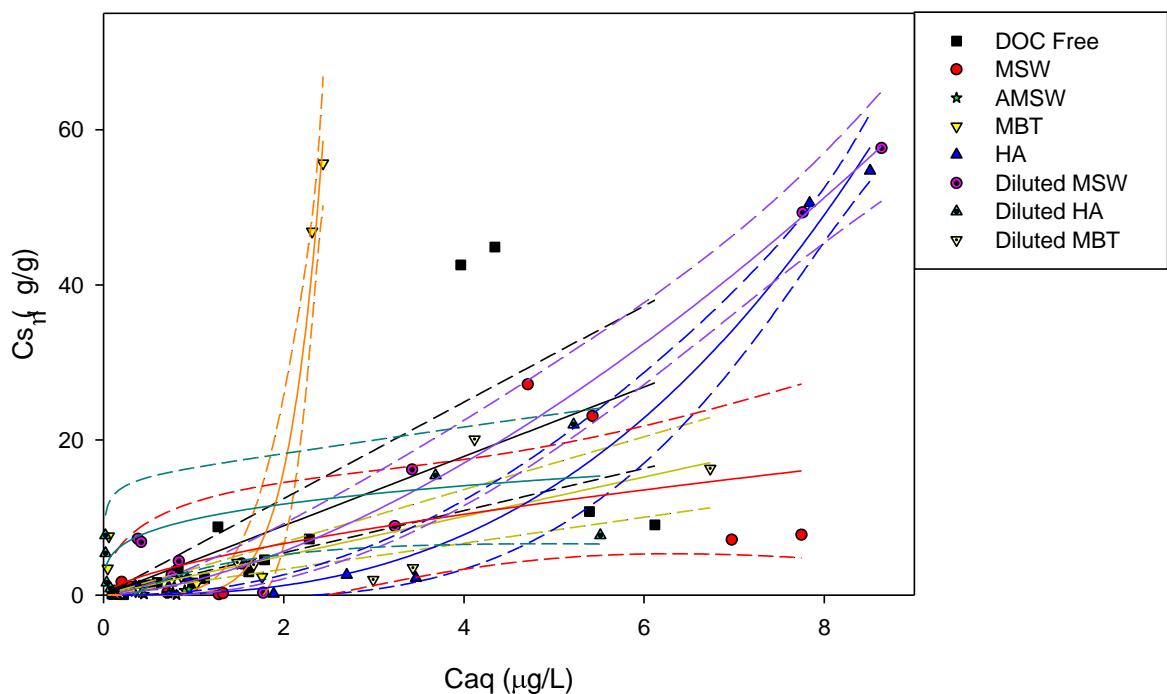


Figure 38: All naphthalene desorption isotherms from the Oxford Clay in leachates of differing DOC character.

From their t values, only the desorption of naphthalene in the AMSW and MBT leachates were statistically separate from the DOC free leachate isotherm ($t= 0.85$ and 1.14 for MBT and AMSW respectively). Isotherms in all other leachates were statistically similar to the desorption of naphthalene in DOC free leachate. The desorption of naphthalene in MBT leachate was the only isotherm that was statistically separate from isotherms in all the other leachates ($t=0.34-1.57$). The isotherms for neat MSW, MBT and HA were also separate from their diluted counterparts ($t=1.96$, 1.20 and 1.34 for MSW, MBT and HA respectively). Although the diluted HA isotherm was not different from the AMSW isotherm ($t=-0.57$); isotherms in diluted MSW and diluted MBT were ($t=6.40$ and 0.97 respectively). This allows some comparison of naphthalene desorption in these leachates.

In comparison to naphthalene desorption into DOC free leachate, the addition of DOC to the leachate solution increased the desorption of naphthalene from the Oxford Clay in AMSW leachate (Figure 38). In the case of MBT leachate the addition of DOC to the leachate solution decreased the amount of desorption from the Oxford Clay relative to desorption in the DOC free leachate. The other leachates were statistically similar to naphthalene desorption in DOC free leachate and so are not offered for comparison. This may be because the presence of higher maturity DOC in solution decreases

naphthalene sorption due to competition of DOC with the naphthalene for sorption sites during the sorption step resulting in less naphthalene available for desorption. Alternatively it may be due to the naphthalene having a greater affinity for the more mature DOC in solution than the solid phase OC (Section 2.2.6.2). Conversely, lower maturity DOC in solution may be enhancing the desorption of naphthalene from the clay OC due to weaker binding of naphthalene during the sorption step, resulting in easier desorption from the solid phase, or by aqueous phase DOC providing an organic phase which the hydrophobic naphthalene can partition onto from the solid. The DOC in solution may also decrease the desorption of naphthalene either by limiting the naphthalene sorbed during the sorption step, reducing the amount available for desorption, or by the DOC, HOCs or DOC and HOC complexes undergoing irreversible binding to the solid phase.

In comparison with naphthalene desorption in AMSW leachate, desorption were seen to increase in all the diluted leachates. Desorption isotherms in the higher maturity AMSW and diluted HA (K_d 0.46 and 3.07 L/g respectively) were statistically similar ($t=-0.57$). However the desorption of AMSW leachate and the diluted MSW and MBT leachates (K_f 5.99 and 2.53 L/g respectively) were statistically separate from each other ($t=6.44$ and 0.97 respectively). Desorption in diluted MSW leachate was distinct from diluted MBT leachate ($t=2.28$). However, isotherms in diluted MBT leachate were not statistically separate from diluted HA leachate ($t=-1.91$). Therefore, overall the desorption of naphthalene from Oxford Clay in leachates of analogous DOC concentration can be resolved into the order;

$$(\text{AMSW} \approx [\text{diluted HA}] \approx \text{diluted MBT}) < \text{diluted MSW}.$$

The diluted MSW leachate showed greater desorption of naphthalene from the clay than the other leachates and at a higher aqueous naphthalene concentration than any of the other leachates. This may be due to the naphthalene sorbing more strongly to the solid phase in the presence of the more mature AMSW, diluted HA and diluted MBT leachates than in the less mature diluted MSW leachate. However, it may also be attributable to the increased amount of naphthalene sorption to the Oxford Clay in diluted MSW

leachate (C_s up to ~80 µg/g) in comparison to the sorption of naphthalene in AMSW (~1 µg/g), diluted MBT (~35 µg/g) and diluted HA (also ~35 µg/g).

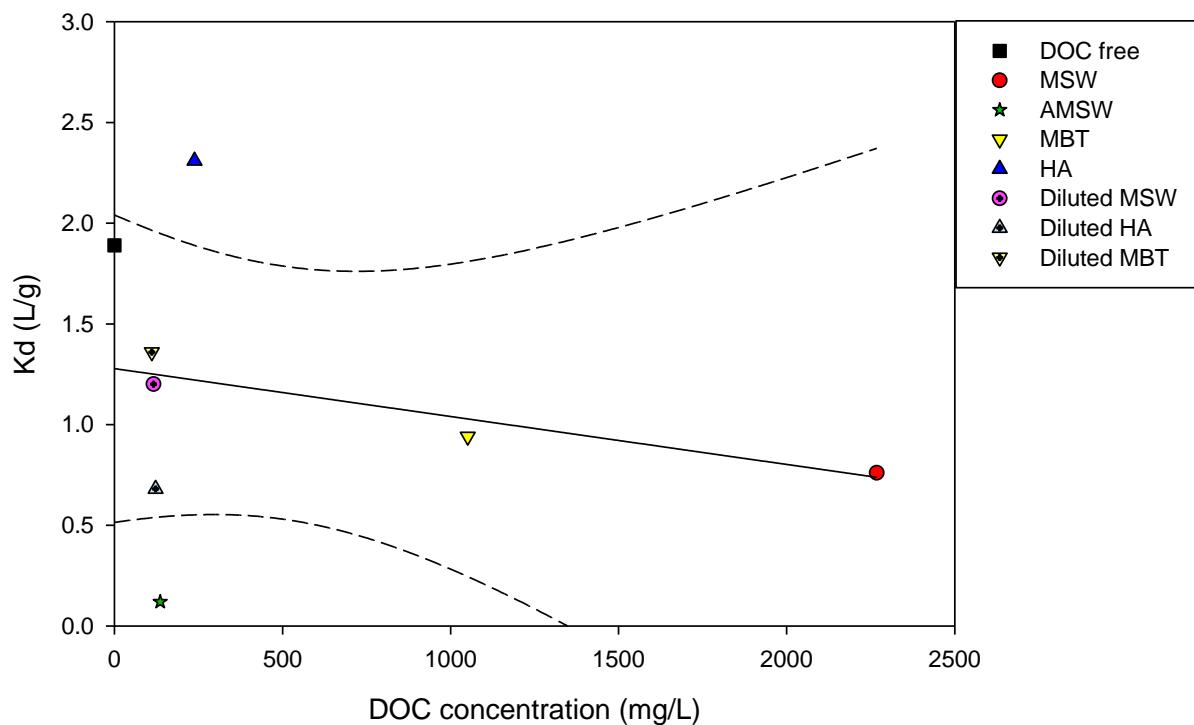


Figure 39: DOC concentration of leachates plotted against desorption coefficient K_d .

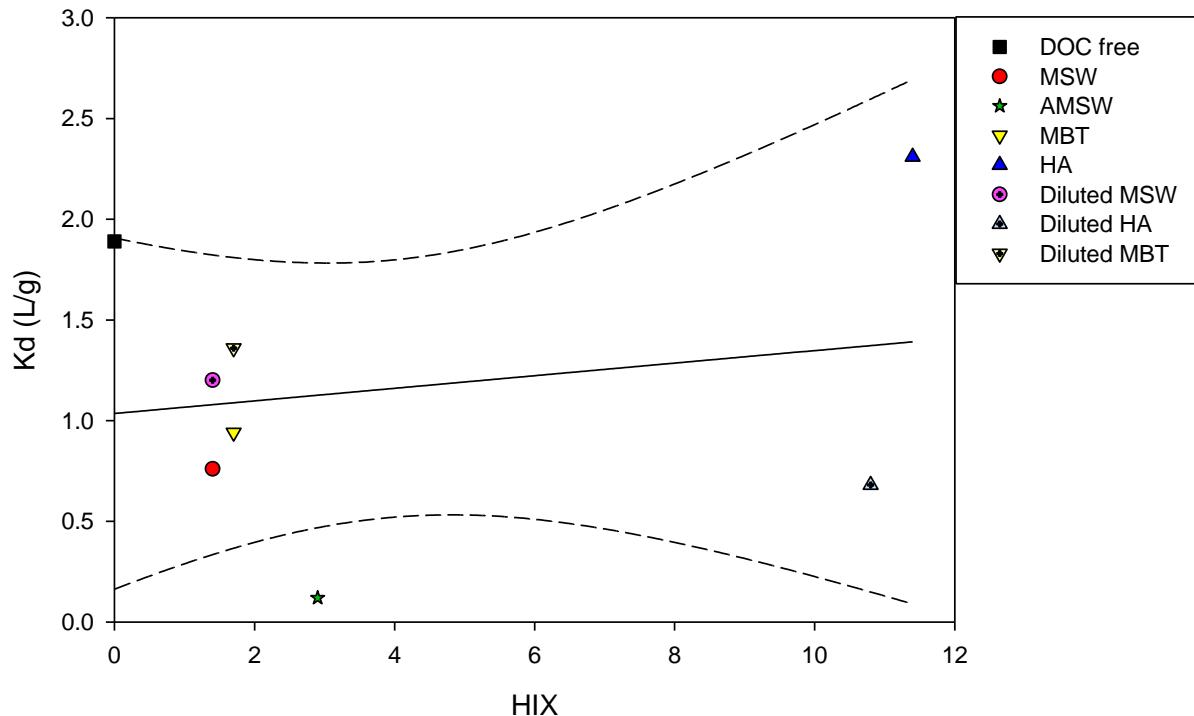


Figure 40: DOC concentration of leachates plotted against maturity of the leachates (HIX).

As shown in Figure 39, there was no relationship between DOC concentration and the amount of desorption observed from the Oxford Clay. The R^2 of the regression was 0.072 and a high p value of 0.52 indicated that the variation in the results was as likely to be due to random variation as them following the regression, Section 4.4.4. Similarly, Figure 40 shows that there was no relationship between the amount of naphthalene desorption and the maturity of the leachates (R^2 0.041 and p value of 0.63).

Unlike the desorption of toluene from the Oxford Clay, desorption was observed in all naphthalene desorption tests. This was in agreement with the findings of Bayard *et al* (1998) that naphthalene sorption was reversible at low aqueous concentrations of naphthalene. This may be due to the sterically smaller toluene being able to sorb to sites which are inaccessible to the naphthalene. Sorption sites within the clay will vary in size due to the chemistry of the site and interactions between functional groups within the site (Section 2.2.2). Because of this, sites may be small enough that they only allow compounds of certain sizes to access the sites (sterics). Therefore as toluene is a smaller molecule than naphthalene it can potentially bind to sterically smaller sites than the larger naphthalene. The methyl group on toluene may also allow toluene to bind more tightly to the surface sorption sites than naphthalene as it can undergo substitution with the site. This may also result in a covalent bond being formed leading to irreversible sorption or the toluene molecule being torn apart during bonding to the surface so it is irrecoverable.

Desorption isotherms for all leachates had K_d values for desorption which were higher than the K_d values for sorption. The shape of the isotherms for all leachates apart from DOC free and diluted MBT leachates were non-linear, with all but HA, diluted MSW and diluted HA (where n was close to one), having n values less than one, indicating that while sorption was reversible, desorption was likely to be a two stage process desorbing toward a desorption maximum. This observation is in agreement with literature that also models naphthalene desorption as a two stage process (Oren and Chefetz, 2005; Kan *et al*, 2000), with an initial fast desorption step, followed by a slower desorption phase (Ahn *et al*, 1999).

From the calculation of a hysteresis index (HI) for naphthalene sorption and desorption isotherms (Table 31), hysteresis was apparent in DOC free, AMSW, diluted MSW,

diluted MBT and diluted HA leachates (indicated by a positive HI). No hysteresis was observed for MSW, MBT and HA leachates.

| Leachate | KD _s | KD _d | HI |
|-------------|-----------------|-----------------|-------|
| DOC free | 1.89 | 4.47 | 2.58 |
| MSW | 0.76 | 0.53 | -0.23 |
| AMSW | 0.12 | 0.3 | 0.18 |
| MBT | 0.94 | 0.21 | -0.73 |
| HA | 1.26 | 1.14 | -0.12 |
| Diluted MSW | 1.2 | 2.81 | 1.61 |
| Diluted HA | 0.68 | 1.36 | 0.68 |
| Diluted MBT | 1.36 | 2.53 | 1.17 |

Table 31: Hysteresis index values for naphthalene sorption and desorption from the Oxford Clay at an aqueous concentration of 10 µg/L. Hysteresis is apparent when HI is positive (KD_d > KD_s) (Section 2.2.5, Equation 10).

The desorption isotherms of naphthalene in the four leachates of analogous DOC concentration exhibited hysteresis in comparison to the sorption isotherms of the leachates. This may indicate that the desorption of naphthalene from the Oxford Clay occurs via a different mechanism to its sorption, for example, by a two stage process of desorption (Kan *et al*, 2000) or that a portion of the naphthalene remains irreversibly bound to the clay (Oren and Chefetz, 2005). In addition to this, due to the differences between the sorption and desorption behaviour of naphthalene in the HA and diluted HA leachates in comparison to the other leachates (illustrated in Figures 35 and 38), it is suggested that sorption in commercially available HA occurs in a different manner to sorption in waste derived leachate DOC. Therefore it would not be appropriate to use it as a substitute for a mature leachate in predictive testing for landfill risk assessments.

As desorption was observed in all leachates, the sorption of naphthalene was found to be reversible. This was in keeping with the literature (Connaughton *et al*, 1993; Bayard *et al*, 1998; Burgos *et al*, 1996; Karickhoff, 1981; Karickhoff *et al*, 1979; Mihelcic and Luthy, 1991). However, the higher K_d and K_f values observed for desorption in comparison to sorption indicates that hysteresis between the sorption and desorption behaviour of naphthalene occurred and that a portion of the naphthalene remained bound to the clay when using a contact time for sorption and desorption of seven days. Similar results were found by Connaughton *et al* (1993) and Bayard *et al* (1998) who attributed

the hysteresis to either the contact time or the polarity of the aqueous phase. This may also be due to desorption being a multistep process.

6. Discussion

6.1 Discussion of Results of DOC and Contaminant Sorption and Desorption Behaviour in Relation to the Literature

Tables 32 shows the results of DOC sorption tests in this work alongside values for sorption in the literature.

| Aqueous phase (DOC mg/L) | Solid phase (% organic carbon) | K _d (L/g) (x10 ³) | K _{oc} (L/g) | Freundlich isotherm K _f (mg ¹⁻ⁿ L ⁿ /g) unless otherwise stated and (n) | Ref |
|---|---|---|--------------------------|---|-----|
| MSW (2268) | Oxford Clay (5.49) | 1.4 | 0.026 | 0.0039 (0.86) | e |
| Rhinebeck soil DOM (103) | Dark Sand (0.4) | 0.132 | 0.12 ^a | --- | 1 |
| Sinclair inlet porewater NOM (138) | Sinclair inlet bulk sediment (<0.05%) | 120 | 0.24 ^a | 0.08 L/g (1.06) | 2 |
| | Montmorillonite (N/A) | 120 | nd | 0.43 L/g (0.74) | |
| Sinclair inlet extracted NOM (175) | Sinclair inlet bulk sediment (<0.05%) | 80 | 0.16 ^a | 1.82 L/g (0.38) | |
| | Montmorillonite (N/A) | 330 | nd | 0.07 L/g (1.36) | |
| Peat Humic Acid | Montmorillonite Na ⁺ pH 7 (N/A) | 0.00002 -0.00026 | nd | 0.07-0.32 (0.44-0.58) | 3 |
| | Montmorillonite Ca ²⁺ pH 7 | 0.00056 -0.00083 | nd | 0.54-0.87 (0.46-0.49) | |
| | Kaolinite Na ⁺ pH 7 (N/A) | 0.00008 -0.00028 | nd | 0.12-0.48 (0.24-0.72) | |
| | Kaolinite Ca ²⁺ pH 7 (N/A) | 0.0009 -0.0019 | nd | 0.75-1.42 (0.34-1.73) | |
| Liberty Bay porewater NOM <1000 Da | Na-Montmorillonite (N/A) | 1.2 | nd | --- | 4 |
| Liberty Bay porewater NOM >1000 Da | | 1.9 | nd | --- | |
| Liberty Bay extracted NOM <1000 Da | | 1 | nd | --- | |
| Liberty Bay extracted NOM >1000 Da | | 1.8 | nd | --- | |
| Suwannee River FA (TOC 482 mg/L) | Goethite (N/A) | 73000 ^L | nd | --- | 5 |
| Polymaleic acid (TOC 889 mg/L) | | 266000 ^L | nd | --- | |
| 10 mg/L NaCl, 20 mg/L CaCl ₂ ·2H ₂ O and 24 mg/L | Kaolinite (N/A) | 56000 ^L | nd | --- | 6 |
| | Kaolinite + Goethite (N/A) | 35000 ^L | nd | --- | |

| | | | | | |
|---|--|---|-------------------|----------------|---|
| K ₂ SO ₄ , pH 6 with DOC extracted from Medicago truncatula shoots (0-200) | Smectite (N/A) | 13000 ^L | nd | | 7 |
| | Smectite + Goethite (N/A) | 9000 ^L | nd | --- | |
| | Illite(N/A) | 32000 ^L | nd | --- | |
| | Illite + Goethite (N/A) | 33000 ^L | nd | --- | |
| | Illite + Haematite (N/A) | 32000 ^L | nd | --- | |
| | Illite + Ferrihydrite (N/A) | 38000 ^L | nd | --- | |
| Fulvic acid | Kaolinite (N/A) | --- | nd | 0.00759 (0.79) | |
| | Vermiculite (N/A) | --- | nd | 0.01803 (0.82) | |
| | Smectite (N/A) | --- | nd | 0.00741 (0.89) | |
| Humic acid | Smectite (N/A) | --- | nd | 0.01886 (0.86) | |
| | Kaolinite (N/A) | --- | nd | 0.01638 (0.68) | |
| | Vermiculite (N/A) | --- | nd | 0.04789 (0.52) | |
| Artificial Leaf litter leachate 134 mg/L | Forest soil (10-19cm depth) (0.598) | 0.81 | 0.14 ^a | 0.00023 (0.79) | 8 |
| | Forest soil (19-22cm depth) (6.12) | 3.32 | 0.05 ^a | 0.03338 (1.75) | |
| | Forest soil (22-32cm depth) (1.39) | 8.96 | 0.64 ^a | 0.42766 (3.97) | |
| | Forest soil (32-59cm depth) (0.14) | 7.77 | 5.55 ^a | 0.49212 (5.73) | |
| | Forest soil (59-/cm depth) (0.046) | 4.13 | 8.98 ^a | 0.38416 (7.21) | |
| Soil humic acid IHSS #1R102H | Kaolinite clay (N/A) | Langmuir-type behaviour but no values given as focus of study was phenanthrene. | | | 9 |

Table 32: Sorption parameters for MSW leachate DOC sorption to the Oxford Clay (e) alongside literature values for DOC sorption. (1) Magee *et al* (1991) (2) Thimsem and Keil (1998) (3) Feng *et al* (2005) (4) Arnarson and Keil (2000) (5) Wang *et al* (1997) (6) Saidy *et al* (2013) (7) Zhang *et al* (2012) (8) Vandenbruwane *et al* (2007) (9) Jones and Tiller (1999). ^(a) Calculated from literature parameters.

^(nd) Could not be determined. ^(L) Langmuir adsorption constant derived from the Langmuir isotherm (Section 2.2.3.3) corrected from L/mg to L/g (1 L/mg=1000 L/g).

6.1.1 MSW leachate DOC Sorption and Desorption

The sorption isotherm for MSW DOC sorption to Oxford Clay fitted equally well to linear and non-linear (Freundlich) models and was therefore modelled as linear for simplicity. This disagreed with a large portion of the literature which found DOC sorption to be non-linear in nature, and best fitted to either a Freundlich or Langmuir isotherm (Jones and Tiller, 1999; Thimsen and Keil, 1998; Wang *et al*, 1997; Saidy *et al*, 2013; Vandenbruwane *et al*, 2007). Unlike the non-linear models to which DOC sorption was fitted in the literature, no apparent tailing off in the sorption capacity toward a maximum at higher DOC concentrations was observed in this work indicating a difference in the sorption behaviour of DOC between this work and that of the literature studies. This work used a DOC concentration range in the MSW leachate of 1.8-2348 mg/L, which was larger than the range of 103 to 889 mg/L used in the literature (Magee *et al*, 1999; Wang *et al*, 1997). This was done in order to better cover the range of DOC concentrations present in landfill leachates (59-40000 mg/L), as shown in Table 1 (Kjeldsen *et al*, 2002). For example, Saidy *et al* (2013) found the sorption behaviour of DOC for (in a pH 6 solution at 22°C with a 12 hour contact time) fit the Langmuir isotherm with a clear sorption maxima being approached at less than 50 mg/L and less than 250 mg/L of DOC respectively. Despite the larger DOC concentration range of 1.8-2348 mg/L used in this study, no clear sorption maximum was apparent. It is unlikely that the clay mineral composition of the Oxford Clay caused the sorption behaviour to become linear since Saidy *et al* (2013) found that DOC sorption to each of the mineral fractions present in the Oxford Clay (smectite (32%), kaolinite (15%) and illite (9%)) (Environment Agency, 2009) Table 10, Section 4.2.1) in isolation was non-linear, Langmuir-type. Therefore, the difference in sorption behaviour is likely to be due to the OC content of the sediments, with the sorption of DOC being enhanced by the greater OC content of the Oxford Clay in comparison to other solid phases (Bright *et al*, 2000). However, in the case of solid phases with low OC content, DOC sorption may be largely governed by the reactive mineral phase, as discussed by Kaiser and Guggenberger (2000). For example, if DOC sorbs to the solid phase through chemisorptive processes such as hydrophobic interactions or ligand exchange then the presence of OC in the sorbent will increase the chemical functionality of the solid phase; thus increasing the potential for these reactions to occur due to the presence of more potential binding sites for the aqueous phase DOC to sorb to. This is plausible since the

majority of the literature used either low organic carbon sediments such as sand (0.4% OC) (Magee *et al*, 1991) or organic free clay minerals such as montmorillonite (Arnanson and Keil 2000) or kaolinite (Feng *et al*, 2005) all of which exhibited lower K_d values for DOC sorption than this work. The literature also used marine sediments at <0.05% OC (Thimsen and Keil, 1998), goethite (Wang *et al*, 1997), smectite (Saidy *et al*, 2013), and vermiculite (Zhang *et al*, 2012) which displayed non-linear sorption behaviour.

Assuming linearity of the isotherm, the K_d value found in this study for leachate DOC sorption to Oxford Clay (1.4×10^3 L/g) was comparable to that found by Arnanson and Keil (2000) for the sorption of NOM onto montmorillonite ($1.00\text{--}1.90 \times 10^3$ L/g). The K_d value for leachate DOC sorption obtained by this study was however higher; indicating more sorption than observed by Feng *et al* (2005) for peat HA extract onto montmorillonite and kaolinite ($2 \times 10^{-5}\text{--}1.9 \times 10^{-3} \times 10^3$ L/g), and by Vandenbruwane *et al* (2007) for the sorption of leaf litter leachate DOC onto a forest soil horizon (0.6% OC) from 10-19 cm depth (0.81×10^3 L/g). It was also higher than the sorption of soil DOM onto sand (0.11% OC), Magee *et al* (1991), (0.132×10^3 L/g). This increase in sorption in relation to the literature was likely to be attributable to the increased OC content of the Oxford Clay in comparison to the sediment used in literature studies.

The bulk inlet sediments and montmorillonite used as sorbents by Thimsen and Keil (1998) both also had significantly lower OC contents (<0.05% OC) than the Oxford Clay. Despite this the K_d values obtained in this work (1.4×10^3 L/g) were lower than the values of Thimsen and Keil (1998). This indicated less sorption of DOC to the Oxford Clay than observed by Thimsen and Keil (1998) for the sorption of marine NOM to montmorillonite or an OM extracted sediment ($80\text{--}330 \times 10^3$ L/g). This is contrary to the theory that the variation in K_d value was due to the OC content of the sorbent, as proposed above. Higher K_d values were also observed by Vandenbruwane *et al* (2007) for the sorption of DOC from leaf litter leachate DOC onto forest soils from 19-59 cm depth ($3.3\text{--}8.96 \times 10^3$ L/g); compared to the sorption of MSW leachate to the Oxford Clay (K_d of 1.4×10^{-3} L/g) in this work. Unlike the sorbents used by Thimsen and Keil (1998) the OC content of the soils used by Vandenbruwane *et al* (2007) had a range that included that of the Oxford Clay (0.046-6.12%). This indicated that the OC content of the sorbent was not the only factor affecting DOC sorption behaviour. The K_{oc} values for sorption calculated using parameters from Magee *et al* (1991), Thimsen and Keil

(1998) (assuming 0.05% OC), and Vandenbruwane *et al* (2007) were 0.12 L/g, 20-660 L/g and 0.05-8.98 L/g respectively. All of these were higher than the K_{oc} observed for sorption of DOC to the Oxford Clay (0.026 L/g). If the differences in K_d were solely attributable to the OC content of the sorbent then the K_{oc} values would be similar. However, Since this was not the case, the differences in sorption coefficient cannot be entirely attributed to the OC content of the sorbent.

The differences in sorption behaviour may also be partly attributable to the structure of the OC present in the solid phase. The presence of more geologically mature OC, such as kerogen (Taylor *et al*, 1998) has been shown to enhance sorption of organic compounds to sediments when present in the solid phase compared to geologically younger carbon type such as inertinite and fusinite (Grathwohl, 1990). The OC in the Oxford Clay is composed mainly of geologically immature OC, as demonstrated by Simoes (2005) who found the composition of Oxford Clay OC to be 92% liptinite (mainly amorphous organic matter (AOM)) with the remaining 8% of the OC being composed of inertinite, semifusinite and vitrinite. However, while this may explain the difference in sorption coefficient between the Oxford Clay and the forest soils whose OC would have been geologically even younger and more unaltered than the Oxford Clay (Vandenbruwane *et al*, 2007), it does not explain the variation in K_d between clay minerals with no OC. It also does not address why, in the case of Thimsen and Keil (1998) increased sorption was observed with a OC free or very low OC sorbent compared to the higher OC Oxford Clay. Mineral influences on the sorption may, therefore be responsible for this variation (Karickhoff, 1984).

The aqueous phase DOC used in the literature was extracted from a variety of natural sources such as plant shoots (Saidy *et al*, 2013), soil DOM (Magee *et al*, 1991), leaf litter (Vandenbruwane *et al*, 2007) and marine sediments (Thimsen and Keil, 1998; Arnarson and Keil, 2000). In the case of Arnarson and Keil (2000), a range of DOC molecular weights were obtained (<1000 Da and >1000 Da). DOC with a range of molecular weights was also obtained from HA and FA extracted from peat (Zhang *et al*, 2012) and purified HA (Feng *et al*, 2005) which were used to examine humic substance (HS) fractionation during DOC sorption. The DOC from the MSW leachate used in this study also contained a range of different DOC compounds (as indicated by fluorescence spectroscopy). However, unlike the DOC used in the literature which was derived from

natural sources, the DOC in the MSW leachate was derived from an anthropogenic source (waste). Leachates derived from wastes will be more complex chemically than natural leachates since they are derived from a wider variety of sources than naturally occurs in a single environment. For example, a landfill leachate may have DOC originating from biodegradable organic waste such as raw, or cooked foods and garden wastes, high lignin and cellulose paper products (most of which have been chemically treated and contain dyes), fabrics, hydrocarbon sources such as petrochemical products and residues from bottled substances such as paints, detergents, personal hygiene products, oils and household chemicals. Leachate DOC from wastes has also been shown to differ from both natural and commercially available DOC as it contained more aliphatic components than the humic acids and fulvic acids in DOC of terrestrial and freshwater origin (Nanny and Ratasuk, 2002) and less aromatic character with a higher percentage of smaller (<10000 Da) molecules than Aldrich HA (Kang *et al*, 2002). Therefore, the chemical nature (and so behaviour) of the DOC compounds in solution is dependent on the origin of the DOC, as well as the type of DOC present (e.g. PL or HSL). This may affect the sorption of DOC to the solid phase due to the reactivity and functionality of the DOC present in different leachates, and may, therefore, result in the observed differences in DOC sorption behaviour between this work and the literature.

The fluorescence ratios of MSW leachate before and after the sorption of leachate DOC to the Oxford Clay indicated an increase in the proportion of HSL DOC relative to the PL DOC in solution. This indicated that HSL DOC was preferentially sorbed to the clay. PL DOC is sterically smaller and less hydrophobic than HSL DOC, containing fewer organic functional groups. Arnarson and Keil (2000) demonstrated that an increased presence of functional groups on larger molecules increased sorption. This was supported by Zhou *et al* (2001) who observed the preferential sorption of high molecular weight compounds to the solid phase, while smaller molecular weight compounds remained in solution. This was attributed to competition of low MW compounds for sorption sites with larger molecular weight compounds, and is in agreement with the findings of this work that HSL DOC was preferentially sorbed to the Oxford Clay.

DOC has been shown to form complexes with HOCs (Chiou *et al*, 1986). Preliminary work (appendix 9.1, Section 5.1) showed that up to 3% of the OC content of the Oxford Clay could desorb into solution in the form of DOC dependant on the m:v ratio used.

The HOC sorption tests (Section 4.1.3) were performed with a m:v ratio at which desorption of OC from the clay into solution was negligible. However, at higher m:v ratios, an increase in the DOC concentration of aqueous phases, especially those with a low initial DOC concentration, may occur due to OC desorbing from the clay into solution as an equilibrium between the aqueous and solid phase OC is reached.

At leachate concentrations in solution greater than two percent by volume (42 mg/L), the difference in fluorescence ratios between sorption to the bottle alone and sorption to the bottle and clay did not show as clear a trend as those at less than two percent leachate by volume in solution. Figure 41 is based on the sorption equilibrium model proposed by Magee *et al* (1991) and outlines the possible sorption equilibrium processes for DOC at low (e.g. <42 mg/L) and high (e.g. >42 mg/L) concentrations. At low concentrations of DOC, the predominant DOC behaviour may be the desorption of DOC from the clay material (a), whereas at higher leachate concentrations, sorption of DOC from solution to the clay (b) may also occur alongside process (a) (Figure 41).

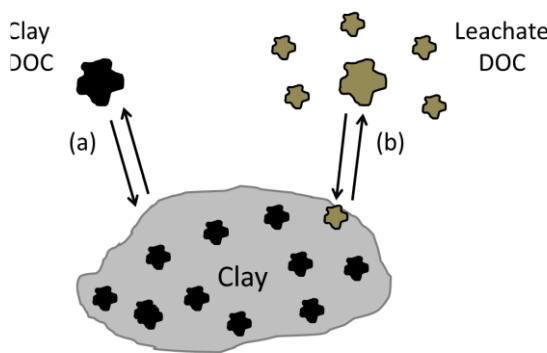


Figure 41: Schematic outlining the sorption equilibrium processes that may occur during DOC sorption to Oxford Clay at (a) low and (b) high DOC concentration in solution. Based on the sorption equilibrium model for DOM and phenanthrene proposed by Magee *et al* (1991).

In solutions with leachate volume greater than two percent, the E:F fluorescence ratios were only very slightly changed (from 0.72-0.9 to 0.68-0.89). This indicated that the overall proportion of the HL to FL DOC in solution was not largely altered by sorption to the clay. A small decrease in the B:D ratios (from 1.1-1.4 to 0.89-1.01) and increase in D:F ratio (from 0.42-0.63 to 0.59-0.76) were observed alongside an increase in the D:E ratio (from 0.47-0.87 to 0.72-1.12). These changes in the ratio were likely to be due to either an increase in the proportion of D (tyrosine like) DOC in solution or a decrease in

the proportion of E (FL) and F (HL) DOC in solution. If this was due to a decrease in HSL DOC in solution, the lack of significant alteration in the E:F ratio indicated that the decrease was likely to be in both HL and FL DOC. This could be attributable to the desorption of protein-like DOC already present in the clay into solution or sorption of HSL DOC from the leachate to the clay. However, preliminary work (Appendix A) showed that the proportion of DOC desorbed from the Oxford Clay into DOC free leachate with HSL character was greater than that with PL character, as indicated by fluorescence ratios of less than one (Table 26). Therefore, the alteration in fluorescence ratio at low leachate DOC concentration was unlikely to be due to desorption of PL DOC from the clay. It was therefore more likely that preferential sorption of the more hydrophobic HSL DOC to the clay explains the observed ratio changes in solutions of greater than two percent leachate in solution. This was in agreement with work by Zhou *et al* (2001) and Meier *et al* (1999) who also found that in DOC mixtures, HSL DOC was preferentially sorbed to clay and sediments and that the fractionation of DOC compounds during adsorption increased with an increase in MW. Therefore, the findings of this work, HSL DOC preferentially sorbs to the Oxford Clay, was in agreement with the literature.

Since DOC can form complexes with HOCs (Chiou *et al*, 1986) the desorption of DOC from the solid phase may also result in the desorption of any previously sorbed contaminants alongside the DOC. This could be due to OC desorption from the clay itself once the aqueous phase DOC concentration falls to sufficiently low levels (<42 mg/L based on preliminary testing). Therefore, desorption of HOCs from the solid phase alongside DOC has the potential to result in a secondary pollution source from the landfill liner. Levels of DOC have been measured at the g/L level decades post closure (Christensen *et al*, 1998). It may therefore be necessary to extend the post closure monitoring period of the landfill to incorporate HOC/DOC complex desorption from the liner. The risks posed would, however, be dependent on the sorption behaviours of HOCs in conjunction with leachate DOC and may not realistically be an issue. For example, if HOC sorption is easily reversible and HOC levels in the liner reduce before the DOC concentrations in the leachates fall, or if the DOC concentration falls within the monitored lifetime of the landfill. Whilst bound to the liner, biodegradation processes may also reduce the HOCs to a level that is no longer environmentally significant.

All the leachates used in this experimental work apart from the DOC free control leachate were within the higher DOC concentration range (>42 mg/L) (111-2268 mg/L DOC). Therefore, the sorption of HOCs was predicted to be impacted by the preferential sorption of HSL DOC. The preferential sorption of the HSL DOC from solution onto the clay may result in three different outcomes for HOC sorption, Section 2.2.6.2.

- 1- The HSL DOC in solution may compete with HOCs for sorption sites on the clay which would result in a reduction in HOC sorption to the clay.
- 2- HOCs may sorb to the HSL DOC in solution and co-sorb to the clay alongside the HSL DOC resulting in an increase in HOC sorption to the clay.
- 3- HSL DOC sorbing to the clay may increase the sorption capacity of the clay providing more organic sorption sites for the HOCs to bind to, increasing the sorption of HOCs.

The desorption of DOC from the Oxford Clay was non-linear and fitted better to the Freundlich isotherm than a linear isotherm with K_f and n equal to $0.0026 \mu\text{g}^{1-n} \text{L}^n/\text{g}$ and 1.42 respectively. Thimson and Keil (1998) also modelled desorption of DOC as non-linear and, when fitted to the Freundlich isotherm, obtained a desorption K_f value of $0.1-0.3 \mu\text{g}^{1-n} \text{L}^n/\text{g}$ which is two orders of magnitude higher than observed in this work. As with the sorption isotherms, the discrepancy between the literature and experimental values may be due to the difference in OC content of the sorbents used. Thimson and Keil (1998) used a low OC extracted marine sediment (<0.05% OC) whereas the Oxford Clay contained 5.49% OC. The n values of Thimson and Keil (1998) were, however close to one (1.05 and 1 for pore water NOM and extracted NOM respectively) indicating that the isotherm was in fact approximately linear; though they argue that it becomes non-linear at lower aqueous concentrations. The results of this study were in agreement with the results obtained by Thimson and Keil (1998). However, since the majority of the literature use the percentage of DOC desorbed after a number of desorption steps relative to the amount sorbed to quantify desorption rather than a sorption coefficient such as K_f for a single step desorption, this complicates comparison to the literature. Negligible desorption into a DOC free solution was observed by Jones and Tiller (1999) for soil humic acid desorbing from kaolinite. This was in agreement with the low levels of DOC desorption observed by Kaiser and Guggenberger (2000) (<3%) and Mikutta *et al* (2007) (2-3%) from a clay mineral solid phase. However, this was not in agreement with the DOC desorption from clay minerals (6-14%) observed by Saidy *et al* (2013),

from vermiculite (18-35%) (Mikutta *et al*, 2007) and from soils and clay minerals (13-50%) (Kahle *et al*, 2004).

The differences between the negligible desorption observed by Jones and Tiller (1999) and the 2-50% desorption observed in the other literature may be attributable to the type of DOC in solution. Jones and Tiller (1999) used soil HA (IHSS) as a DOC source, whereas the other DOC sources used in the literature were derived from plants or forest floor environments. The majority of the literature also used OM free clay minerals as sorbent (e.g. Jones and Tiller, 1999). Therefore, variation in DOC desorption behaviour due to a difference in the OC percentage content of the sediments studied is unlikely. However, the variation observed in the literature between different clay minerals (negligible to 50% desorption) indicates that the clay mineral is affecting the desorption of DOC from the clay when there is no OC component to the sorbent, in agreement with Mikutta *et al* (2007) and Saidy *et al* (2013). Sorption hysteresis was also observed for DOC (Figure 24). This was in agreement with Kaiser and Guggenberger (2000) who found DOC sorption to not be easily reversible, with significant hysteresis observed. Hysteresis of the isotherm may be due to desorption from the Oxford Clay being a multistep process rather than a single step process (Kleber *et al*, 2007; Zhang and Liu, 2010).

6.1.2 Sorption and Desorption of Toluene to the Oxford Clay

Table 33 shows a summary of the experimental data obtained in this study alongside literature data. In the case of DOC free, MBT, diluted MSW and diluted HA leachate, the toluene K_d values obtained for sorption (0.078, 0.10, 0.11 and 0.085 L/g respectively) were comparable to the value for synthetic leachate containing tannic acid (0.094 L/g) observed by Simoes *et al* (2011) and Environment Agency (2009). The K_{oc} value for Simoes *et al* (2011) and Environment Agency (2009) in synthetic leachate (1.72 L/g) was also within the range of these four leachates (1.42, 1.82, 2.00 and 1.55 L/g respectively). Since the solid phase, and its f_{oc} , is identical in this work to that used by Simoes *et al*

(2011) any K_d variations observed in toluene sorption isotherms are likely to be due to variation in the solution phase DOC rather than differences in solid phase OC.

| Aqueous phase | Solid phase (% organic carbon) | K _a (L/g) (x10 ³) | K _{oc} (L/g) | Freundlich isotherm K _f (mg ¹⁻ⁿ L ⁿ /g) unless otherwise stated and (n) | Ref. |
|-------------------|---|--|-----------------------|--|------|
| DOC free | Oxford Clay (5.49) | 78 | 1.42 | 0.081 (0.99) | e |
| MSW | Oxford Clay (5.49) | 46 | 0.84 | 0.047 (1.00) | |
| AMSW | Oxford Clay (5.49) | 38 | 0.69 | 0.03(0.93) ⁺ | |
| MBT | Oxford Clay (5.49) | 100 | 1.82 | 0.62 (0.72) | |
| HA | Oxford Clay (5.49) | 310 | 5.65 | 0.39 (1.35) ⁺ | |
| MSW (1:20) | Oxford Clay (5.49) | 110 | 2.00 | 0.10 (1.02) | |
| HA (1:2) | Oxford Clay (5.49) | 85 | 1.55 | 0.084 (0.29) ⁺ | |
| Synthetic with TA | Oxford Clay (5.49) | 94 | 1.72 ^a | 0.15 (0.93) ⁺ | 1 |
| Water | Humic acid coated Al ₂ O ₃ (0.54) | 400 | 74 | --- | 2 |
| | Humic acid (33.5) | 62500 | 187 | --- | |
| | Offhut Soil (0.23) | 440 | 191 | --- | |
| | Whiteman soil (0.41) | 320 | 77 | --- | |
| Phosphate buffer | Sapsucker woods HA | 10.1 | 0.081 | --- | 3 |
| | Sapsucker woods FA | 2.59 | 0.014 | --- | |
| | Tannic acid | 7.76 | 0.015 | --- | |

| | | | | | |
|-----------------------------|--|--------|-------------------|-----|---|
| | Lignin | 97.2 | 0.15 | --- | |
| | Zein | 70.3 | 0.13 | --- | |
| | Cellulose | 0.02 | 0.00005 | --- | |
| | Aldrich Humic acid | 42.4 | 0.088 | --- | |
| Synthetic ground water | Natural aquifer | 0.37 | 0.25 ^a | --- | 4 |
| Methanogenic phase leachate | Triassic sandstone West midlands (0.026) | 0.0077 | 0.03 | --- | 5 |
| Acetogenic phase leachate | Triassic sandstone Nottingham (0.147) | 0.046 | 0.031 | --- | |
| | | 0.018 | 0.012 | --- | |

Table 33: Experimental sorption parameters for toluene sorption to the Oxford Clay (e) alongside literature values for DOC sorption. (1) Simoes *et al* (2011) and Environment Agency (2009) (2) Garbarini and Lion (1985) (3) Garbarini and Lion (1986) (4) Schwarzenbach and Westall (1981) (5) Thornton *et al* (2000). ⁺ From the linearized logarithmic form of the Freundlich isotherm $\text{Log}(C_s) = \text{Log}(K_f) + n \text{Log}(C_{aq})$ (otherwise K_f and n are from the original Freundlich isotherm $C_s = K_f C_{aq}^n$). K_{oc} is either directly taken from the literature or calculated (^a) (as detailed in Section 2.2.3.1).

The linear nature of the DOC free, MSW, MBT and diluted MBT toluene sorption isotherms was in agreement with the literature observations (Garbarini and Lion, 1985; Garbarini and Lion, 1986; Schwarzenbach and Westall, 1981; Thornton *et al*, 2000) where toluene sorption to soil OC was studied. However, the non-linear nature of the AMSW, HA and diluted HA leachate isotherms was contrary to the literature, which largely modelled toluene sorption onto soil derived DOC and natural aquifer materials as linear (Garbarini and Lion, 1985; Garbarini and Lion, 1986; Schwarzenbach and Westall, 1981). The sorbents used in all of these literature studies were, however, different in OC content to the Oxford Clay. Garbarini and Lion (1986) used OC extracts from soils (100% OC) as a sorbent, Schwarzenbach and Westall (1981) used a natural aquifer material (0.37% OC) and Garbarini and Lion (1985) used either a low OC soil or HA (0.23-0.54% and 33.5% respectively) as a sorbent. Since the Oxford Clay has a higher OC content than these low OC soils, but a lower OC content than the OC extracts used as sorbents; and the OC content of the sorbent can affect the sorption of HOCs, Section 2.2.6.1. Differences in OC content of the sorbents may therefore be affecting the sorption behaviour of toluene. For example, an increase in OC in the sorbent may provide additional sorption sites for toluene due to the OC increasing the functionality of the surface. This may result in a linear isotherm as opposed to a Freundlich or Langmuir type isotherm with a sorption maximum, at which sorption may be limited by sorption sites on the surface.

While toluene sorption in the DOC free leachate of this work was a reasonable match to the toluene sorption observed by Simoes *et al* (2011) (K_d 0.078 and 0.094 L/g and K_{oc} 1.42 and 1.72 L/g respectively), a better fit was achieved by sorption in diluted HA leachate (K_d 0.085 L/g, K_{oc} 1.55 L/g). As the only difference between these three batch tests was the inclusion of tannic acid as a DOC source in the synthetic leachate by Simoes *et al* (2011) and Aldrich HA for diluted HA, this indicates that inclusion of a ‘synthetic’ DOC source in the leachate increased sorption of HOCs to the Oxford Clay. The K_f value from the Log linearization of the Freundlich isotherm for toluene sorption in the presence of tannic acid (Environment Agency, 2009) ($0.15 \mu\text{g}^{1-n} \text{L}^n/\text{g}$) was between those obtained in this study for HA, diluted HA, MBT and AMSW leachates (0.39, 0.84, 0.62 and $0.03 \mu\text{g}^{1-n} \text{L}^n/\text{g}$ respectively). The K_f values for the commercially sourced HA, diluted HA and tannic acid leachates (Environment Agency, 2009) were much higher than that of the waste derived AMSW leachate. This may indicate that waste derived

DOC and commercially sourced DOC surrogates (e.g. TA and HA) interact with the toluene, the clay, or both in different ways and therefore have different effects on the sorption of toluene. This may be due to the more uniform nature or higher functionality of commercially available DOC sources in comparison to waste derived DOC. The MBT leachate, however, had a higher K_f value than observed in the tannic acid containing aqueous phase. This is likely to be due to the higher concentration of DOC in the MBT leachate in comparison to the other aqueous phases.

Toluene sorption in the MBT and diluted MSW leachates exhibited K_{oc} and K_d values slightly greater than those observed by Simoes *et al* (2011) (K_d 0.10, 0.11 and 0.094 L/g and K_{oc} 1.82, 2.00 and 1.72 L/g respectively). In the case of HA leachate (K_d 0.31 L/g, K_{oc} 5.61 L/g) more sorption of toluene was observed than reported by Simoes *et al* (2011) and the Environment Agency (2009). The commercially available humic acid used in the HA leachate also differed from the tannic acid. The HA leachate is very mature (HIX 11.4) and though tannic acid has no fluorescence activity to compare it to the other leachates, the HA consists of a mixture of larger molecular weight compounds (MW 1->300 kDa (Shin *et al*, 1999)) than the tannic acid (MW 1701.2 g/mol). Differences in the K_{oc} values indicated that differences in sorption behaviour were not due to the OC of the solid phase (the sorbents used in this work and by Simoes *et al* (2011) were the same). Therefore differences in sorption behaviour are likely to be attributable to the DOC in solution. While the MBT DOC is more mature in nature in comparison to the diluted MSW DOC (HIX 1.7 and 1.4 respectively), they are both waste derived DOC sources. This differs from the tannic acid used by Simoes *et al* (2011) in which the tannic acid used was from a commercially available source and consisted of a single defined empirical formula ($C_{76}H_{52}O_{46}$) and molecular weight (1701.2 g/mol) (Sigma-Aldrich Company Ltd). Structural and chemical differences between the more uniform tannic acid DOC compounds and the complex and highly variable waste derived DOC may account for differences in sorption behaviour as suggested by the Environment Agency (2009) who found that leachate DOC sorbed more strongly to the Oxford Clay than tannic acid. This may result in an increase in toluene sorption to the Oxford Clay when in the presence of leachate DOC compared to commercially available DOC due to increased co-sorption of DOC-toluene complexes to the sorbent (Section 2.2.6.2) or enhancement of sorption sites on the solid phase due to DOC sorption increasing the functionality of the surface via cumulative sorption, Section 2.2.6.2. This may be driven by the leachate

DOC sorbing more strongly to the solid phase than the tannic acid. Co and cumulative sorption processes between the DOC and toluene may still be occurring in the presence of tannic acid to a lesser degree, however, as tannic acid may be sorbing less strongly to the clay, which would result in lower K_d values for tannic acid than for the waste derived leachate DOC.

The values of K_d and K_{oc} obtained for toluene sorption to Oxford Clay in MSW, AMSW and diluted HA leachate (K_d 0.046, 0.038 and 0.085 L/g, and K_{oc} 0.84, 0.69 and 1.55 L/g respectively) were lower than those observed by Simoes *et al* (2011) and Environment Agency (2009) (K_d 0.094 L/g, K_{oc} 1.72 L/g). MSW and AMSW leachate DOC differs from the tannic acid used as a DOC surrogate by Simoes *et al* (2011) and the Environment Agency (2009) as they contain waste derived DOC. The MSW leachate contained both PL and HSL DOC with a lower maturity (HIX 1.4) than the more mature, largely HSL DOC of the AMSW leachate (HIX 2.9). Compared to the more uniform DOC structure of the tannic acid (Environment Agency, 2009; Sigma-Aldrich Company LTD). This difference in DOC structure may be the reason for the observed differences in sorption behaviour.

K_d values for toluene sorption in all leachates in this study (0.038-0.31 L/g) were higher than those seen in the sorption of toluene to a natural aquifer material in synthetic groundwater (0.37×10^{-3} L/g) (Schwarzenbach and Westall, 1981) and a low OC aquifer in leachates ($0.77-1.8 \times 10^{-5}$ L/g) (Thornton *et al*, 2000). K_{oc} values for the leachates in this study (0.69-5.65 L/g) were also higher than those observed by Schwarzenbach and Westall (1981) and Thornton *et al* (2000) (0.25 and 0.012-0.03 respectively) indicating that this difference is likely to be attributable to the DOC in solution rather than the sorbent OC.

K_d values for all leachates in this work (0.038-0.31 L/g) were, however, lower than those found for toluene sorption to soils and HAs in water (0.32-62.5 L/g) (Garbarini and Lion, 1985). The K_d value for toluene sorption in HA leachate (0.31 L/g) was comparable with the sorption of toluene to the Whiteman soil (K_d 0.32 L/g) (Garbarini and Lion, 1985). K_{oc} values for the sorption data of Garbarini and Lion (1985) (74-191 L/g) were, however, much higher than those obtained in this study (0.69-5.65 L/g). Although variations in the K_{oc} values indicate that DOC rather than the sorbent OC alone is

attributable for the differences in sorption, the nature of the sorbent OC may also play a role.

Experimental K_d values for the leachates (0.038-0.31 L/g) were within the range given by Garbarini and Lion (1986) for lignin, zein and Aldrich HA sorbents (0.04-0.097 L/g). The K_d value for lignin (0.097 L/g) was comparable to that of MBT leachate (0.10 L/g) and the K_d value for Aldrich HA (0.04 L/g) was comparable to that of MSW leachate (0.046 L/g). The K_d values for all the leachates in this study were, however, higher than the other substrates examined by Garbarini and Lion (1986) (0.2×10^{-4} -0.01 L/g). This may be due to the type of OC used as the sorbent as AHA was shown to behave differently to natural HA and FA compounds. K_{oc} values obtained by Garbarini and Lion (1986) (0.5×10^{-4} -0.15 L/g) were, however, up to two orders of magnitude lower than those obtained in this study (0.44-5.61 L/g). The variation in K_{oc} between this study and the literature indicates that the DOC in solution and not just the solid phase OC may impact toluene sorption

From comparing K_{oc} values from this study to those from the literature with varying levels of sorption; differences in the aqueous phases used may also have an impact on the sorption behaviour of toluene. The literature studies predominantly used DOC free aqueous phases. For example, the solution phase used by Schwarzenbach and Westall (1981) was a synthetic groundwater containing <0.2 mg/L DOC; the solution phase used by Garbarini and Lion (1985 and 1986) was water and phosphate buffer respectively. This work used leachates containing different types of DOC in addition to a DOC free leachate. Toluene sorption in the DOC free leachate used in this study (K_d 0.078 L/g) exhibited linear behaviour and was close to the values for sorption observed by Simoes *et al* (2011) and the Environment Agency (2009) for the sorption of toluene to the Oxford Clay in a tannic acid containing leachate (K_d 0.094 L/g). It was also in agreement with the sorption of toluene to lignin and zein in a phosphate buffer leachate (K_d 0.097 and 0.070 L/g respectively) observed by Garbarini and Lion (1986). Some of the OC extracts used in the literature as sorbents, such as the humic acid used by Garbarini and Lion (1985 and 1986) and the fulvic and tannic acids used by Garbarini and Lion (1986) may not only exist as a solid phase sorbent, but may also reside in solution as DOC. This was supported by Garbarini and Lion (1986) who found that all of the Sapsucker woods FA, and a portion of the other sorbents were dissolved in the solution phase acting

as DOC rather than solid phase OC. It is therefore obvious that the system in which toluene is sorbing differs from that of this work, where toluene was sorbing to the solid phase Oxford Clay in aqueous phases of varying DOC character. Differences in both the solid and solution phase in comparison to this work therefore mean that differences in the sorption behaviour of toluene between this work and the literature discussed above are to be expected. It should also be noted that, in this work, DOC may compete with toluene for sorption sites on the solid phase (Section 2.2.6.2). Whereas in the case of Garbarini and Lion (1985 and 1986) the toluene is simply partitioning onto a single sorbent (OC extracts; either dissolved or solid phase) in the absence of any secondary DOC competition for sorption sites.

The composition of the DOC, for example its maturity and associated structural and chemical behaviour, therefore must also affect the sorption of toluene to the Oxford Clay alongside the DOC concentration. This is apparent when plotting the graph of K_d vs DOC concentration or maturity where no trend was observed. This was also supported by Thornton *et al* (2000), who found that leachates of different ages, and so different DOC composition (Section 2.1.4) altered the sorption of toluene. Thornton *et al* (2000) also demonstrated that leachates of different ages impacted the sorption behaviour of toluene. The difference in K_d value for toluene sorption between the acetogenic leachate used by Thornton *et al* (2000) and the MSW leachate used in this work ($0.018\text{-}0.046 \times 10^3 \text{ L/g}$ and $46 \times 10^3 \text{ L/g}$ respectively) indicated that much less sorption was observed by Thornton *et al* (2000) than in this work. “*No significant sorption*” of solution phase OC to the aquifer material was reported by Thornton *et al* (2000). This may be due to the higher OC concentration of the leachate used by Thornton *et al* (2000) (18900 mg/L compared to 2388 mg/L for MSW leachate). The decreased sorption observed by Thornton *et al* (2000) in comparison to the MSW leachate of this work may, therefore, be due to sorption of toluene to aqueous phase DOC rather than the solid phase. This would, therefore, result in a decrease in the sorption of toluene to the sorbent as it is residing in solution bound to the DOC.

Thornton *et al* (2000) also noted that the sorption of toluene to aquifer materials (Triassic sandstone) was greater in younger, acetogenic phase (A-phase) (K_d $0.018\text{-}0.046 \times 10^3 \text{ L/g}$) (Section 2.1.4) leachates than in more mature methanogenic phase (M-phase) leachates (K_d $0.0077 \times 10^3 \text{ L/g}$). This was three to four orders of magnitude lower than

the sorption coefficients obtained in this work in the case of both leachates. As the K_{oc} values obtained by Thornton *et al* (2000) were also one to two orders of magnitude lower than this work (0.012-0.031 L/g compared with 0.44-5.65 L/g), the organic carbon content of the sorbent was not the sole reason for the variation in K_d values. Therefore, the type of DOC present in solution must also have an effect on toluene sorption. This highlights the variability in sorption behaviour between different leachates.

As DOC has been shown to sorb reversibly to the Oxford Clay when there is no HOC in solution (Section 5.1) it is reasonable to assume that the DOC present in solution will also move toward a sorption equilibrium with the Oxford Clay when HOCs are present. In this case as the DOC is moving toward equilibrium with the clay toluene is also moving toward equilibrium with both the DOC in solution and the Oxford Clay. As toluene can form complexes with DOC (Garbarini and Lion, 1986) an increase in DOC sorbed to the clay, and therefore an increase in toluene-DOC complexes sorbed to the clay, could result as the DOC-clay system moves towards equilibrium. This was supported by Magee *et al* (1991) who found that DOM acted as a carrier molecule and enhanced the transport phenanthrene, a larger PAH containing 3 benzene rings, which is expected to behave similarly in solution to naphthalene due to their structural similarity.

The relationship between the toluene-DOC complexes and sorption is further complicated since greater toluene sorption was observed with the less mature diluted MSW leachate than with the more mature diluted HA or AMSW leachates despite them being of similar DOC concentration. This indicated that DOC type as well as concentration had an effect on toluene sorption. This could be due to availability of sorption sites for PL DOC that are inaccessible to HL DOC (e.g. for steric reasons) (Sykes, 1986). In this scenario, toluene could be undergoing co-sorption with the protein-like DOC to the surface of the clay in sites that are sterically inaccessible to the larger HSL DOC. Alternatively, the PL DOC could be enhancing the surface of the clay, making it easier for the toluene (alone or bound to humic-like DOC) to sorb to the clay surface.

The solution phases used by Thornton *et al* (2000) were UK domestic waste (MSW) landfill leachates from both the acetogenic and methanogenic phases of landfill stabilisation. Although details of the DOC concentration or the nature of the OC in the leachates were not given, the TOC concentration of the acetogenic leachate was

significantly higher than the TOC concentration of the leachates used in this work (18900 mg/L compared to 2348 mg/L for the MSW leachate (2268 mg/L DOC)). The K_{oc} values obtained in this study (0.44-5.61 L/g) were again higher than those of Thornton *et al* (2000) (0.012-0.03 L/g). Therefore, variation in K_d was not due to differences in the OC content of the sorbent. The work of Thornton *et al* (2000), again showed that changes in K_{oc} are likely to be due to differences in the solution phase, further highlighting the complex chemical nature of landfill leachates and the difficulty of reliably reproducing a real leachate media on which to base the prediction of sorption behaviour.

Desorption of toluene from the Oxford Clay was observed in DOC free, MSW, MBT and diluted MSW leachates. No desorption of toluene was observed from the clay in AMSW, HA or diluted HA leachates. The desorption of toluene was non-linear in all cases where it was observed. In comparison to DOC free leachate, more desorption of toluene was observed from the clay in DOC containing aqueous phases.

The literature for toluene desorption from clays into an aqueous phase is limited; with the focus of the literature being mainly gaseous phase toluene, solid phase micro-extraction and thermal desorption (Arthur and Pawliszyn, 1990; Keyes and Silcox, 1994; Liu *et al*, 2005; Owens *et al*, 1992; Potter and Pawliszyn, 1994). Chatzopoulos *et al* (1995) however, observed that the desorption of toluene from activated carbon (200x325 mesh) into deionised (DI) water was 95% reversible, with only a 5% fraction irreversibly sorbed. In this study, hysteresis was observed between toluene sorption and desorption, which was in agreement with the Environment Agency (2009) who observed that desorption from the Oxford Clay had an irreversible fraction. Although slightly less desorption of toluene from the Oxford Clay into a DOC free leachate was observed by the Environment Agency (2009) (K_d 0.19 L/g) than in this study (K_d 0.14 L/g), more desorption was observed into MSW, MBT and diluted MSW leachates (0.070, 0.11 and 0.068 L/g respectively) than into DOC free leachate, indicating that DOC in the aqueous phase increased the desorption of toluene from the Oxford Clay relative to toluene desorption in a DOC free aqueous phase.

As there was no change in the solid phase between experiments in this work, the differences in desorption observed between the DOC free leachate and the MSW, MBT

and diluted MSW leachates was attributed to the organic carbon present in the leachate. This was supported by Garoma and Skidmore (2011) who observed an increase in the rate of toluene desorption from a bentonite clay with increasing ethanol content in solution. Although this is a different DOC source to leachate DOC, both in molecular character and complexity, it does indicate that an increase in the organic component of a solution may result in more rapid desorption of toluene from clays. However, in this study, while toluene desorption was greater in the high concentration MSW leachate (2268 mg/L) than the MBT leachate (1051 mg/L) toluene desorption in diluted MSW leachate (116 mg/L) was greater than desorption in MBT leachate (1051 mg/L). This does not fit with the literature trend that an increase in DOC concentration in solution results in an increase in desorption of toluene. This was attributed to the DOC in leachates not being directly chemically analogous to ethanol due to the more complex molecular structure and composition of leachate DOC. It also further confirms that the type of DOC in solution as well as the concentration in solution affects the desorption behaviour of toluene. Desorption was greater when MSW DOC (from either neat or diluted MSW leachates) was present in solution than MBT leachate DOC. This indicated that it was not just the concentration of DOC in solution facilitating the partitioning of toluene from the clay into the aqueous phase. This may be due to the greater HSL maturity of the DOC in the MBT leachate than in MSW leachate (HIX 1.71 and 1.38 respectively) promoting stronger binding of toluene to the clay during the sorption step (Murphy *et al*, 1992) which could occur through co-sorption or cumulative sorption. This was supported by the lack of desorption observed in the three leachates with the highest maturity; AMSW, HA and diluted HA leachates (HIX 2.94-11.4).

The relationship between the amount of desorption observed and the DOC present in solution could not be explained simply by virtue of the concentration or maturity of the DOC in solution alone, as both increases and decreases in toluene desorption were observed in leachates containing DOC and with comparable HSL maturity, compared to desorption in the DOC free leachate. Therefore, both the HSL maturity and the DOC concentration of leachates must affect desorption of toluene from the Oxford Clay. This may be due to HSL DOC binding toluene more strongly to clay surfaces in the presence of DOC, resulting in decreased desorption from the clay. High concentrations of DOC in solution may also be creating a more hydrophobic aqueous environment, facilitating an increase in desorption in a DOC containing leachate relative to desorption in the DOC

free leachate and lower DOC concentration leachates may also be a possible explanation for this.

6.1.3 Sorption and Desorption of Naphthalene to the Oxford Clay

Tables 34 and 35 show a summary of the experimental data obtained in this study alongside literature data for sorption and desorption respectively. For non-linear isotherms, K_f values compared are derived from the linearized Freundlich isotherm.

| Aqueous phase | Solid phase (% organic carbon) | K_d (L/g) ($\times 10^3$) | K_{oc} (L/g) (*=from K_f) | Freundlich isotherm K_f ($mg^{1-n}L^n/g$) unless otherwise stated and (n) | Ref. |
|-----------------------------|--|----------------------------------|--------------------------------------|--|------|
| DOC free | Oxford Clay (5.49) | 1890 | 34.43 | 2.37 (0.9) | e |
| MSW | Oxford Clay (5.49) | 760 | 13.84 | 0.79 (0.65) ⁺ | |
| AMSW | Oxford Clay (5.49) | 120 | 2.19 | 0.11 (1.15) ⁺ | |
| MBT | Oxford Clay (5.49) | 940 | 17.12 | 1.16 (0.94) | |
| HA | Oxford Clay (5.49) | 2310 | 42.08 | 2.14 (0.59) ⁺ | |
| MSW 1:20 | Oxford Clay (5.49) | 1200 | 21.86 | 0.85 (1.09) | |
| HA 1:2 | Oxford Clay (5.49) | 680 | 12.39 | 0.89 (1.16) ⁺ | |
| MBT 1:10 | Oxford Clay (5.49) | 1360 | 24.77 | 0.81 (1.18) | |
| Synthetic with TA | Oxford Clay (5.49) | 2140 | 38.93 ^a | 3.14 (0.91) ⁺ | |
| Synthetic no TA | Oxford Clay (5.49) | 2330 | 49.40 ^a | 2.52 (1.0) ⁺ | |
| Methanogenic phase leachate | Triassic sandstone West midlands (0.026) | 0.527 | 2.03 | --- | 2 |
| DI water | Cote st andre cultured soil (1.4) | 4.23 | 0.30 ^a | --- | 3 |
| | Cote st andre meadow soil (3.2) | 9.4 | 0.29 ^a | --- | |
| | Pequest (1.4) | 4.8 | 0.34 ^a | --- | |
| | Eurosoil III (3.4) | 14.2 | 0.42 ^a | --- | 3 |
| | Eurosoil IV (1.5) | 5.1 | 0.34 ^a | --- | |
| 0.01 M $CaCl_2$ | Eustis soil (0.66-0.68) | 3 | 0.45 | --- | 4 |
| | | 5.47 | 0.80 | --- | |
| | Lincoln soil (0.036) | 0.136 | 0.38 | --- | |
| | Lincoln soil (0.12) | 9.8 | 8.17 | --- | |
| | Lincoln soil (0.063) | 2.3 | 3.65 | --- | |
| | Soil O1 (49) | --- | 0.45* | 0.223 (0.97) ⁺ | 5 |

| | | | | | |
|---|-------------------------------------|------------|-------------------|----------------------------|----|
| Aq. solution 0.005 M $CaSO_4$ & 0.02% NaN_3 | Soil O2 (39) | --- | 0.59* | 0.232 (0.97) ⁺ | 6 |
| | Soil O3 (41) | --- | 0.59* | 0.24 (0.97) ⁺ | |
| | Soil A1 (5.9) | --- | 3.73* | 0.22 (0.92) ⁺ | |
| | Soil A2 (2.1) | --- | 10.33* | 0.217 (0.89) ⁺ | |
| | Soil A3 (0.5) | --- | 44.4* | 0.222 (0.87) ⁺ | |
| 0.01 M $CaCl_2$ | Columbus aquifer material A (0.027) | 0.11 | 0.41 ^a | --- | 7 |
| | Columbus aquifer material B (0.064) | 0.15 | 0.23 ^a | --- | |
| | Columbus aquifer material C (0.026) | 0.07 | 0.27 ^a | --- | |
| | Soil 1 (53.4) | 781 | 1.46 | 0.775 (1) ⁺ | |
| | Soil2 (32.2) | 158 | 0.49 | 0.164 (0.99) ⁺ | |
| 0.15 M $NaCl$, 0.004 M Na_2HPO_4 and 0.002M KH_2PO_4 | Soil 3 (7.38) | 45.4 | 0.62 | 0.0565 (0.88) ⁺ | 7 |
| | Soil 4 (4.53) | 31.9 | 0.70 | 0.0357 (0.96) ⁺ | |
| | Soil 5 (2.55) | 13.4 | 0.55 | 0.0165 (0.9) ⁺ | |
| | Coarse silt (2.78-3.27) | | 0.0013 | | 8 |
| | Baker Soil (1.99) | 23 | 1.16 ^a | --- | |
| 0.01 M $CaCl_2$ | Baxter Soil (6.06) | 36.8 | 0.61 ^a | --- | 9 |
| | Colwood whole Soil (10.8) | 72 | 0.67 ^a | --- | |
| | Colwood Organic (20.3) | 250 | 1.23 ^a | --- | |
| | Lee Soil (9.82) | 94.3 | 0.96 ^a | --- | |
| | River Sediment (2.96) | 23.8 | 0.80 ^a | --- | |
| | Synthetic sorbents (nd) | 1010-20600 | nd | --- | |
| | High OC soil (3.2) | 18.2 | 0.56 ^a | --- | |
| 0.01 M $CaCl_2$ | Low OC soil (0.52) | 0.96 | 0.18 ^a | --- | 10 |
| | Hagerstown silt loam (1.94) | 8 | 0.41 ^a | --- | |
| | Berkley silt loam (2.85) | 8.5 | 0.30 ^a | --- | |
| | Tifton sand (0.5) | 2 | 0.4 ^a | --- | |
| | Hagerstown silt | 4 | 0.21 ^a | --- | |

| | | | | | |
|---|--------------------------------|---------|------------------------|-----|----|
| 20% by vol. CH_3OH in DI water | loam (1.94) | | | | 11 |
| | Berkley silt loam (2.85) | 4.4 | 0.15 ^a | --- | |
| | Tifton sand (0.5) | 1 | 0.2 ^a | --- | |
| 0.01 M CaCl_2 30-50% by vol. CH_3OH in DI water | Hagerstown silt loam (1.94) | 0.7-1.8 | 0.04-0.09 ^a | --- | 11 |
| | Hagerstown silt loam (1.94) | 0.5-4.7 | 0.03-0.24 ^a | --- | |

Table 34: Isotherm parameters for experimental data obtained in this study (e) alongside literature data for naphthalene sorption. (1) Simoes *et al* (2011) and Environment Agency (2009) (2) Thornton *et al* (2000) (3) Bayard *et al* (1998) (4) Bouchard *et al* (1990) (5) Xing (2001) (6) Macintyre *et al* (1992) (7) Xing (1997) (8) Karickhoff *et al* (1979) (9) Guerin and Boyd (1997) (10) Burgos *et al* (1996) (11) Fu and Luthy (1986).

⁺ From the linearized logarithmic form of the Freundlich isotherm; otherwise K_f and n are from the standard Freundlich isotherm. K_{oc} is either directly taken from the literature or calculated (^a) Section (2.2.3.1).

| Aqueous phase | Solid phase (% organic carbon) | K_d (L/g) ($\times 10^3$) | Freundlich isotherm K_f ($\text{mg}^{1-n}\text{L}^n/\text{g}$) unless otherwise stated and (n) | Ref. |
|----------------------|-----------------------------------|----------------------------------|---|------|
| DOC free | Oxford Clay (5.49) | 1.85 | 1.35 (1.48) ⁺ | e |
| MSW | Oxford Clay (5.49) | 1.02 | 2.09 (0.65) ⁺ | |
| AMSW | Oxford Clay (5.49) | 0.47 | 0.3 (0.95) ⁺ | |
| MBT | Oxford Clay (5.49) | 0.048 | 0.38 (0.48) ⁺ | |
| HA | Oxford Clay (5.49) | 0.48 | 0.83 (0.39) ⁺ | |
| MSW 1:20 | Oxford Clay (5.49) | 0.16 | 0.51 (0.58) ⁺ | |
| HA 1:2 | Oxford Clay (5.49) | 0.40 | 0.01 (1.88) ⁺ | |
| MBT 1:10 | Oxford Clay (5.49) | 0.32 | 0.55 (0.87) ⁺ | |
| Synthetic with TA | Oxford Clay (5.49) | 4.51 | 10.23 (0.74) ⁺ | 1 |
| DI water | Cote st andre cultured soil (1.4) | 0.00417 | --- | 3 |
| | Cote st andre meadow soil (3.2) | 0.00854 | --- | |
| | Pequest (1.4) | 0.00428 | --- | |
| | Eurosoil III (3.4) | 0.01097 | --- | |
| | Eurosoil IV (1.5) | 0.00468 | --- | |

Table 35: Isotherm parameters for experimental data obtained in this study (e) alongside literature data for naphthalene desorption. (1) Simoes *et al* (2011) and Environment Agency (2009) (3) Bayard *et al* (1998).

⁺ From the linearized logarithmic form of the Freundlich isotherm; otherwise K_f and n are from the standard Freundlich isotherm. K_{oc} is either directly taken from the literature or calculated (^a) Section (2.2.3.1).

The sorption isotherms in DOC free, MSW, AMSW, MBT, diluted MSW and diluted MBT leachates were linear, which was in agreement with some of the literature which used aqueous phases both containing and omitting DOC. Guerin and Boyd (1997) observed that the sorption of naphthalene to both natural and synthetic sorbent materials in phosphate buffered saline was linear. Sorption of naphthalene to soils was also found to be linear in 0.01 M CaCl₂ solution (Burgos *et al*, 1996; Bouchard *et al*, 1990). Naphthalene sorption to Aquifer materials in 0.005M CaSO₄ and to silt and soils in DI water (Bayard *et al*, 1998; Karickhoff *et al*, 1979; Macintyre *et al*, 1992) was also linear. The linear behaviour of naphthalene sorption has also been observed when DOC was present in the aqueous phase in the form of organic solvents (Fu and Luthy, 1986) and in a methanogenic landfill leachate (Thornton *et al*, 2000).

Naphthalene sorption in DOC free leachate had a higher K_d value than all of the leachates except HA. This indicated that sorption of naphthalene to the clay in the presence of a DOC containing aqueous phase was reduced. This was in agreement with the findings of the Environment Agency (2009) that sorption of HOCs to liner materials increased when there was no DOC in solution compared to when it was present. This may either be due to competitive sorption of DOC to the clay alongside naphthalene, or sorption of the naphthalene to the aqueous phase DOC, allowing naphthalene to remain in solution. The values of K_d obtained for naphthalene sorption to Oxford Clay in all leachates except the HA leachate were also lower than those observed by Environment Agency (2009) in a DOC free leachate (2.33 L/g) supporting the decrease in naphthalene sorption observed with the addition of DOC to the aqueous phase.

The K_d values for naphthalene sorption to Oxford Clay in all leachates except the HA leachate were also lower than those observed by Environment Agency (2009) where tannic acid was used as a DOC surrogate (K_d 3.14 L/g). Naphthalene sorption in HA leachate (K_d 2.14 L/g) was, however, greater than that obtained in tannic acid (K_d 3.14 L/g). This could be attributed to the type of DOC in the HA and tannic acid leachates being different or to the concentrations of DOC in solution (238 mg/L and 1000 mg/L respectively). As the diluted HA exhibited a lower K_d than that of both HA and tannic acid, it is likely that a combination of these factors is responsible. The sorption of naphthalene to the Oxford Clay using tannic acid as a DOC surrogate was, however,

performed twice by the Environment Agency (2009), once alongside a leachate containing no tannic acid (values as above), and once as a stand-alone experiment yielding a K_f value of $3.14 \mu\text{g}^{1-n} \text{L}^n/\text{g}$. Reasons for this difference in K_d value obtained in repeat experiments were not given. However, this additional value was higher than the K_f of HA ($2.14 \mu\text{g}^{1-n} \text{L}^n/\text{g}$) and placed the sorption of naphthalene to the Oxford Clay in the presence of HA leachate within the range of that observed by the Environment Agency (2009) when using tannic acid as a DOC surrogate. Both the tannic acid and HA were commercially available DOC sources which may account for their larger K_d values in comparison to the MSW and AMSW leachates, which contained DOC derived from wastes. The sorption isotherms for naphthalene to the Oxford Clay in HA and diluted HA leachates were better fitted to a non-linear, Freundlich isotherm rather than to a linear isotherm. This was contrary to sorption in all the other leachates, and indicated further that DOC in commercially available HA affects the sorption of HOCs differently to waste derived DOC.

As with the findings of the Environment Agency (2009), the results of Fu and Luthy (1986) indicated that the addition of dissolved organic compounds to the aqueous phase (specifically methanol and acetone) decreased the sorption of naphthalene. This was reflected in the results of this study, which found the sorption of naphthalene to decrease in the presence of aqueous phases containing DOC (K_d 0.12-1.36 L/g) in comparison to the DOC free leachate (K_d 1.89 L/g).

K_{oc} values obtained by the Environment Agency (2009) for naphthalene sorption to the Oxford Clay (with tannic acid; 38.93 L/g and DOC free; 49.4 L/g leachates) were higher than those seen for all leachates used in this work except HA leachate (42.08 L/g for HA leachate and 2.19-34.43 L/g for the other leachates). The difference in K_{oc} values between sorption tests in this study and the literature supports the theory that it is the DOC in solution rather than the solid phase OC that is causing these differences. This may be due to the presence of different concentrations and compositions of DOC in the leachates of this study (DOC concentration range, 2268-122 mg/L; HIX values, 1.38-11.42). The mechanisms by which the presence of DOC in solution may result in a decrease of naphthalene sorption to the clay are therefore either competitive sorption of the HOC with the DOC, preventing naphthalene from sorbing to the clay, or by providing a more organic aqueous phase so allowing the naphthalene to remain in solution. This

may occur by the more mature DOC blocking sorption sites either due to steric factors (Sykes, 1986) or by direct competition of the DOC with naphthalene for sorption sites.

K_f values for naphthalene sorption in all the leachates except AMSW ($0.79\text{-}2.37 \mu\text{g}^{1\text{-n}} \text{L}^n/\text{g}$) were larger than those observed by Xing (1997 and 2001) (0.017-0.78 and 0.22-0.24 respectively) indicating more sorption of naphthalene to the Oxford Clay in this study than was observed in soils and soil extracts with OC contents ranging between 0.5 and 53 percent (Xing, 2001; Xing, 1997). The K_{oc} values provided by Xing (2001) were, in fact, K_{oc-f} values and so, although they appear to differ from the K_{oc} values for naphthalene in leachates, they are not directly comparable to the K_{oc} values due to differences in the units of K_{oc} and K_{oc-f} . K_{oc} values for all leachates in this work ($K_{oc} 2.19\text{-}42.08 \text{ L/g}$) were, however, all greater than the K_{oc} values for naphthalene sorption to soils (0.49-1.46 L/g) obtained by Xing (1997). This difference in K_{oc} values indicated that the differences in naphthalene sorption between this study and the literature were due to solution phase DOC rather than the OC content of the sorbent. This was supported by the results of Xing (1997 and 2001) that were obtained using a DOC free solution of 0.01 M CaCl_2 as the aqueous phase and all of the leachates with non-linear sorption behaviour containing DOC.

K_d values for naphthalene sorption in all leachates which exhibited linear behaviour (Table 34; $K_d 120\text{-}1890 (\times 10^3) \text{ L/g}$) were higher than those seen in the literature for sorption to natural sorbents. Literature values for naphthalene sorption to natural sorbents varied by five orders of magnitude from natural aquifer materials ($K_d 0.07\text{-}0.15 (\times 10^3) \text{ L/g}$) (MacIntyre *et al*, 1991) to soils and soil extracts ($K_d 23\text{-}250 (\times 10^3) \text{ L/g}$) (Guerin and Boyd, 1997). Lower K_d values were also observed for sandy soils with OC content 0.5-3.2 percent ($0.5\text{-}18.2 (\times 10^3) \text{ L/g}$) (Burgos *et al*, 1996; Fu and Luthy, 1986) soils with OC content 2.55-53.4 percent ($13.4\text{-}781 (\times 10^3) \text{ L/g}$) (Xing 1997) and to sandy soil with OC content 0.06-0.68 percent amended with high molecular weight hydrocarbons from unleaded petrol ($0.14\text{-}9.8 (\times 10^3) \text{ L/g}$) (Bouchard *et al*, 1990). The exceptions to this were the K_d values obtained by Xing (1997) in soils one and two (OC 53.4% and 32.2% respectively, K_d values 781 and 158 ($\times 10^3$) L/g) and values obtained by Guerin and Boyd, (1997) ($K_d 1010\text{-}20600 (\times 10^3) \text{ L/g}$) for naphthalene sorption to synthetic sorbents. The OC contents of the sorbents used in the literature varied over

three orders of magnitude (0.026-20.3 percent) and in all cases differed from that of the Oxford Clay (5.49%).

The OC content of the sorbent may have an effect on the sorption of naphthalene to the solid phase. However, the K_{oc} values for most of the literature (0.0013-1.46 L/g) were lower than those found in this study (2.19-34.43 L/g). There were, however, a few exceptions to this. The K_{oc} for sorption of naphthalene to aquifer material in methanogenic phase leachate (2.03 L/g) (Thornton *et al*, 2000) was similar to that of sorption to Oxford Clay in AMSW leachate (2.19 L/g). This indicated that the differences in OC of the sorbent was responsible for the variation in K_d between these two experiments, and so that the methanogenic leachate and the AMSW leachates may be behaving in a similar fashion in solution. The K_{oc} values obtained by Bouchard *et al* (1990) in Lincoln Rtd and Lincoln Rh soils (3.65 and 8.17 L/g respectively) and by Xing (2001) for naphthalene sorption to soils A1 and A2 (3.73 and 10.33 L/g respectively) were within the range of K_{oc} values found in experimental work (2.19-42.08 L/g). The variation in K_{oc} values from experimentally determined sorption isotherms in this work, however, reinforces the theory that it is the DOC present in the aqueous phase as well as the OC content of the solid phase which affects the sorption behaviour of naphthalene.

Observed differences in K_d values for naphthalene sorption are therefore likely to be attributable to the differences in the DOC present in solution, as indicated by the differences in K_{oc} values between the literature isotherms and those obtained for naphthalene sorption to Oxford Clay in this study. This was supported by the fact that the majority of the literature used deionised water or an inorganic salt solution; CaCl_2 , CaSO_4 or a NaCl and phosphate buffer solution as their aqueous phases (detailed in Table 34).

Desorption of naphthalene from the Oxford Clay was observed in all leachates. Desorption isotherms were linear in DOC free and diluted MBT leachates and was better fitted to a Freundlich (non-linear) isotherm in the case of all other leachates. As with toluene desorption there were literature references for naphthalene desorption which focused on the thermal desorption of naphthalene from a variety of solid phases (Choudhary and Mantri, 2000 and 2001). The literature for naphthalene desorption from

sediments back into solution was, however, more extensive than that for toluene desorption.

The K_d values for naphthalene desorption from the Oxford Clay obtained by Bayard *et al* (1998) ($0.00417\text{-}0.011 \times 10^3 \text{ L/g}$) were lower than those from this study, indicating more desorption of naphthalene into DI water from the lower organic carbon soils used by Bayard *et al* (1998) than from the Oxford Clay into both DOC free and DOC containing aqueous phases. This may be due to naphthalene sorbing more strongly to the higher OC (5.49%) Oxford clay used in this work than the lower OC (1.4-3.4%) sediments used by Bayard *et al* (1998) resulting in more desorption from the weakly sorbed naphthalene from the sediments of Bayard *et al* (1998). However, despite using the same solid phase as this work (the Oxford Clay) the K_d values for naphthalene desorption observed by Simoes *et al* (2011) ($4.51 \times 10^3 \text{ L/g}$) were all higher than those in this work (0.68-15.88 L/g). This indicated less desorption of naphthalene in this work than into a synthetic leachate when using tannic acid as the DOC surrogate (Simoes *et al*, 2011). Therefore, the variation in desorption behaviour is likely to be attributable to the DOC in solution.

Alternatively, this difference in desorption behaviour may be due to the variation in DOC sorbed during the sorption step. Less sorption was observed by Bayard *et al* (1998) in DI water than in the leachates of this work. This was attributed to the presence of DOC in solution enhancing sorption of naphthalene to the sorbent in this work in comparison with that of Bayard *et al* (1998). If this is the case, then the presence of DOC during the sorption step may have resulted in stronger sorption of naphthalene to the solid phase, which in turn would inhibit naphthalene desorption in this work, compared to desorption following a DOC free sorption step.

The results of this study indicated that the presence of DOC in solution reduced sorption and increased desorption of naphthalene to the Oxford Clay relative to a DOC free leachate. Therefore this may indicate that the type of DOC in solution affects the sorption and desorption behaviour of naphthalene. This may be due to the naphthalene, which is more sterically inhibited than the toluene, not being able to approach sorption sites or penetrate the surface for the Oxford Clay due to the presence of DOC, resulting in weaker surface sorption of the HOCs (Wang *et al*, 2010; Murphy and Zachara 1995; Lion *et al*, 1990). This fits with the decrease in sorption observed in this work with the

addition of DOC to solution. However, reduced sorption in this work did not directly relate to a reduction in desorption, as discussed above.

6.2 Discussion of Whole Work

6.2.1 Sorption

| Aqueous phase (Leachate) | | Toluene | | Naphthalene | |
|--------------------------|------------|----------------------|--|----------------------|--|
| | | K _d (L/g) | K _f ($\mu\text{g}^{1-n} \text{L}^n/\text{g}$) (n) | K _d (L/g) | K _f ($\mu\text{g}^{1-n} \text{L}^n/\text{g}$) (n) |
| DOC Free | Sorption | 0.078 | 0.081 (0.99) | 1.89 | 1.36 (0.99) |
| | Desorption | 0.14 | 0.80 (0.55) | 4.47 | 5.55 (0.85) |
| MSW | Sorption | 0.046 | 0.047 (1.00) | 0.76 | 0.68 (1.03) |
| | Desorption | 0.070 | 0.16 (1.35) | 2.21 | 1.15 (0.81) |
| AMSW | Sorption | 0.038 | 0.03 (1.93) | 0.12 | 0.44 (0.86) |
| | Desorption | --- | --- | 0.46 | 0.55 (0.82) |
| MBT | Sorption | 0.10 | 0.62 (0.73) | 0.94 | 1.10 (0.96) |
| | Desorption | 0.11 | 0.66 (0.61) | 15.88 | 1.86 (0.52) |
| HA | Sorption | 0.31 | 0.39 (1.35) | 2.31 | 1.16 (1.02) |
| | Desorption | --- | --- | 5.56 | 1.29 (0.97) |
| Diluted MSW (1:20) | Sorption | 0.11 | 0.10 (1.02) | 1.20 | 1.07 (1.03) |
| | Desorption | 0.67 | 0.46 (0.54) | 5.99 | 1.95 (1.08) |
| Diluted HA (1:2) | Sorption | 0.085 | 0.84 (0.29) | 0.68 | 1.14 (0.98) |
| | Desorption | --- | --- | 3.07 | 1.36 (1.00) |
| Diluted MBT (1:10) | Sorption | n/a | n/a | 1.36 | 0.92 (1.11) |
| | Desorption | n/a | n/a | 2.53 | 2.44 (0.27) |

Table 36: Sorption and desorption coefficients for toluene and naphthalene. Values have been taken from Tables 27 and 30.

The K_d values obtained in this work show increased sorption of naphthalene to the Oxford Clay in all leachates compared to toluene sorption in the same leachate (Table 36). This was attributed to the relative hydrophobicity of the contaminants, with the more hydrophobic naphthalene having a lower affinity for the aqueous phase than toluene, and so showing increased sorption to the clay relative to toluene. This was in agreement with the findings of Simoes *et al* (2005) Weber and Miller (1988) Nourmoradi *et al* (2012) and Piwoni and Banerjee (1989) who all found that sorption was increased with increasing hydrophobicity of the target compounds. Toluene sorption was linear in all but three leachates and naphthalene sorption was linear in all but HA and diluted HA leachates.

Toluene sorption was non-linear in AMSW, HA and diluted HA leachates. The n values for both AMSW and HA leachates (1.93 and 1.35 respectively) indicated that toluene sorption had some exponential non-linear character, becoming more favourable with increasing sorption. This may be due to the high maturity of the DOC in the AMSW and HA leachates (HIX 2.9 and 11.4 respectively) coating the surface of the sorbent (cumulative sorption) and enabling multilayer sorption of toluene. Alternatively this may be due to the toluene being able to access additional sorption sites on more humic DOC in comparison to other DOC sources due to the higher functionality of HSL DOC and so enabling co-sorption to the surface with the DOC.

The n value for toluene sorption to the clay in diluted HA was less than one (0.29) indicating that as the toluene sorbed to the clay further sorption became less favourable towards a sorption maximum, which would indicate a monolayer coverage of the contaminant with a limited number of sorption sites available (Song *et al*, 2013; Atkins and de Paula, 1992 and 2006). This was unlikely to be due to the humic nature of the DOC as the maturity of diluted HA was similar to that of HA (HIX 11.4 and 10.8 respectively). Therefore it may be attributable to the concentration of the DOC in solution. HA leachate (233 mg/L) had an n value of greater than one indicating more exponential sorption behaviour and diluted HA had an n value less than one indicating Freundlich-type behaviour. The higher concentration of the HA leachate may be facilitating bilayer sorption, whilst lower concentrations (e.g. diluted HA) is not. However, the AMSW leachate had a DOC concentration in between the HA and diluted HA DOC concentrations (136 mg/L) and had an n value greater than one, indicating that there may be multilayer sorption occurring. This may indicate that, at a certain concentration of more mature DOC in the aqueous phase, bilayers can form during contaminant sorption to the Oxford Clay.

Naphthalene sorption was non-linear in HA and diluted HA leachates only. Naphthalene sorption in HA and diluted HA leachate had n values close to one (1.08 and 0.98 L/g respectively) indicating that sorption of naphthalene in these leachates was close to linear and became more favourable as sorption progressed with little evidence of reaching a sorption maximum. This may be explained by a combination of HOC sorption being reduced on humic substance coated surfaces that were formed at higher ionic strengths due to it having a more closed conformation (Murphy *et al*, 1992) and the

larger naphthalene molecule being more sterically hindered than the smaller toluene and so being unable to access the sorption sites on the HA layers (Wang *et al*, 2010). The non-linear nature of both the toluene and naphthalene sorption isotherms in the presence of HA and diluted HA leachates (Aldrich HA) may indicate that commercially available sources of DOC behave differently from DOC derived from wastes. This may be due to the chemical composition of the DOC since Aldrich HA only contained DOC compounds from a set molecular weight range; whereas DOC derived from wastes is highly variable in molecular weight and character and is dependent on many factors including the type and age of the waste in question. This was supported by the difference in K_d for toluene sorption between HA and FA extracted from woodland soils (10.1 and 2.59×10^3 L/g respectively) and Aldrich HA (42.4×10^3 L/g) as found by Garbarini and Lion (1986).

6.2.2 Desorption

The K_d values for toluene desorption were lower in each leachate than those for naphthalene desorption (0.070-0.67 and 0.46-15.88 L/g respectively). Therefore, more desorption of toluene was seen from the solid phase than naphthalene. This was in agreement with Lee *et al* (1992) who found that increasing hydrophobicity of PAHs decreased the amount leached from coal tar into an aqueous phase. It also agrees with Zhou and Zhu (2007) who found that the K_d for desorption increased (so desorption decreased) with increasing hydrophobicity (where hydrophobicity was indicated by the $\log K_{ow}$ values of the contaminant).

The decreased desorption of naphthalene in comparison with toluene may be due to the processes occurring in the sorption stage. Naphthalene exhibited increased sorption to the clay due to its hydrophobicity, and had a lower affinity for the aqueous phase. Therefore, reduced naphthalene desorption from the solid phase relative to toluene may be due to naphthalene being more strongly bound to the sorbent due to its hydrophobicity. In comparison to the less hydrophobic toluene, which exhibited less sorption but more desorption; the naphthalene results indicate that an increase in hydrophobicity results in stronger binding of the contaminant to the solid phase during sorption. Lion *et al* (1990) observed sorption to be more reversible when it occurred at the surface of the sorbent compared to when the target compound penetrated the surface. Based on the results of

this work, this would indicate that toluene sorption occurred at the surface of the solid phase and naphthalene penetrated the sorbent to a greater extent. However, Wu and Gschwend (1986) found that more hydrophobic compounds penetrated surfaces more slowly due to lower diffusivity which would result in greater naphthalene desorption than toluene desorption from the Oxford Clay. Therefore, the DOC in solution may be enabling naphthalene to penetrate the sorbent surface or to sorb to the solid phase irreversibly; whereas in a DOC free leachate, the naphthalene cannot penetrate to deeper sorption sites on the Oxford Clay. Mature DOC in the leachate may also provide an aqueous phase that is more hydrophobic than the solid phase, thus allowing increased irreversible naphthalene sorption over toluene sorption due to the hydrophobicity of the contaminants.

The desorption of both toluene and naphthalene from Oxford Clay was non-linear in MSW, MBT, and diluted MSW leachates. As with the K_d values for desorption, the K_f values of naphthalene were also higher than those of toluene, indicating that more desorption of toluene than naphthalene from Oxford Clay occurred in these leachates. Compared to desorption in DOC free leachates there was more desorption of both toluene and naphthalene from the Oxford Clay when DOC was present in the aqueous phase. The increased desorption of toluene relative to naphthalene may be due to the sterically smaller toluene being able to access sorption sites on the clay that naphthalene cannot; avoiding competition from DOC for sorption sites on the solid phase or being irreversibly bound to the solid phase. This was supported by Murphy and Zachara (1995) who found that smaller molecules have longer retention times on surfaces as they can sorb to pore spaces which are inaccessible to larger molecules and Lion *et al* (1990) who observed that sorption became less reversible as pollutants penetrated the surface. When DOC was present in the aqueous phase it may compete with toluene for sorption sites but enhance the sorption of the more sterically hindered naphthalene, allowing it to approach sorption sites which otherwise would be accessible only to smaller molecules (Wang *et al*, 2010). This would account for naphthalene being less easily desorbed from the solid phase into the aqueous phase than toluene, as sorbing alongside DOC may mean the HOC is more tightly bound to the solid phase during the sorption step.

No toluene desorption was observed in AMSW, HA and diluted HA leachates. This may be attributable to irreversible sorption of toluene or slow desorption kinetics in these

leachates. Irreversible sorption of toluene may be attributed to the sterically smaller toluene molecule being able to bind tighter to the solid phase alongside the mature leachate DOC or deeper within the surface by diffusive transport (Wu and Gschwend, 1986); Lion *et al*, 1990). However, naphthalene desorption was observed in the presence of these three leachates, and was best fitted by non-linear isotherms. The n values for naphthalene desorption in AMSW and HA leachates were less than one (0.86 and 0.97 respectively) indicating that desorption may occur as a two stage process with an initial desorption of naphthalene from the clay towards a plateau, implying that a portion of naphthalene may remain bound to the clay (Kan *et al*, 1994). The n value for naphthalene desorption in diluted HA leachate was, however, one, indicating that desorption increased with increased aqueous naphthalene concentration. Less desorption was also seen in the diluted HA leachate, which had a higher K_f than the AMSW or HA leachates (K_f 1.36, 0.55 and 1.29 $\mu\text{g}^{1-n} \text{L}^n/\text{g}$ respectively). This may be due to the lower ionic strength of the diluted HA leachate resulting in a more open conformation of the HA when complexed to the clay during the sorption step (Murphy *et al*, 1992). This may be due to a greater hydrophobic surface area of the DOC being available for sorption (Murphy *et al*, 1992). This may result in increased penetration of naphthalene into the surface, allowing naphthalene to sorb more strongly to the solid phase in the diluted leachates (Lion *et al*, 1990; Mechlinška, 2009) than in the higher ionic strength HA leachate, (higher ionic strength so more closed conformation) (Murphy *et al*, 1992). Although the ionic strength of the AMSW was lower than that of the diluted HA, it was also significantly less mature (HIX 2.9 compared to 10.8 and 11.4). Therefore it is possible that the impact of ionic strength on the sorption and desorption behaviour is only applicable in the case of the high maturity commercially available HA.

6.2.3 Applications of Research and Relevance to Industry

From the results of this study, sorption behaviours in different leachates of comparable DOC concentrations were distinct from each other. This was attributed to the type of DOC in solution and could result in the incorrect estimation of levels of contaminant sorption within the landfill liner system. For example, if a diluted MSW leachate or a commercially available DOC source such as Aldrich HA (diluted HA leachate) was used to model a leachate from an aged waste (AMSW) in a study to determine toluene sorption

behaviour then, from the results of this study, the sorption coefficients obtained would be expected to be higher than those for an AMSW leachate. The use of a higher sorption coefficient would result in an overly high estimate of toluene sorption to the Oxford Clay occurring within the landfill. This could subsequently lead to under-engineering of liner systems due to an over estimate of the extent of contaminant attenuation by the liner material.

While over estimation of K_d values may result in a higher estimate of contaminant sorption and a lower estimate of contaminant desorption than is actually the case; underestimation of K_d values may result in a lower estimation of sorption and a higher estimation for desorption than is actually the case. The underestimation of these coefficients could therefore lead to over-estimation of the polluting potential of the leachate as the removal of contaminants from the system by the liner is underestimated and the release of contaminants from the liner into solution is underestimated. Therefore the pollution potential of the landfill leachate may be overestimated, which may result in unnecessary additional costs. However, if there was any doubt as to the validity of the K_d values being used, in this situation it would be better to under estimate the K_d values rather than over estimating them. This would ensure that the risk of contaminant release into the environment (and incurring remediation costs) due to inaccurate prediction of attenuation behaviour was avoided.

It is clear that estimating the sorption and desorption of contaminants for Oxford Clay using a ‘surrogate’ leachate, which is likely to have different DOC character to the actual leachate produced by the landfill due to the complexity of leachate formation process, may therefore result in the incorrect estimation of sorption and desorption from the liner material, which may then result in:

- Overestimation of contaminant sorption to the liner, leading to under engineering of containment systems and possible environmental release of contaminants.
- Underestimation of contaminant sorption to the liner, leading to additional costs to the landfill operator due to over engineering containment systems.

- Overestimation of contaminant desorption from the liner, leading to additional costs to the landfill operator due to over engineering containment and monitoring systems.
- Underestimation of contaminant desorption from the liner, leading to under engineering of containment systems, inadequate aftercare of the landfill due to incorrect estimates of the polluting lifetime of the site and possible release of contaminants into the environment.

It is therefore suggested that it would be prudent to use a ‘worst case’ prediction of the sorption and desorption of contaminants for the liner material. Although this may result in a rise in the construction and operating costs of the landfill due to possible over-engineering of the liners and extension of the monitoring period of the landfill, it would ensure environmental protection and avoid the expense of environmental remediation works. In this situation the lowest sorption coefficient predicting the least sorption and the highest desorption coefficient predicting the most desorption should be used to model the attenuation of contaminants to liner materials.

When considering chemical interactions within the landfill cell system it becomes apparent that, even at its most basic level of detail, the system is highly complex. At its most basic, a landfill cell is an excavation with a basal liner (which may extend up the sides of the excavation to either partial depth or the full depth of the cell). There is often a drainage layer included in the base of a landfill in order to facilitate leachate collection and prevent damage to the liner due to direct contact of the liner with the waste. Above this layer the waste is deposited. As the influx of waste may not be constant some landfill sites may use a temporary covering of soil, or a similar material, in between waste deposition in order to prevent windblown waste and discourage pests. Assuming that the (very basic) leachate in this system contains only DOC, HOCs, heavy metals and inorganic compounds, there are still numerous interactions in the system which occur in addition to the sorption of HOCs to the liner. These include heavy metal complexation with DOC and alteration of DOC structure due to the ionic strength of the solution, swelling of liner clays, sorption of all leachate compounds to waste materials, biodegradation, biofilm formation and precipitation of heavy metals out of solution. This list is far from exhaustive and, although interactions within a leachate system have

been briefly discussed in Section 2.2.2 (Table 2), the reality of the interactions in a landfill cell is that they are highly complex and difficult to account for. Therefore, the landfill leachate system has been simplified for this work, with each experiment only considering the sorption of a single contaminant to a single liner material with a leachate of varying DOC character.

In addition to sorption, biodegradation is another mechanism through which contaminants may be attenuated in a landfill system. Biodegradation was not considered in this work as over the short contact times used in the batch tests toluene and naphthalene were found by the literature to be resistant to biodegradation (Simoes, 2005; Environment Agency, 2002). In a landfill system, however, sorption processes occur over a much longer time period. As a landfill may be actively receiving waste for years and continues to degrade and produce leachate for years post-closure (Kjeldsen, 2002; Christensen *et al*, 1998) the biodegradation of contaminants is likely to affect the concentrations of both the solution phase and sorbed contaminants in the landfill system.

While in a lab scale experimental study the biodegradation of contaminants can be prevented using a biological inhibitor; in a landfill this is neither practical nor desirable. This is because a reduction in contaminant concentration is a desirable outcome for leachate maturation and attenuation. Biological inhibitors (e.g. mercuric chloride or sodium azide) are also often toxic in their own right and have the potential to be a greater risk to the environment than the original contaminant. Over large timescales, should biodegradation of contaminants which are sorbed to the clay occur, the reduction of contaminant concentration would mean the likelihood of contaminants desorbing from the solid phase would be reduced. This may also mimic the irreversible sorption of contaminants over a longer time period.

Due to the inherent complexity of a landfill cell and the interactions taking place within it, in relation to a working landfill cell this work provides only a tiny proportion of the information required to fully model the effect of DOC in landfill leachate on the sorption of HOCs to the liner material. However, it does provide a starting point for further research in order to elucidate the effect of DOC on contaminant sorption behaviour. While this study looked at different DOC environments in solution, it did not follow the maturation of leachates from a given waste from start to finish. The selection of a K_d

value to model contaminant attenuation via sorption taken from a methanogenic-phase leachate is recommended as methanogenic leachates are in contact with the liner for the majority of a landfill's lifetime. However, as a waste degrades and the leachate matures, the concentrations and type of DOC in solution changes (Section 2.1.4). This study did not, therefore account for all the types of leachate from the same original waste that may come into contact with the liner material during the lifetime of the landfill cell.

As discussed in Section 3.3, the use of batch testing as an approach to measure sorption, while recommended by the Environment Agency (2000a and 2000b), is not a perfect method for modelling the interaction at the leachate-liner interface. This is because in batch testing the contact area between the clay and the leachate is proportionally greater in batch testing than it would be in the case of an actual liner. The contact area of the clay with the leachate through a cross section of the liner may also not be uniform due to preferential pathways forming throughout the material due to cracking, compaction and the hydraulic gradient of the system. This may result in the over-estimation of contaminant sorption to the liner material and is a source of error within the experimental work.

Due to the high variation and complexity of leachate composition, it is therefore suggested that it is best to select a K_d value for the target contaminant that is representative of sorption and desorption behaviour in a methanogenic leachate. Ideally this leachate should be from a waste identical to that expected to be deposited in the landfill cell. However, this is not realistic as although in the UK some individual authorities and councils do collect information about the composition of MSW that is produced by their area (DEFRA, 2014) the final waste in the landfill site cannot be guaranteed to be as predicted.

This work has highlighted not only the variation in literature values for the sorption of different contaminants, but the lack of literature values for the sorption of contaminants to liner materials within the landfill system. This is due to the focus of the literature on the remediation of environments that are already contaminated by landfill leachates, as opposed to their behaviour as they are being contained in order to prevent environmental contamination. This may be due in part to the legacy of uncontained and unlined landfill sites worldwide and the problems of environmental remediation in these situations.

While very little information on desorption of contaminants from liner materials was apparent in the literature, the disparity between the experimentally obtained sorption and desorption coefficients and the available literature values for sorption coefficients serves to highlight the importance of selecting a coefficient that is relevant to the landfill environment and the sorbent being used, even if the exact system conditions cannot be accurately predicted or modelled.

It is therefore suggested that the sorption and desorption coefficient values are selected for modelling contaminant attenuation within the landfill system on a ‘worst case scenario’ basis. Where the prediction of contaminant sorption to the liner material is minimised and assumed readily reversible and desorption is maximised. Figure 42 is a graphical summary for the decision making process recommended as a result of this study when selecting a K_d value for modelling contaminant attenuation. Although K_d values are automatically provided for use in the case of the landfill risk assessment tool, LandSim, it is the opinion of this study that they should be used only if better information is unavailable, and if it represents a ‘worst case scenario’ outcome of attenuation modelling.

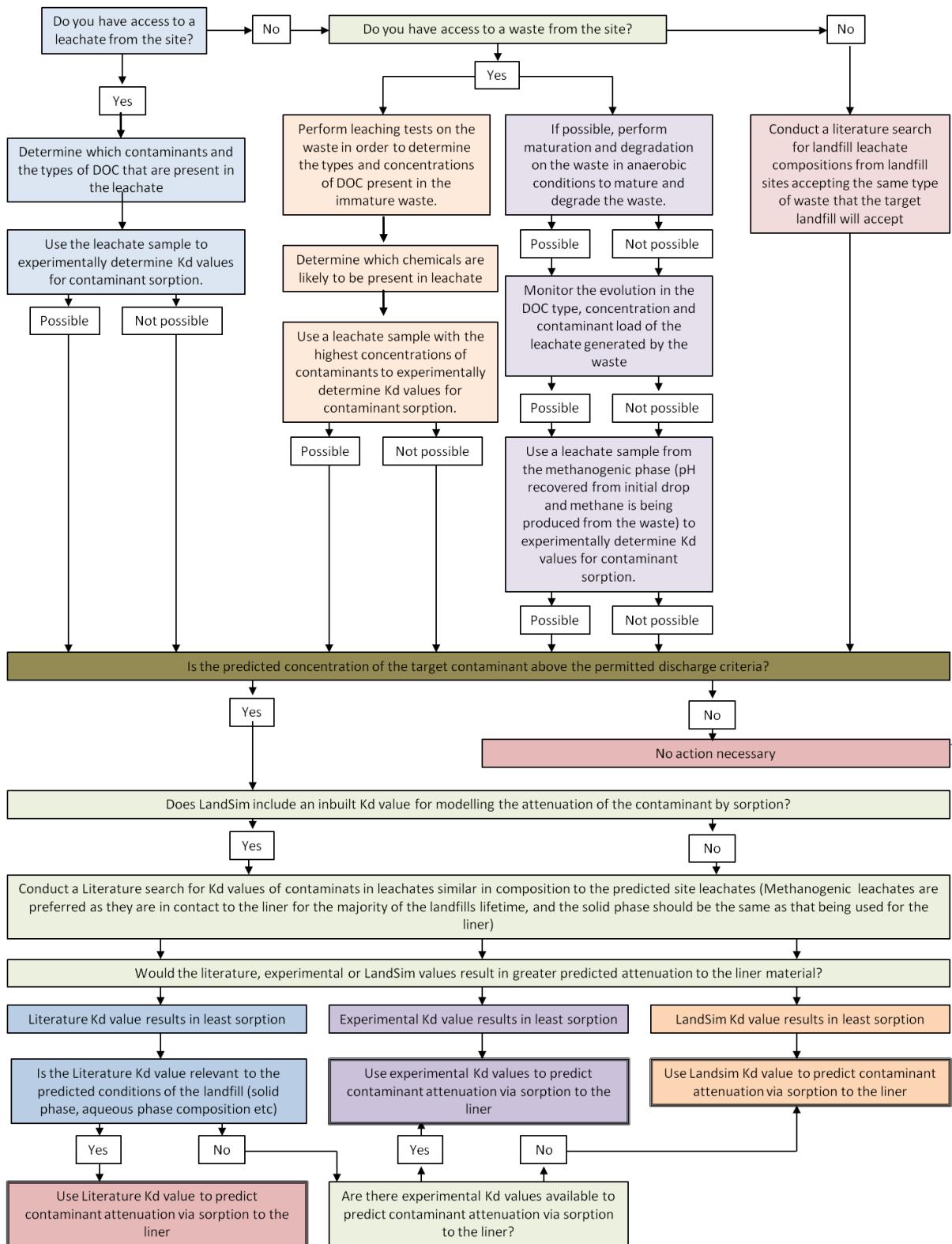


Figure 42: The recommended decision making process for selecting sorption coefficients for use with landfill risk assessment software such as LandSim.

As highlighted by Figure 42, it is recommended that all available sources for potential sorption and desorption coefficients are considered. In the case of an already active landfill site or a site that will be accepting the same waste as a previous cell (for example

in the case of an application for a new cell to expand an existing landfilling facility) sorption and desorption experiments should be conducted using a sample of the leachate and the proposed liner material. Failing this, a waste sample from the landfill (or a sample of the waste intended for disposal at the new site) should be obtained, matured throughout its stabilisation phases and leachates collected at each stage. These leachates should then be used to assess the sorption and desorption behaviour of each predicted contaminant in the leachate solution. It is, however, recognised that this will not always be plausible or possible. Therefore a literature search may also be conducted focussing on the waste type, stage of maturation and country of origin of the waste. This should also include a solid phase as similar to the proposed liner material as possible.

The type of leachate expected and its predicted contaminant load should also be taken into account. Sorption and desorption coefficients from all of these sources should then be assessed alongside the default LandSim value(s) for each given contaminant and the coefficient resulting in the ‘worst case scenario’ outcome from the point of view of environmental protection should be selected for use (i.e. least sorption and most desorption).

6.2.4 Limitations of this Work

Due to the complexity of the problem posed in this thesis there are significant limitations to the findings of this work. In the leachate solution, due to its complexity and the variety of compounds that it contains, the adsorption behaviour of HOCs was not straightforward. This was due to the presence of other compounds in solution which had the potential to interact with the leachate, sorbent and sorbate. The huge number of potential interactions that are possible within the landfill system means that the determination of sorption trends was an incredibly complex problem. While this work aims to draw conclusions from the observed impact of different groups of DOC on HOC sorption behaviour, it recognised that pH, EC, heavy metals, and the presence of other compounds in the system remain unaccounted for. While this work uses the overall unpredictability of the leachate system and the impact that their normalisation may have on the chemical nature of the DOC in a real landfill as justification for not normalising all

of these factors, it is recognised that they will have an effect on the sorption behaviours of both the DOC and HOCs in solution.

While industry uses a literature derived K_d for the prediction of sorption, there are many literature sources for data from this study to be compared to. The lack of application of values of K_d from the literature and experimentally obtained in this work using risk assessment software such as LandSim; and comparison of the results of these K_d values with those provided by LandSim to determine whether the differences in K_d values between different sources is significant, is a major limitation of this work. This comparative study is a body of work that would be extremely useful for the validation of these results and the further justification of using a ‘worst case scenario’ approach to sorption coefficient selection. This would, however, require access to the full LandSim programme which unfortunately was not available for use during this work.

The amount of data for each leachate is, in itself, a limitation of the results of this work. This limits the power of any statistical analysis applied to the data gathered in this work, and so the degree of confidence that is able to be assigned to the results. Ideally a larger data set should be obtained for each contaminant and leachate combination across a much larger concentration range than that currently used in this research. This would allow the determination of the overall isotherm shape for sorption and desorption. This full isotherm would then have the potential to be broken down into sections which correspond to narrower concentration ranges, and so provide a better idea of the K_d values for contaminant sorption across a given contaminant concentration range.

The key limiting factor of this work was therefore the complexity of the leachate-clay sorption system. This was largely due to the complex and unpredictable nature of leachates and the change in their character throughout their formation and maturation. Because the formation of a leachate is dependent on so many different factors; moisture content, age of the landfill, compaction, temperature, the origin of the waste, infiltration, bacterial flora and the surface area of the waste to name but a few; it is therefore practically impossible to predict the composition of a leachate from its starting waste. It is also possible (as demonstrated in Section 4.2.4.1) that two leachates from different areas of the same cell can produce leachates with differing compositions from the same waste. This variation in the leachate composition means that the prediction of sorption

and desorption behavioural trends is an extremely complex problem, even ignoring factors such as EC, pH and biodegradation.

7. Conclusions

The addition of DOC to the aqueous phase altered the sorption and desorption behaviour of the HOCs toluene and naphthalene. The relationship between toluene sorption and desorption and the addition of DOC was complex and could not be completely elucidated. The addition of DOC to the naphthalene system, however, resulted in a decrease in sorption to, and an increase in desorption from, Oxford Clay for all DOC types relative to sorption and desorption in a DOC free leachate. Both DOC concentration and character were found to affect the sorption and desorption behaviour of toluene and naphthalene to the Oxford Clay. This relationship was not straightforward and neither factor was able to solely account for the observed impacts of DOC addition to the aqueous phase on sorption and desorption behaviour.

In the sorption of a mixed-type DOC from a contaminant (toluene and naphthalene) free MSW leachate HSL DOC was observed to preferentially sorb to the Oxford Clay over PL DOC. DOC was also observed desorbing from the Oxford Clay where high m:v ratios of clay were used. In this case, preferential desorption of HSL DOC over PL DOC was also observed. Therefore, if HOCs form complexes with HSL DOC then an increase in HOC sorption to the Oxford Clay may result via cumulative sorption or co-sorption, and at low aqueous DOC concentrations HOC-DOC complexes may preferentially desorb into the aqueous phase. If the HOCs do not interact with HSL DOC then the HSL DOC may compete with HOCs for sorption sites, reducing HOC sorption to the Oxford Clay

The non-conformity of diluted HA DOC to the other leachates throughout this work indicated that the origin of the DOC may also be important, and that commercially available DOC sources are not analogous in behaviour to waste derived leachate DOC. The use of a commercially available DOC source (e.g. AHA) to model a leachate DOC may, therefore, result in significantly different estimates of alteration of sorption and desorption behaviour than the use of waste derived leachates, even at comparable concentrations. The use of synthetic DOC based sorption coefficients may, therefore, lead to incorrect estimation of attenuation of a contaminant compound to the liner. This could lead to over or under engineering of the liner system resulting in unnecessary expense or an environmental pollution risk.

Therefore, it is suggested that when selecting a K_d value to model the attenuation of a contaminant for Landfill Risk assessment a ‘worst case scenario’ is employed, where the least sorption and most desorption of a contaminant occurs. This will ensure environmental protection measures are adequate by preventing the over-prediction of sorption and under prediction of desorption. Further to this, where literature values for K_d are used it is recommended that they are selected carefully in order to account for both the solid and solution phase (DOC) effects on sorption. Ideally K_d values should be either selected from a literature source or determined experimentally using a system with a similar OC content of the sediment and similar DOC concentration and character to that of the predicted leachate composition. In practice, however, the highly complex and variable nature of leachates means that this may not be achievable.

This study has shown that the relationship between DOC in leachates and the sorption behaviour of toluene to the Oxford Clay is complex and dependant not only on the concentration of DOC in solution but also its character. From this work, it was also clear that this relationship is complex and its further elucidation will require significant further study. It was, therefore, suggested that when selecting a K_d value for estimating attenuation, that it is more appropriate to use a leachate in contaminant sorption tests that produces a ‘worst case’ scenario result, which predicts the lowest contribution of sorption to contaminant attenuation; rather than a leachate that is closer in HSL character to an aged leachate, but may overestimate sorption and underestimate desorption behaviour, in order to ensure environmental protection is adequate.

The variation in the system was a major limitation of this work. Although contaminant sorption behaviour was shown to be affected by the DOC in solution, the relationship between DOC and its effect on sorption and desorption behaviour was unable to be resolved. This uncertainty meant that a direct recommendation on how to select the correct sorption or desorption coefficients for the purpose of modelling the attenuation of contaminants by sorptive processes could not be achieved. It is due to these limitations that the recommendation for K_d selection based on a worst case scenario was made.

8. Recommendations for Further Research

This work has established that the character of DOC in leachates solutions alters the sorption and desorption behaviour of the HOCs toluene and naphthalene. Due to the complexity of the leachate system the exact relationships between DOC type, DOC concentration and the sorption and desorption coefficients of the contaminants was not able to be fully resolved. Therefore, suggestions are given for further research in order to more completely elucidate the effect that specific types of DOC and their concentrations have on sorption and desorption behaviours of contaminants.

8.1 pH and Ionic Strength (EC) Effects

In this work the pH and EC of leachate solutions was not standardised or normalised to the same level. Both of these factors have been shown in the literature to impact the molecular conformation of DOC and, therefore, may affect the DOC behaviour. Therefore, a study to determine the pH and EC dependence of sorption coefficients in different aqueous DOC conditions would be beneficial. This could be achieved by measuring sorption of contaminants in a selected leachate and adjusting the EC whilst observing the change in sorption behaviour. The pH of the leachate solution will also affect the solubility of heavy metals and humic and fulvic acids in solution, as well as the conformation of the DOC compounds. An experiment where the pH for a selected leachate is altered and the affect of pH alteration on the sorption behaviour of contaminants and the DOC in solution would elucidate the effect of pH on the system. This could be achieved either using a suitable buffer system or by directly altering the pH of the aqueous phase using an acid or a base. This would allow determination of any relationship between sorption and desorption behaviour of the contaminants and DOC under different pH and EC conditions. Since the pH and EC of leachates varies during the stabilisation of a landfill waste (most notably during the acetogenic and initial methanogenic stages of stabilisation) this is particularly relevant to leachate systems.

8.2 The Contribution of DOC Type to Sorption and Desorption

This study has found that the type of DOC in solutions does affect the sorption behaviour of HOCs, and that DOC derived from wastes and from a commercially extracted source effect sorption behaviour to differing degrees. Therefore, it is recommended that this work is repeated with both a larger range of waste derived leachates and a number of commercially available DOC sources and compounds, including both humic substance-like and protein-like compounds. IHSS standard compounds, humin, fulvic acids, humic acids, tannic acid, tyrosine, tryptophan, sugars, cellulose, and lignins are suggested as possible candidates for further commercially available DOC solution studies.

In addition to the use of a number of different ‘bulk’ DOC sources in experimental work, the contribution of the different types of DOC in DOC mixtures to the sorption and desorption behaviour of contaminants should be determined. This could be achieved by size fractionating the leachates or DOC solutions (e.g. by ultra-filtration) and then repeating the sorption tests using the size fractions from each leachate. This would allow comparison of the sorption behaviour of contaminants in the bulk leachate with the sorption in each size fraction. Information on the relative contributions of each size fraction to the overall sorption behaviour may then be deduced. This may allow the prediction of the impact a leachate will have on contaminant sorption behaviour based on the size fractions present in the leachate.

8.3 DOC Characterisation

More in depth characterisation of both bulk leachate DOC and the DOC present in size fractionated leachates will allow more concise discussion of the findings of sorption and desorption testing. In addition to fluorescence spectroscopy, UV spectroscopy, pH, EC and DOC concentration; analysis of the leachate DOC could be achieved by methods such as FTIR, NMR, size exclusion chromatography, GC/GCMS, LC/LCMS, ICPMS (for heavy metals), X-ray diffraction, X-ray fluorescence and atomic abundance analysis. Some of these methods would require significant work to develop into working methods

for each leachate (e.g. GCMS and LCMS) and while many of these techniques will produce spectra that are challenging to interpret, it may be possible for a ‘test suite’ of methods to be developed in order to maximise the information gathered whilst reducing the amount of time required for interpretation. Improved characterisation data for the DOC present in solution will allow greater levels of confidence when attributing observed experimental effects to particular groups of DOC.

8.4 DOC Sorption to the Solid Phase

Sorption of DOC to the solid phase in the absence of contaminants should also be repeated with DOC from landfill leachates derived from both different wastes and commercially available sources. This should be done for both the bulk leachate solutions and their size fractionated components in order to determine whether preferential sorption of HSL DOC to the solid phase over PL DOC is a phenomenon which is reproducible in other leachate environments with different types of DOC being present in solution. The sorption capacity of the clays for the DOC could also be determined by attempting to saturate the solid phase with very high concentration DOC leachates.

8.5 The Solid Phase

It would also be beneficial to repeat all of the above experimental suggestions using a number of other liner materials as solid phases. The Mercia Mudstone, Kimmeridge Clay and materials used as sorbents in GCLs are suggested as potential solid phases for use in order to allow for the effects of OC content in the solid phases alongside the effects of aqueous phase DOC to be accounted for. The interaction of different leachate DOC types with clays of differing OC content (both independent of and alongside contaminant sorption and desorption) is also an area which warrants further study.

8.6 DOC and HOC Fate

While the fate of DOC and HOCs from solutions is broadly determined via mass balance, where they reside, either on the solid phase (mineral or OC component) or in solution (e.g. on types of solution phase DOC) could not be determined. In order to better identify the fate of the DOC and target HOCs in solution, chemical labelling of target compounds (for example a specific contaminant or DOC compound) either in the bulk solution or in different size fractions could be undertaken. For both DOC and target HOCs this could be achieved through C¹³ labelling, with the fractions analysed by NMR. Alternatively, labelling of compounds could be achieved through marking the compounds with a fluorophore and analysis by spectroscopic techniques. Due to the complexity of the DOC fluorescence and absorbance spectroscopy, C13 labelling is likely to be the better choice. Labelling specific individual DOC compounds in a real leachate and ensuring that only one type of DOC is labelled would be highly complex due to the unknown nature of leachate DOC, whereas the introduction of a pre-labelled DOC compound into solution is relatively simple. Therefore, labelling of DOC is likely to only be of greater benefit to determining the fate of DOC compounds in a synthetic leachate, or when using a commercial DOC source (or mixture). In the same way, labelling of HOCs or other contaminants and monitoring their fate would be relatively simple as they are artificially added to the solution in the case of this experimental procedure. The leachate and solid could then be separated, with the leachate DOC being size fractionated if desired, allowing identification of the fate of the HOCs.

8.7 Range of HOCs

Currently the effect of leachate DOC on the sorption of only two HOCs (toluene and naphthalene) has been examined. The use of a wider range of contaminants would allow determination of the effect of contaminant hydrophobicity on sorption behaviour and its contribution to the overall effect of DOC type on sorption behaviour. For example, if DOC has a greater effect on the sorption behaviour of contaminants of differing hydrophobicities. One way to do this would be to continue to progress through the PAHs, phenanthrene, anthracene, tetracene, pentacene and so on. As their chemical structures consist only of benzene rings with no additional functional groups, their interactions with DOC are likely to occur by similar mechanisms through their delocalised electron systems. The chemical conformation of the molecules may also be a

factor since different isomers of the same chemical composition exist (e.g. phenanthrene and anthracene). Results from a wider range of contaminants could allow trends in sorption behaviour to be extrapolated into a wider range of compounds with more confidence than those based on only toluene and naphthalene. Using benzene for experimental work rather than toluene would also be beneficial as the methyl group on toluene adds functionality to the compound that means its behaviour is not directly analogous to that of benzene. As well as HOCs, other contaminant groups present in leachates such as pesticides, inorganic components, heavy metals and XOCs (Section 2.1.3) may also be candidates for the further extension of this work.

8.8 Kinetics and Biodegradation

Experimental work conducting sorption and desorption testing over a larger timescale, in order to ensure that both the DOC and HOC have reached equilibrium in solution, would be a beneficial addition to this work. Also kinetic studies for DOC and HOC sorption independently and together to see if co-sorption effects affect the kinetics of the contaminant or DOC sorption behaviour. Performing multistep desorption in order to assess how the desorption would occur if the contaminant diffused away from the interface, allowing secondary, tertiary and quaternary desorption stages to be assessed would allow the determination of whether the amount desorption from the clay would be environmentally significant. Desorption of contaminants from the clay into solutions with varying aqueous contaminant concentrations could also be used to identify whether desorption only occurs below a particular aqueous contaminant concentration, if more sorption of contaminant would occur above this level and if this level would be realistically reached in a landfill stabilisation scenario and timescale. This should be done both with and without bio inhibitors in order to ascertain whether degradation of the contaminants is significant over the longer equilibrium timescales used experimentally. Biodegradation rates should also be assessed for the DOC in solution, HOCs sorbed to solution phase DOC and HOCs sorbed to the solid phase as the rate of biodegradation of sorbed contaminants may impact the concentrations available on the sorbent for desorption, so affecting whether the contaminant release from the clay would be realistically significant to industry post closure.

8.9 Data Collection Using LandSim

This study was limited by the use of the demonstration version of LandSim, as its functionality for sorption is minimal. Using a full copy of the LandSim programme would allow the practical comparison of experimentally determined K_d values with literature values in order to quantify whether the impact of K_d variation is significant in the context of landfill risk assessments. In addition to this, the establishment of a database for HOC or contaminant sorption to a range of solid phases in aqueous phases containing different leachate DOC characters would be beneficial for the landfill industry as a whole for the selection of sorption coefficients and prediction of sorption and desorption of contaminants.

8.10 Other Work

- Performing column testing alongside batch testing would allow validation of the batch method and offer a comparison that more effectively models the solid phase interface of the liner and the leachate. These results should be compared to the results of the batch tests, however, the limitations of both testing methods should be considered and explored.
- To monitor the evolution of the leachate character from a landfill from the date that it is opened through to post closure, and to obtain and characterise the leachate character and contaminants present in the leachates. This would be a long term project (lasting until 40+ years post-closure) with samples taken from different wells in the same cell and/or different cells in order to compare the leachates and to assess the variability of leachate composition from the same waste source.

9. Appendices

9.1 Appendix A - Preliminary Testing. Desorption of DOC From the Oxford Clay into a DOC Free Leachate.

Overview

Appendix A presents the results of a batch desorption test to determine the desorption of DOC present in the Oxford Clay into a DOC free synthetic leachate. The results of this preliminary experiment at a single mass to volume ratio of 0.17 g/mL were used in Section 5.1 as supporting data for the theory that at low DOC concentration in solution the preferential desorption of humic substance-like DOC from the Oxford Clay is the cause for observed alterations in the fluorescence ratios during the sorption of MSW leachate DOC to the Oxford Clay (Section 4.1.2.1). The data points at 20 g clay (0.17 g/mL) are highlighted in the Figure A1 presenting this preliminary work.

The DOC free leachate was based on the recipe for synthetic MSW leachate (Environment Agency, 2009) the composition of which has been previously detailed in Section 4.2.4.2, the solid phase for this work was a sample of the Oxford Clay (Section 4.2.1) and all reagents used were of analytical grade purchased from Sigma Aldrich Ltd or Fisher Scientific Ltd diluted with ultra-high quality (UHQ) deionised water.

Clay (0.01 to 60 g) was added to pre-weighed acid washed bottles of average internal volume 120ml (mass to volume ratios 8.3×10^{-5} -0.5). Each clay mass was repeated in triplicate and bottles containing no clay were prepared to assess the extent of sorption to the bottle, septa and cap. The bottles were partially filled with DOC free leachate, capped and left to stand for 2 hours in an anaerobic cabinet (gas mix 5% carbon dioxide in background gas (5% hydrogen in nitrogen)) to eliminate air bubbles. The bottles were then filled with leachate and sealed using pre-weighed PTFE septa and aluminium caps taking care to keep the headspace to a minimum. The samples were agitated on a

roller mixer stirrer for 7 days at 20°C then centrifuged at 1200 rpm for 20 minutes to separate the leachate from the clay. Samples (20 ml) were taken from the supernatant for fluorescence, UV, DOC concentration, pH and EC analysis.

pH and EC

a decrease in the pH with increasing mass of clay from pH 8±0.2 at 0 g clay to pH 7±0.3 at 40 g clay and a steady increase in EC with increasing mass of clay in solution was observed. The increase in EC and decrease in pH seen may be due to release of ionic compounds or inorganic salts by the clay. In the case of pH, sorption of compounds that would otherwise buffer the pH may result in an increase in free hydrogen ions in solution.

Fluorescence

Figure A1 shows results from fluorescence spectroscopy of samples from the desorption of DOC from the Oxford Clay. All six fluorescence peaks identified in Section 2.3.1.3 were observed, indicating that both humic substance-like and protein-like DOC compounds desorb from the Oxford Clay into a DOC free solution. Peaks A-D and F (tyrosine-like, tryptophan-like and humic-like) showed an initial increase in fluorescence peak intensity with increasing clay mass, after which a decline in intensity was seen with an increase in mass to volume ratio. The decline in intensity occurred for peaks F, A and B-D when the mass to volume ratios in the reaction vessels exceeded 0.004, 0.17 and 0.08 g/mL respectively. The most prominent peak intensity was from humic-like compounds at low clay concentrations ($m:v < 0.17$ g/mL). This may indicate that humic-like compounds are either the larger proportion of desorbable organic carbon from the clay, or the most easily desorbed from the Oxford Clay. While the fluorescence peak intensities cannot be used to directly compare the concentrations of a compound in different systems, the comparison of peak intensities within the same system can be used to indicate alterations in the proportion of the compounds within that system. Once a certain $m:v$ ratio was reached (as above) the fluorescence peaks showed a decrease in intensity, indicating that at higher clay masses either re-sorption of DOC compounds to the clay occurs or the DOC does not desorb from the clay. The exception to this was peak E (fulvic-like) which showed a steady increase in intensity with increasing clay mass and was the most prominent peak when the $m:v$ ratio > 0.17 g/mL. This may

indicate that fulvic-like organic carbon from the Oxford Clay was not easily re-sorbed to the clay or that there was a greater proportion on the clay to desorb.

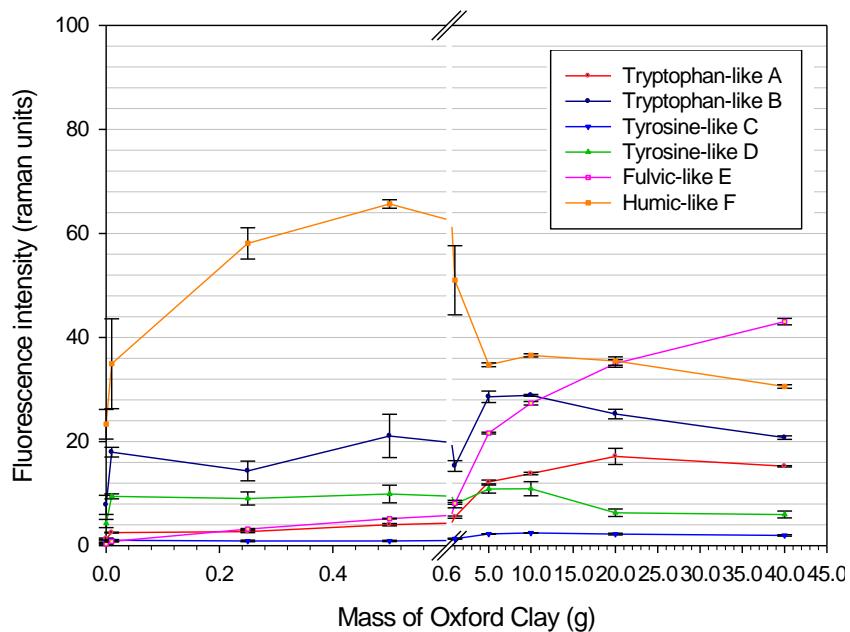


Figure A1: Change in fluorescence peak intensities with increasing mass of clay for desorption of DOC from the Oxford Clay. Data is dilution and blank corrected and Raman normalised to the Raman peak of water at excitation 348 nm.

UV

The UV absorbance at 254 nm showed an increase with increasing mass to volume ratio until 20 g of clay (m:v ratio 0.17 g/mL) when the UV absorbance at 254 nm began to decrease (Figure A2). This indicated that the desorption of aromatic compounds into solution increased at m:v ratio less than 0.17 g/mL (before 20 g clay) but then decreased at higher clay masses, either through a lack of desorption or re-sorption onto the surface.

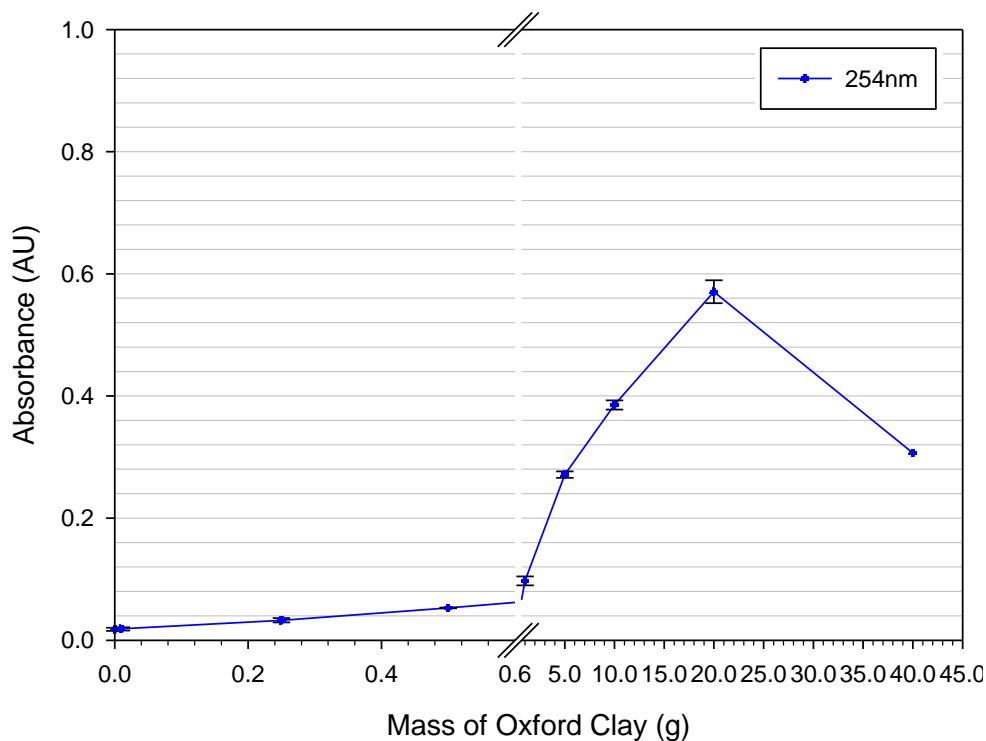


Figure A2: Change in UV absorbance at 254 nm with increasing mass of clay for desorption of DOC from the Oxford Clay. Data is dilution and blank corrected.

DOC and TOC

Figures A3 and A4 show the percentage of the total organic carbon content of the Oxford Clay (5.49% by mass) that was desorbed into solution either as DOC or TOC. The concentrations of TOC and DOC desorbed from the Oxford clay into the DOC free aqueous phase are presented in Table A1 alongside their standard errors. The majority of the organic carbon desorbed from the Oxford Clay at low massed of clay was in the

form of TOC, with DOC levels being undetectable when there was a mass to volume ratio of 0.008 g/mL or less. This indicated that at low m:v ratios the organic carbon desorbed from the clay was particulate rather than dissolved. As the mass of clay was increased, a larger contribution to organic matter in solution was in the form of DOC until the TOC:DOC contribution was approximately 50:50 at 20 g clay (m:v 0.17 g/mL).

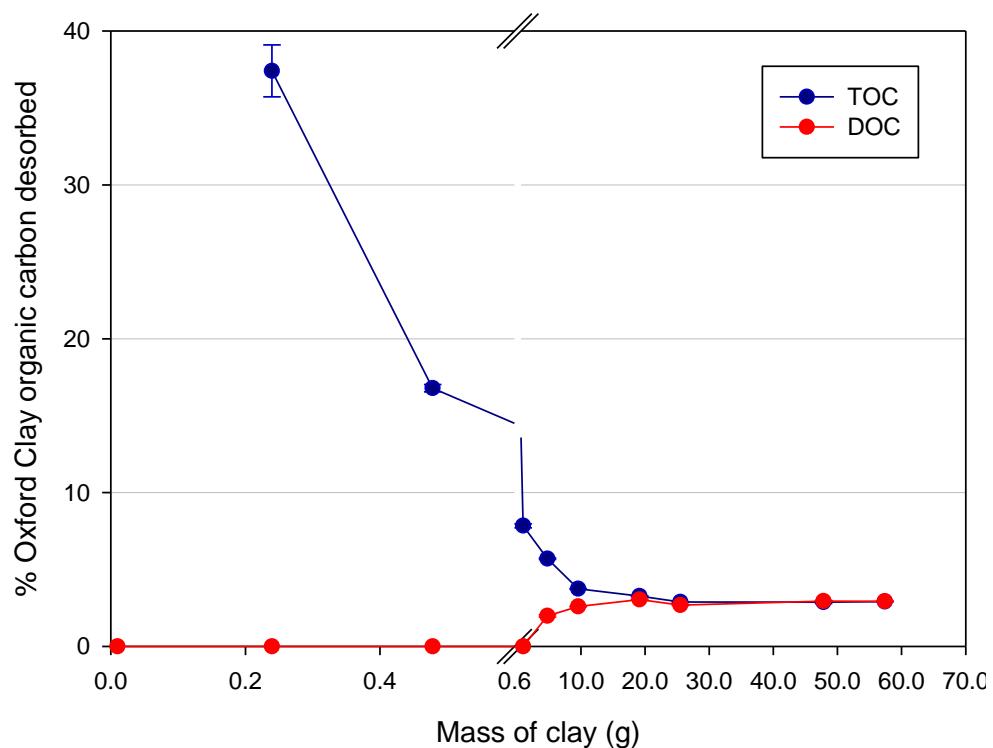


Figure A3: Change in percentage of the total organic carbon content of Oxford Clay that is desorbed into a DOC free synthetic leachate with increasing mass of clay in the forms of DOC and TOC. Data is dilution corrected and standard error is indicated by the error bars.

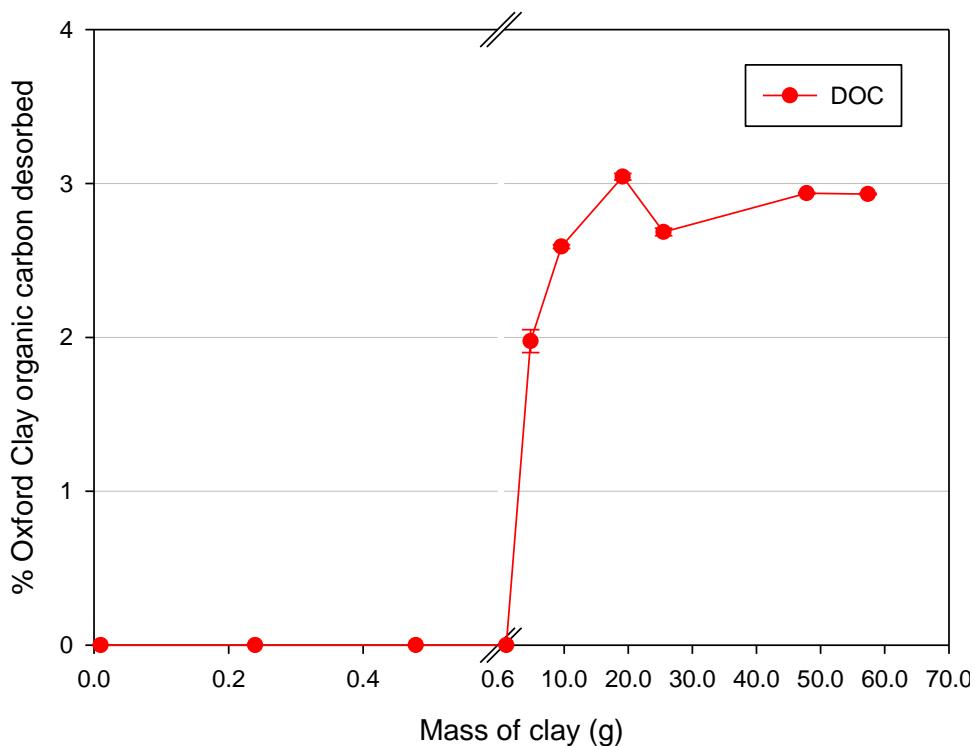


Figure A4: Change in percentage of the total organic carbon content of Oxford Clay that is desorbed into a DOC free synthetic leachate with increasing mass of clay in the form of DOC. Data is dilution corrected and standard error is indicated by the error bars.

| Mass clay (g) | M:V ratio (g/mL) | DOC (mg/L) | TOC (mg/L) | DOC std error (+/- mg/L) | TOC std error (+/- mg/L) |
|---------------|-----------------------|------------|------------|--------------------------|--------------------------|
| 0 | 0 | 0 | 0 | 0 | 0 |
| 0.01 | 8.33×10^{-5} | 0 | 1.29 | 0 | 0.61 |
| 0.25 | 0.002 | 0 | 5.14 | 0 | 1.88 |
| 0.5 | 0.004 | 0 | 4.61 | 0 | 0.54 |
| 1 | 0.008 | 0 | 4.30 | 0 | 0.58 |
| 5 | 0.042 | 5.43 | 15.63 | 1.67 | 1.06 |
| 10 | 0.083 | 14.22 | 20.54 | 0.34 | 5.47 |
| 20 | 0.167 | 33.43 | 35.91 | 2.02 | 0.78 |
| 40 | 0.333 | 58.98 | 63.38 | 4.82 | 2.17 |
| 50 | 0.417 | 80.61 | 78.96 | 1.70 | 0.83 |
| 60 | 0.500 | 96.58 | 95.87 | 1.46 | 2.04 |

Table A1: The amount of clay in each desorption stage and the m:v ratio in the desorption bottle are shown alongside the DOC and TOC concentrations measured from the aqueous phase after the desorption step and their respective standard errors. The data for the mass to volume ratio used in Section 5.1 is highlighted.

In the DOC sorption to the Oxford Clay (Section 5.1) the m:v ratio used (0.17 g/mL) would have resulted in the desorption of 69.3 mg/L of organic carbon from the oxford clay into solution, of which 33.4 mg/L is attributable to DOC. This equates to only 3%

of the total organic carbon content of the Oxford Clay. In the case of the m:v ratios used in contaminant sorption (0.013 g/mL for toluene and 0.0004 g/mL for naphthalene). From the results of this desorption study, less than 2% of the total organic carbon in the clay would desorb into solution during toluene sorption in DOC free leachate (equating to <5.4 mg/L carbon) making its contribution negligible when dealing with most leachates. However, it may need to be taken into account when using leachates that are DOC free or contain very low levels of DOC. At m:v ratios of >0.008 g/mL, no DOC desorption into solution was observed. This indicates that DOC desorption from the Oxford Clay into the aqueous phase was not significant enough to affect naphthalene sorption tests at m:v ratio 0.0004 g/mL in any aqueous phase and can be ignored.

The TOC and DOC concentrations that resulted from the desorption of organic carbon from the Oxford Clay at m:v ratios relevant to the sorption batch tests (Sections 4.1.2 and 4.1.3) was low (0-33.4 mg/L for DOC and 1.3-35.9 mg/L for TOC) and was therefore one to two orders of magnitude smaller than the concentration of the leachates being studied (111-2268 mg/L). This difference in magnitude was also observed between the fluorescence peak intensities and UV absorbance of the OC desorbed from the Oxford Clay and the leachates used in sorption testing. Therefore, the effect desorption of organic carbon from the Oxford Clay has on sorption experiments would be negligible for the majority of leachates. However, for low organic carbon leachates, such as the DOC free synthetic leachate, the effect of organic carbon desorbing from the sorbent may need to be considered.

9.2 Appendix B – The Maturation of Artificially Produced Leachates

Appendix B presents the monitoring data during the stabilisation of the MBT and AMSW leachates which were artificially produced from waste; including DOC character and evolution of DOC via fluorescence and UV spectroscopy. The methodology for the artificial production of leachates is detailed in Section 4.2.4.2.

pH and EC Measurements

An initial drop in pH was observed for both the AMSW leachate (pH 7.5 to pH 6.8) and the MBT leachate (pH 6.7 to pH 5.7). This was indicative of the waste moving through the acetogenic and into the methanogenic maturation phase (Kjeldsen *et al*, 2002). The initial pH drop was more prominent in the MBT leachate, which also had a lower initial pH value than the AMSW leachate. This may be attributable to either the leached state of the AMSW waste or the treatment process undergone by the MBT waste. Both leachates then stabilised at pH 7.2 and 7.3 for AMSW and MBT respectively.

The EC of the MBT and AMSW leachates also showed an initial drop followed by stabilisation. Again this drop was more prominent in the MBT (14 to 8 milli Siemens per meter (mS/m), stabilising at 7.7 mS/m) in comparison to the AMSW (6 to 3 mS/m, stabilising at 2.9 mS/m). This again may be due to the leached nature of the AMSW resulting in fewer mobile inorganic compounds in the waste compared to the MBT. Alternatively, it may be due to the MBT treatment process which does not specifically aim for the removal of inorganic compounds (e.g. salts) which would therefore affect EC.

Gas Production

Gas was collected from the MBT reaction vessel using a gas bag (Teldar). Gas measurement began after 900 hours for the MBT waste, which was when gas production from the vessel became measurable. Although the total volume of gas produced by the waste was not measured, an initial increase in the daily gas volume produced was noted. This was followed by a steady reduction in the volume of gas produced daily. This drop

was likely to be attributable to substrates within the waste being consumed by bacterial action.

An increase in the percentage volumes of both methane and carbon dioxide was seen from the MBT waste until 1700 hours when the percentage volumes of gas production peaked at 37:65% ($\text{CH}_4:\text{CO}_2$ %). The percentage volumes of both gases then stabilised and began to decline until 6200 hours at 14:18%, when a second peak in percentage volume was seen. The second peak reached a maximum after 8690 hours at 39:48%, after which the percentage volumes of the gasses again declined. The increases in methane production observed corresponded to the increase in MBT pH and, therefore, was indicative of the waste moving through the acetogenic and into the methanogenic maturation phase.

No gas was collected from the AMSW vessel. Samples were drawn from the surface of the waste, however no methane was observed. Carbon dioxide was observable in the majority of the samples but despite showing a small increase in volume after 3200 hours never exceeded 2.71% by volume. The lack of gas production is likely to be due to the stabilised nature of the waste.

Fluorescence Spectroscopy Results

Samples of the leachate were analysed by fluorescence spectroscopy as they matured. The peaks, picked from the leachate fluorescence EEMs for AMSW and MBT, and their variation with time are plotted (Figures B1 and B2). The peak intensities seen for the AMSW waste (Figure B1) are an order of magnitude less than those for MBT (Figure B2). This is likely to be due to the leached nature of the original AMSW waste. In the AMSW leachate, peaks E and F (Fulvic-like and Humic-like) are present with the highest intensity. Tryptophan-like peaks A and B are also present, however their intensities are 30-50% lower than those of the humic and fulvic-like peaks. As discussed in Section 2.3.1.4, this is not an indication of the relative compound concentration in solution since the fluorescence of DOC compounds varies depending on the chemical structure of the DOC. Tyrosine-like peaks were largely removed when the blank values for 2% sewage sludge solution and the original rainwater were subtracted. Peak D, however, was intermittently present at very low intensity (<40 Raman units). An increase in peaks A,

B, E and F was seen until 4000 hours, after which the peak intensities levelled out, indicating leachate stabilisation. The sharp peak and drop between 1000 and 1500 hours was attributable to the transfer of the waste to a new reaction vessel due to a leak in the outlet valve. Drain/fill cycles to ensure mixing (indicated by vertical lines) did not have a distinguishable effect on the peak intensities.

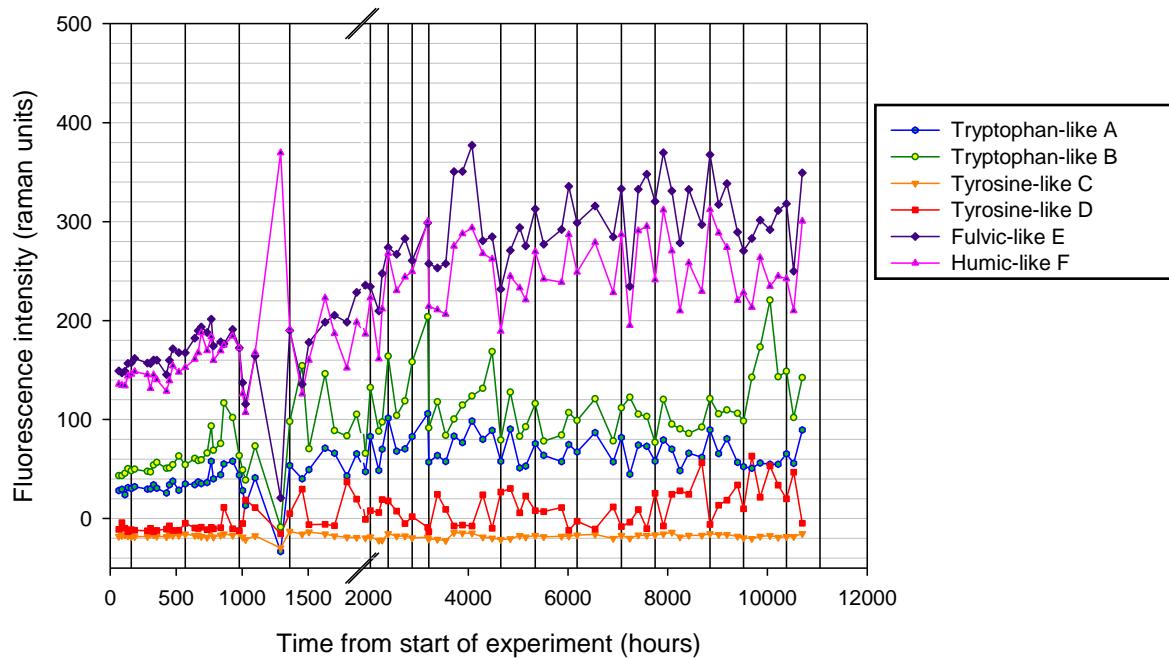


Figure B1: Change in fluorescence peak intensities with time for AMSW leachate. Data is dilution and blank corrected and Raman normalised to the Raman peak of water at excitation 348 nm.

The MBT leachate exhibited all 6 fluorescence peaks (Figure B2). As in the AMSW leachate, the protein-like peaks (A-D) were of a lower intensity than the humic substance-like peaks (E and F). This difference in intensity was approximately 30-50% for both the AMSW and MBT leachates, which highlights that differences in intensity may be due to variations in molecular structure altering fluorescence rather than the concentration of DOC in solution. As humic substance-like molecules are generally larger and more aromatic than protein-like molecules they may fluoresce with a greater intensity due to increased electron resonance within their structure.

Peaks A-D showed an initial increase in intensity until approximately 1800 hours followed by a decrease in intensity, stabilising at approximately 6000 hours. Peaks E and F showed an initial decrease in intensity until 1000 hours before following the same increase and decrease pattern as the protein-like peaks (A-D). Though peak E increased

in intensity until 4000 hours and peak F increased in intensity until 2000 hours, they stabilised at the same time as the other peaks. This may be due to an initial degradation process such as initial aerobic digestion of the humic substance-like compounds, as anaerobic conditions were not confirmed until ~900 hours, followed by a build-up of humic substance-like compounds during the methanogenic phase. This was feasible as the increase in intensity corresponded to the onset of methane production (and so confirmation of anaerobic conditions) within the vessel.

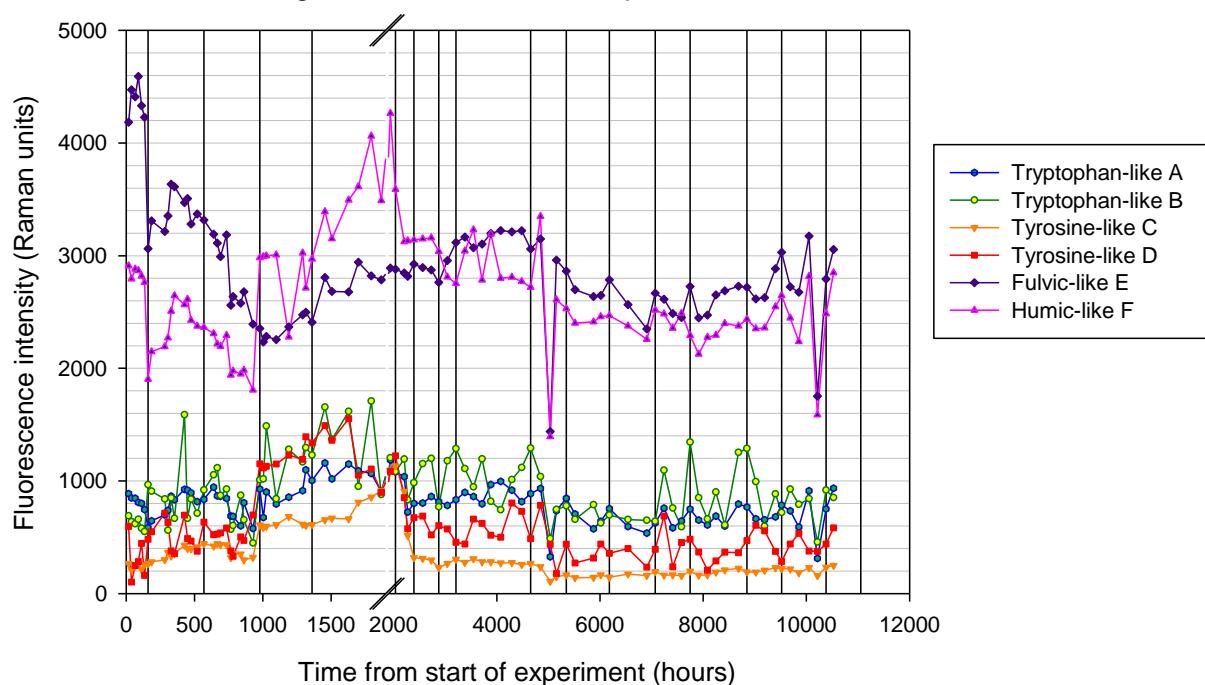


Figure B2: Change in fluorescence peak intensities with time for MBT leachate. Data is dilution and blank corrected and Raman normalised to the Raman peak of water at excitation 348 nm.

The wavelengths of the fluorescence peaks observed corresponded well with literature values (Table 6). There was a lack of peak movement due to red-shifting. Therefore the fluorescence sample dilutions used were deemed adequate to reduce IFE to negligible values.

UV Spectroscopy Results

The UV absorbance at 254 nm for AMSW showed an increase in absorbance until 4000 hours, followed by stabilisation (Figure B3). This was consistent with the increase in fluorescence peak intensity observed in peaks E and F and indicated an increase in

aromatic character of the leachate DOC which was likely to be attributable to a build-up of humic substance-like compounds.

The UV absorbance at 254 nm for MBT leachate showed a steady decrease in absorbance until 4000 hours, followed by stabilisation (Figure B3). This indicated a decrease in aromatic character of the leachate as it approached stabilisation. The UV absorbance peak at 1000-2000 hours was consistent with the increase in fluorescence peak intensity observed in the humic substance-like peaks as methane production began. This indicated an increase in humic substances during the initial methanogenic stages which then quickly began to decline.

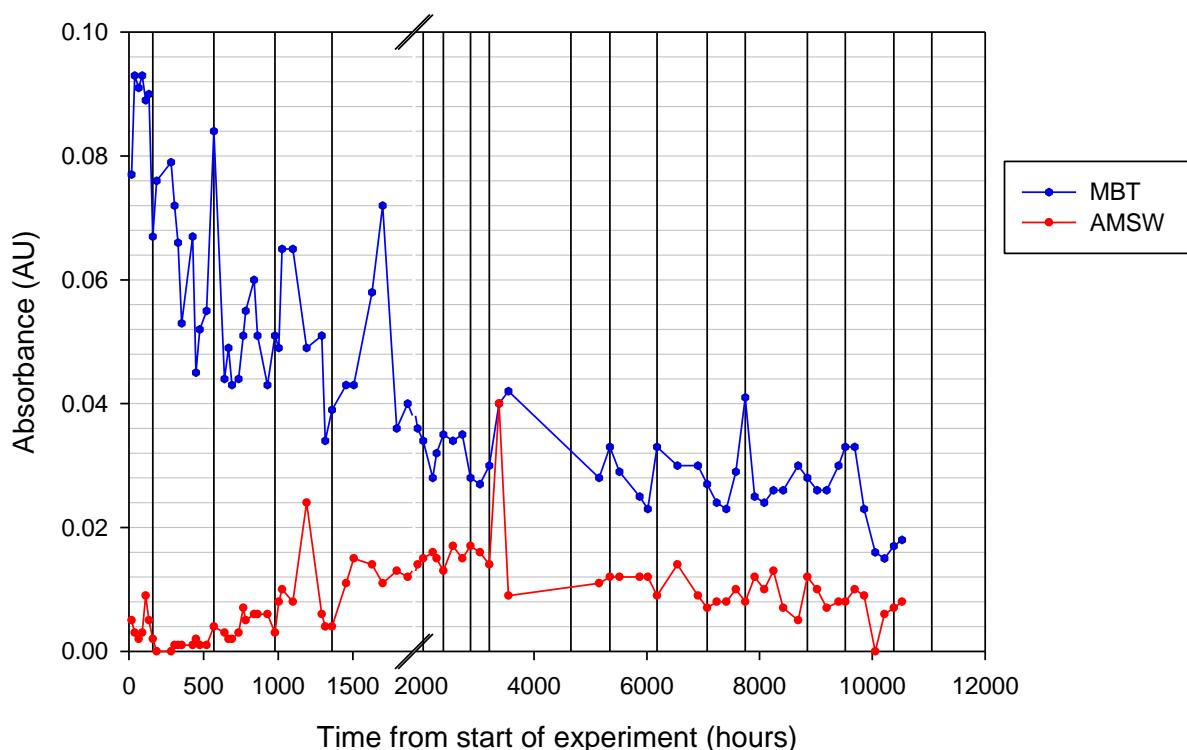


Figure B3: Change in UV peak absorbance with time for MBT and AMSW leachates at 254 nm. Data is blank corrected at 1:1000 dilution for both samples.

DOC

In AMSW leachate, the DOC concentration showed an initial increase and decrease followed by a further increase in concentration to stabilisation (Figure B4). The increase in concentration before stabilisation was also observed in all AMSW fluorescence peaks, indicating that the increase in fluorescence peaks was linked to an increase in DOC. The initial increase in DOC concentration may indicate dissolution of DOC from the waste

into solution, which reduced when the reaction vessel was changed before continuing to increase in concentration.

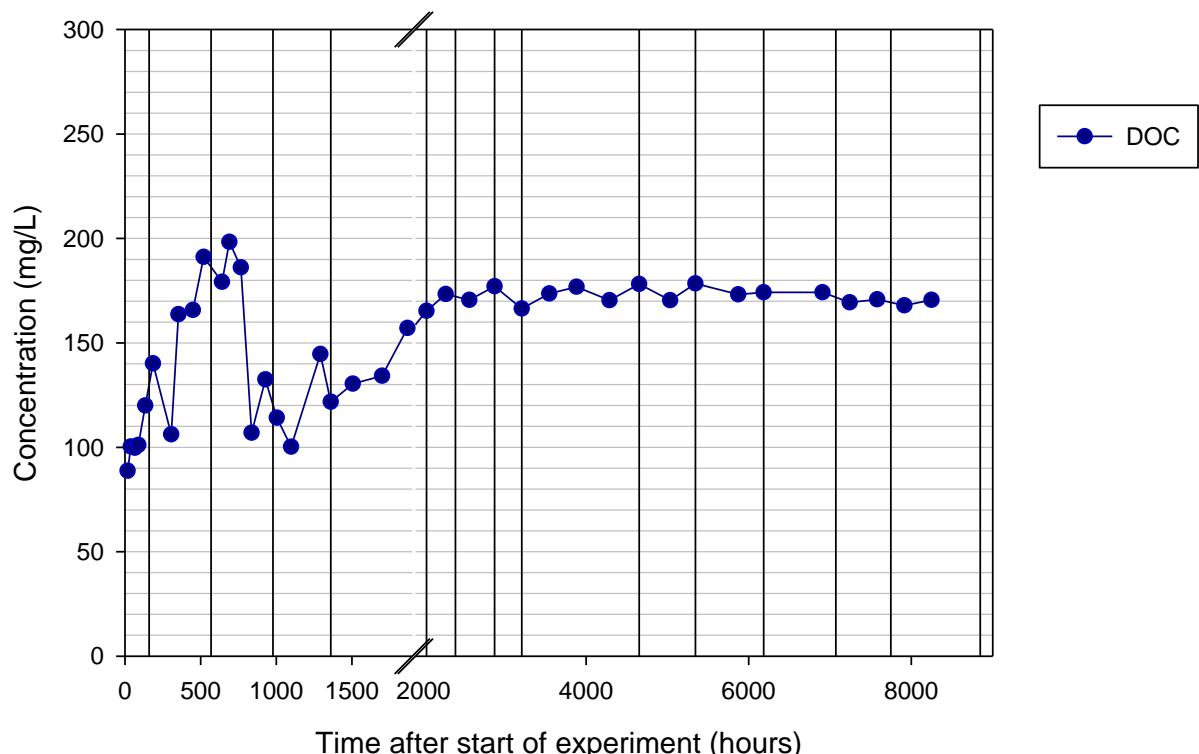


Figure B4: Change in DOC concentration with time for AMSW leachate. Data is dilution corrected.

The DOC concentration of the MBT leachate (Figure B5) shows an initial sharp decrease with time. This then recovers to a greater concentration than the initial value and then sharply declines again before stabilising at approximately 4000 hours. The initial drop in DOC concentration may be due to initial desorption and subsequent degradation of DOC from the waste due to initial aerobic degradation, followed by an increase in concentration which may be due to increased leaching of compounds from the waste. The second sharp decrease in concentration before stabilisation coincides with the onset of the methanogenic phases of stabilisation, and so may indicate the degradation of DOC by methanogens.

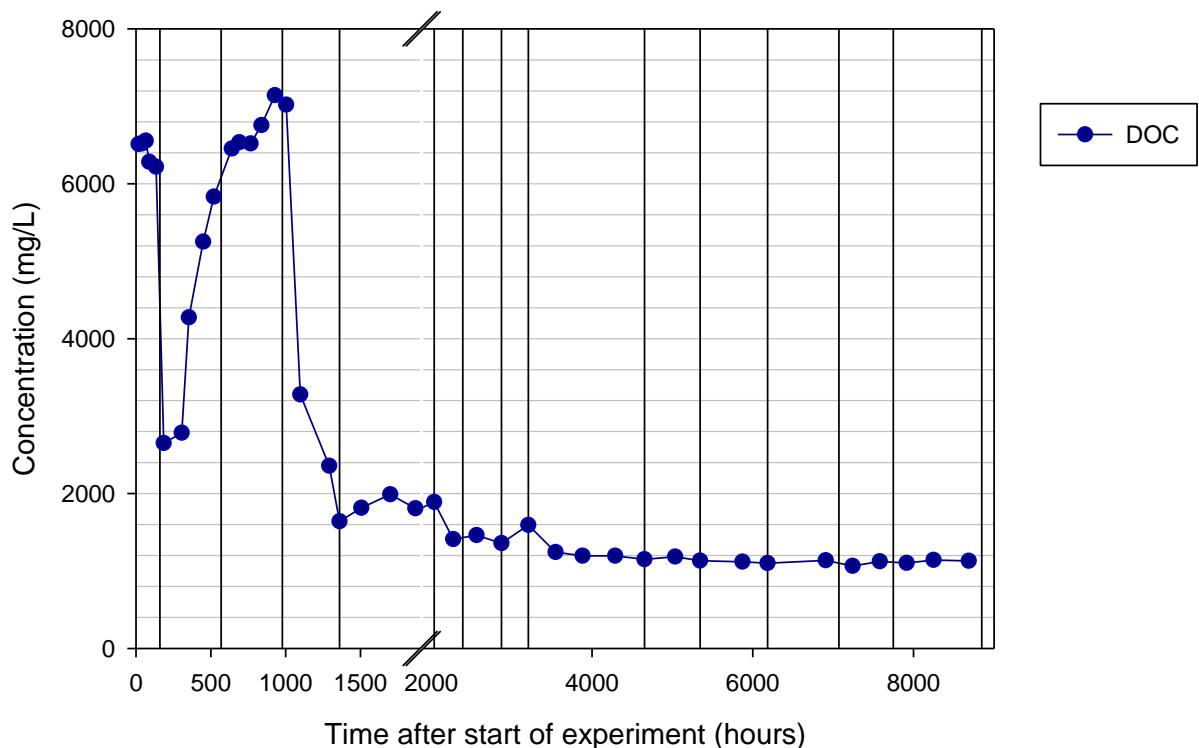


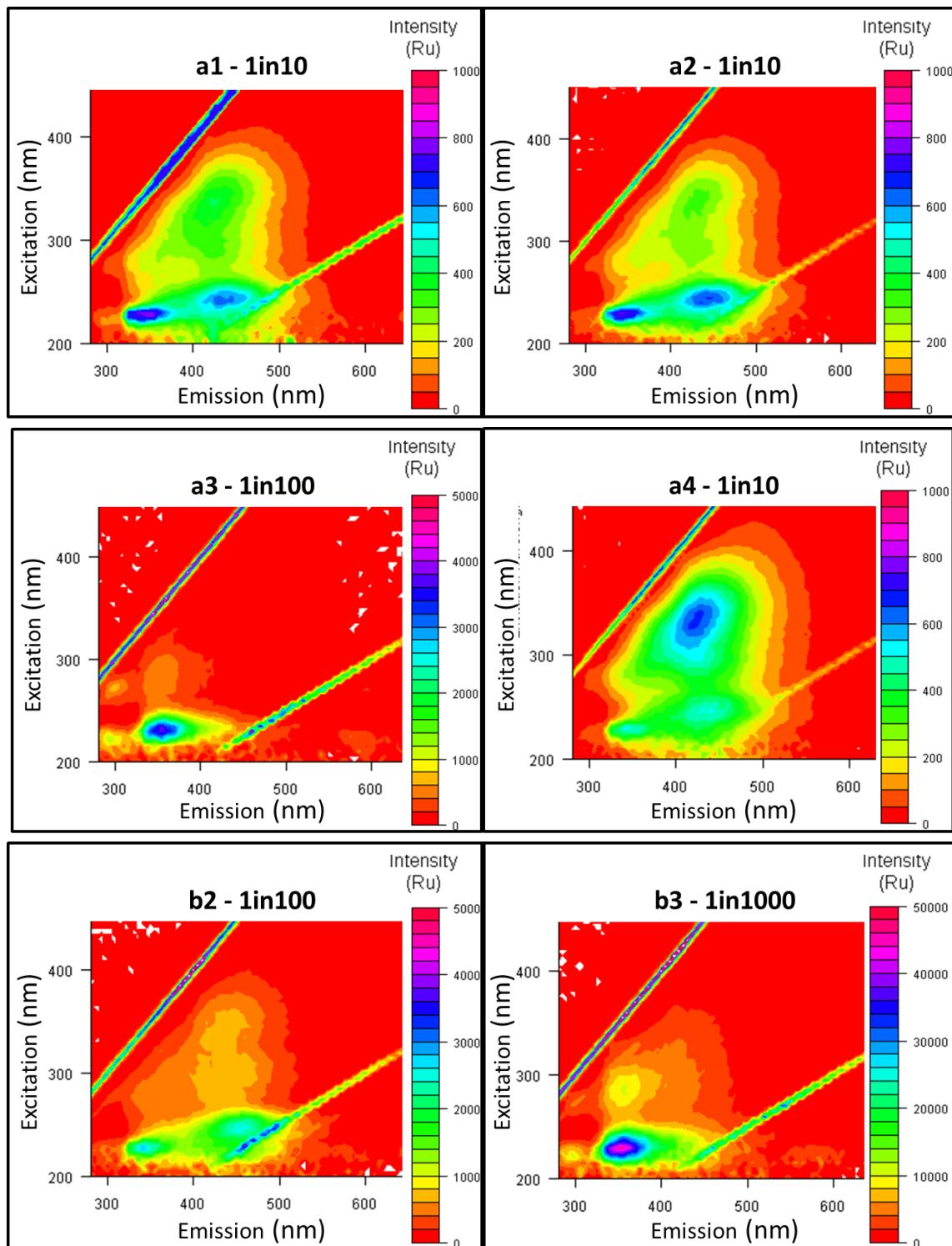
Figure B5: Change in DOC concentration with time for MSW leachate. Data is dilution corrected.

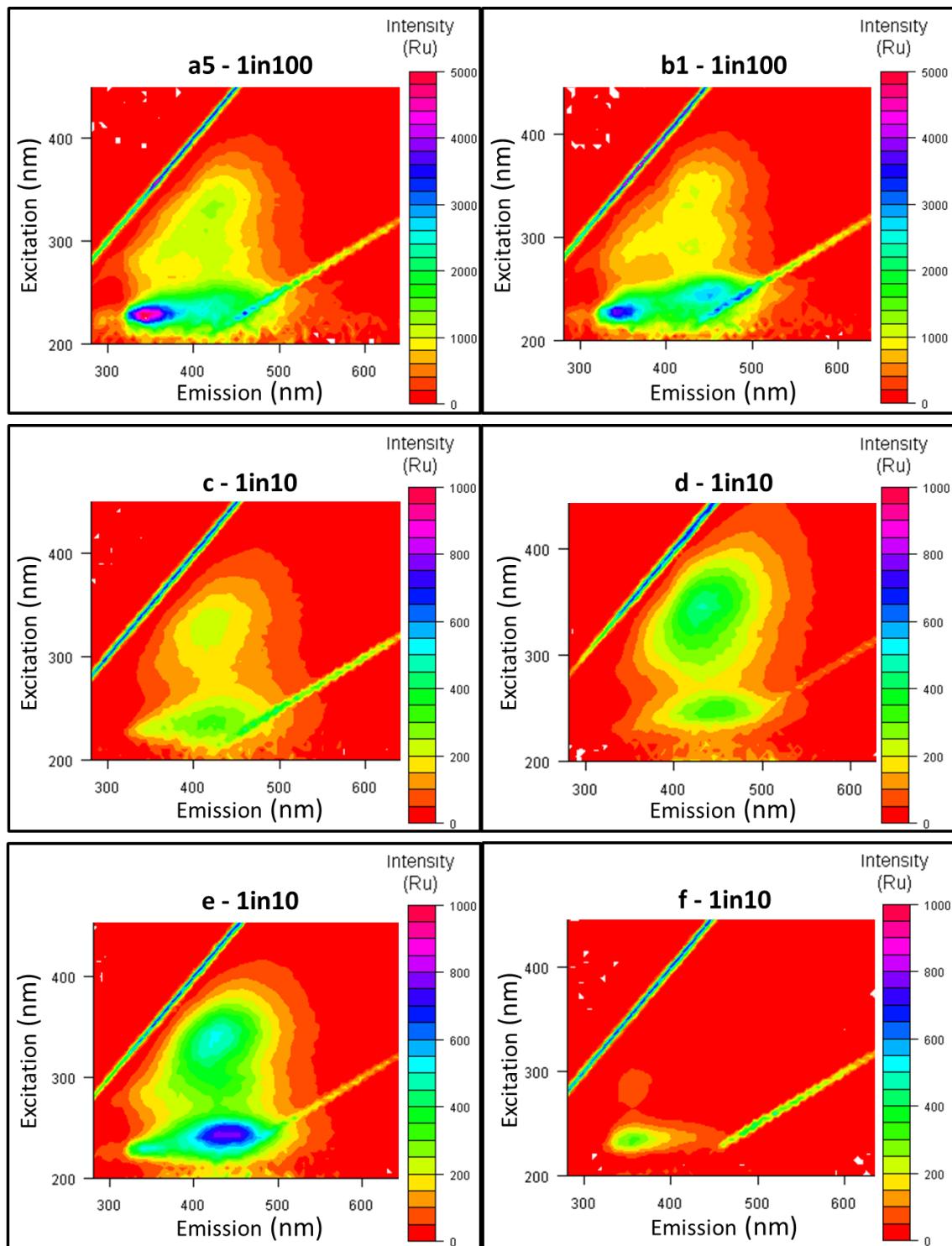
Summary of leachate stabilisation

The AMSW and MBT leachates produced fluorescence peaks which were directly comparable to the literature (Table 6). Both leachates stabilised at around 4000 hours and were then ready to be used in batch testing work. Monitoring of the leachates did, however, continue until approximately 10000 hours in order to ensure full stabilisation of the leachate had occurred. Fluorescence for AMSW showed a steady increase in peak intensity for all peaks before stabilization. The MBT fluorescence showed an initial increase in peak intensity for peaks A-D, but a drop in peak intensity for peaks E and F which then began to increase once anaerobic conditions had been established and gas production began. This was attributed to initial aerobic degradation of fulvic-like compounds followed by their build up until an equilibrium in solution was reached and the leachate stabilised. UV absorbance at 254 nm for AMSW mirrored the increasing trend observed in fluorescence results. The MBT UV absorbance showed a decline in aromatic character of the leachate as it approached stabilisation. AMSW DOC showed an initial increase and decline before again increasing to stabilisation. The trend

followed by the DOC concentration matches that seen in the fluorescence results, indicating that the change in fluorescence may be partly due to DOC concentration in solution. MBT DOC concentrations showed an initial decrease followed by an increase which was attributed to an initial aerobic degradation of DOC followed by increased leaching of compounds from the waste. This was followed by a second decrease in concentration which coincided with the onset of gas production, indicating methanogenic degradation processes occurring within the vessel.

9.3 Appendix C - Fluorescence EEMs for Leachates Characterised in Section 4.2.5.





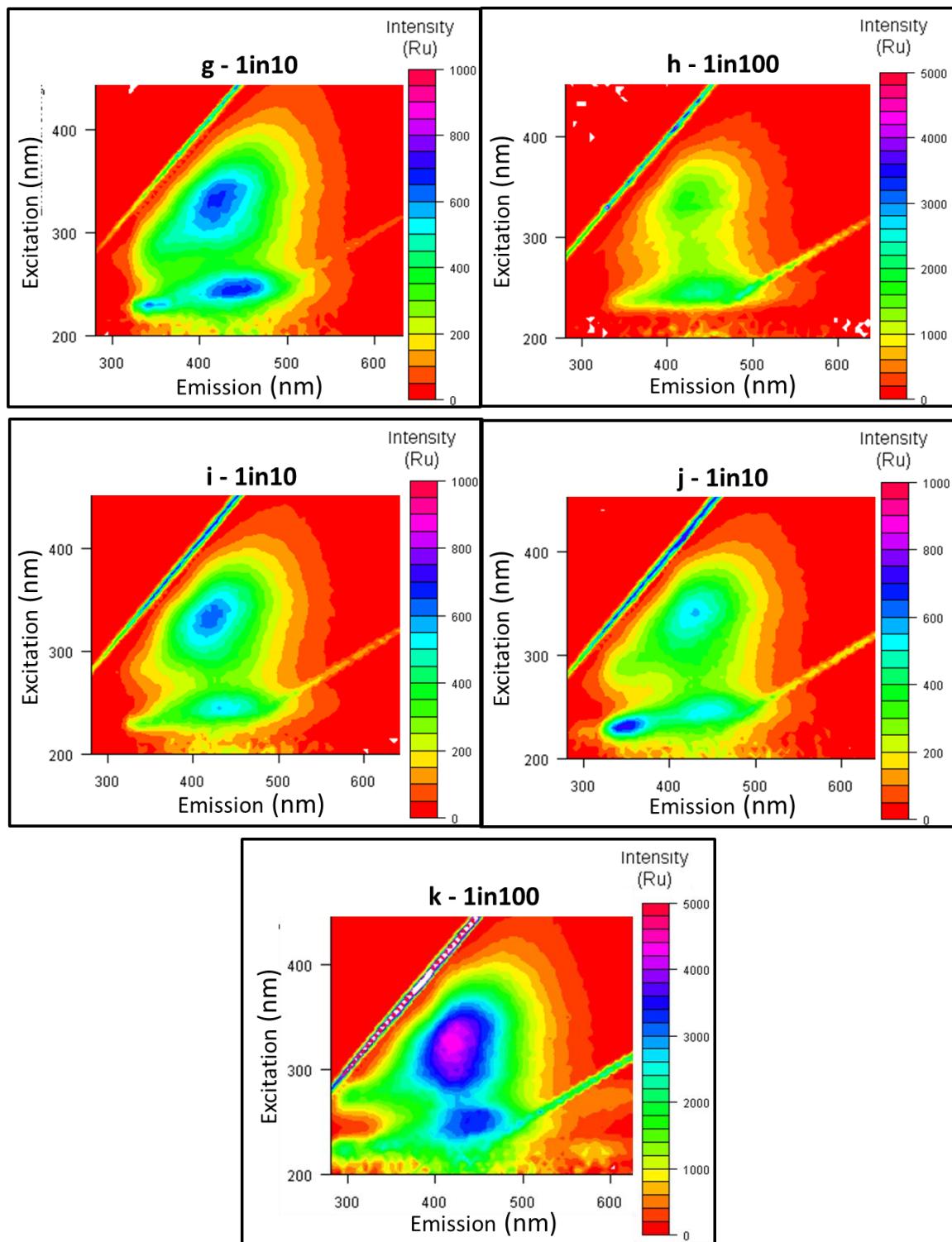


Figure C1: Fluorescence EEM spectra of leachates from different landfill sites (a-k), and between different wells on the same landfill site (a1-5 and b1-3).

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