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Attenuation of organic contaminants in leachate by mineral landfill liners

Integrated Catchment Science programme
Science report: SC020039/SR5 Project record

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Steve Killeen

Head of Science

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1 Introduction

This document contains the project record which accompanies the Environment Agency report *Attenuation of organic contaminants in leachate by mineral landfill liners (SC020039-5/SR)*. This record collates the interim reports made to the Environment Agency steering committee throughout the project and includes details of the initial review of UK mineral liner materials, UK leachates and contaminants likely to be found in UK landfill leachates. Details of the methods used in the project to measure attenuation (through sorption and biodegradation) of certain List I organic contaminants are given. The document includes results from all the experiments undertaken during the project.

2 Characteristics of UK landfills

2.1 UK landfill leachates

2.1.1 Introduction

Landfill leachate has been described as a water-based solution of compounds derived from waste (Christensen *et al.*, 2001). Leachate is mainly generated by rainwater percolating through layers of waste, although the inherent moisture content of the waste and other types of water inputs may also contribute. Chemical conditions found in the landfill liner environment are influenced by leachate, which in turn is determined by waste composition and biological, chemical and physical processes occurring in the landfill.

In terms of waste composition, four broad classes of landfill have been identified for the purpose of this review:

- conventional municipal solid waste (MSW) and non-hazardous landfill;
- mechanically separated and biologically treated municipal solid waste (MBP);
- bottom ash from incineration of municipal solid waste (MSWI);
- treated hazardous wastes meeting European acceptance criteria.

2.1.2 Municipal solid waste/Non-hazardous landfill

The leachate derived from MSW landfill contains four main groups of compounds: biodegradable and recalcitrant organic matter, inorganic compounds (such as Na, Mg, K, Ca, Fe, Mn, Cl, ammonia, sulphate and bicarbonate), heavy metals (such as Cd, Cu, Cr, Pb, Ni, and Zn) and xenobiotic organic compounds (such as aromatic hydrocarbons, chlorinated aliphatics and phenols). Typical “bulk chemistry” values for leachate from MSW are shown in Table 2.1. Very high concentrations of dissolved organic carbon (DOC) and inorganic compounds may be found; the concentrations of these components may be 1,000 to 5,000 times greater than groundwater (Christensen *et al.*, 2001). The concentration of xenobiotic organic compounds is generally very low, but many are toxic even at low concentrations.

The composition of leachate from MSW landfills changes as the waste ages and biodegrades (for example, Statom *et al.*, 2003). The initial load of organic matter in the leachate is high (Table 2.1) but decreases as the landfill matures, albeit slowly: for example, Belevi and Baccini (1989) suggested that it may take 500 to 1,700 years to reduce the organic carbon content of leachate to 20 mg/l. Similarly, MSW leachates have high nitrogen content, and nitrogen concentrations tend to remain high for many years (Hjelmar, 2000).

MSW decomposes over time and, in general, up to five biodegradative phases may be identified:

Phase 1: aerobic microbial decomposition.

Putrescible wastes undergo aerobic biodegradation until the available oxygen is used up. During this time, generally less than one month, carbon dioxide is the main gas produced and heat is generated, the leachate contains low molecular weight carbon compounds and ammonia and its pH is approximately neutral .

Phase 2: acidogenesis

Aerobic bacteria are superseded by anaerobes as oxygen levels drop. Complex organic material is hydrolysed and volatile fatty acids are produced by acidogenesis. The leachate pH drops as volatile fatty acids accumulate; carbon dioxide and hydrogen are produced.

Phase 3: acetogenic acid phase

Long chain fatty acids are broken down by acetogenic bacteria to acetate, carbon dioxide and hydrogen. The pH of the leachate may drop to less than five.

Phase 4: methanogenic phase

Anaerobic methanogenic bacteria convert the products of acetogenesis into carbon dioxide and methane. The pH rises (pH7.5-9.0) and the degradability of the residual leachate dissolved organic carbon is reduced. The methanogenic phase may last for decades or even centuries (Belevi and Baccini, 1989).

Phase 5: aerobic phase

Final stage when aerobic conditions are re-established and aerobic microorganisms replace the anaerobes.

Table 2.1 Composition of municipal solid waste landfill leachate in various phases

	Young MSW	Acid phase	Methanogenic phase	Overall
pH	5.6-7	4.5-7.5	7.5-9	4.5-9
COD (mg/l)	35-50 x 10 ³	6-60 x 10 ³	500-4,500	140-152,000
BOD ₅ (mg/l)	21-25 x 10 ³	4-40 x 10 ³	20-550	20-57,000
SS (mg/l)	2,630-3,950			
TKN (mg/l)	2,370			14-2,500
NH ₃ -N (mg/l)	2,020			50-2,200
Total-P (mg/l)	5-6			0.1-23

References: Ozturk *et al.*, 2003; Ehrig, 1988; Christensen *et al.*, 2001

COD = chemical oxygen demand; BOD₅ = biological oxygen demand (5 day);
SS=suspended solids; TKN = total Kjeldahl nitrogen; NH₃-N = ammonia-nitrogen; Total-P = total phosphorus

2.1.3 Mechanical biological pre-treatment

During mechanical biological pre-treatment (MBP), municipal solid waste is subjected to mechanical extraction processes to remove glass, plastics and metals, and the remaining organic fraction is treated by composting (or a combination of composting and anaerobic treatment) before deposition in a landfill or use in agriculture, horticulture or landscaping. The quality of leachate from MBP waste depends on the:

- waste inputs and extent of source separation;
- type of mechanical pre-treatment;
- type and duration of biological treatment (Environment Agency, 2003b).

The residual waste after mechanical extraction (without biological treatment) produces a significantly higher strength leachate compared to non-separated waste (for example, COD = 172,000 mg/l, BOD₅ = 123,000 mg/l, NH₃-N = 4,000 mg/l; Environment Agency, 2003b). Aerobic treatment stabilizes residual waste to a degree, reducing the COD, BOD₅ and total nitrogen content in the leachate compared to untreated residual waste (Leikam and Stegmann, 1999). Analysis of stabilized MBP-waste has shown that some easily degradable organic material may remain, although humification of the residual material may have started (Zach *et al.*, 2000).

2.1.4 Residues from incineration of MSW

Incineration of MSW creates different types of ash residues; these may be considered to fall into two waste streams:

- bottom ash – the clinker that falls through the grate and may contain unburned fractions;
- fly ash and APC residues – fine particulates from the incinerator flue gas or air pollution control (APC) scrubbers.

Bottom ash residues contain a high proportion of silicates, calcium oxide, soluble salts (particularly chlorides and metals), and a small amount of unburned organic material (generally less than five per cent) (Environment Agency, 2003b). Hydration of calcium oxide to slaked lime (calcium hydroxide) leads to heating and produces a strongly alkaline leachate (> pH 11.5). Carbonation of slaked lime to calcium carbonate causes the pH to fall to 8.0-8.5, increasing the solubility of some metals. Analysis of the extractable carbon remaining in MSW bottom ash reveals that it is water soluble, polar in nature and comprises low molecular weight aliphatic and aromatic acids (Ferrari *et al.*, 2002). The nitrogen content and COD of leachate from incinerated MSW bottom ash is much lower than untreated waste; sulphate concentrations are high compared to MSW leachate but may decrease as the landfill matures and sulphide concentrations may rise if reducing conditions develop (Environment Agency, 2003b).

The waste residues from the flue gas and APC scrubbers may be landfilled separately or together. The fine particulates in flue gas may be collected by electrostatic precipitation. Scrubbing for removal of gaseous trace inorganic and organic compounds may involve wet or dry processes, and produce sludges or filter cakes. Fly ash and APC sludges contain a high proportion of soluble inorganic calcium salts, mainly chloride, sulphate and hydroxide, plus sodium chloride and heavy metals (particularly zinc, iron and lead, but also cadmium, copper, chromium

and nickel, plus trace amounts of mercury) (Hjelmar, 1996; Hjelmar *et al.*, 2000). Fly ash may contain traces of unburned organic material.

2.1.5 Treated hazardous waste

The Landfill Directive (Council Directive 1999/31/EC) prohibits the co-disposal of hazardous wastes with biodegradable MSW; thus, the leachate from hazardous waste landfills is likely to be dominated by chemical rather than biological processes (Environment Agency, 2003b). A wide range of components may be present in hazardous waste (including filter cakes and sludges, incinerator ash and cement-stabilised wastes) leading to leachates of varying quality. Extremely high concentrations of dissolved salts, halogenated organics and trace elements may be found, but organic carbon and nitrogen contents are low. The limited data available show a tendency of decreasing leachate strengths with landfill age (Environment Agency, 2003b).

2.1.6 Characteristics of dissolved and colloidal organic matter in leachate

Landfill leachate from MSW landfills and MBP wastes contains a mixture of dissolved organic matter (DOM) typically composed of a heterogeneous assortment of low molecular weight polysaccharides, cellulose, hemicellulose, proteins, volatile fatty acids, lipids and waxes, and higher molecular weight compounds such as humic and fulvic acids (Christensen *et al.*, 1998; Nanny and Ratasuk, 2002). Studies have shown that DOM in landfill leachate changes as the landfill ages, with an increase in humic relative to fulvic acids (Artiola-Fortuny and Fuller, 1982) and increasing aromaticity and molecular weight in old leachates (Kang *et al.*, 2002; Calace *et al.*, 2001). Landfill leachate also contains colloidal material (0.1-1 μm particulates) which is predominantly organic in nature, but also includes an inorganic fraction comprising Al, Fe and Si (Gounaris *et al.*, 1993; Jensen and Christensen, 1999).

DOM and colloids may bind with organic pollutants, but may also compete with organic compounds for sorption sites on solid surfaces (Chiou *et al.*, 1986). Competition leads to a decrease in sorption of organic contaminants relative to when organic material is not present. However, DOM can also associate with low organic carbon materials increasing their sorption of organic contaminants (Larsen *et al.*, 1992), thus increasing sorption coefficients. The retention of colloids by porous media may also increase apparent sorption affinity of a solid phase if the colloid material sorbs organic contaminants. Thus, the presence of DOM and colloidal material in leachate may have an impact on sorption coefficients, depending on the relative partitioning of organic material and hydrophobic contaminants between the different phases.

2.1.7 Redox conditions in landfill leachate

Aerobic and anaerobic biodegradation of waste is accompanied by changes in redox potential in the landfill. In freshly deposited wastes, the organic matter in the leachate is oxidised first by oxygen, then nitrate, manganese, iron and sulphate, before methanogenesis commences. The concentration of such oxidising agents and their reduced species in the leachate can therefore be used to indicate the principal redox conditions (US EPA, 1996). The type of emplaced waste also influences the redox environment. In high sulphate-low organic carbon leachates such as those formed

when bottom ash is present, sulphate-reducing conditions may predominate in an anoxic environment.

While redox conditions in landfill leachate may not significantly impact on sorption-desorption processes for non-polar organic contaminants, many organic compounds may only undergo biodegradation under specific conditions such as aerobic, nitrate-reducing or sulphate-reducing. Physico-chemical parameters in a landfill liner are likely to be dominated by the redox conditions in the landfill, therefore the potential for biodegradation in the liner depends to an extent on the leachate chemistry.

2.2 UK liner materials

2.2.1 Introduction

The Landfill Regulations require groundwater to be protected from pollution by landfill leachate by the incorporation of a geological barrier and, in landfills where leachate needs to be collected, a bottom liner. The broad categories of artificial liners used in the UK include:

- compacted clay liners (local reworked clays or bentonite-enriched soils);
- geosynthetic liners (comprising a thin layer of sodium or calcium bentonite bonded to a layer or layers of geotextile);
- composite liners (a geosynthetic liner used with a mineral liner or bentonite).

This report concentrates solely on mineral liner materials.

Any material used as a mineral liner needs to be engineered to meet certain performance criteria, which will include a maximum hydraulic conductivity of 1×10^{-9} m/s (Environment Agency, 2003d). The high cost of haulage means that there is an obvious preference to use local materials in the construction of compacted clay liners. Fortunately, most UK clays and many mudrocks (with a reasonable degree of plasticity) can be engineered to meet engineering requirements, and consequently a wide range of geological strata are currently in use as landfill mineral liners. In the UK the available materials range in age from Carboniferous to recent, and have very varied mineralogies. Some of the characteristics of commonly used mineral liner materials are given in Table 2.2. There is considerable variation in organic content and mineral abundance in any given formation; only rarely is the composition constant.

Table 2.2 Some commonly used mineral landfill liner materials

Strata	Region	Organic carbon cont. %	Clay content %	Principal clay mineral composition	Smectite content %
Kimmeridge Clay	Dorset, East England	1.8-9.4 ^a	57 ^d	illite-smectite, illite, kaolinite	low
Coal Measures ¹	NE/NW England, Wales, Scotland	0-10	15-80	kaolinite & illite	<10
Oxford Clay	Oxfordshire	4-8	30-70 ^d	illite	low ²
Lias Clay	Dorset, Somerset, Midlands, Yorkshire	0.25-12 ^b	18-68 ^d	illite, illite-smectite, kaolinite	low
London Clay	London basin	2-4	40-60	smectite, illite	30-40
Gault Clay	Cambridgeshire, Oxfordshire, Buckinghamshire	1-4	40-60 ^d	smectite, kaolinite, illite	10-25
Mercia Mudstone	Midlands & South Yorkshire	very low	10-50 ^c	illite	very low
Fullers Earth	Southern and Southwest England	very low	40-70 ^d	smectite	90
Etruria	Midlands	very low	40-60	illite, illite-smectite	low
Boulder Clay/ Glacial Till	Widespread		10-55 ^c	illite-smectite, chlorite	variable
Weald Clay	Kent, Surrey, Sussex		20-74 ^d	illite-smectite, illite, kaolinite,	low
Lacustrine Clay	Widespread	8.3-9.5 ^c		illite	

¹Including colliery waste; ²smectite is abundant in the clay fraction of coexisting limestones such as the Great Oolite. References: ^aScotchman, 1987; ^bDeconink *et al.*, 2003; ^cReeves *et al.*, 2006; ^dCripps and Taylor, 1986 and 1987.

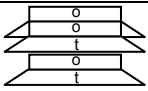
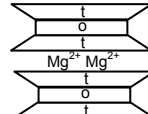
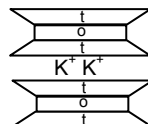
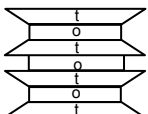
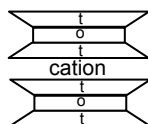
2.2.2 Liner composition

UK liner materials exhibit wide variation in rock types and ages, clay content and mineralogy, and organic matter content and composition. The two factors which influence attenuation in mineral liner materials are clay mineralogy and organic carbon (Section 2.2.3). The clay fraction of a soil or sediment has long been considered important as a chemically active component of the solid phase. The composition of clay minerals and their net negative charge lends a relatively polar nature to the solid surfaces which leads to a natural affinity between the solid and polar or ionic solutes. Natural soils often contain a mixture of two or more clay mineral species, combined with quartz, carbonates, calcite and other non-clay minerals. The

clay mineral species include kaolinite, illite, smectite, vermiculite and chlorite; the structure of these is shown in Table 2.3 (see Horseman *et al.*, 1996; Rowe *et al.*, 1995; Reeves *et al.*, 2006). Kaolinite has a low surface charge and surface area, therefore little adsorptive capacity for ionic or polar contaminants; it is difficult to achieve a hydraulic conductivity of less than 10^{-8} m/s with this clay, thus advective transport is greater than required. Illite, chlorite and smectite are all important mineral species used in landfill liners. Illite, a form of mica, consists of stacks of 2:1 layered units held together by a strong potassium bond. Isomorphous substitution leads to illites maintaining a negative charge which permits adsorption of positively charged species. Illite is readily compacted to form liners with a hydraulic conductivity of 10^{-9} m/s to 10^{-11} m/s. Chlorite also has a strongly bonded, 2:1 clay layer structure, and similar properties to illite. Some chlorites contain iron which may oxidise, reducing the negative charge and permitting swelling and formation of vermiculites or smectites. Smectites, or swelling clays, have a low negative charge so layers are not strongly bound together and interlayer swelling may occur. However, smectites show very low hydraulic conductivities (10^{-11} to 10^{-15} m/s) and can be mixed with sand to make clay liners, or combined with geotextiles to form geosynthetic clay liners. Mixed layer clays such as illite-smectites may be formed during periods of diagenesis and weathering.

While the large surface area of the clay fraction has been shown to be important for sorption of heavy metals and neutral hydrophobic organic compounds (Sawney and Gent, 1990; Aochi *et al.*, 1992), it is generally of secondary importance for non-ionic hydrophobic organic compounds which preferentially bind to organic material in soils and sediments (Section 2.2.3). In terms of a liner's ability to attenuate trace organic substances, there is evidence that both the quantity and type of organic matter is important for sorption of hydrophobic organic compounds.

Table 2.3 Basic structure of clay mineral species (from Horseman *et al.*, 1996)

	Layers	General crystal structure	Crystal Habit	Surface area m ² /g
Kaolinite	1:1		often euhedral hexagonal plates; 0.05 – 2 µm thick	10-20
Vermiculite	2:1		usually mixed with other clay minerals	40-80 (up to 870 if interlayer surfaces included)
Illite	2:1		irregular, thin flakes; 300nm thick	65-100
Chlorite	2:1		platey	
Smectite	2:1		small, filmy sheets, 100nm to 200nm thick	50-120; (700-840 if interlayer surfaces included)

o= octahedral layer ($n(\text{Al}_2(\text{OH})_6)$) or ($n(\text{Mg}_3(\text{OH})_6)$); t= tetrahedral layer ($n(\text{Si}_2\text{O}_5)^{2-}$).

2.2.3 Organic carbon in liner materials

If a solid contains greater than 0.1 per cent ($f_{oc} > 0.001$) organic carbon, sorption of hydrophobic organic contaminants (HOCs) is dominated by the organic carbon content (OC) (Karickhoff *et al.*, 1979; Schwarzenbach and Westall, 1981). In low carbon environments, mineral content may affect the mobility of HOCs. Researchers in the 1970s and 1980s found that sorption of HOCs was driven by hydrophobic interactions with soil organic matter and described sorption in terms of a linear partitioning model, in which sorption was envisaged as a partition of the HOCs from the aqueous phase into the solid organic phase which was relatively homogeneous and amorphous (Chiou *et al.*, 1979; Karickhoff *et al.*, 1979). Other more complex partitioning models have since been developed and are discussed in Section 3.2.

In recent years, it has been recognised that the structural type of organic carbon is as important as the quantity for sorption of HOCs. This is further discussed in Section 3.3.6, but briefly the following processes are important: organic material changes as it ages, undergoing degradative processes, reduction and oxidation, varying degrees of heat and pressure until it is extensively altered from the parent material. Over geological time, humic material may be transformed into kerogen, peat, coal or shales. Soils and sediments contain a mixture of relatively young humic material and older more diagenetically altered material (Song *et al.*, 2002). HOCs sorb strongly to more complex and thermally altered organic carbon, such that sorption coefficients may be much greater than predicted from simple empirical models based on the organic carbon content of a soil or sediment (Kloneidam *et al.*, 1999; Ghosh *et al.*, 2000; Karapanagioti *et al.*, 2000; Accardi-Dey and Gschwend, 2002).

3 Review of natural attenuation processes

3.1 Overview of natural attenuation processes

Attenuation of an environmental contaminant occurs when there is a reduction in load, concentration, flux, or toxicity of the contaminant in soil or groundwater. The term 'natural' is used to indicate that these processes occur *in situ* and without human intervention. Other terms associated with natural attenuation in the literature include "intrinsic bioremediation", "intrinsic remediation", "passive bioremediation" and "natural recovery".

Natural attenuation processes can be divided into three groups: physical (sorption, dispersion, diffusion, dilution and volatilisation), chemical (chemical and abiotic reactions) and biological (biodegradation) processes. Brief descriptions of each of these mechanisms are given in Table 3.1 (McCallister and Chiang, 1994; Christensen *et al.*, 2001). A combination of these processes may contribute to attenuation, with anaerobic biodegradation and sorption being particularly important in a landfill liner environment.

Table 3.1 Summary of the attenuation processes affecting contaminant transport and fate in the subsurface

Process		Description
Physical	Volatilisation	Transfer of contaminants from an aqueous phase to the vapour phase
	Dispersion	Spreading of contaminants due to heterogeneities in groundwater systems
	Diffusion	Spreading of contaminant in response to concentration gradient within a fluid
	Sorption	Association of a contaminant in a gaseous or aqueous phase with a solid material
Biological	Aerobic	Microorganisms use oxygen as an electron acceptor to degrade contaminants
	Anaerobic	Alternative electron acceptors (e.g., NO_3^- , SO_4^{2-} , Fe^{3+} and CO_2) are used by microorganisms to degrade contaminants
Chemical	Hydrolysis, dehydrohalogenation, and other chemical reactions	Chemical transformations that degrade contaminants without microbial facilitation

3.2 Sorption

3.2.1 Introduction

Sorption is a generic term which describes the processes by which a contaminant partitions between solid and aqueous phases. A number of processes may be involved, including adsorption, in which a compound attaches onto a solid surface, and absorption, in which a compound diffuses into the structure of a porous particle. Detachment from the surface and back into solution is referred to as desorption. Sorption retards the diffusion and advection of contaminants through a solid matrix and may also reduce bioavailability by sheltering contaminants from direct uptake by microorganisms (Chiou *et al.*, 1983; Karickhoff, 1984; Pignatello, 1998; Delle Site, 2001).

The extent of sorption depends on the properties of the sorbent and the contaminant, which may include size, shape, molecular structure, functional groups, solubility, polarity, charge distribution and acid-base characteristics (Bailey and White, 1970; Pignatello and Xing, 1996). Sorption may include chemical processes (such as chemisorption) in which reactions occur between compounds, or physical processes in which binding between particles is through hydrophobic bonding (such as van der Waals' forces (Horseman *et al.*, 1996)). In physical sorption, the energy exchange is low and the chemical nature of the sorptive species is preserved. Chemical sorption can be endo- or exothermic with an activation energy and tends to occur only at specific sites and with particular species. Many sorption processes may be considered intermediate between chemical and physical sorption, including hydrogen bonding, dipole interactions and charge transfer interactions. Sorption may be "sorbent-motivated", in which there is a high affinity between the sorbent and the sorbate (such as cation exchange reactions), or "solvent-motivated", in which the sorbate reacts adversely with the solution phase. Hydrophobic substances (such as substituted or unsubstituted aromatic and aliphatic hydrocarbons) repel water and accumulate at the soil-water interface or sorb to organic matter (Weber *et al.*, 1991; Delle Site, 2001) by partitioning (in which the soil organic matter may be regarded as a water-immiscible liquid phase (Karickhoff, 1981)). Ionic polar compounds (including many pesticides) may bind to surfaces by cation exchange or hydrogen bonding.

At any given contaminant concentration, the contaminant will sorb to the solid matrix until equilibrium is reached between the amount of contaminant on the surface and that in solution. Sorption equilibrium may take hours, days or years depending on the sorbent/sorbate system. In the case of HOCs sorption is biphasic: the uptake of sorbate by the solid is initially rapid, followed by a slower sorption rate towards equilibrium (Leenheer and Ahlrichs, 1971; Karickhoff, 1980; Karickhoff and Morris, 1985; Ball and Roberts, 1991; Wu and Gschwend, 1986; Brusseau *et al.*, 1991). The rapid phase may last for a matter of hours, whereas the slow phase can take days or months or even years (Morrisey and Grismer, 1999).

In this report the term sorption refers to adsorption or absorption of the solute (namely the List I contaminant present in the leachate in aqueous solution) to the solid (or mineral liner). Desorption refers to the process of contaminants detaching from the solid surface and re-entering solution. Sorption and desorption are frequently quantified by the partition coefficient, K_d . Sorption may be measured by experiments involving batch tests or column tests. In batch testing, the uncontaminated solid is placed in a vessel into which solutions of varying concentrations of the contaminant are added. The vessels are sealed and shaken until equilibrium is reached. For each contaminant concentration, the sorbed concentration is plotted against the dissolved

concentration at equilibrium. In the case of linear sorption, the slope of the graph is a straight line, passing through the origin, with gradient K_d (the soil-water partition (or distribution) coefficient, l/kg). In column testing, the contaminant solution is passed through the uncontaminated solid in a laboratory column. Here, sorption is a function of the retardation of the contaminant relative to the flow rate of the solution. Further details of the batch and column tests used to determine natural attenuation in this study are given in Sections 7, 8 and 9.

3.2.2 Sorption models

A sorption isotherm is the relationship between the amount of a substance sorbed and its concentration in solution (or in the gas phase) measured at a constant temperature. Three equilibrium models are generally used to describe sorption of contaminants. Two of these (Freundlich and Langmuir) describe different types of non-linear sorption behaviour, while the third, linear sorption, is a special case of Freundlich sorption in which the slope of the isotherm is constant.

3.2.3 The Freundlich adsorption model

The Freundlich non-linear sorption model describes a system in which the number of sorption sites is large relative to the number of contaminant molecules, but where sorption decreases with increasing contaminant concentration (Figure 3.1). The Freundlich isotherm is described by the equation:

$$C_s = K_F C^n \quad (3.1)$$

where:

C_s = sorbed contaminant concentration (mass of contaminant/mass of solid, $\mu\text{g/g}$)

K_F = equilibrium coefficient for the sorption reaction ($\mu\text{g}^{1-n} \text{l}^n/\text{g}$)

C = dissolved contaminant concentration ($\mu\text{g/l}$)

n = chemical specific constant to take account of heterogeneity, normally $0 < n < 1$.

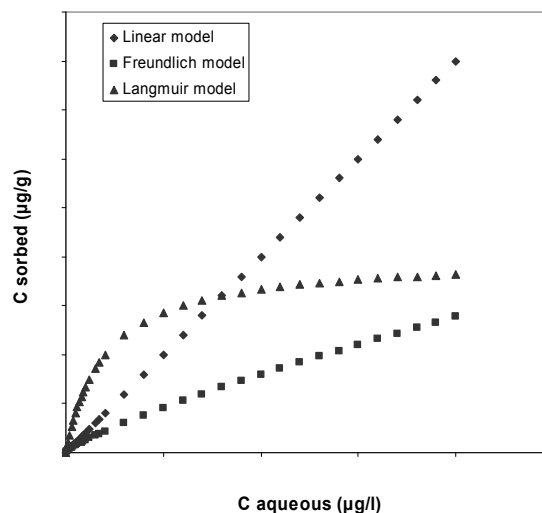


Figure 3.1 Freundlich, Langmuir and Linear models for the sorption isotherm

The Freundlich isotherm is widely used for simple applications to “real” situations and implicitly takes into account the heterogeneity or variability found in the environment. The Freundlich isotherm has been widely used for trace metal adsorption to soils and sediments and the sorption of organics, including pesticides, to soils. Typically n is in the range 0.5 to 0.8. For $n < 1$ or $n > 1$, the Freundlich isotherm is nonlinear; when $n = 1$, it reverts to the linear isotherm. A plot of $\log C_s$ vs $\log C$ (called a ‘Freundlich’ plot) is linear with a slope n and an intercept at $\log C = 0$ equal to $\log K_F$. The lower the slope of the Freundlich plot, the more the apparent heterogeneity of the material.

The partition coefficient K_d for the Freundlich isotherm (which illustrates that like the Langmuir isotherm, K_d decreases with increasing concentration) is given by:

$$K_d = K_F C^{n-1} \quad (3.2)$$

3.2.4 The Langmuir isotherm

The Langmuir non-linear model describes a case where the sorbed concentration increases linearly with dissolved concentration at low contaminant concentrations, then approaches a constant value at higher contaminant concentrations as the number of sorption sites on the solid becomes limiting (Figure 3.1). The Langmuir model is described by the equation below:

$$C_s = \frac{K_L C M}{(1 + K_L C)} \quad (3.3)$$

where:

C = dissolved contaminant concentration (ug/l)

C_s = sorbed contaminant concentration (mass of contaminant/mass of solid, $\mu\text{g/g}$)

K_L = Langmuir adsorption or affinity constant (dimensionless)

M = total number of sorption sites (a constant related to the area occupied by a monolayer of sorbate, $\mu\text{g/g}$).

This equation can be re-written in terms of the partition coefficient, K_d :

$$K_d = \frac{K_L M}{(1 + K_L C)} \quad (3.4)$$

since

$$K_d = \frac{C_s}{C} \quad (3.5)$$

Both Freundlich and Langmuir isotherms are essentially linear when low concentrations and a limited concentration range is considered, as in a dilute groundwater contaminant plumes. Where dissolved concentrations are sufficiently high, isotherm nonlinearity may be important (Allen-King, 1996).

3.2.5 Organic carbon partition coefficient, K_{oc}

For non-polar organic contaminants, including many of the List I organic substances, sorption is controlled by the fraction of organic carbon in the matrix when f_{oc} is greater than 0.001 (0.1% organic carbon) (Karickhoff *et al.*, 1979; Schwarzenbach and Westal, 1981). The partition coefficient for organic carbon, K_{oc} , is defined as K_d normalised to the fraction of organic carbon in a matrix, f_{oc} . If a matrix is dominated by organic matter and sorption is assumed to be linear, then:

$$K_{oc} = \frac{K_d}{f_{oc}} \quad (3.6)$$

where

K_{oc} = partition coefficient for organic carbon

K_d = partition coefficient

f_{oc} = fraction of organic carbon in the matrix

Using K_{oc} reduces the variation in reported K_d values which results from the different organic carbon content found in different matrices.

The tendency of HOCs to partition into organic carbon is inversely related to their water solubility; hence, sorption to organic carbon is also a function of the hydrophobicity of a compound which can be measured in terms of the octanol-water partition coefficient (K_{ow}) (Mackay *et al.*, 1980; Chiou *et al.*, 1982; Piatt and Brusseau, 1998; Kleineidam, *et al.*, 1999). K_{ow} values and water solubility (S) of typical landfill leachate contaminants are given in Table 3.2.

K_{oc} can be estimated from solubility or from the octanol-water partition coefficient K_{ow} :

$$\log K_{oc} = -a \log S + b \quad (3.7)$$

and

$$\log K_{oc} = a \log K_{ow} - b \quad (3.8)$$

where

K_{oc} = organic carbon partition coefficient (l/kg)



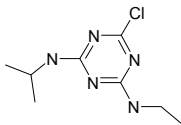
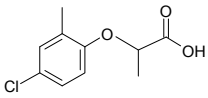

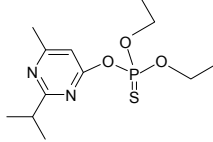
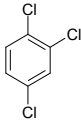
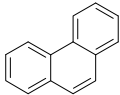
S = aqueous solubility of the solute ($\mu\text{g/l}$)

K_{ow} = octanol-water partition coefficient (ratio of concentration of a contaminant in n-octanol to its concentration in water at equilibrium under defined conditions)

a and b are determined by measurement of multiple contaminant/soil combinations

A number of empirical models have been developed for HOCs which take into account both the hydrophobicity of the compound and the fraction of organic carbon in the matrix (Table 3.3). Databases of K_{oc} values are available via the internet (such as Environmental Fate Database, Syracuse Research Corporation) or in the literature (see Verschuere, 1983; Delle Site, 2001).

Table 3.2 Chemical characteristics of landfill leachate contaminants

List I substance	Structure	log K _{ow} (-)	S (mg/l)*
Trichloroethene (TCE)		2.47	778.7
Toluene (BTEX)		2.54	573.1
Atrazine		2.82	214.1
Mecoprop		2.94 ^a	193.7
Naphthalene		3.17	142.1
Diazinon		3.86	6.46
1,2,4-trichlorobenzene		3.93	20.0
Phenanthrene (PAH)		4.35	0.677

NOTES: K_{ow} - octanol-water partition coefficients and S - water solubility (SRC, 1988)

*Measured at 25°C

^aMecoprop in neutral (non-ionised) form

Table 3.3 Empirical models for sorption of hydrophobic organic contaminants

Models	Soil or sediment	Contaminants
$\log K_{oc} = \log K_{ow} - 0.21^a$	River and pond sediments	Polycyclic aromatic (PAH) and chlorinated hydrocarbons
$\log K_d = 0.72 \log K_{ow} + \log f_{oc} + 0.49^b$	River, lake and aquifer sediments, ($f_{oc} = 0.0004-0.058$)	Aromatic hydrocarbons, chlorinated aromatic hydrocarbons and alkenes
$\log K_{OM} = 0.904 \log K_{ow} - 0.543^c$	Silt loam soil, ($f_{oc} = 0.019$)	Aromatic hydrocarbons, chlorinated aromatics hydrocarbons and PCBs
$\log K_d = 1.07 \log K_{ow} + \log f_{oc} - 0.51^d$	Silt loam soil, ($f_{oc} = 0.015$)	Benzene, chlorinated aromatic hydrocarbons, PAHs ^d

^aKarickhoff *et al.*, 1979; ^bSchwarzenbach and Westal, 1981; ^cChiou *et al.*, 1983; ^dXia and Ball, 1999

While many of the empirical models available for sorption of hydrophobic contaminants are based on batch sorption tests of soils and sediments, a number of other methods have been employed to generate estimates of partition coefficients. Gawlik (1997) reviewed numerous models for estimating K_{oc} based on water solubility and K_{ow} , as discussed above, while others were derived from experimental work done with reverse phase high performance liquid chromatography (HPLC) using columns with similar properties to soil organic carbon such as octadecylsilicate, or chemical or physically immobilised humic acid. Gawlik also reviewed partition models which related sorption to the molecular topology of contaminants. Sabljic *et al.* (1987) proposed a partition model which related the molecular connectivity index of range of compounds (including a range of PAHs, chlorinated aromatic and aliphatic hydrocarbons, polychlorinated biphenyls (PCBs), chlorophenols, DDT and DDE) to their organic matter partition coefficients (derived from a number of literature sources including Karickhoff, 1979; Chiou *et al.*, 1979, Chiou *et al.*, 1983; Kenaga and Goring, 1980; Kock, 1983):

$$\log K_{OM} = 0.55({}^1\chi) + 0.45 \quad (3.9)$$

where

K_{OM} = the organic matter partition coefficient

${}^1\chi$ = first-order molecular connectivity index for the contaminant

The molecular connectivity index ${}^1\chi$ is calculated from the non-hydrogen parts of the molecular skeleton. Each non-hydrogen atom is described by its atomic δ value, which is equal to the number of adjacent non-hydrogen atoms. The molecular connectivity index is then calculated from the sum of atomic δ values:

$${}^1\chi = \sum (\delta_i \delta_j)^{-0.5} \quad (3.10)$$

Where i and j correspond to pairs of adjacent non-hydrogen atoms and summation is over all of the bonds between non-hydrogen atoms.

The model predicts K_{OM} for HOCs, and has been adapted to predict partition coefficients for ionic and polar compounds such as anilines, carbamates, triazines, pyridines, uracils, and organic acids, by use of a semi-empirical correction factor that accounts for the polarity of the compound (Sabljic *et al.*, 1987).

3.2.6 Organic matter quality

Organic matter in soils and sediments occurs as a heterogeneous mixture of substances derived from a variety of source materials (including plant and animal remains) which have been modified by a combination of physical, chemical and biological processes. These processes may bring about significant alterations to the structure and composition of the parent material. Soil organic matter is typically divided into two groups of non-humic or humic substances. Non-humic substances are easily degradable compounds whereas humic substances (which form the greatest fraction of organic material in soils and sediments (Huang *et al.*, 2003) are large heterogeneous molecules which are resistant to chemical and biological degradation (Pignatello, 1998; Sparks, 1999). Humic substances may be subdivided into three fractions, based on their relative solubility in acids and alkalis:

- Humic acid – soluble in dilute alkaline solution and precipitated at pH2.
- Fulvic acid – soluble at any pH value.
- Humin – insoluble in both alkalis and acids.

Humic acids have a relatively low molecular weight and high proportion of carboxylic acid groups, whereas fulvic acids have higher molecular weight and have more aromatic components. Humin comprises materials such as kerogen and black carbon. Kerogen is formed from organic matter by geological processes, such as near-surface diagenesis and deep burial condensation reactions under high temperatures and pressures. Black carbon comprises soots, chars and other materials with elemental carbon at their surfaces; it is formed from incomplete combustion of organic material (Allen-King *et al.*, 2002).

The presence of kerogen and black carbon in soils and sediments can significantly alter their sorption potential (Grathwohl, 1990; Huang *et al.*, 1997; Allen-King *et al.*, 2002). If such thermally altered material is present in soils, K_{oc} , and other empirical models, may not always adequately describe the relationship between sorption and OC content. Studies have shown that the diversity in composition and structure of the organic matter can result in a variation in the sorptivity of HOCs (Kloneidam *et al.*, 1999). In particular, for low concentrations of hydrophobic contaminants, sorption may be much greater than predicted from simple empirical models when the solid phase contains thermally altered organic matter such as kerogens, coals, charcoals and soots (Kloneidam *et al.*, 1999; Ghosh *et al.*, 2000; Karapanagioti *et al.*, 2000; Accardi-Dey and Gschwend, 2002). Thermal alteration of organic matter can produce non-polar surfaces with porosity and high specific surface area which promotes adsorption and leads to non-linear sorption isotherms for HOCs characterized by very high sorption at low aqueous concentrations (Allen-King *et al.*, 2002).

In simple terms, this type of sorption can be described by the Langmuir model, but it is more common to fit non-linear sorption by Freundlich isotherms. However, non-linear sorption resulting from thermally altered organic matter may arise from a combination of an adsorption component which dominates at low aqueous concentrations and a partitioning component which prevails at higher concentrations. A number of composite or dual mode models which attempt to describe the combination of linear and non-linear sorption have been presented in the literature (see Xing and Pignatello, 1997; Huang *et al.*, 1997; Weber *et al.*, 1999; Xia and Ball,

1999; Chiou *et al.*, 2000). In addition, some researchers have tried to model sorption in terms of the oxidation state of organic matter (see Grathwohl, 1990; Young and Weber, 1995):

$$\log K_{oc} = 1.52 \log(H/O) + 1.54 \quad (3.11)$$

Because of the variability in organic matter quality, sorption coefficients and retardation rates determined for contaminants in soils and aquifers may not apply to mineral liner materials because of the type of organic carbon in the liner, and the application of K_{oc} values determined from such matrices to materials which have thermally altered organic matter can be problematic.

3.2.7 Binding to dissolved organic carbon

The organic content, and to a lesser extent the mineralogy of a clay (illite, smectite, kaolinite), will determine the available surface area for sorption of HOCs in a mineral liner. There is a high potential for sorption on the liner, but contaminants contained in leachate are in competition with other leachate chemicals for sorption sites, and the concentration of organic contaminants is usually low compared to other organic compounds in the leachate, such as dissolved organic carbon. Studies with aquifer materials have shown that leachate DOC may increase or decrease the partition coefficient for some hydrophobic organic contaminants (Larsen *et al.*, 1992) and heavy metals (Calace *et al.*, 2001). The association of a specific HOC with particular type of DOC depends on the origin and molecular properties of the DOC (Mott, 2002). For example, Chin *et al.* (1997) demonstrated a direct correlation between uptake of the polycyclic aromatic hydrocarbon (PAH) compound pyrene and the aromaticity, molecular weight and oxygen content of different types of DOC, whereas the relationship was inversely correlated to the dissolved aliphatic carbon. A sorption coefficient determined for a contaminant dissolved in groundwater may not apply to the same contaminant in leachate.

3.2.8 Sorption to mineral surfaces

Below 0.1 per cent organic carbon content, sorption to mineral surfaces may become the dominant mechanism (McCarty *et al.*, 1981; Chiou *et al.*, 1983; Karickhoff, 1984; Grathwohl, 1990; Murphy *et al.*, 1990). It has been reported that clay minerals, particularly expansive clay minerals, are associated with enhanced sorption of some non-ionic compounds when the fraction of clay is large relative to the f_{oc} (Karickhoff, 1984; Laird *et al.*, 1992). In this case, sorption increases with increasing surface area of the mineral and decreasing hydrophobicity of the contaminant. McCarty *et al.* (1981) determined the critical lower value of carbon content (f_{oc}^*) in a sediment below which sorption to mineral surfaces is greater than sorption to organic carbon:

$$f_{oc}^* = \frac{SA}{2 \times 10^5 K_{ow}^{0.84}} \quad (3.12)$$

Where SA is the specific surface area of the sediment (mm^2/g).

The above relationship was derived from sorption on silica of HOCs (including benzene, naphthalene, tri and tetra chloroethylene) with K_{ow} ranging from 10^2 to 10^4 . The relationship may not be appropriate for use with HOCs of greater or lesser hydrophobicity and on other mineral types.

3.3 Desorption

Sorption is often modelled as a reversible process, but frequently models fail to predict long-term release or desorption of contaminants to the environment. Desorption is the release of a sorbed compound from the solid phase to the aqueous phase. Similar to sorption processes, a contaminant will desorb from the solid matrix into the aqueous phase until equilibrium is reached between the amount of contaminant on the surface of the solid and that in solution. In the landfill liner environment, any contaminant sorbed to the liner may desorb when flushed with uncontaminated leachate. While desorption of contaminants from a landfill liner may lead to contamination of groundwater, it also has the potential to make compounds more bioavailable, since those that are entrapped within the solid matrix are considered unavailable to microbial degradation (Alexander, 1995; Lueking *et al.*, 2000), and consequently lead to reduction of contaminant concentrations.

It has been frequently demonstrated, however, that desorption processes are often not the same as sorption (Di Toro and Horzempa, 1982; Abdul and Gibson, 1986; Pignatello, 1990; Kan *et al.*, 1994) and sorption may be irreversible, that is, less than 100 per cent of the sorbed contaminant is desorbed. Sorption and desorption hysteresis (in which the distribution coefficient for desorption, is greater than the corresponding sorption distribution coefficient K_d at a constant aqueous phase concentration) has often been reported in laboratory studies on HOCs (Karickhoff and Morris, 1985; Pignatello, 1990; Paviostathis and Mathavan, 1992; Di Toro and Horzempa, 1982; Kan *et al.*, 1994; Huang *et al.*, 1998; Huang *et al.*, 2003).

Hysteresis and irreversible sorption has been attributed to a number of mechanisms. The sorbed molecules may be entrapped within soil organic matter or in meso- or micro-pores of the inorganic components of soils with low OC content (Huang *et al.*, 2003). Alternatively, a portion of the sorbate may be irreversibly bound to the soil due to physical changes in the soil matrix which might prevent or inhibit the diffusion of the sorbed compound back into solution (Pignatello, 1990; Kan *et al.*, 1997) and decrease the rate of desorption compared to that of sorption (Farrell and Reinhard, 1994; Huang and Weber, 1998; Huang *et al.*, 1998; Weber *et al.*, 1998). Very slow desorption processes may also account for desorption hysteresis. It is frequently found that desorption from soils and sediments can be biphasic (with fast and slow desorbing fractions) (Cornelissen *et al.*, 1997a and 1997b) or triphasic (with fast, slow and very slow fractions) (Ten Hulscher *et al.*, 1999). Typically, a fraction of the sorbed compound is desorbed relatively rapidly (over minutes or hours), depending upon the prevailing physical and chemical conditions, and a significant amount is released more slowly over days, months or years (see Karickhoff, 1980; Paviostathis and Mathavan, 1992; Pignatello and Xing, 1996). Since complete desorption may take a considerable period of time, it is important to take account of the effect of both sorption and desorption kinetics when constructing sorption/desorption isotherms. Where contaminants have been sorbed to the solid matrix for a substantial period of time, less of the sorbate may be removed by desorption, due to a process known as "ageing" (Paviostathis and Mathavan, 1992; Hatzinger and Alexander, 1995). Over time, the more easily desorbed contaminant becomes less available and may become non-extractable (Macleod and Semple, 2000) because of processes which include the slow diffusion of HOCs into the solid organic fraction of the soil matrix, and entrapment within soil micro-pores (Hatzinger and Alexander, 1995).

A simple model may be used to describe the portions of available and unavailable contaminant (Kan *et al.*, 1997):

$$C_{SORBED,total} = C_{SORBED,rev} + C_{SORBED,irr} \quad (3.13)$$

where

$C_{SORBED,total}$ = total solid phase contaminant concentration ($\mu\text{g/g}$)

$C_{SORBED,rev}$ = solid phase contaminant concentration in the reversible compartment ($\mu\text{g/g}$)

$C_{SORBED,irr}$ = solid phase contaminant concentration in the irreversible compartment ($\mu\text{g/g}$).

and

$$C_{SORBED,rev} = K_d C \quad (3.14)$$

where

K_d = partition coefficient (l/g)

C = dissolved contaminant concentration ($\mu\text{g/l}$)

$C_{SORBED,irr}$ may be obtained from batch sorption/desorption experiments in which the contaminant is sorbed onto the matrix then desorbed until the aqueous concentration reaches detection limits, Figure 3.2. If the contaminant aqueous concentration is greater than one third to one-half of its aqueous solubility, the irreversible compartment will be filled (Kan *et al.*, 1998) during one sorption step. The value of $C_{SORBED,irr}$ may be obtained by extrapolating the desorption values to the vertical axis.

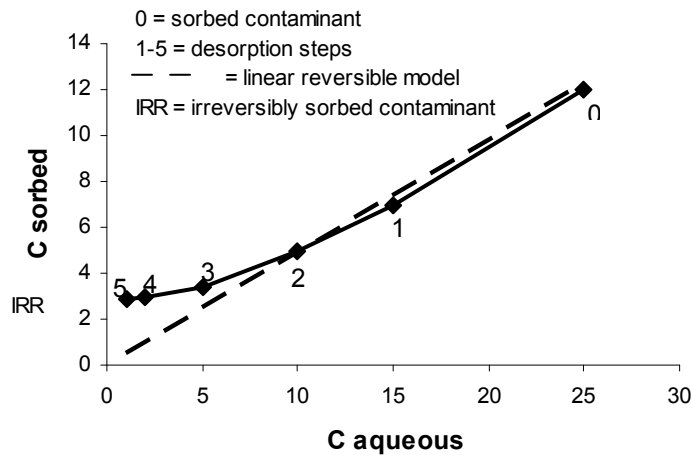


Figure 3.2 Desorption of solid phase contaminant over a number of steps. Shows the linear reversible sorption model and potential irreversibly sorbed phase.

Kan *et al.* (1998) developed a semi-empirical irreversible sorption model. Sorption to the reversible compartment was represented by a linear sorption isotherm, and sorption in the irreversible portion (which has a well-defined maximum for each contaminant/sediment combination) was defined by a Langmuir-type isotherm:

$$C_{SORBED,total} = K_{OC} \times f_{oc} \times C + \frac{K_{OC}^{irr} \times f_{oc} \times Q \times C}{1 + K_{OC}^{irr} \times f_{oc} \times C} \quad (3.15)$$

where

K_{OC}^{irr} = partition coefficient of the irreversible compartment normalised to the organic carbon content of the solid phase

and

$$Q = C_{SORBED,irr}^{MAX} F \quad (3.16)$$

where

$C_{SORBED,irr}^{MAX}$ = maximum sorption capacity of the irreversible compartment

F = the fraction of the irreversible compartment that is filled during sorption (assumed to be one when the aqueous concentration is greater than half the aqueous solubility of the contaminant)

The maximum irreversible sorption capacity for a range of non-polar hydrophobic contaminants (including aromatic hydrocarbons, polyaromatic hydrocarbons, chlorinated benzenes and biphenyls, and DDT) has been related to the OC content of a sediment and the contaminant hydrophobicity (Kan *et al.*, 1998; Chen *et al.*, 2000):

$$C_{SORBED,irr}^{MAX} = 37765 f_{oc} K_{OW}^{-0.23} \quad (3.17)$$

where

$C_{SORBED,irr}^{MAX}$ = maximum solid phase contaminant concentration in the irreversible compartment ($\mu\text{g/g}$)

The potential for contaminant sorption in an irreversible compartment has implications for fate and contaminant transport models. The use of reversible isotherms in transport models leads to optimistic predictions of the number of pore volumes required to reach minimum required concentrations, whereas incorporation of the irreversible sorption model may result in a more realistic prediction of the amount of flushing required to remove the contaminant from a sediment or liner.

3.4 Chemical degradation

Chemical degradation involving HOCs may include hydrolysis and oxidation-reduction reactions.

Clays are able to catalyse a number of chemical reactions by acting as acids, or promoting redox reactions. Clays have a large surface area, and their negatively charged aluminosilicate sheets are conjugate bases of oxyacids with resulting acidity derived from the terminal hydroxyl groups and bridging oxygen molecules (Lazlo, 1987). Reactions catalysed by clays include protonation of alkenes, addition reactions, esterifications and oxidation reactions. The potential for detoxification of dioxins by catalysis with Cu-smectites was demonstrated under relatively mild conditions (Boyd and Mortland, 1985).

3.5 Biodegradation

3.5.1 Introduction

Biodegradation is generally regarded as the principal mechanism via which organic contaminants are permanently removed from the environment, in contrast to sorption processes where the chemical is simply made unavailable. The mechanism is generally microbially mediated. The propensity for a contaminant to undergo biodegradation depends on an array of interacting biological and physicochemical parameters including the structure of the compound and its associated properties, the presence of a microbial population and associated enzyme systems capable of degrading the chemical and availability of terminal electron acceptors ranging from oxygen under aerobic conditions to nitrate, ferric iron, sulphate and carbon dioxide under anaerobic conditions. Consequently, the rates of biodegradation of specific chemicals can vary widely (orders of magnitude), depending on the environmental niche under evaluation. Intermediate products formed from contaminants during biodegradation may be more or less persistent, and more or less hazardous, than the parent compound. For biodegradation to occur the contaminant must be in aqueous solution since sorption onto the matrix generally renders contaminants less available to microbial transformation.

Microorganisms oxidise organic substances (electron donors) as a source of carbon and energy, while using a respiratory substrate (the terminal electron acceptor). Aerobic processes occur when there is a significant concentration of dissolved oxygen (above 0.5 mg/l). In a landfill, biodegradation of organic material will lead to consumption of the available oxygen and the rapid generation of anaerobic conditions and the production of methane (landfill gas).

Anaerobic biodegradation can involve the direct use of contaminants as sources of carbon and energy. Some organic compounds cannot be biodegraded in this way, but other processes, such as co-metabolism, may lead to the microbial degradation of such contaminants. This requires the presence of other biodegradable materials, which can be other contaminants. For example, chlorinated aliphatic hydrocarbons undergo biodegradation by a number of processes, some of which are common to both aerobic and anaerobic conditions: (1) as a primary substrate, (2) by reductive dechlorination, or (3) by co-metabolism. In addition, abiotic hydrolysis reactions are known to be involved in some of the degradative pathways.

3.5.2 Measuring biodegradability

The biodegradability of organic contaminants in soils and aquifers contaminated with leachate is usually investigated by three different approaches: (i) microcosm studies, (ii) detailed monitoring of the organic contaminant distribution in a leachate plume, and (iii) field injection experiments (Christensen *et al.*, 2001). Microcosm studies typically involve isolating a volume of aquifer or soil material and groundwater containing the organic contaminant, and subsequent measurement of the fate of the contaminant in a reactor. Field injection experiments involve the injection of a stock solution of the organic contaminants into the subsurface soil and monitoring of the plume formed. The methods used to determine biodegradation rates in this study are described in Section 10. The biodegradation rates given in Section 4 have been reported from plume or injection experiments in aquifers or from microcosm studies involving soils, because of the paucity of data available for some organic contaminants in mineral liner environments.

Lag periods are often seen in microcosm studies because the microbes need to acclimate to the conditions imposed. The length of the lag period will depend on the number and type of microbial species present, their ability to acclimate, their metabolic state, and the environmental conditions, in terms of temperature, pH, redox potential, oxygen concentration, and presence or absence of electron acceptors and donors.

3.5.3 Biodegradation kinetics

A compound will biodegrade at a particular rate subject to environmental conditions, including the availability of nutrients and the presence and growth of the microbiota. Biodegradation rates used in natural attenuation studies are often expressed in terms of Monod, zero-order and first-order kinetics.

The Monod equation was developed to describe the growth of a population of microbes in the presence of a carbon source that is growth limiting (that is, all other requirements are present in excess). Biomass increases as a result of metabolism of the substrate. At low concentrations of substrate, the population of microbes is small, and with increasing substrate concentration, the microbial population grows until it reaches a maximum growth rate. This is described mathematically as:

$$\mu = \frac{\mu_{\max} S}{K_s + S} - k_d \quad (3.18)$$

where

- μ = growth rate of the microbe
- S = substrate concentration
- μ_{\max} = maximum growth rate of the microbe
- K_s = a constant defined as the value of S at which $\mu = 0.5\mu_{\max}$
- k_d = microbial decay rate

The change in substrate concentration is given by

$$\frac{dS}{dt} = \frac{-\mu_{\max} B}{Y} \frac{(S)}{K_s + S} \quad (3.19)$$

where

- Y = biomass yield (mg biomass/mg substrate used)
- B = biomass concentration (mg/l).

The Monod equation is best used when the microbial population is growing in size in relation to the substrate. It is only practical to use Monod kinetics to derive biodegradation rates under laboratory conditions since a number of variables have to be determined.

3.5.4 Zero-order kinetics

Zero-order kinetics apply when the biodegradation rate is independent of the concentration of the substrate being biodegraded. The rate of a zero-order reaction is linear (a constant amount of substrate is lost per unit time). The reaction rate can be expressed as:

$$\frac{dS}{dt} = k_0 \quad (3.20)$$

and

$$k_0 = \frac{S_0 - S_t}{t} \quad (3.21)$$

where

- k_0 = rate constant (such as $\mu\text{g/l/day}$)
- S_0 = initial substrate concentration
- S = substrate concentration at time t

3.5.5 First-order kinetics

Under conditions where there is no growth of the microbial population and a low concentration of substrate (typically less than one mg/l), first-order rate constants are often used. In this situation, the concentration of the substrate and the rate of biodegradation drop in proportion to each other, that is, the rate of biodegradation is dependent of substrate concentration. Loss of substrate is exponential and follows a logarithmic curve. First-order rate constants are represented by:

$$\frac{dS}{dt} = k_1 S \quad (3.22)$$

where

- k_1 = rate constant (units are often 'per days' in natural attenuation studies).

In first-order reactions, a constant percentage of the substrate is lost with time and rate can be described by either percent per time or half-life, that is, the time required for the original contaminant to be reduced to one half of its initial concentration. Half-lives are usually stated in days, months or years. From the integration of the first-order rate constant equation:

$$t_{\frac{1}{2}} = -\frac{\ln 2}{k_1} \quad (3.23)$$

3.6 Impact of attenuation of contaminant transport

Transport of contaminants is governed by advection, dispersion and diffusion through a solid medium, and by reactions such as sorption and degradation. The velocity of compounds which sorb to a sediment is less than the porewater flow velocity, since sorption sites must be filled to attain the correct distribution between the solid and aqueous phases. Thus, the contaminant flow is retarded relative to porewater flow. In well-constructed mineral landfill liners, hydraulic conductivity is low (less than 10^{-9} m/s) so advection is limited and diffusion (in which contaminant migration is driven by concentration differences) is the predominant contaminant transport process (Rowe, 1987; Kim *et al.*, 2001).

In order to predict contaminant transport through a mineral liner, mass transport parameters such as the retardation coefficient, the hydrodynamic dispersion coefficient and seepage velocity are required (Kim *et al.*, 1997). These parameters can be estimated using laboratory-scale column tests. Column studies have the advantage of approximating field conditions more closely than sorption batch tests by allowing solids to be at rest relative to the mobile solutes, and by maintaining representative solid to solution ratios (between aquifer material and contaminated water). They therefore couple the effects of transport and chemical reactions on the sorption processes being evaluated. However, non-equilibrium and transport effects often complicate the interpretation of column experiments (see Griffin *et al.*, 1976; Brusseau *et al.*, 1991). Estimates of sorption and retardation obtained from different methods (batch tests, column or field experiments) may vary by more than one order of magnitude (for example, Bourg *et al.*, 1993; Benker *et al.*, 1998). Factors that are particularly important contributors to this variability are:

- composition of the aqueous phase;
- non-linear isotherms;
- non-equilibrium behaviour;
- non-ideal behaviour (due to field-scale heterogeneity in determining the magnitude of hydraulic conductivity and K_d).

The consequences of non-linear isotherms on contaminant transport are that pollutant breakthrough can be significantly retarded relative to that which would occur if sorption was linear. Similarly, during flushing the tail of the mass transport curve will be longer if isotherms are non-linear (Miller and Weber, 1988; Weber *et al.*, 1991; Appelo and Postma, 1993). It is possible that a solute is not sorbed rapidly during its passage through a medium, such that non-equilibrium conditions prevail (Horseman *et al.*, 1996). Van Genuchten and Cleary (1981) provide examples from the soils literature.

3.6.1 Column tests

Transport of contaminants is often estimated from the contaminant sorption coefficient K_d because batch sorption tests are relatively inexpensive, but more realistic results are likely to be obtained from column studies. In a one-dimensional column test, mass transport of a biodegradable solute through a porous medium with linear sorption under steady-state conditions and assuming first-order degradation, can be expressed using the retardation factor R (Freeze and Cherry, 1979):

$$R \frac{\partial C}{\partial t} = D_h \frac{\partial^2 C}{\partial x^2} - v \frac{\partial C}{\partial x} - k_d C \quad (3.24)$$

where

- R = retardation factor
- C = concentration of the tracer (Mass/Length³)
- x = distance from the inlet (L)
- t = time (Time)
- v = pore water velocity (L/T)
- D_h = hydrodynamic dispersion coefficient (L²/T)
- k_d = the first-order degradation constant (1/T)

The retardation factor R is related to sorption parameters by:

$$R = 1 + \frac{\rho_b}{\theta} K_d \quad (3.25)$$

where

- ρ_b = soil dry density (M/L³)
- θ = total porosity of the medium
- K_d = partition coefficient (L³/M).

D_h can be determined by:

$$D_h = \alpha v + D \quad (3.26)$$

where

- α = longitudinal dispersivity (L)
- D = effective molecular diffusion coefficient (L²/T).

In the column test, the pore water velocity v is a function of hydraulic conductivity, hydraulic gradient and the effective porosity of the sample. The pore water velocity can be calculated as follows:

$$v = \frac{K_h i}{\theta_e} \quad (3.27)$$

where

- K_h = hydraulic conductivity (L/T)
- i = hydraulic gradient
- θ_e = effective porosity of the sample.

In a well built mineral liner, with low leachate head, advective flow will be very low, and if biodegradation does not occur, Equation 3.6.1 reduces to a diffusion equation (Fick's second law):

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} \quad (3.28)$$

where

C, t, and x are as in Equation 3.6.1, and D is the effective molecular diffusion coefficient as in Equation 3.6.3.

A range of mathematical solutions to the advection-dispersion equation and the diffusion equation are available. Van Genuchten and Alves (1982) provide a review of solutions for a variety of conditions and processes.

4 List I organic compounds in UK leachates

4.1 Presence of List I organic compounds in UK landfill leachate

As described in the introduction to this report, a wide variety of organic contaminants are found in UK MSW leachates. The following principal sources were used to review the prevalence and concentrations of List I organic substances in landfill leachates:

- Pollution Inventory (PI) study Phase 1: comprehensive trace organic analysis on 72 raw leachates (Environment Agency, 2001).
- Pollution Inventory (PI) study Phase 2: comprehensive trace organic analysis on 24 raw leachates (Environment Agency, 2003a).
- In-house analyses of trace organics for private sector clients of Knox Associates (UK) Ltd.
- Published literature.

Xenobiotic organic compounds found in landfill leachate originate from household or industrial chemicals. They are generally present in low concentrations in the leachate (for example, under one mg/l). Some examples of List I compounds, their frequency and typical concentrations found in non-inert landfill leachates, are given in Table 4.1. Examples of List II compounds are given in Table 4.2.

4.2 Sorption coefficients and biodegradation rates for selected List I contaminants

There was a need to restrict the number of List I substances reviewed in detail in this report, and consequently the substances were grouped according to their:

- status as a List I substance under the Groundwater Regulations 1998;
- occurrence and concentration in UK leachates.

In addition, substances investigated in other natural attenuation projects and those that the Environment Agency had a particular interest in (such as from foot-and-mouth disposal sites) were assessed. Substances included in the literature review are shown in Table 4.3 along with the criteria used for prioritisation.

A literature review was compiled from peer-reviewed journals, official reports (US Environmental Protection Agency, Environment Agency (England and Wales)), online abstracting services (ISI Web of Science) and search facilities of the BIOLOG and DATALOC files of the Environment Fate Database (EPS, 2000). The review is presented in Appendix 1. Table 4.4 lists the selected List I substances and their hydrophobicity (K_{ow}) and solubility (S) characteristics together with a range of sorption coefficients and biodegradation rates obtained from the literature.

Table 4.1 List I trace organic substances in municipal solid waste landfill leachates

Group	Examples	Typical median concentration µg/l	Frequency in UK leachates
BTEX	Benzene		Toluene is the most commonly found of the BTEX compounds, and is found in the highest concentration. (Some BTEX compounds have been found in leachate from landfilled fly ash and APC residues; EA 2004, European landfills).
	Toluene	21	
	Ethylbenzene	10	
	Xylenes	35	
Polycyclic aromatic hydrocarbons (PAHs)	Naphthalene	0.46	Naphthalene is frequently found in landfill leachates. Phenanthrene is commonly detected.
	Total PAHs excluding naphthalene	5.25	
Aromatic hydrocarbons	Biphenyl	0.1	
Pesticides	Mecoprop (MCPP)	11	Mecoprop has been found in almost all UK leachates.
	Dichlorprop (2,4,DP)		
	2,4-Dichlorophenoxyacetic acid (2,4 D)		
	2,4,5-Trichlorophenoxy acetic acid (2,4,5-T)	~1.5	
	Diuron		
Phenols	Pentachlorophenol	0.1	
Chlorinated aromatic compounds	1,2,4-trichlorobenzene	~1	Not widely found in UK leachates.
Volatile halogenated aliphatics	Tetrachloroethene (PCE)	3.2	Not widely found in UK leachates, but frequently reported in USA and European studies.
	Trichloroethene (TCE)	5.6	
	AOX (adsorbable organic halogens/halides)	177	
Paraffins	Short, medium and long chain		Widespread use and distribution in the environment. No reliable analytical protocol applicable to leachates developed.
Organotin compounds	Tributyltin Dibutyltin	0.2	Frequently detected in UK leachates. Analysis for organotin compounds in leachates rarely carried out.
Brominated diphenyl ethers	Bisphenol A		Tentatively identified in leachates from mechanically-biologically treated municipal solid waste (MBP-MSW). However, no accredited method yet exists for leachates.
Mineral oils		3000-80,0000	

References: Environment Agency, 2001, 2003a; Knox *et al.*, 2000.

Table 4.2 List II trace organic substances in municipal solid waste landfill leachates

Group	Examples	Typical median concentration µg/l	Frequency in UK leachates
Pesticides	2-methyl-4-chlorophenoxyacetic acid (MCPA)	0.1	
Fuel additives	Methyl tertiary butyl ether (MTBE)	1	
Formaldehyde		~1	
Phenols	Total phenols	30	
Diazinon			Present in landfills after disposal of carcasses from 2001 foot-and-mouth outbreak.
Atrazine			Detected in very few UK leachates, but present in groundwater.
Phthalates	Bis(2-ethylhexyl)phthalate (DEHP)	1	Widespread in leachates.
Nonylphenol		1	Detected in 83% of raw leachates in the PI Phase 2 study and are endocrine disrupting substances. Not currently classified as List I or List II, despite being on the PI list.

References: Environment Agency, 2001, 2003a; Knox *et al.*, 2000.

Table 4.3 Summary of substances for literature review

Priority for literature review	Priority for literature review	Possible inclusion in literature review	Not included
<i>Substances that are List I and widely present in UK landfill leachates</i>	<i>Requested for review by EA but not widely present in UK landfill leachates</i>	<i>Either, List I but not widely found, Or, not List I but widely found</i>	<i>Either not List I, or not widely found</i>
Benzene, toluene, ethylbenzene, xylenes (BTEX compounds)	Trichlorobenzenes	1,1-dichloroethane	Tetrachloroethene
Polycyclic aromatic hydrocarbons (PAHs), e.g. phenanthrene	Trichloroethene	Mineral oils	MCPA ((4-chloro-2-methyl phenoxy) acetic acid)
Naphthalene (bicyclic aromatic hydrocarbon)	Atrazine	2,4-Dichlorophenoxyacetic acid (2,4 D) or 2,4,5 Trichlorophenoxy acetic acid (2,4,5-T)	Nonylphenols
Mecoprop (MCP)	Diazinon		Pentachlorophenol
Organotin compounds	Phthalates		Aniline
	Bisphenol A		Methyl tertiary butyl ether (MTBE)
	Propetamphos		Dichloprop
			Diuron
			Formaldehyde
			Brominated diphenyl ethers
			Short-chain chlorinated paraffins, SCCPs
			Medium-chain chlorinated paraffins, MCCPs
			Long-chain chlorinated paraffins, LCCPs
			Biphenyl

Table 4.4 Characteristics of selected List I substances

List I substance	log K _{ow} (-)	S (mg/l)*	log K _{oc} (ml/g)	Anaerobic biodegradation half life, t _{1/2} (days)
Trichloroethene	2.47	778.7	2.09 - 3.43	17 – 4,950
Toluene (BTEX)	2.54	573.1	1.59 - 2.43	
Atrazine	2.5	214.1	1.04 - 3.79	124
Mecoprop	2.94	193.7	0 - 2.95	--
Naphthalene	3.17	142.1	2.71 - 3.92	0 - 96
Propetamphos	3.82	110	2.99	19
Diazinon	3.86	40	1.8 - 3.2	16
1,2,4-Trichlorobenzene	3.93	20.0	2.5 - 4.0	
Phenanthrene (PAH)	4.35	0.677	3.95 - 4.92	49

NOTES:

K_{ow} - octanol-water partition coefficients and S - water solubility (SRC, 1988)

*measured at 25°C

Literature sources for soils and sediments listed are:

(a) for TCE; Ong and Lion (1991); Garbarini and Lion (1986); Smith *et al.* (1990); Stauffer and MacIntyre (1986); Grathwohl and Reinhard (1993); Mehran *et al.* (1987); Piwoni and Banerjee (1989); Lee *et al.* (1988); Pavlostathis and Jaglal (1991); Allen-King *et al.* (1997); Myrand *et al.* (1992).

(b) for toluene: Garbarini and Lion (1985); Garbarini and Lion (1986); Hu *et al.* (1995); Vowles and Mantoura (1987); Seip *et al.* (1986); Walton, *et al.* (1992). Abdul *et al.* (1990); Brusseau (1991 and 1993); Schwarzenbach and Westall (1981); Brusseau and Rao (1991); Wilson *et al.* (1981).

(c) for atrazine: Spark and Swift (2002); Ruge *et al.* (1999); Helweg *et al.* (2001); Croquet *et al.* (2005); Accinelli *et al.* (2001).

(d) for mecoprop: Tomlin (1998); Williams *et al.* (2001); Fomsgaard (1997); Madsen *et al.* (2000); Helweg (1993); Clausen *et al.* (2001); Clausen and Fabricius (2001);

(e) for naphthalene: Xing (1997); Xia and Ball (1999); King *et al.* (1999); Piatt *et al.* (1996); Xiao *et al.* (2004).

(f) for propetamphos: Kid and James (1991); Cooke *et al.* (2004); Garcia-Ortega *et al.* (2006).

(g) for diazinon: Kid and James (1991); PAN Pesticide Database; Arienzo *et al.* (1994); Cooke *et al.* (2004).

(h) for TCB: Bosma *et al.* (1988); Middeldorp *et al.* (1997); Adrian *et al.* (1998); Chiou *et al.* (1983); Wilson *et al.* (1981); Hu *et al.* (1995); Schwarzenbach and Westal (1981); Walton *et al.* (1992); Brusseau *et al.* (1990); Brusseau and Rao (1991); Voice *et al.* (1983); Acton and Barker (1992); Oliver and Charlton (1984); Southworth and Keller (1986); Wu and Gschwend (1986); Paya-Perez *et al.* (1991); Lee *et al.* (1989); and Njoroge *et al.* (1998).

(h) for phenanthrene: King *et al.* (1999); Rockne and Strand (1998); Karickhoff (1997); Chiou *et al.* (1998); Xia and Ball (1999).

5 List I contaminants and synthetic landfill leachate

5.1 Choice of List I compounds used in the experimental work

The compounds chosen for laboratory investigation in this project were selected as representatives of major contaminant groups likely to be found in UK landfill leachates. Five substances were listed as a priority for this study. The concentrations of the substances used in the experimental work are shown in Table 5.1. They were derived using three criteria:

- The concentration should not be less than the median found in UK leachates, to make the findings as relevant as possible to UK conditions.
- Concentrations should be at least 10 times greater than the readily achievable analytical detection limit, to ensure that attenuation processes can be determined with conventional analytical techniques.
- Concentrations should not be excessively high compared with typical UK leachates, to ensure experimental results will not produce behaviour that would not occur at lower concentrations.

These criteria can potentially conflict with one other. In practice, the values in Table 5.1 are reasonably consistent with all three criteria for the first three substances listed, toluene, naphthalene and Mecoprop. For the remaining two, trichloroethylene (TCE) and 1,2,4-trichlorobenzene (TCB), the values are dictated by the analytical detection limits although they may be unrealistically high for most UK landfill leachates.

Table 5.1 Leachate concentrations of the List I organic substances used in this study

Substance	Contaminant Group	Median conc. in UK leachates µg/l	Typical detection limit in leachate µg/l	Conc. for biodegradation tests µg/l	Conc. for sorption tests µg/l
Toluene	Aromatic hydrocarbons, BTEX compounds ^a	21	10	100	10-1,000
Naphthalene	Polyaromatic hydrocarbon	0.46	0.1	5	0.5-50
Mecoprop	Phenoxyalkanoic herbicide	11	0.1	15	1-100
TCB ^b	Chlorinated aromatic hydrocarbons	1 ^c	0.3	3	0.3-30
TCE ^d	Chlorinated aliphatic hydrocarbons	5.6 ^e	1	10	1-100

^a BTEX compounds include benzene, toluene, ethyl benzene and xylene;

^b 1,2,4-Trichlorobenzene; ^c Approximate median in those UK leachates where found;

^d Trichloroethene; ^e Mean values reported in study of US landfills, where compound was present in around 70 per cent of samples

5.2 Preparation of synthetic leachate

Synthetic leachates were used in the experiments to ensure consistency throughout the study period. Two classes of landfill leachate were simulated, namely:

- conventional MSW/non-hazardous landfill (representing leachate from a methanogenic landfill);
- MSWI leachate resulting from landfilling of bottom ash from incineration of MSW (representing leachate from a landfill with primarily sulphate-reducing conditions).

Both leachates were used in biodegradation tests, whereas only the MSW leachate was used in batch sorption and desorption tests. The characteristics of leachates from these landfill types have been the subject of Environment Agency research projects (Environment Agency, 2003b; 2003c).

The compositions of the synthetic leachates are given in Table 5.2. They are intended to mimic the major ion content, organic carbon content, ammoniacal nitrogen and pH values of these classes of leachate. The organic carbon content of the leachates is particularly important as it is known that hydrophobic organic pollutants sorb to DOC. Tannic acid is used to simulate DOC in the leachates: it is a reasonable surrogate for the hard COD (chemical oxygen demand) found in methanogenic MSW leachates. The suitability of tannic acid in synthetic bottom ash leachates is questionable but in the absence of more detailed investigations of those leachates, tannic acid is used by default.

During the experimental work it was found that the tannic acid precipitated from solution on exposure to air and therefore all the tests were prepared in an anaerobic cabinet. The composition of the MSWI leachate in the original recipe was found to be above the solubility limit of one or more of the leachate components at the resulting pH of 7.8. Due to the difficulty of removing the precipitate (by filtering and heating) from the large amount of leachate required for the biodegradation tests (34 litres), an alternative recipe was investigated. CaCl_2 and H_2SO_4 were used as the sources of calcium and sulphate, respectively, instead of CaSO_4 (Table 5.2). This resulted in a 21 per cent increase in the chloride concentration in solution and a pH of 6.15. The leachate was then adjusted using NaOH to pH 6.8, resulting in an eight per cent increase of sodium in solution. No precipitation was observed in the resultant synthetic MSWI leachate.

5.3 Limitations of synthetic leachate

Because the quality of landfill leachate changes over time as the landfill matures, and DOC concentrations may also fluctuate in the short term (Statom *et al.*, 2004), it was deemed necessary to use a stable source of DOC in the synthetic leachates in order to ensure reproducible results during the experimental study. Commercial humic and fulvic acids (which are extracted from terrestrial or aquatic sources) have been used in previous research as surrogates for DOC (Malcolm and McCarthy, 1986). Tannic acid has also been used in place of natural organic matter in studies investigating sorption of organic pollutants to sediments (Dentel *et al.*, 1998; Flores-Cespedes *et al.*, 2006). In the case of the current project, it was decided that tannic acid (Sigma Aldrich UK) would provide the best surrogate for DOC in leachate from a relatively young methanogenic landfill, in which the dissolved organic fraction has been shown to resemble fulvic acid rather than humic acid.

It is known that there are differences between commercially available humic and fulvic acids and natural DOC (Malcolm and McCarthy, 1986). The degree of aromaticity, molecular weight, carbon/nitrogen ratio and reactivity of these commercial materials may not be representative of leachate humic or fulvic acids. Sorption of hydrophobic compounds by DOC has been shown to be dependent on aromaticity (Gauthier *et al.*, 1987; Chin *et al.*, 1997), molecular size and polarity (Chiou *et al.*, 1979). Thus, it is possible that tannic acid may not react with the chosen List I compounds in exactly the same way as natural leachate DOC; however, it is more representative of the landfill liner environment to include DOC in sorption batch tests and biodegradation tests than to perform the tests in water. To assess the impact of DOC on sorption, batch tests for the List I substances were also carried out with no tannic acid present (Section 7.6.1). Sorption of tannic acid to the mineral liner materials was also measured (Section 7.6.2)

Table 5.2 Composition of synthetic leachates to be used in the study.

Leachate component	MSW leachate	MSWI leachate*	
	(mg/l)	Original composition (mg/l)	Alternative composition (mg/l)
Reagents added:			
tannic acid, C ₇₆ H ₅₂ O ₄₆	1,000	500	500
ammonium chloride, NH ₄ Cl	2,000	150	150
sodium chloride, NaCl	2,000	4,000	4,000
sodium bicarbonate, NaHCO ₃	4,000	2,000	2,000
calcium sulphate, CaSO ₄		1,000	-
sodium hydroxide, NaOH		50	297
calcium chloride, CaCl ₂		-	816
sulphuric acid, H ₂ SO ₄		-	721
Resulting calculated concentrations:			
TOC	540	270	270
Cl ⁻	2,541	2,527	3,049
Na ⁺	1,882	2,149	2,322
NH ₄ -N	523	39	39
Ca ²⁺	2,381	294	294
SO ₄ ²⁻		706	706
pH	7.6	7.8	6.8

Both leachates were used in the biodegradation studies; the sorption tests were carried out in MSW leachate only.

*The alternative composition of MSWI leachate was used in the biodegradation experiments after it was found that a precipitate was formed with the original composition of leachate (Section 5.2).

6 Mineral liner materials

6.1 UK liner materials

In order to select liner materials for laboratory testing, geological groups with different characteristics were investigated. Because of the wide variation in rock types and mineralogy of materials used in landfill liners, it was necessary to use a simplified characterisation system to aid the choice of material for laboratory testing. The amount of organic material in a liner has a large effect on sorption of HOCs (Section 2.2), whereas, the ratio of smectite to total solids provides an approximate indication of the plasticity of a material, and its suitability for landfill liner construction. These two parameters have been plotted in Figure 6.1a for different geological formations. Many contain less than 10 per cent smectite, but can be differentiated by their organic content, whereas pure bentonite (smectite/montmorillonite) and bentonite enhanced sand contain greater proportions of smectite but have a low organic content. London Clay and Gault Clay contain between 10 and 40 per cent smectite with organic contents between one and four per cent. A trilinear diagram showing the ratio of the three dominant clay groups, smectite, illite and kaolinite, is shown in Figure 6.1b. This plot is useful for differentiating some of the units that lie in close proximity in Figure 6.1a.

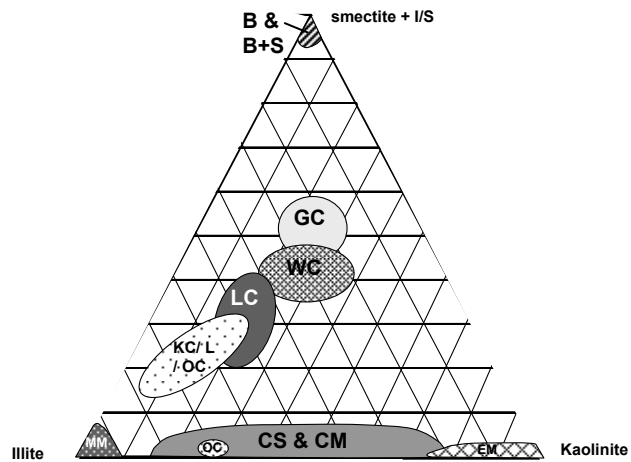
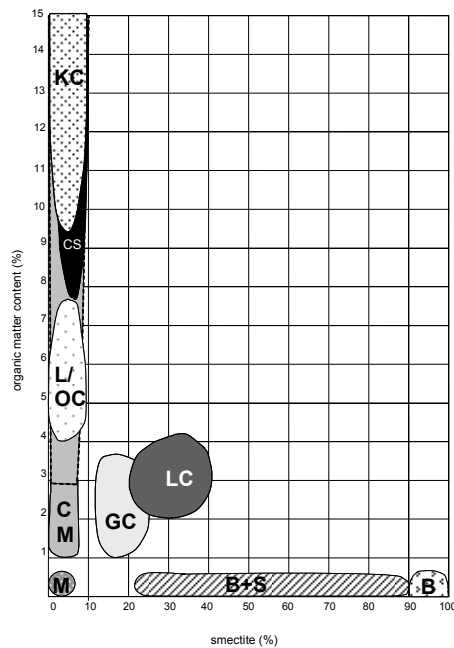
In discussion with the Environment Agency, it was decided that only natural mineral liner materials would be studied. Three materials, with a range of organic matter contents, were chosen for laboratory testing:

- Mercia Mudstone
- London Clay
- Oxford Clay

The liner materials are described briefly in Table 6.1. Characterisation of the samples was carried out and results are provided in Section 6.2.

Table 6.1 Description and moisture content of freshly dug samples of the liner materials

Liner material	Site	Moisture content (%)	Sample description
Mercia Mudstone	Waresbury Quarry (Hartlebury, UK)	6.7	Firm to stiff, friable red clay
London Clay	Ockendon landfill (Essex, UK)	28.7	Firm brown clay
Oxford Clay	Bletchley landfill (Buckinghamshire, UK)	33.0	Soft, moist, dark grey clay with carbonaceous shells and rootlets



(a)

(b)

Figure 6.1 Geochemical of mudrocks used in landfill liners: (a) Organic matter and smectite, (b) representation of clay mineralogy. LC= London Clay, GC= Gault Clay, M= Mercia Mudstone, B= Bentonite, B+S = Bentonite and Sand, CM= Coal Measures, L= Lias, OC= Oxford Clay, CS= Colliery Spoil, KC= Kimmeridge Clay, WC= Weald Clay, EM= Etruria Marl.

6.2 Characterisation of liner materials

Samples of Mercia Mudstone, London Clay and Oxford Clay were collected, dried and characterised with respect to: (i) organic carbon content, (ii) cation exchange capacity (CEC), (iii) specific surface area, and (iv) mineralogical composition. The results of the characterisation tests are summarised in Table 6.2; results from particle size analysis are shown in Table 6.3. Details of the experimental procedures involved in the characterisation, and further results (such as particle size analysis, elemental analysis, X-ray diffraction (XRD) and X-ray fluorescence (XRF)) are given in Appendix 3.

Table 6.2 Characterisation of Mercia Mudstone, London Clay and Oxford Clay

Parameter		Mercia Mudstone	London Clay	Oxford Clay
TC (%)		2.02 [6]	0.64[20]	7.22 [6] ^a
OC ^b (%)		0.30	0.6	5.49
CEC (meq/100g)		22.1 [3]	26.5[3]	30.63 [3]
Specific surface area (m ² /g)		31.6 ^d [2] 45.0 ^e [2]	54.0 ^e [2]	55.5 ^d [2] 50.2 ^e [2]
Total Fe ₂ O ₃		6.3 ^f	8.33 ^f	4.5 ^f
Extractable Fe		2.8 ^g	2.36	1.4 ^g
Clay minerals ^c (%)	Smectite	18	31	32
	Illite	36	29	15
	Kaolinite	0	11	9
	Chlorite	3	2	0.5
Major non-clay minerals (%)	Quartz	15	18	18
	Dolomite	17	0	0
	Calcite	1	9	9

Notes: TC-total carbon (CE Instruments 1112 Flash Elemental Analyser); OC-organic carbon (Rosemount Analytical Dohrmann DC-190 Carbon Analyser); CEC-cation exchange capacity (Environment Agency 2000); ^a average [no. replicates]; ^b calculated from difference between total carbon and inorganic carbon; ^c smectite reported as smectite+illite/smectite +chlorite/smectite (determined using Philips PW 3040/60 X-ray Diffractometer); ^d determined by PVP sorption (Blum and Eberl, 2004); ^e determined by EGME sorption (Cihacek and Bremmer, 1975); ^f Philips Magix-Pro wavelength XRF spectrometer; ^g Dithionite-citrate method (Mehru and Jackson, 1960).

Table 6.3 Laser diffraction analysis of the <0.2 mm fraction of Mercia Mudstone, London Clay and Oxford Clay

Particle size (%)	Mercia Mudstone	London Clay	Oxford Clay
Clay	29.6	24.3	20.0
Fine silt	33.9	30.9	31.1
Medium silt	26.6	28.4	35.6
Coarse silt-sand	7.1	16.8	13.4

Clay <2 µm; Fine silt 2-6 µm; Medium silt 6-20 µm; Course silt 20-60 µm; Fine sand 60-200 µm

6.2.1 Mercia Mudstone

The Mercia Mudstone Group, formerly known as the Keuper Marl, is part of the Triassic series and outcrops extensively in the UK Midlands and South Yorkshire. It is dominated by mudstones but also contains evaporite minerals, mainly halite (sodium chloride), anhydrite (calcium sulphate) and gypsum. The iron oxide minerals present (hematite; two per cent) give rise the subsequent red colour of the resulting rock. The Mercia Mudstone is low in OC (0.3 per cent) and has substantial carbonate content, mainly from dolomite (17 per cent).

6.2.2 London Clay

The London Clay is a member of the Lower Eocene strata which outcrops principally in the London basin, but also across southeast England. It is a stiff, bluish clay which becomes brown on weathering. Calcareous marine fossils are common, and pyrite is often found. The mineralogy of London Clay is dominated by illite and smectite in Central London, becoming more kaolinitic westwards. Samples of London Clay were obtained from Ockenden landfill in Essex. The OC content of London Clay samples (0.6 per cent) was less than expected from the literature (two to four per cent).

6.2.3 Oxford Clay

Oxford Clay is a marine argillaceous formation of Middle Callovian to Lower Oxfordian age which outcrops in central and southern UK; it is subdivided into the Peterborough Member, an OC rich and fossiliferous shale, and the Stewartby and Weymoth members, a calcareous mudstone with relatively low contents of OC (Kenig *et al.*, 1994). The variations in the lithology and OC content of the Oxford Clay have been attributed to varying depositional environmental conditions, including the depth of the sea floor and oxic-anoxic conditions. The laminated shales high in OC are thought to represent oxygen-deficient depositional bottom conditions with low benthic faunal activity while the non-laminated mudstones are thought to have been deposited in oxic environments (Ebukanson and Kinghorn, 1985).

Samples of the Peterborough Member of the Oxford Clay Formation were obtained from a waste disposal site in Bletchley, UK. The OC content of the Oxford Clay samples, 5.5 per cent, was in agreement with the contents usually found for the Peterborough Member (three to 16.6 per cent; Kenig *et al.*, 1994). The inorganic carbon (IC) content was mainly calcareous (calcite nine per cent).

6.3 Organic matter characterisation

Because of the importance of organic matter in sorption of HOCs, a further investigation was undertaken to characterise the OC in the samples. Because of the low OC of Mercia Mudstone and London Clay, OC characterisation was only carried out for the Oxford Clay.

The OC in the Oxford Clay sample was isolated using a decarbonation-demineralisation (HF/HCl) procedure (Appendix 1) and classified according to commonly used classifications in organic petrography for kerogen (see Taylor *et al.*, 1998) in terms of liptinites, vitrinite and inertinite. The kerogen components present in the isolated organic matter from the Oxford Clay were found to comprise liptinite (amorphous organic matter (AOM), spores, pollen and algae), vitrinite, semi-fusinite and inertinite (Figure 6.2). Liptinite (mainly AOM) was the dominant type of organic matter (92 per cent) whereas inertinite+semi-fusinite+vitrinite were minor components of the organic material (eight per cent). This is in accordance with previous petrographic studies of the Oxford Clay Formation which reported AOM of phytoplanktonic origin as the dominant organic matter (85 to 95 per cent of total organic matter) in the Peterborough Member with lignitic debris and well-preserved plant fragments comprising the remaining 5-15 per cent (Belin and Kenig, 1994).

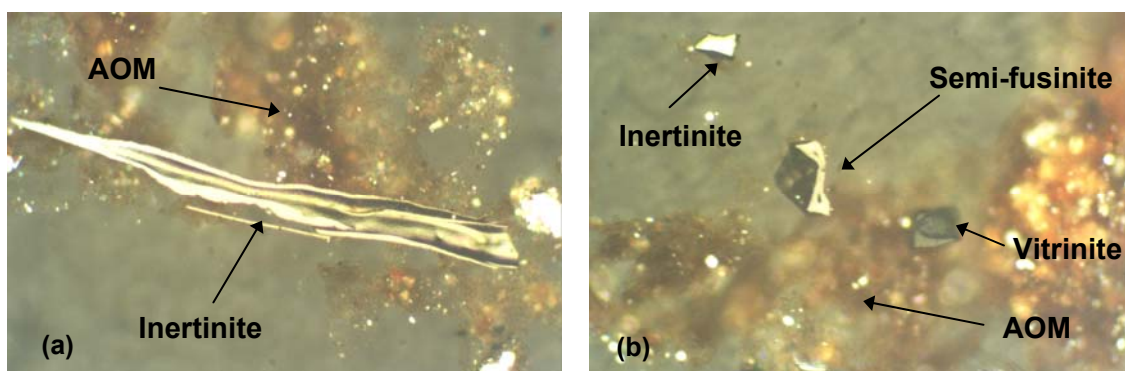


Figure 6.2 Photomicrographs of the different organic matter components present in the Oxford Clay. (a) Inertinite with well preserved cellular structure and high reflectance and AOM containing highly reflective pyrite; reflected light; and (b) inertinite with high reflectance, semi-fusinite with median reflectance, and vitrinite with low reflectance; reflected light (field of view 260 μm by 170 μm).

7 Batch sorption tests

7.1 Overview of methodology

Batch shake tests are a quick and relatively inexpensive method of producing estimates of sorption parameters. Batch testing involves placing uncontaminated materials into a number of reaction vessels (Figure 7.1). A solution containing the contaminant under investigation is added to the required concentration, then the vessels are sealed and agitated until chemical equilibrium is reached between the solute and the sorbent. The resulting concentration remaining in solution is analysed and the sorbed mass derived; this value represents a data point on a plot of aqueous against sorbed contaminant concentration.

The batch sorption tests for the five different contaminants (Section 7.3) were carried out in synthetic MSW leachate. For the substances with low aqueous solubility (under 779mg/l), stock solutions were prepared prior to the batch tests by adding the appropriate amount of each compound to methanol. Sodium azide (100 mg/l) and mercuric chloride (0.05 mg/l) were added to the leachate to inhibit biological activity during the tests (Nielsen *et al.*, 1996).

The batch tests were carried out in glass crimp-top bottles (122 ml internal volume, Sigma Aldrich, UK) which were cleaned prior to use (acid wash in 0.1M HCl, followed by rinsing in Milli-Q Plus and oven drying). The liner material was weighed into the bottles and these were then filled with leachate in an anaerobic glovebox (Wolf labs Model A Vinyl cabinet). The contaminants under investigation were then added to the bottles, further leachate added to leave no headspace, and the bottles sealed immediately with aluminium caps and Teflon®-coated septa to avoid any volatilisation of the compound. The bottles containing the clay or mudstone and leachate were mixed by horizontal rotary agitation, at $20 \pm 2^\circ\text{C}$. Bottles containing leachate and the List I compounds, but no solid sample, were also prepared to assess losses of contaminant by volatilisation or sorption to the bottle or septa. Losses of contaminant from the aqueous solution other than by sorption to the solid matrix (sorption to glass or septa, or biodegradation) were found to be negligible for the contaminants and experimental conditions used in this study. At the end of the contact time, the solid and liquid phases were separated by centrifugation (1,400 rpm for 10-30 minutes). Duplicate samples of the supernatant liquid (10 ml) were then collected from each bottle in 20 ml headspace vials (Sigma-Aldrich, UK) for determination of the contaminant aqueous concentration.

Initial tests (Section 7.2) were carried out to determine the ratio that provided 20 to 80 per cent sorption of contaminant. A kinetic investigation was then carried out over 30 days to establish the time necessary for each system to reach sorption equilibrium (constant aqueous concentration of the compound) (Section 7.3). Each test was carried out in duplicate with destructive sampling occurring regularly during the 30 day period; each bottle was only sampled once and then discarded. Sorption isotherms were determined over a range of two orders of magnitude difference of the proposed concentration of each substance. Sorption of each List I substance was studied individually (single solute isotherms; (Section 7.4)) and competitive sorption was studied for the combination of TCB and toluene (Section 7.5). The effect of DOC (in the form of tannic acid) in the synthetic MSW leachate on the sorption of List I substances is discussed in Section 7.6., while sorption of tannic acid by the mineral liner materials is described in Section 7.7.

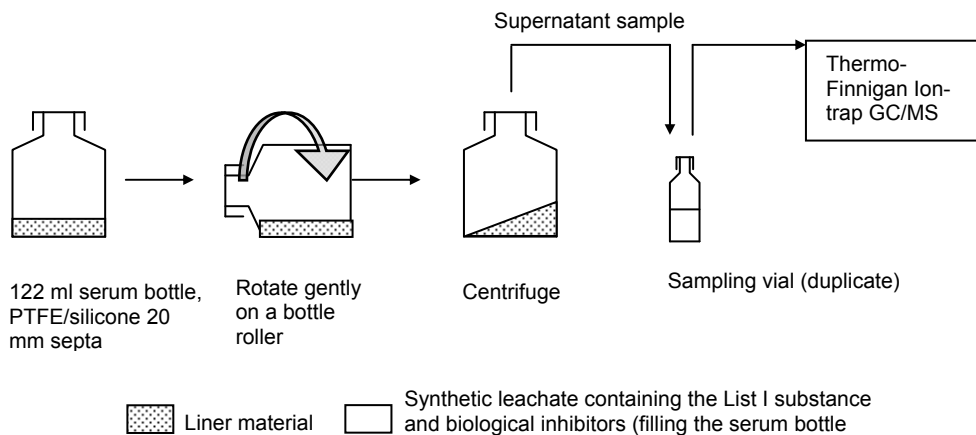


Figure 7.1 Experimental set-up of sorption batch tests

The concentration of contaminant sorbed to the solid matrix was determined by a mass balance based on the variation in contaminant aqueous concentrations between the start of the test and at each sampling event (Equations 7.1.1 and 7.1.2).

$$C_{sorbed}(t) = \frac{C_i - C_{aqueous}(t)}{M} V \quad (7.1)$$

where

- $C_{sorbed}(t)$ = concentration of contaminant sorbed to the solid matrix at time t ($\mu\text{g/g}$)
- C_i = contaminant aqueous concentration at the start of sorption tests ($\mu\text{g/l}$)
- $C_{aqueous}(t)$ = contaminant aqueous concentration at time t , ($\mu\text{g/l}$)
- M = dry weight of mineral liner material in the sorption bottle (g)
- V = volume of leachate added (litres).

$$\%sorbed(t) = \frac{C_i - C_{aqueous}(t)}{C_i} 100 \quad (7.2)$$

where

$\%sorbed(t)$ = percentage of contaminant sorbed to the liner material at time t

C_i and $C_{aqueous}(t)$ are as in Equation 7.1.1.

7.2 Solid/liquid ratios

Tests were carried out to determine the sorbent mass to liquid in order to achieve 20 to 80 per cent sorption of each List I contaminant; outside this range relative measurement errors become dominant (Delle Site, 2001). An example is shown in Figure 7.2 and the solid/liquid ratios used for the different mineral liner material/contaminants combinations are shown in Table 7. 1

In the case of Oxford Clay, only small quantities of clay were needed to achieve 50 to 60 per cent sorption of the hydrophobic contaminants. In fact, less clay was used than predicted from K_d values found in the literature; the reasons for this are discussed in Section 7.5. High solid/liquid ratios were needed with some contaminants (see TCE and Mecoprop) and Mercia Mudstone in order to achieve sufficient sorption. At these ratios, the mass of mudstone needed (for example, 120 g in a 122 ml serum bottle; density of the mudstone was around $1.5 \text{ g/cm}^3 \text{ d.w.}$) resulted in problems with mixing the solid sample and the leachate. Attempts were made to remove air from the mixture by swirling the bottle and leaving to stand overnight (in the anaerobic glovebox), but it was often difficult or, in some cases, impossible to remove all the air bubbles prior to sealing the bottle. The presence of air bubbles (generally less than 0.5 ml in a 122 ml bottle) may have provided an additional partitioning phase for volatile substances such as TCE.

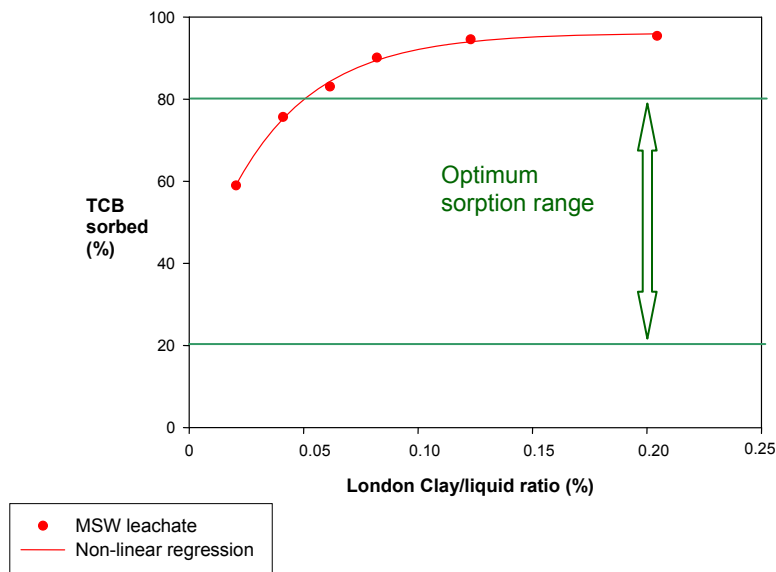


Figure 7.2 Sorption of TCB on London Clay at different solid/liquid ratios

Table 7.1 Percentage sorption of List I contaminants by Mercia Mudstone, London Clay and Oxford Clay at different solid/liquid ratios

	London Clay		Mercia Mudstone		Oxford Clay	
	solid:liquid ratio (m/v)	% sorption	solid:liquid ratio (m/v)	% sorption	solid:liquid ratio (m/v)	% sorption
Mecoprop	0.08	50-60	0.5	50-60	0.11	50-60
Naphthalene	n/c	n/c	0.82	20	0.0004	50-60
Toluene	0.31	30-45	0.82	20	0.0125	50-65
TCB	0.02	50	0.74	40	0.0004	40-60
TCE	n/c	n/c	0.98	10	0.01	50-60

(n/c = tests not carried out)

7.3 Sorption kinetics

Although sorption is often regarded as instantaneous for modelling purposes, it may take weeks, months or years to reach equilibrium. Many researchers have observed that in most cases, the uptake or release of hydrophobic organic contaminants is biphasic, occurring in fast, then slow stages (Leenheer and Ahlrichs, 1971; Karickhoff, 1980; Ball and Roberts, 1991; Arocha, 1996). The slow stage of sorption is often referred to as non-equilibrium sorption because of the long periods of time required to reach full sorption equilibrium for some compounds (Morrisey and Grismer, 1999). If sorption batch tests are not allowed to reach equilibrium, there is potential for the sorption coefficient K_d to be significantly underestimated. An understanding of sorption kinetics is critical therefore to natural attenuation studies.

Prior to the sorption isotherm tests conducted in this study (Section 7.4), sorption kinetics tests were carried out over 30 days to determine the contact time to reach equilibrium for each of the mineral liner material/contaminant combinations. The contact times established are shown in Table 7.2 for the particular solid:liquid ratios determined in earlier tests (Section 7.2). Figure 7.3 shows the sorption of TCB by London Clay and that of the control samples; the concentration of the control increases initially from mixing, then remains relatively constant, demonstrating negligible losses of contaminant over the period of the test (29 days). The results of the kinetics tests showed that sorption of the List I substances was biphasic, having a fast uptake stage over the first 24 to 48 hours of the test, followed by slower uptake towards equilibrium (Figures 7.4 and 7.5).

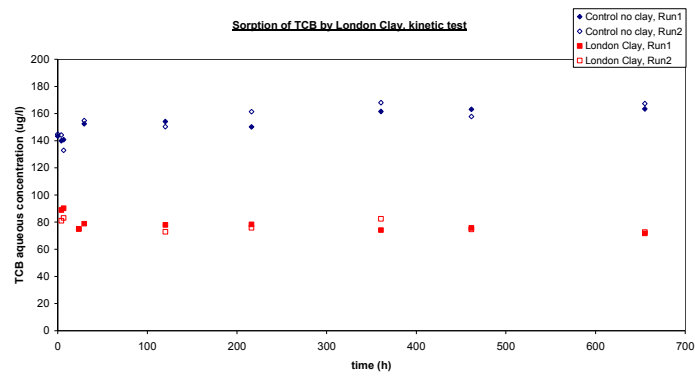
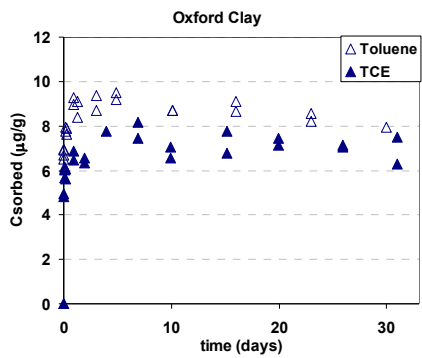


Figure 7.3 Sorption kinetics of TCB on London Clay
 Closely coupled data points represent duplicate samples.

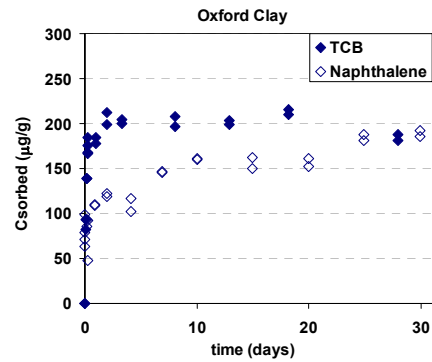
Table 7.2 Contact time for equilibrium sorption of List I contaminants on Mercia Mudstone, London Clay and Oxford Clay

	London Clay	Mercia Mudstone	Oxford Clay
	contact time (days)	contact time (days)	contact time (days)
Mecoprop	5	5	5
Naphthalene	n/c	7	7
Toluene	7	4	7
TCB	5	4	7
TCE	n/c	5	5

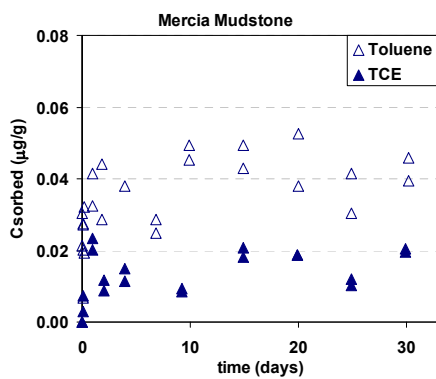
(n/c = not carried out)



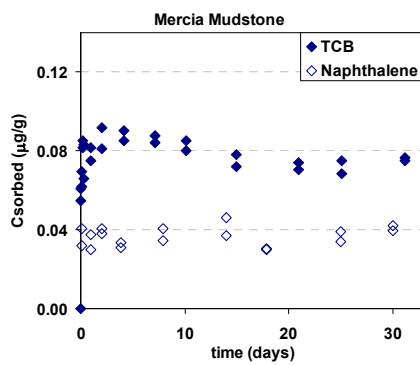
(a)



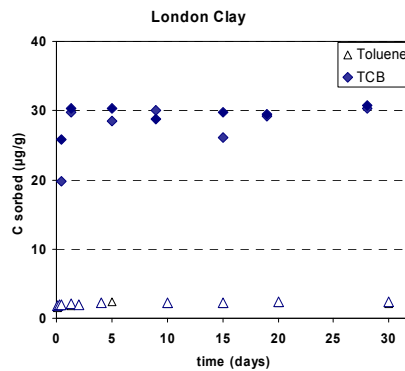
(b)



(c)

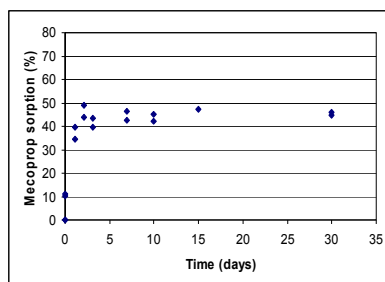


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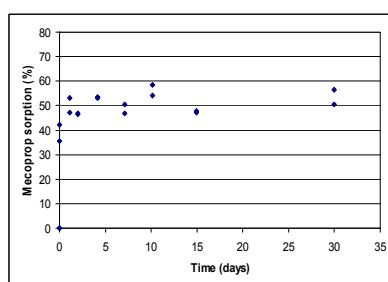


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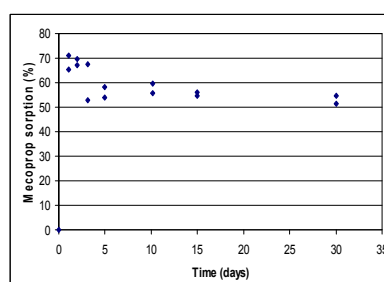
Figure 7.4 Sorption kinetics of leachate organic pollutants on Oxford Clay (a) Toluene and TCE, b) TCB and naphthalene; Mercia Mudstone (c) Toluene and TCE, d) TCB and naphthalene; and London Clay (e) Toluene and TCB.



(a)



(b)



(c)

Figure 7.5 Sorption kinetics of Mecoprop on (a) Mercia Mudstone (b) London Clay and (c) Oxford Clay

7.4 Sorption isotherms

7.4.1 Introduction

Batch sorption tests were carried out according to the method given in Section 7.1 to obtain data for sorption isotherms over a range of two orders of magnitude as given in Table 6.3. The equilibrium sorption data was fitted by two sorption models, the linear model and the Freundlich model (Section 3.2). Least squares regression analysis was carried out to obtain the sorption parameters of the linear isotherm and the linearised logarithmic Freundlich isotherm.

7.4.2 Sorption isotherms of HOCs

Freundlich model fits to the sorption equilibrium data for naphthalene toluene, TCB, and TCE on each of the three liner materials are shown in Figure 7.6. Sorption parameters for the linear and Freundlich models are summarised in Table 7.3.

Sorption was found to increase with increasing contaminant hydrophobicity (TCE < toluene < naphthalene < TCB) and with the f_{oc} of the liner materials. The observed increase in sorption of the organic pollutants with increasing OC content suggests that this component dominates sorption of the contaminants to these materials. This has also been observed in previous studies which have shown that sorption of HOCs is dominated by the OC content in soils and sediments where OC content is greater than 0.1 per cent (Karickhoff *et al.*, 1979; Schwarzenbach and Westall, 1981).

K_{oc} values for toluene, TCB and naphthalene determined in this study were compared with literature K_{oc} values (Table 7.4) and with empirical K_{oc} - K_{ow} correlations found in the literature. While K_{oc} values determined in this study for London Clay fall within the range of literature values, K_{oc} values determined for Oxford Clay are much greater, and those for Mercia Mudstone are generally lower, see Figure 7.7.

Table 7.3 Parameters of linear and Freundlich models fit for sorption data for naphthalene toluene, TCB, and TCE on Mercia Mudstone, London Clay and Oxford Clay

Clay liner	Contaminant	Linear Model		Freundlich Model			Log K_{oc} (ml/g)
		$K_d \times 10^3$ (l/g)	R^2	$K_F \times 10^3$ ($\mu\text{g}^{1-n} \text{l}^n/\text{g}$)	n	R^2	
Mercia Mudstone	Naphthalene	0.18	0.85	0.5	0.80	0.94	1.8
	Toluene	0.10	0.92	0.1	0.99	0.97	1.5
	TCB	0.6	0.97	2.0	0.75	0.96	2.3
	TCE	0.11	0.82	0.1	0.98	0.81	1.6
London Clay	Toluene	1.7	0.932	1.8	1.01	0.98	2.5
	TCB	49.8	0.884	137	0.77	0.96	3.9
Oxford Clay	Naphthalene	2,137	0.95	3,142	0.91	0.89	4.6
	Toluene	94	0.96	150	0.93	0.99	3.2
	TCB	2,152	0.80	4,498	0.86	0.96	4.6
	TCE	82	0.98	86	0.99	0.99	3.2

R^2 - correlation coefficient

Several K_{oc} - K_{ow} correlations describing the sorption dependence on contaminant hydrophobicity have been developed in the literature for a range of HOCs and soils/sediments (Section 3.2.5). The correlations were applied to the compounds and materials under investigation and were found to significantly underestimate the sorption of the contaminants by Oxford Clay observed in this study (Table 7.3 and Figure 7.8).

Sorption coefficients higher than those predicted by empirical correlations have been attributed in the literature to sorption onto soil mineral fraction and/or differences in soil organic matter composition (Allen-King *et al.*, 1997). Given that the Oxford Clay has an OC content greater than 0.1 per cent, the enhanced sorption capacity of the clay is not thought to be due to sorption onto the mineral fraction. Recent studies have shown that the diversity in composition and structure of the organic matter can give a variation in the sorptivity of HOCs, due to the presence of different organic fractions such as humic and fulvic acids and kerogen (Kleneidam *et al.*, 1999). The kerogen components in the isolated organic matter from the Oxford Clay were found to comprise liptinite (AOM, spores, pollen and algae), vitrinite, semi-fusinite and inertinite (Figure 6.2). AOM has been shown to exhibit higher K_{oc} values (higher sorption) than other organic matter components for phenanthrene (Kleneidam *et al.*, 1999). The high K_{oc} values obtained in this study for Oxford Clay may be the result of an extremely high sorptive form of AOM.

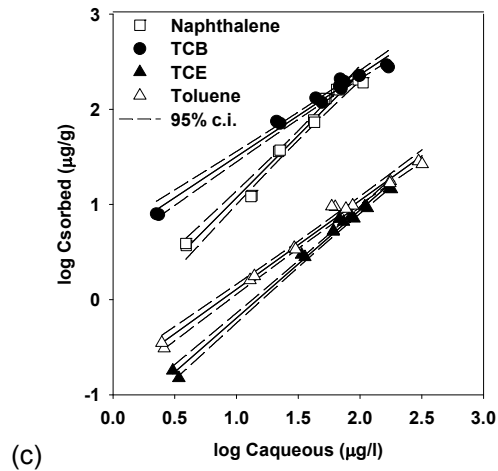
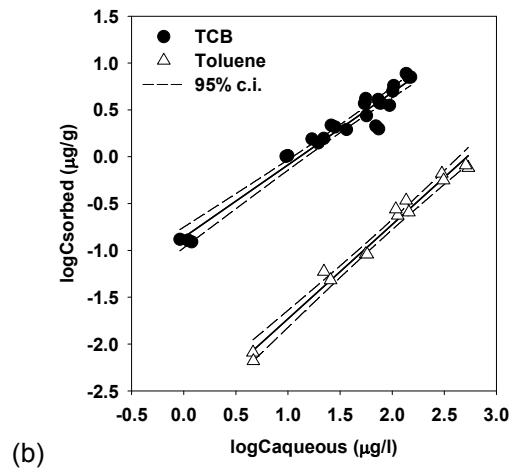
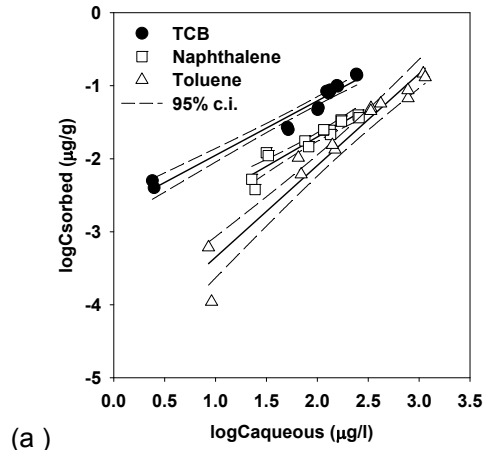
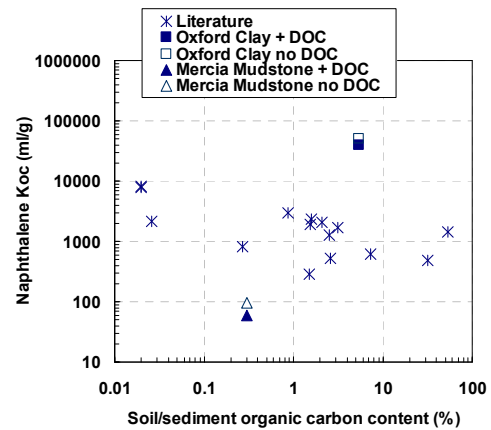
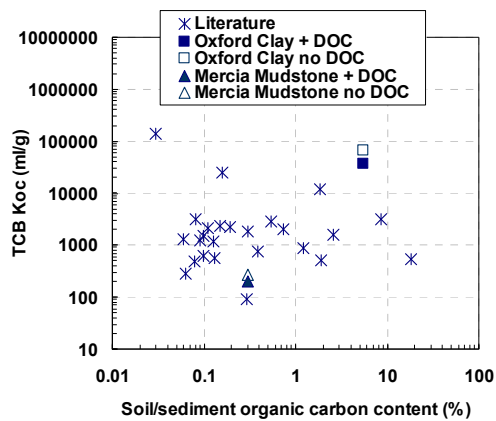
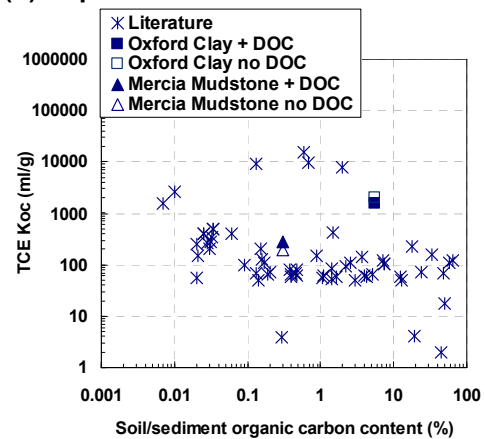
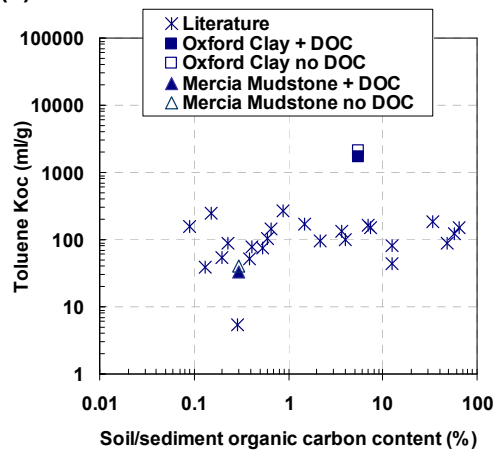


Figure 7.6 Freundlich sorption isotherms for toluene, naphthalene, TCB TCE.
 (a) Mercia Mudstone, (b) London Clay, and (c) Oxford Clay. Closely coupled data points represent duplicate results.



(a) TCB

(b) Naphthalene



(c) Toluene

(d) TCE

Literature sources for soils and sediments listed are:

- (a) for TCB, Chiou *et al.* (1983); Wilson *et al.* (1981); Hu *et al.* (1995); Schwarzenbach and Westall (1981); Walton *et al.* (1992); Brusseau *et al.* (1990); Brusseau and Rao (1991); Voice *et al.* (1983); Acton and Barker (1992); Oliver and Charlton (1984); Southworth and Keller (1986); Wu and Gschwend (1986); Paya-Perez *et al.* (1991); Lee *et al.* (1989); and Njoroge *et al.* (1998);
- (b) for naphthalene, Xing (1997); Xia and Ball (1999); King *et al.* (1999); Piatt *et al.* (1996), Xiao *et al.* (2004).
- (c) for toluene, Garbarini and Lion (1985, 1986); Hu *et al.* (1995); Vowles, and Mantoura (1987); Seip *et al.* (1986). Walton *et al.* (1992). Abdul *et al.* (1990); Brusseau (1993); Schwarzenbach and Westall (1981); Brusseau and Rao (1991); Wilson *et al.* (1981).
- (d) for TCE, Ong and Lion (1991); Garbarini and Lion (1986); Smith *et al.* (1990); Stauffer and MacIntyre (1986); Grathwohl and Reinhard (1993); Mehran *et al.* (1987); Piwoni and Banerjee (1989); Lee *et al.* (1988); Pavlostathis and Jaglal (1991); Allen-King *et al.* (1997); Myrand *et al.* (1992).

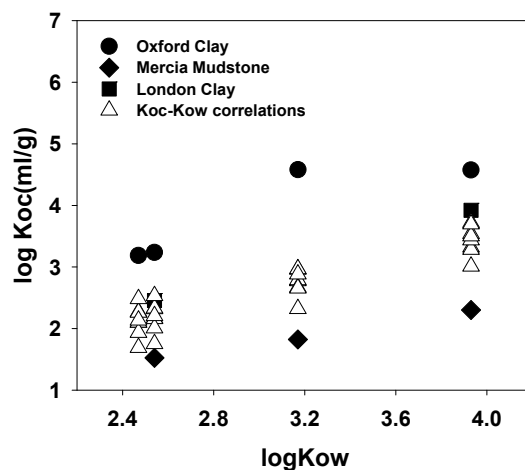
Figure 7.7 K_{oc} values for TCB, naphthalene, toluene and TCE in natural soil and sediments as a function of the sorbent organic carbon content

Table 7.4 Comparison of K_{oc} values determined from this study for selected List I compounds with values found in literature and predicted by empirical correlations

List I compound	Log K_{ow}	Solubility	Literature values Log K_{oc} (ml/g)	Predicted values* Log K_{oc} (ml/g)	This study Log K_{oc} (ml/g)		
					Mercia Mudstone	London Clay	Oxford Clay
					Naphthalene	3.17	142
Toluene	2.54	573.1	1.59 - 2.43	1.75 - 2.33	1.5	2.5	3.2
TCB	3.95	20	1.9 - 5.05	3.03 - 3.74	2.3	3.9	4.6
TCE	2.47	778.7	2.09 - 3.43	1.69 - 2.27	1.6	-	3.2

Literature values from Karickhoff *et al.* (1979); Schwarzenbach and Westall (1981); Chiou *et al.*, (1983); Sabljic (1987); Xia and Ball (1999); Seth *et al.* (1999); Chu and Chan (2000).

*Values determined from empirical correlations: Schwarzenbach and Westall (1981); Karickhoff *et al.* (1979); Chiou *et al.* (1983); Xia and Ball (1999).



Predicted K_{oc} values (Δ) using K_{oc} - K_{ow} correlations from literature: Schwarzenbach and Westall 1981; Karickhoff *et al.* (1979); Chiou *et al.* (1983); Karickhoff (1981); Sabljic (1987); Seth *et al.* (1999); Chu and Chan (2000); Xia and Ball (1999). TCE ($\log K_{ow}$ 2.47), toluene ($\log K_{ow}$ 2.54), naphthalene ($\log K_{ow}$ 3.17), and TCB ($\log K_{ow}$ 3.93).

Figure 7.8 Experimental K_{oc} values derived in this study for Oxford Clay, Mercia Mudstone and London Clay

7.4.3 Sorption isotherms of Mecoprop

Least squares regression analysis was carried out to obtain the sorption parameters of the linear isotherms and linearised logarithmic Freundlich isotherms for Mecoprop (MCP) on the three liner materials (Figure 7.9). The model fits for MCP sorption on London Clay and Oxford Clay are linear (the fitted values for n being approximately one) for sorption in both synthetic leachate and tap water (Table 7.5). Sorption of MCP on Mercia Mudstone appeared to be non-linear in synthetic leachate ($n=0.87$).

Table 7.5 Parameters of linear and Freundlich models fit to sorption data for Mecoprop on Mercia Mudstone, London Clay and Oxford Clay in synthetic leachate

Contaminant	Clay liner	Linear Model		Freundlich Model		
		$K_d \times 10^3$ (l/g)	R^2	$K_F \times 10^3$ ($\mu\text{g}^{1-n} \text{l}^n/\text{g}$)	n	R^2
Mecoprop	Mercia Mudstone	1.2	0.67	2.8	0.87	0.85
	London Clay	17.8	0.96	18.3	1.01	0.95
	Oxford Clay	8.4	0.98	8.4	0.98	0.97

R^2 - correlation coefficient

K_d values determined from the linear sorption coefficient model for MCP in soils and sediments are more frequently available in the literature. Literature K_d values for sorption of MCP range from zero to 2.8 ml/g (Helweg, 1993; Fomsgaard, 1997; Harris *et al.*, 2000), for soils and sediments, and zero to 0.17 ml/g for aquifer materials (Zipper *et al.*, 1998; Tuxen *et al.*, 2000; Madsen, 2000; Environment Agency, 2004). The linear sorption coefficient for MCP on Mercia Mudstone was greater than the literature values for aquifer sediments, but fell within the range of literature K_d values for soils; sorption of MCP by London Clay and Oxford Clay was much greater than literature values for both aquifer sediments and soils (Figure 7.10). The factors which might affect sorption of MCP include interactions of the carboxylic group with negatively charged clay surfaces and organic matter via metal ion bridges (Clausen *et al.*, 2001; Celis *et al.*, 1999) or partitioning via lipophilic interactions with soil organic matter (Chiou *et al.*, 1979; Karickhoff, 1984). The principal physicochemical characteristics of the three liner materials which could account for the differences in the magnitude and sorption/desorption behaviour of MCP can be summarized as: Oxford Clay has the highest OC content and CEC, Oxford and London Clays have a higher specific surface area than Mercia Mudstone, and London Clay has the highest iron oxide content. Analysis by X-ray fluorescence (Philips Magix-Pro wavelength XRF spectrometer) and by dithionite extraction (Table 7.2.) showed that London Clay had the highest percentage of iron oxyhydroxides followed by Mercia Mudstone and Oxford Clay. This does not fully account for the sorption of Mecoprop by these three liner materials, since sorption is in the order London Clay > Oxford Clay > Mercia Mudstone. The greater sorption of Mecoprop by Oxford Clay may be a function of its specific surface area or organic carbon content which is greater than that of Mercia Mudstone.

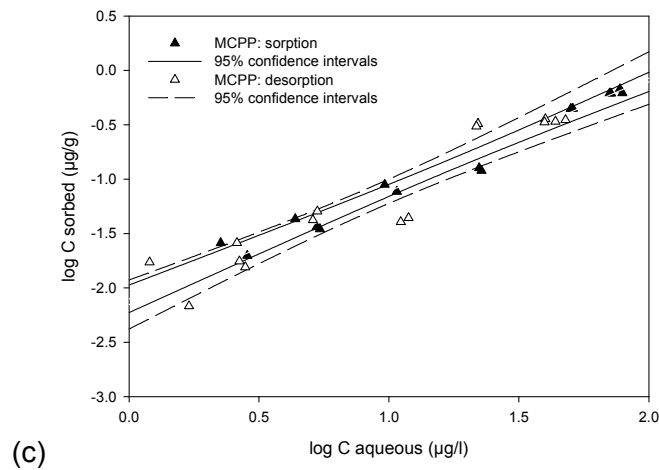
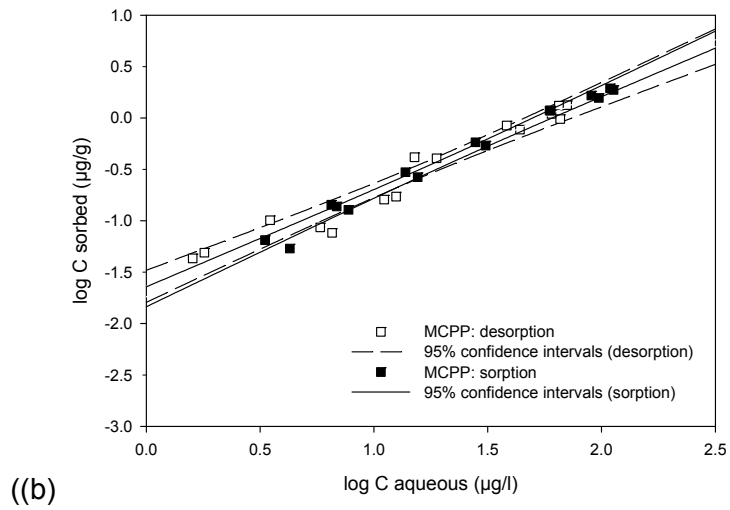
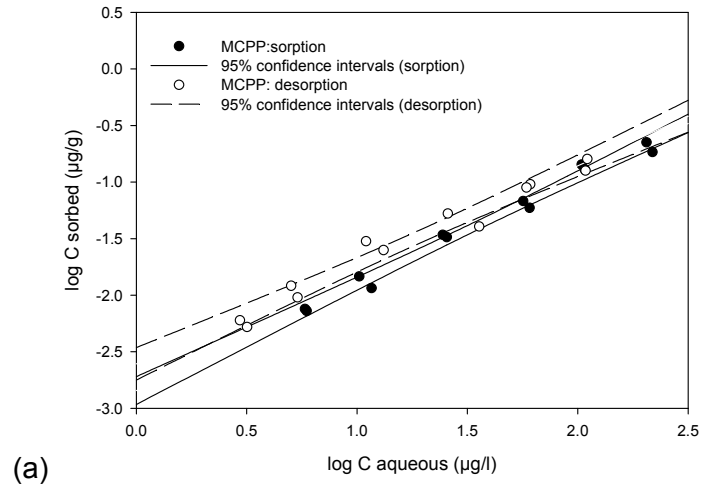


Figure 7.9 Freundlich sorption and desorption of MCPP on (a) Mercia Mudstone (b) London Clay and (c) Oxford Clay in synthetic leachate

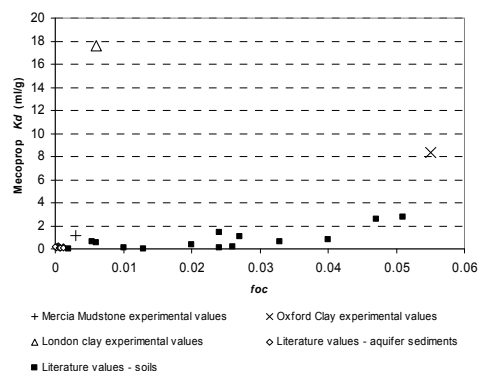


Figure 7.10 Measured and literature K_d values for MCPP.

Literature values from: Hauberhauer *et al.* (2000); Madsen *et al.* (2000); Harris *et al.* (2000).

7.5 Competitive sorption of List I substances

Landfill leachate generally contains a mixture of List I contaminants and consequently sorption isotherms which are constructed with single organic contaminants are not necessarily appropriate when competing compounds are present in a leachate. This is because a mixture of compounds will compete for a finite number of sorption sites (Xing and Pignatello, 1998; White and Pignatello, 1999). The effect of this is that some contaminants will be sorbed to the detriment of others, and consequently the uptake of certain contaminants by the liner could be lower than predicted by sorption coefficients derived from single compound sorption tests (Abdul and Gibson, 1986; Peng and Dural, 1998). In low OC content soils however, sorption of HOCs may be enhanced by the presence of a low polarity co-solute which effectively increases the OC content (Brusseau, 1991). The degree of cooperative sorption in any particular system depends on the f_{oc} of the soil, the mass and hydrophobicity of the co-solute, and that of the solute of interest.

A test was carried out to establish if the presence of TCB affects the sorption of a less hydrophobic contaminant – toluene – on Oxford Clay. The sorption of toluene was assessed with increasing concentrations of TCB (using a seven-day batch sorption test) and the results compared with the sorption of toluene in single solute tests. Duplicate tests were carried out with an initial toluene concentration of 120 µg/l, and initial TCB concentrations of 62 µg/l and 324 µg/l. The results demonstrated that, at these concentrations, there was no decrease in toluene sorption when TCB was present (Figure 7.11). The sorbent/liquid ratio (1.3 per cent) was chosen to match that of the single sorbent sorption tests carried out with toluene and Oxford Clay. At this ratio it appears that there is sufficient sorption capacity in the clay to absorb approximately 60 per cent of the toluene and nearly all of the TCB added.

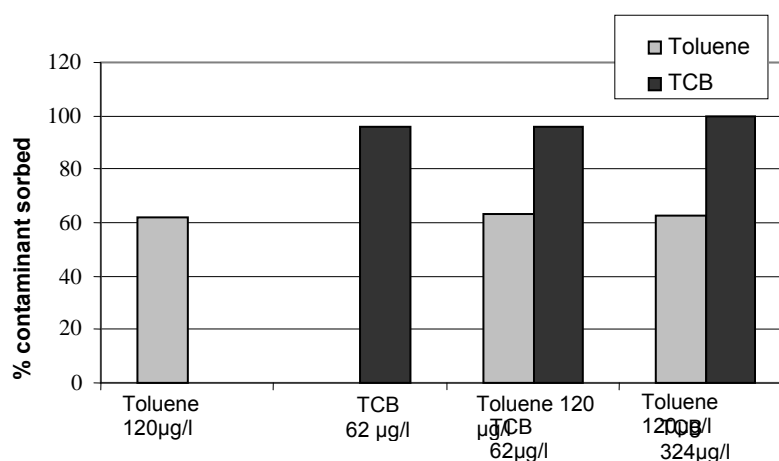


Figure 7.11 Sorption of toluene and TCB by Oxford Clay in single and competitive sorption tests. Initial aqueous concentrations of toluene and TCB are indicated on the x axis.

7.6 The effect of dissolved organic carbon on sorption of List I substances

7.6.1 Effect of tannic acid on sorption of List I substances

Tannic acid was used to mimic the natural DOC of the MSW and MSWI leachates. The sorption of hydrophobic substances to the liner materials may be affected by the presence of a third phase constituted by the DOC. Initial tests showed that sorption of TCB by London Clay with no tannic acid in the MSW leachate was increased relative to sorption when tannic acid was present in the leachate. Sorption isotherms for TCB and naphthalene on Oxford Clay, and TCB on Mercia Mudstone were determined in MSW leachate with and without tannic acid (Figures 7.12 and 7.13). The equilibrium sorption data was fitted by the linear model and the Freundlich model. Least squares regression analysis was carried out to obtain the sorption parameters of the linear isotherm and the linearised logarithmic Freundlich isotherm (Table 7.6).

Table 7.6 Parameters of linear and Freundlich models fit to sorption data for contaminants on Mercia Mudstone and Oxford Clay in synthetic leachate with and without tannic acid

Contaminant/ Clay liner	MSW leachate	Linear Model		Freundlich Model		
		$K_d \times 10^3$ (l/g)	R^2	$K_F \times 10^3$ ($\mu\text{g}^{1-n} \text{l}^n/\text{g}$)	n	R^2
TCB/ Mercia Mudstone	Tannic	0.5	0.94	2.4	0.655	0.92
	No tannic	0.7	0.96	3.8	0.654	0.99
Naphthalene/ Oxford Clay	Tannic	1,702	0.97	1,188	1.078	0.99
	No tannic	2,325	0.95	2,523	1.009	0.98
TCB/ Oxford Clay	Tannic	2,060	0.82	4,364	0.862	0.99
	No tannic	3,623	0.95	9,398	0.782	0.99

R^2 - correlation coefficient

Sorption of the hydrophobic organic contaminants by liner materials (TCB and naphthalene by Oxford Clay and TCB by Mercia Mudstone) without tannic acid in the leachate increased relative to sorption when tannic acid was present in the leachate. This may be caused by sorption of tannic acid (1,000 µg/l) to the solid matrix in preference to TCB and naphthalene which are present in much smaller concentrations (under 300 µg/l). In addition, the difference in molecular size between tannic acid (C₇₆H₅₂O₄₆) and TCB (Cl₃C₆H₃) or naphthalene (C₁₀H₈) suggests that sorbed tannic acid molecules may be blocking access of TCB and naphthalene molecules to sorption sites.

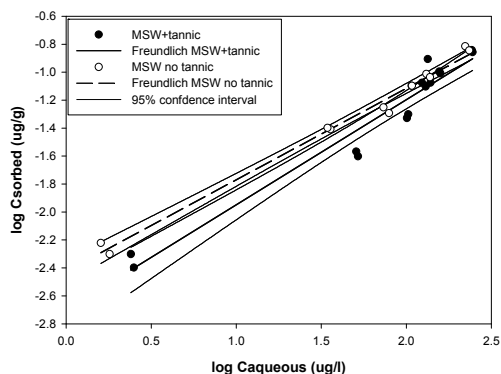


Figure 7.12 Sorption isotherms for TCB on Mercia Mudstone in MSW leachate with and without tannic acid

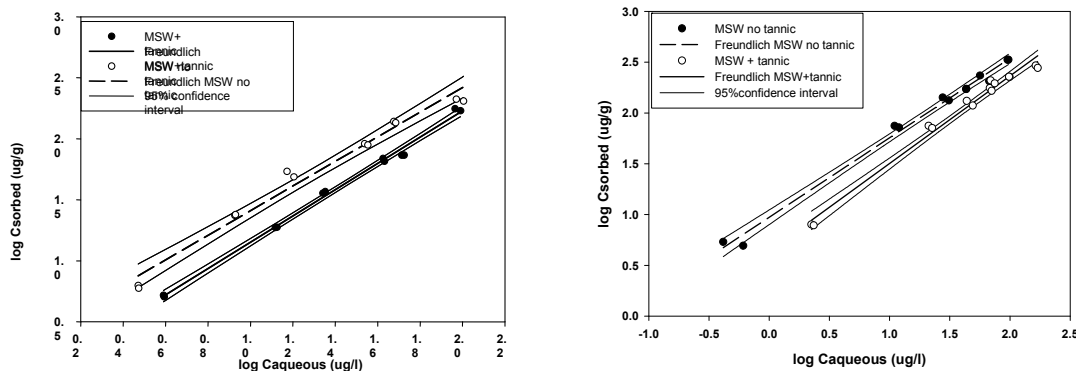


Figure 7.13 Sorption isotherms for naphthalene on Oxford Clay in MSW leachate with and without tannic acid

7.6.2 Sorption of tannic acid by mineral liner materials

Laboratory tests demonstrated that the presence of tannic acid in solution affected the sorption of hydrophobic List I substances (Section 7.5). Therefore, a study of the extent to which tannic acid was removed from solution by sorption to the mineral liner materials was undertaken. Sorption of tannic acid by Oxford Clay and Mercia Mudstone was investigated at the same solid/liquid ratios used in the List I

substances sorption tests (Table 7.7) and the tests were carried out under the same conditions with the exception that the List I contaminants were not added. DOC measurements were carried out at the National Oceanography Centre by high temperature catalytic combustion (Pan *et al.*, 2003).

Table 7.7 Experimental conditions of sorption tests of tannic acid on Oxford Clay

Variables	Experimental conditions
Liner material	Oxford Clay, air-dried and ground Mercia mudstone, air-dried and ground
Oxford Clay/leachate ratio (w/v)	0.0004 (as used in TCB and naphthalene sorption) 0.0125 (as used in toluene sorption) 0.0424 (expected to be the highest ratio used)
Mercia Mudstone/leachate ratio (w/v)	0.74 (as used in TCB sorption) 0.82 (as used in toluene and naphthalene sorption) 0.98 (as used in TCE sorption)
Contact time	7 days (duration of isotherm tests) 1 month (duration of kinetic tests)
Biological inhibitors	NaN ₃ 100 mg/l, HgCl ₂ 50 µg/l
Temperature	20 ± 2°C

The colour of the synthetic MSW leachate was found to vary from the original yellow colour at the lowest solid/liquid ratio to a grey colour at the highest ratio (Figure 7.14). In addition to the colour change, a decrease of up to 50 and 90 per cent in DOC in solution was also detected which indicates sorption of tannic acid by the Oxford Clay and Mercia Mudstone, respectively (Figure 7.15). This appears to confirm that hydrophobic List I substances and tannic acid compete for sorption sites on these two mineral liner materials (see Section 7.6). Tannic acid sorption increased with the amount of solid present in the bottles. The greatest amount of tannic acid removed from solution was observed in the bottles containing Mercia Mudstone; this is related to a higher solid/liquid ratio used rather than a higher sorption affinity. However, 90 per cent sorption of DOC by Mercia Mudstone corresponds to 0.5 mg DOC sorbed per gram of mudstone, while 50 per cent sorption of DOC by Oxford Clay corresponds to 6 mg DOC sorbed per gram of clay: that is, Oxford Clay has a greater sorption capacity per gram of clay than Mercia Mudstone.

Kinetic tests were carried out over 60 days to assess sorption of DOC by Mercia Mudstone and Oxford Clay. The limited tests (Figure 7.15) showed that sorption increased between 15 and 30 days after which no further sorption was observed (data not shown). This would suggest that the contact time needed to reach sorption equilibrium for DOC is longer than that of the List I contaminants (approximately five to seven days), but further tests would need to be carried out to confirm this.



Figure 7.14 Synthetic MSW leachate containing tannic acid after seven days of contact with Oxford Clay. (Clay/leachate ratio (w/v) from left: no solid, 0.0004, 0.0125, 0.0424)

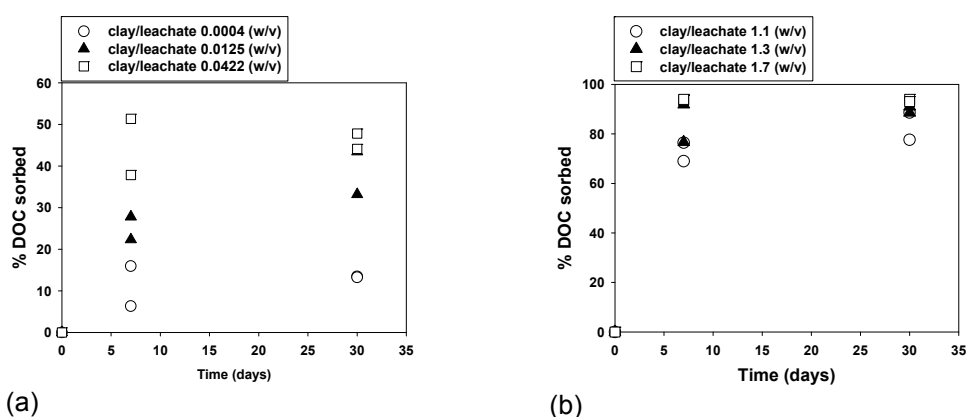


Figure 7.15 Variation with time of DOC sorption by (a) Oxford Clay and (b) Mercia Mudstone in synthetic MSW leachate at different solid/leachate ratios

7.6.3 Sorption of real leachate DOC by liner materials

A further test was undertaken to assess the extent to which DOC was removed from a real methanogenic municipal solid waste leachate by sorption to the mineral liner materials. Sorption of leachate DOC by Oxford Clay, London Clay and Mercia Mudstone was investigated at the same solid/liquid ratios used in the List I substances sorption tests (Table 7.8) and the tests were carried out under the same conditions with the exception that the List I contaminants were not added.

As with the tannic acid experiments discussed in Section 7.5.2, the greatest amount of leachate DOC was removed from solution in the bottles containing Mercia Mudstone (Figure 7.16); this is related to a higher solid/liquid ratio used rather than a higher sorption affinity. An average of 64 per cent sorption of DOC by Mercia Mudstone corresponds to 2.4 mg DOC sorbed/g dry weight, while 13 per cent sorption of DOC by Oxford Clay corresponds to 10 mg DOC sorbed /g dry weight, that is, Oxford Clay has a greater sorption capacity per gram than Mercia Mudstone. Sorption of leachate DOC by London Clay was similar in magnitude to Oxford Clay both in terms of percentage removal and mass of DOC sorbed. Leachate DOC was more strongly sorbed by Oxford Clay and Mercia Mudstone than tannic acid, perhaps indicating different sorption characteristics between the two types of DOC.

Table 7.8 Experimental conditions of sorption tests of leachate DOC on landfill liner materials

Variables	Experimental conditions
Liner material	Oxford Clay, air-dried and ground London Clay, air-dried and ground Mercia mudstone, air-dried and ground
Oxford Clay/leachate ratio (w/v)	0.0004 (as used in TCB and naphthalene sorption) 0.0424 (highest ratio used)
London Clay/leachate ratio (w/v)	0.02 (as used in TCB sorption) 0.11 (as used in Mecoprop sorption)
Mercia Mudstone/leachate ratio (w/v)	0.5 (as used in Mecoprop sorption) 0.98 (as used in TCE sorption)
Contact time	7 days (duration of isotherm tests)
Biological inhibitors	NaN ₃ 100 mg/l, HgCl ₂ 50 µg/l
Temperature	20 ± 2°C

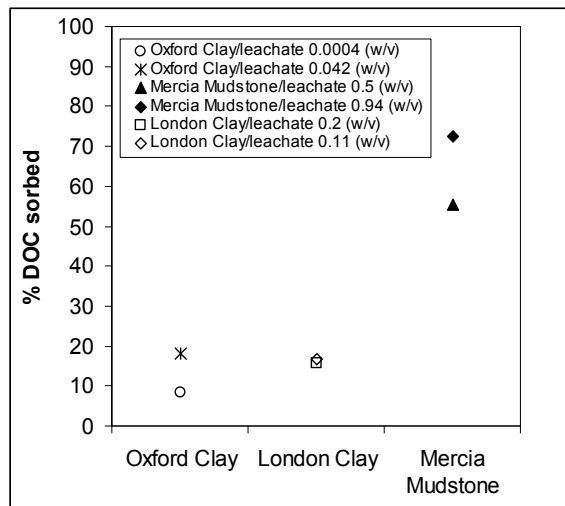


Figure 7.16 DOC sorption from real landfill leachate by Oxford Clay, London Clay and Mercia Mudstone at different solid/liquid ratios (duplicate results)

8 Desorption tests

8.1 Overview of desorption methodology

Desorption equilibria are generally measured by the batch sorption, decant and refill method (Bowman, 1979). In this technique, the supernatant solution is removed after equilibration with the solid in the batch sorption test and replaced with a solute-free solution. This allows the solute sorbed to the solid phase to desorb into the solute-free aqueous phase until a new equilibrium condition is reached. Kinetic tests are first carried out to determine the contact time to reach equilibrium in the desorption phase and then desorption isotherm tests can be performed and the desorption distribution coefficients established.

The solute-free leachate used in the desorption tests was produced by mixing the liner material and fresh synthetic leachate, in the same ratio as in the sorption tests and for the same contact time. This was done so that the solute-free solution in the desorption phase would be as similar as possible, in terms of dissolved organic carbon and colloidal material, to the supernatant solution removed at the end of the sorption step (Huang *et al.*, 1998). However, it was not possible to be certain that the solute-free solution and the solution used in the sorption step would be identical because of the variation in both the content and nature of the organic carbon present in the mineral liner material which might leach into solution during the tests.

At the end of desorption, the concentration of contaminant in supernatant solution includes the contaminant that is not removed at the beginning of desorption (any remaining solution and contaminant trapped in the solid matrix at the end of the sorption test) and that which is desorbed from the solid phase during desorption. Contaminant loss from the solid phase during repeated desorption steps can be expressed as follows (Kan *et al.*, 1994):

$$C_{desorbed} = [C_i - C_{i-1}(1-r)] \frac{V}{M} \quad (8.1)$$

where

- $C_{desorbed}$ = loss of solid phase at the end of the desorption step ($\mu\text{g/g}$ dry weight)
- C_i & C_{i-1} = equilibrium solute concentrations ($\mu\text{g/l}$) at the end of the i th desorption and previous sorption step respectively
- r = fraction of supernatant replaced at each dilution.

The mass of contaminant remaining sorbed to the mineral liner material at the end of desorption can be expressed as follows:

$$C_{sorbed}^d = C_{sorbed}^s - C_{desorbed} \quad (8.2)$$

where

- C_{sorbed}^d = concentration of contaminant sorbed ($\mu\text{g/g}$ dry weight) at the end of the desorption step

C_{sorbed}^s & $C_{desorbed}$ = concentrations of contaminant at the end of the sorption step and the following desorption step ($\mu\text{g/g}$).

In this report the Freundlich isotherm for desorption is therefore given by:

$$C_{sorbed}^d = K_F^d C_i^n \quad (8.3)$$

where:

C_{sorbed}^d = sorbed contaminant concentration (mass of cont./mass of solid, $\mu\text{g/kg}$)

K_F^d = equilibrium coefficient for the desorption reaction

C_i = dissolved contaminant concentration at end of desorption step ($\mu\text{g/l}$)

n = chemical specific constant to account for heterogeneity, normally $0 < n < 1$.

The distribution coefficient for the linear desorption isotherm is denoted by K_d^d .

8.2 Desorption kinetics

In the sorption batch tests, preliminary tests were carried out to establish the best ratio of sorbent to solution in order to obtain measurable changes in aqueous contaminant concentration during sorption (30-60 per cent sorption). If sorption is reversible, the same ratio of sorbent to solution should be suitable for the desorption tests. As discussed in Section 8.3, reversible sorption was not always present and for certain solute/sorbent combinations, the loss of contaminant was low and consequently the results are subject to error (Delle Site, 2001).

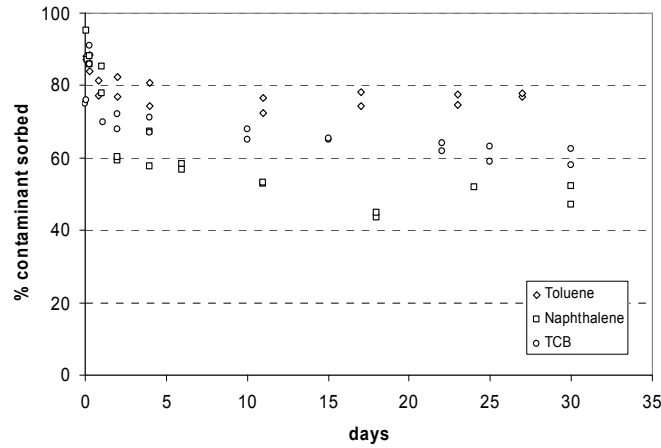
Desorption kinetic tests were carried out as follows: solute was sorbed onto the mineral liner materials using the sorption batch method as described in Section 7; the same initial aqueous concentration was used. After the sorption step (using the sorption contact times given in Table 8.1), samples were collected from all the bottles for analysis of the sorption equilibrium concentration, the supernatant was removed, and the mass of the bottles, remaining solid and entrapped synthetic leachate was noted. The bottles were refilled with solute-free leachate, capped and the mass of the bottles and contents again recorded. The bottles were agitated on horizontal rotary roller. Sample bottles were taken in duplicate with destructive sampling over a 30-day period (each bottle was only sampled once and then discarded) to determine the time required to reach desorption equilibrium for each of the liner/contaminant combinations. Desorption equilibrium was considered to be attained when the contaminant concentration change was too small to measure over a number of days.

The results of the kinetics tests showed that desorption of the List I substances was biphasic, having a fast release stage over the first 24 to 48 hours of the test, followed by slower desorption towards equilibrium (see Figure 8.1). The contact times used in subsequent desorption isotherm tests are shown in Table 8.1 for toluene, TCB, naphthalene and Mecoprop; desorption tests were not carried out for TCE for any of the mineral liner materials, and sorption/desorption tests for naphthalene on London Clay were not carried out.

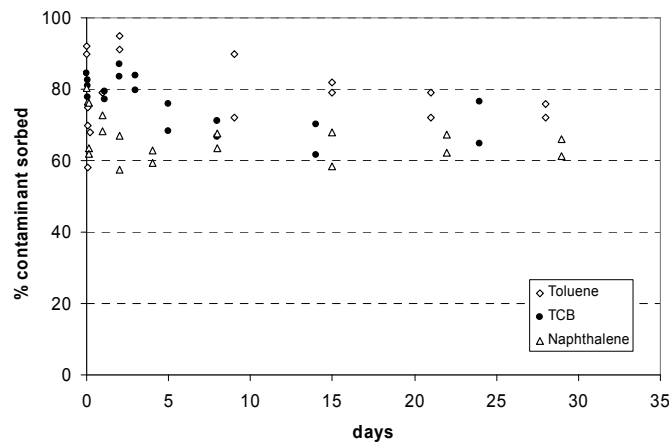
Table 8.1 Contact times for sorption and desorption isotherm tests as determined from kinetic studies

	Mercia Mudstone		London Clay		Oxford Clay	
	sorption	desorption	sorption	desorption	sorption	desorption
Mecoprop	5	10	5	10	5	10
Naphthalene	7	10	n/c	n/c	7	10
Toluene	2	10	7	12	7	12
TCB	4	10	5	15	7	10
TCE	5	n/c	n/c	n/c	5	n/c

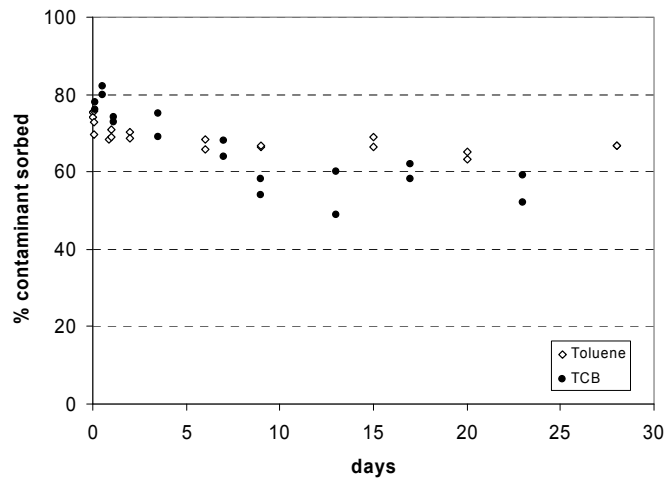
n/c = not carried out



(a)



(b)



(c)

Figure 8.1 Desorption kinetics of organic pollutants from (a) Oxford Clay, (b) Mercia Mudstone, and (c) London Clay. Closely coupled data points represent duplicate samples.

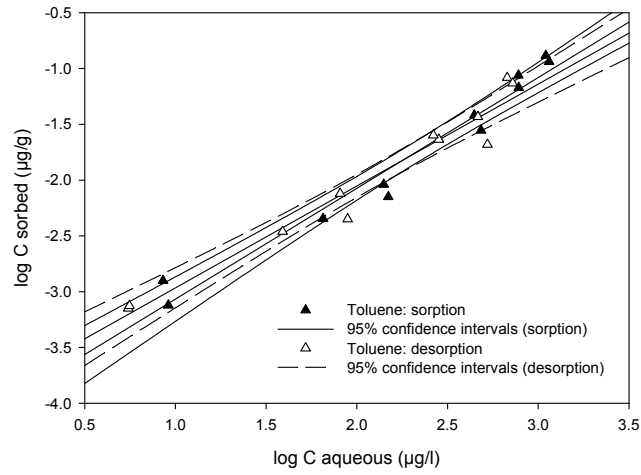
8.3 Desorption isotherms for HOCs

Desorption tests were carried out using the batch sorption, decant and refill technique for three of the contaminants (toluene, TCB and naphthalene) on each of the three mineral liner materials. Sorption and desorption parameters for the linear and Freundlich models are summarised in Table 8.2. Freundlich model fits to the sorption and desorption equilibrium data are shown in Figures 8.2 to 8.4.

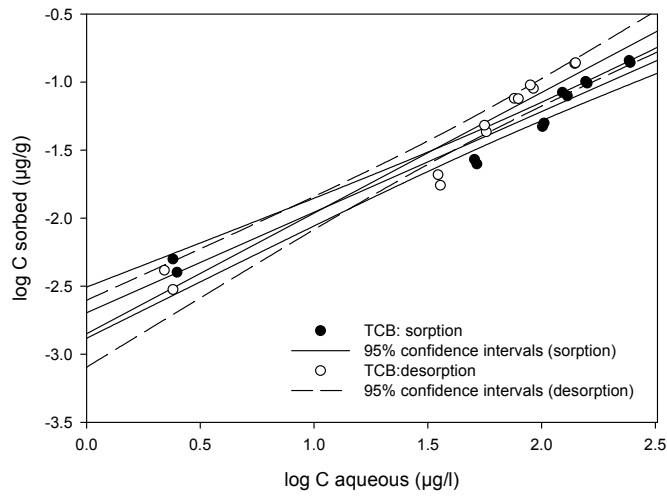
Table 8.2 Parameters of linear and Freundlich models fit to sorption and desorption data for toluene, TCB, TCE and naphthalene on Mercia Mudstone, London Clay and Oxford Clay

Clay	Contaminant	Isotherm	Linear Model		Freundlich Model		
			$K_d \times 10^3$ (l/g)	R ²	$K_F \times 10^3$ ($\mu\text{g}^{1-n} \text{l}^n/\text{g}$)	n	R ²
Mercia Mudstone	Naphthalene	Sorption	0.2	0.84	0.52	0.8	0.94
		Desorption	0.4	0.928	0.68	0.834	0.96
	Toluene	Sorption	0.1	0.96	0.02	1.257	0.943
		Desorption	0.09	0.84	0.13	0.913	0.9575
	TCB	Sorption	0.6	0.98	2.02	0.74	0.96
		Desorption	1.0	0.97	1.4	0.887	0.9451
London Clay	Toluene	Sorption	1.7	0.96	1.97	0.99	0.99
		Desorption	3.4	0.894	4.21	0.98	0.97
	TCB	Sorption	49.8	0.884	137	0.774	0.958
		Desorption	65.6	0.9	165	0.74	0.93
Oxford Clay	Naphthalene	Sorption	2,213	0.95	3,125	0.9	0.82
		Desorption	4,513	0.94	10,227	0.74	0.97
	Toluene	Sorption	94.3	0.957	150	0.93	0.99
		Desorption	186.8	0.879	476	0.84	0.96
	TCB	Sorption	1,860	0.79	4,573	0.81	0.95
		Desorption	4,492	0.96	6,616	0.87	0.82

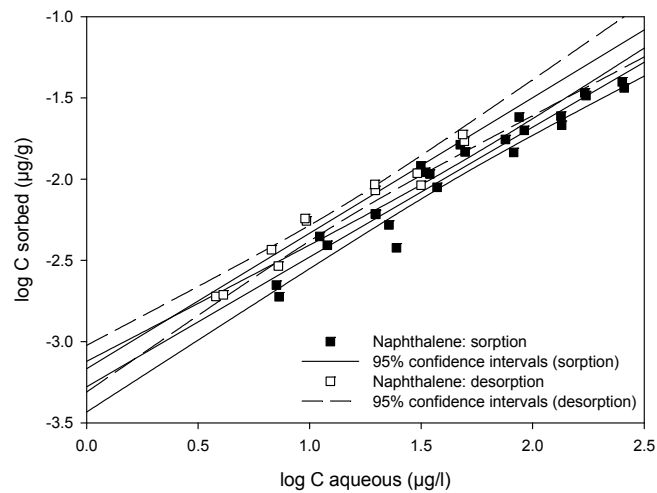
R² - correlation coefficient



(a)

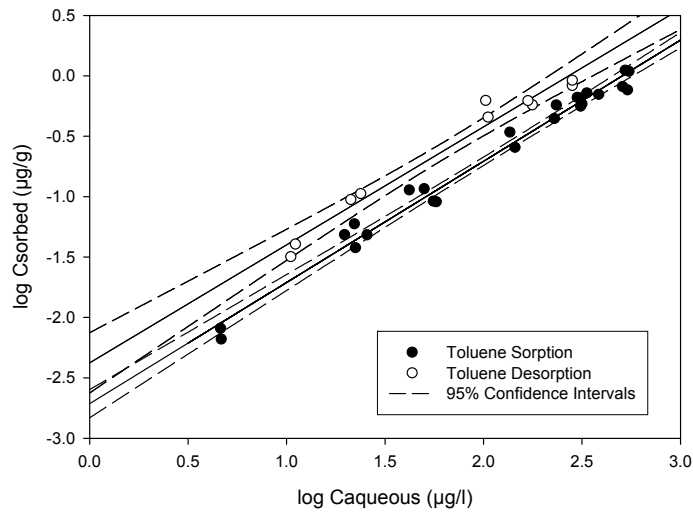


(b)

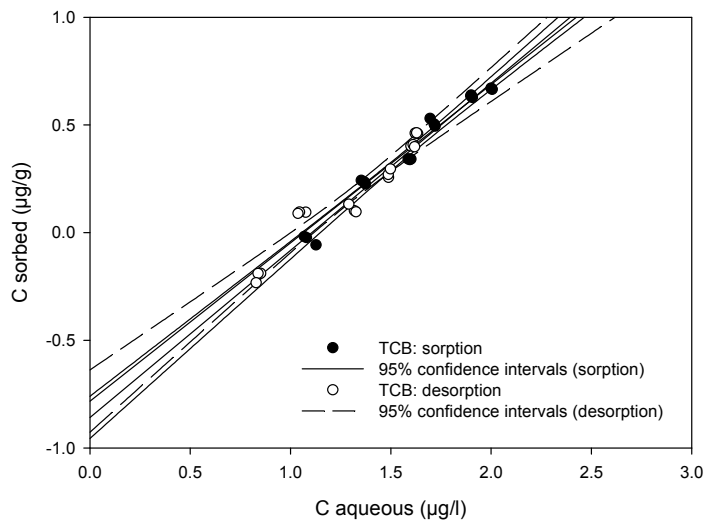


(c)

Figure 8.2 Freundlich sorption and desorption isotherms for (a) toluene, (b) TCB and (c) naphthalene on Mercia Mudstone

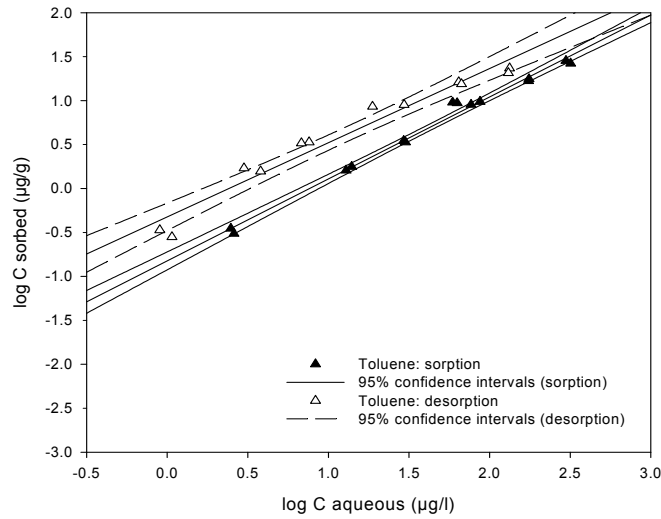


(a)

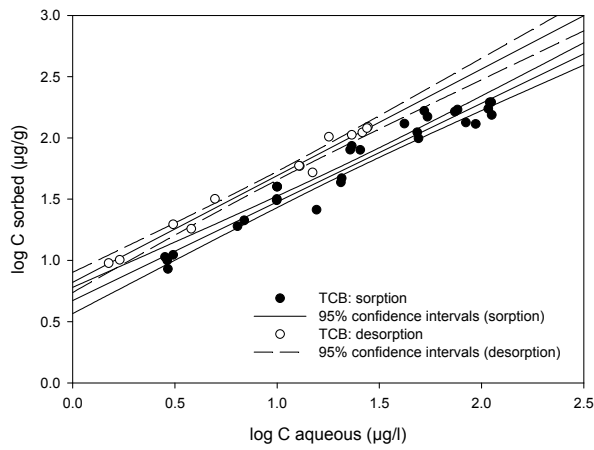


(b)

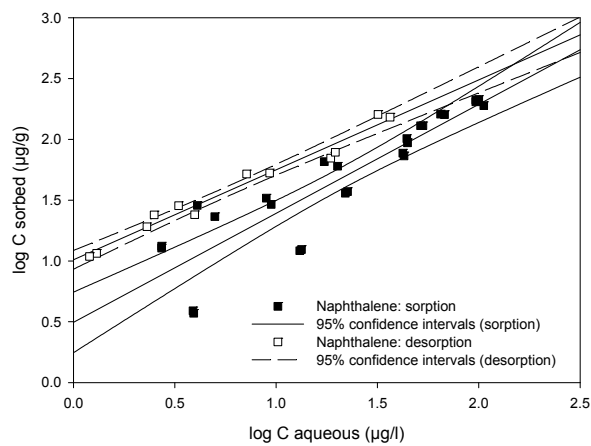
Figure 8.3 Freundlich sorption and desorption isotherms for (a) toluene and (b) TCB on London Clay



(a)



(b)



(c)

Figure 8.4 Freundlich sorption and desorption isotherms for (a) toluene, (b) TCB and (c) naphthalene on Oxford Clay

The Freundlich sorption and desorption isotherms for toluene, TCB and naphthalene on Mercia Mudstone are not significantly different (Figure 8.2) at 95 per cent confidence intervals. Although this is the result of only one sorption step, the overlap of sorption and desorption isotherms suggests that sorption is reversible on this liner material. However, a large amount of Mercia Mudstone was needed to effect sufficient sorption of the contaminants, leading to operational problems when preparing the sorption tests, and again, when re-suspending the solid for the desorption tests.

Sorption of TCB on London Clay appears to be reversible as shown by the Freundlich sorption and desorption isotherms (Figure 8.3). The sorption and desorption isotherms of toluene on London Clay do not overlap, but are not significantly different at 95 per cent confidence intervals.

The results from the first desorption step for toluene and naphthalene on Oxford Clay show significant difference between the sorption and desorption isotherms indicating possible sorption-desorption hysteresis (Figure 8.4). The sorption and desorption isotherms of TCB on Oxford Clay do not overlap, but are not significantly different at 95 per cent confidence intervals. For non-polar hydrophobic organic contaminants sorption-desorption hysteresis, in which the sorbed fraction does not readily desorb to the aqueous phase, has been attributed to (a) entrapment of the sorbed molecules in meso or microporous structures within inorganic components of soil aggregates (see Farrell and Reinhard, 1994), (b) entrapment of sorbed molecules within organic matter matrices (see Carroll *et al.*, 1994), or (c) slow rates of desorption (see Weber *et al.*, 1998). Given the presence of highly sorbent organic carbon in Oxford Clay, it is likely that diffusion and entrapment of toluene and naphthalene into organic matter matrices or slow rates of desorption may be responsible for the hysteresis observed.

8.4 Desorption of Mecoprop

Least squares regression analysis was carried out to obtain the desorption parameters of the linear isotherms and linearised logarithmic Freundlich isotherms for MCP on the three mineral liner materials in synthetic leachate (Figure 8.5); the model parameters are given in Table 8.3. The model fits for MCP desorption from Oxford Clay and London Clay are approximately linear, however desorption on Mercia Mudstone appears to be non-linear ($n=0.88$). There appears to be little difference between the sorption and desorption coefficients, which suggests that sorption of MCP is reversible in synthetic leachate after one desorption step.

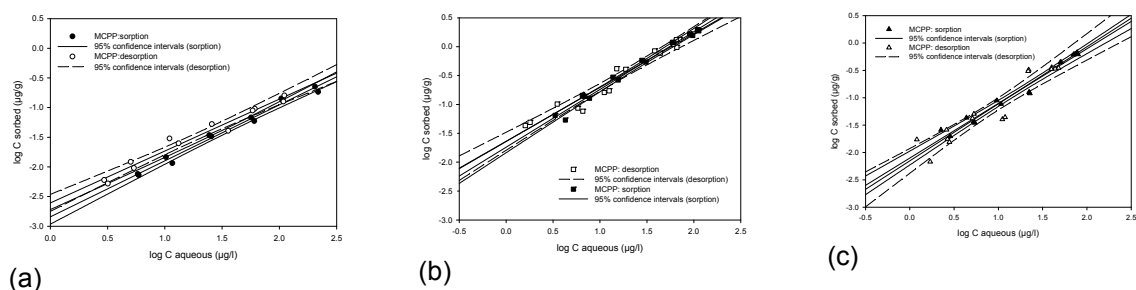


Figure 8.5 Freundlich sorption and desorption of Mecoprop on (a) Mercia Mudstone, (b) London Clay, and (c) Oxford Clay

Table 8.3 Parameters of the linear and Freundlich models fit to the sorption and desorption data for Mecoprop on Mercia Mudstone, London Clay and Oxford Clay

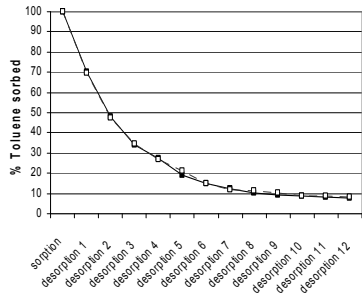
Clay liner	Isotherm	Linear Model		Freundlich Model		
		$K_d \times 10^3$ (l/g)	R^2	$K_F \times 10^3$ ($\mu\text{g}^{1-n} \text{l}^n/\text{g}$)	n	R^2
London Clay	Sorption	17.6	0.99	18.1	1.0	0.99
	Desorption	18.4	0.96	23.7	0.93	0.95
Mercia Mudstone	Sorption	1.2	0.67	2.8	0.87	0.85
	Desorption	1.4	0.949	2.47	0.88	0.97
Oxford Clay	Sorption	8.4	0.99	8.4	0.98	0.97
	Desorption	8.6	0.875	7.6	1.01	0.89

R^2 - correlation coefficient

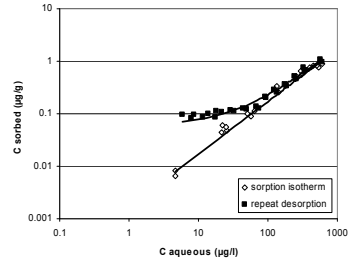
8.5 Repeat desorption tests

Simple contaminant transport models based on classical advection-dispersion equations (such as LandSim) typically assume that sorption is reversible, so that at zero aqueous concentration there is also zero concentration sorbed to the solid phase. Single step desorption tests may demonstrate desorption hysteresis, but to estimate the magnitude of irreversibly sorbed contaminant, multiple step decant-refill cycles must be carried out. If very low aqueous contaminant concentrations are observed after a number of desorption steps, the amount of contaminant remaining sorbed may be approximated to the irreversible fraction. Repeat desorption tests were therefore carried out on a limited number of mineral liner/contaminant combinations. Starting with a standard batch sorption at a high aqueous concentration, the supernatant liquid was replaced until a new equilibrium was reached. Following measurement, this liquid was again replaced until a new equilibrium was reached. Between nine and twelve desorption steps were carried out in this manner.

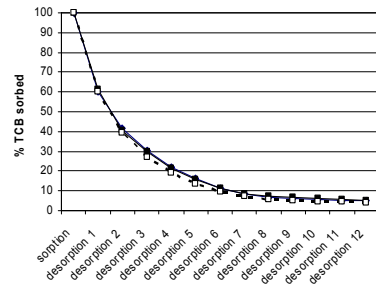
Multi-step desorption tests were undertaken for TCB and toluene on Oxford and London Clay. Sorption/desorption hysteresis was not demonstrated for toluene and TCB on London Clay and TCB in Oxford Clay in the single step desorption batch tests, but results from the multi-step desorption tests indicate that in addition to sorption/desorption hysteresis, there was an element of irreversible sorption in all cases (Figures 8.6 and 8.7). Oxford Clay had the largest capacity with approximately 35 $\mu\text{g/g}$ TCB and 2.5 $\mu\text{g/g}$ toluene sorbed irreversibly by applying a simple linear model. A two-domain model (Kan *et al.*, 1998; Equation 3.6) was also fitted to the data. The model suggests that only a fraction of the irreversible compartment was filled by the contaminant in the sorption stage. Sorbed contaminant concentrations predicted by the irreversible sorption models are significantly greater than those predicted by linear sorption isotherms which assume sorption reversibility. These results demonstrate that some mineral liner materials may have a much greater capacity to retain certain contaminants than might be predicted from conventional models.



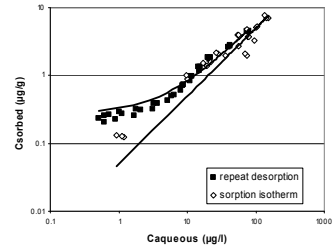
(a)



(b)

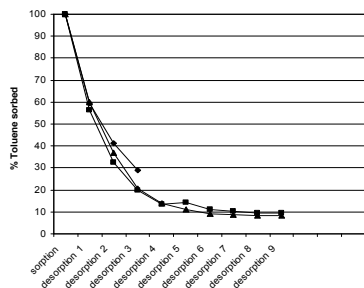


(c)

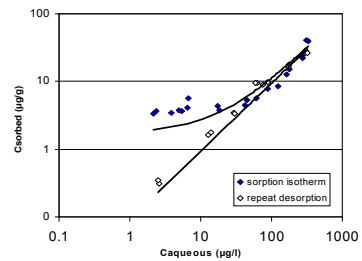


(d)

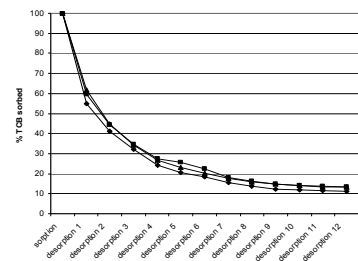
Figure 8.6 Repeat desorption tests of toluene and TCB on London Clay.
 (a) % Toluene sorbed after 12 desorption steps from an initial concentration of 774 µg/l toluene; (b) sorption isotherm of toluene on London Clay and results from repeat desorption test (c) % TCB sorbed after 12 desorption steps from an initial concentration of 172 µg/l TCB; (d) sorption isotherm of TCB on London Clay and results from repeat desorption test.



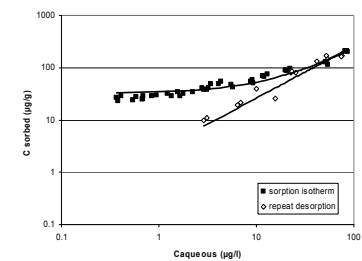
(a)



(b)



(c)



(d)

Figure 8.7 Repeat desorption tests of toluene and TCB on Oxford Clay.
 (a) % Toluene sorbed after nine desorption steps from an initial concentration of 824 µg/l toluene; (b) sorption isotherm of toluene on Oxford Clay and results from repeat desorption test (c) % TCB sorbed after 12 desorption steps from an initial concentration of 165 µg/l TCB; (d) sorption isotherm of TCB on Oxford Clay and results from repeat desorption test.

9 Column tests

9.1 Introduction

Column tests were carried out using inert triaxial cells to determine the scalability of the sorption parameters derived from the batch tests. This study examined the extent of attenuation during transport of MCPP through the mineral liner materials with reference to a 'conservative' tracer. The aim was to establish whether MCPP was subject to any irreversible sorption and to quantify the extent and nature of retardation from sorption.

9.2 Brief overview of methodology

The retardation of Mecoprop by Mercia Mudstone and Oxford Clay was tested. The samples were prepared by drying, grinding, sieving (to under 63 μ m). The ground samples were mixed with freshly de-aired tap water to a moisture content (defined as mass of water to dry mass of solids) of 85-90 per cent, then consolidated in a clear acrylic tube of approximately 39 mm internal diameter mounted in an oedometer loading device (BS 1377:5, 1990) to a maximum vertical stress of 400 kPa. The maximum consolidation stress was sufficient to produce a sample of good stiffness for the use in the triaxial cell. When the maximum stress was reached, the sample was unloaded in stages to the effective stress to be used in the test (90 kPa). The sample was recovered from the oedometer tube, trimmed and transferred to the triaxial cell.

The standard triaxial cell apparatus was modified to minimise any potential for sorption of Mecoprop (Figure 9.1). Polytetrafluoroethylene (PTFE) was used in contact with the sample to prevent sorption of MCPP by the latex membrane. The interaction between Mecoprop and PTFE was evaluated in batch tests and no sorption was found; however, sorption of MCPP (20 per cent) by the latex membrane was observed (method given in Appendix 3). A de-aired porous disc was placed at each end of the sample, which was then positioned on the PTFE base. PTFE tape (RS Thread Seal Tape) and PTFE sheet (Polyflon PTFE sheet 0.25 mm thick) were wrapped around the sample and the PTFE base and top cap. A latex membrane was applied over the PTFE. The cell was closed and filled with de-aired tap water, and the sample subjected to an isotropic stress by pressurising the cell fluid. In the majority of the tests, the cell, base and top pressures were set to 160 kPa, 140 kPa and zero respectively, in order to provide a mean effective stress of 90 kPa, representative of conditions below a landfill. The sample was permeated with tap water until steady flow was obtained. The time for transport through PTFE tubing from the pressure controllers to the cell, assuming piston flow, was calculated to be between 0.01 and 0.06 days for all tests.

A total of 10 tests were performed with Mercia Mudstone and Oxford Clay. Samples were collected at the outlet measured for bromide, used as a conservative tracer. The samples were then acidified to pH 2 and refrigerated to preserve the Mecoprop. Bromide concentrations were measured by ion selective electrode (Thermo Orion) except in Tests 3 and 4 where high NaCl concentrations interfered with the bromide probe and instead a colorimetric method (Presley, 1971) was used. The method for MCPP measurement is described in Appendix 3. Tests showed that the presence of Mecoprop did not influence the analysis of bromide (50 mg Br⁻/l) in tap water; similarly the presence of bromide did not affect the analysis of Mecoprop.

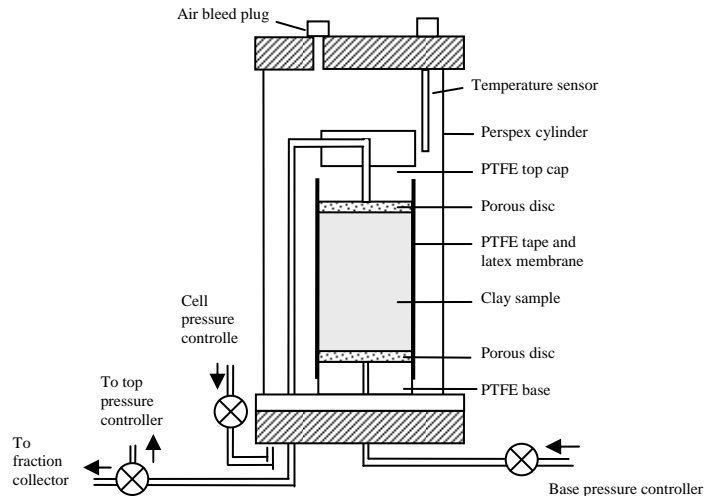


Figure 9.1 Triaxial cell used in the column tests

Ten tests were performed using the triaxial apparatus (Table 9.1). In Test 1, conservative transport in Mercia Mudstone was investigated by using potassium bromide (50 mg Br/l) as a tracer in tap water. The sample was then left undisturbed in the triaxial cell and tracer injection was repeated for Test 2 to establish repeatability. The effect on transport of adding the tracer to synthetic leachate (represented by 6.97 g/l NaCl, an ionic strength typical of municipal solid waste (MSW) leachate ($I = 0.119$)) was investigated in Tests 3 and 4.

In Test 5, tap water containing the contaminant MCPP as well as the reference tracer (50 mg Br/l) was injected. Sodium azide (50 mg/l) was added to prevent biodegradation of mecoprop during the test. Due to analytical difficulties, Test 6 was not assessed further. Test 7 was performed in Oxford Clay, with half the hydraulic gradient of the basic pressure state. Tests 8 and 9 were performed on a new Mercia Mudstone sample with bromide and Mecoprop in tap water. Finally, Test 10 was a further investigation of transport Oxford Clay, with the standard cell condition restored.

The initial concentration of Mecoprop (300 µg/l: Tests 5 and 7; 500 µg/l Tests 8 and 9), while greater than normally found in landfill leachate, was selected to ensure adequate concentrations for the analytical technique (solid phase extraction and GC-MS). The hydraulic gradient used in the tests was greater than would be encountered under normal landfill conditions, but was necessary to produce flow rates suitable for sampling in the limited time available for the tests.

Table 9.1 shows the hydraulic conductivity measured in each test, which gives a useful indication of within-sample variability between tests as well as between-sample variability. Taking the mean values, the hydraulic conductivity of the Mercia Mudstone was 1.7×10^{-9} m/s, whereas for Oxford Clay it was 3.6×10^{-10} m/s. Although the mean for the Oxford Clay was lower, it remained within the range of measured Mercia Mudstone hydraulic conductivities.

Table 9.1 Column details and fitting results

	Test	1	2 [†]	3	4	5	8	9	10
Basic data	Sample number	1	1	1	1	2	5	5	6
	Operator	1	1	1	1	2	3	3	4
	Sample type*	MM	MM	MM	MM	MM	MM	MM	OX
	Br mass recovery (%)	93.2	96.9	90.9	101.5	98.7	95.5	100.0	101.0
	MCPPP mass recovery (%)	-	-	-	-	95.6	96.1	108.0	96.6
	K (m/s×10 ⁻¹⁰)	7.4	9.2	6.3	2.6	11.9	33.8	50.2	4.9
Fixed parameters	v (m/s×10 ⁻⁷)	6.6	8.2	5.6	2.3	8.4	23.3	34.7	3.8
	L (mm)	38	38	38	38	47	48	48	54
	θ_e (-)	0.43	0.43	0.43	0.43	0.43	0.43	0.43	0.32
Fitted parameters	R_{MCP} (-)	-	-	-	-	4.3	3.0	3.5	17.6
	D_{Br} (m ² /d×10 ⁻⁴)	4.5	4.8	2.9	0.8	34.3	99.0	77.6	5.8
	D_{MCP} (m ² /d×10 ⁻⁴)	-	-	-	-	256.1	50.4	66.7	13.5
Derived parameters	Pe (-)	4.8	5.5	6.3	9.0	1.0	1.0	1.9	3.0
	t_A (d)	0.67	0.53	0.78	1.90	0.65	0.24	0.16	1.65
Fit	N (-)	101	131	50	41	259	35	202	134
	r (-)	0.995	0.992	0.976	0.994	0.991	0.993	0.979	0.93

Hydraulic conductivity for the first sample increased for Test 2 and then decreased in both Test 3 and Test 4. Tests 3 and 4 differed from all the other tests due to the fact that a sodium chloride solution was injected instead of tap water. A step change in the hydraulic conductivity for these two tests may have been anticipated, given that Batchelder *et al.* (1998) observed a 20 to 30 per cent shrinkage of clay minerals in the presence of synthetic leachate, yet the observed difference in these tests was undramatic. Algal growth was observed in the PTFE tubing leading from the cell and may have been responsible for progressive blocking of the sample or porous disks. The lack of major changes due to the sodium chloride, justified injection of tap water (rather than 'leachate' simulated by sodium chloride) for the remaining tests.

9.3 Mercia Mudstone column tests

Tests 1-5 and 8-9 were carried out using Mercia Mudstone. Three samples were prepared using the same preparation and consolidation techniques and the triaxial cell was operated under the same conditions (Table 9.1).

Mecoprop and potassium bromide were introduced to the column and samples of the eluant were taken for analysis every 90 minutes during the course of the test. Pressure, temperature and flow rate were monitored constantly. In Test 1, only the bromide tracer was run through the column because of difficulties with Mecoprop analysis. Figure 9.2 shows the flow rates for Test 2. The concentration of bromide and Mecoprop in the samples was measured and compared to the initial concentration (C/C_0). Although the flow had stabilised before the test was started, the flow rate dropped from 0.3 to 0.15 ml/minute during the test. The fall in flow rate could be due to clogging of porous disc used at the top of the sample. After testing, some clogging of the disc was observed. The flow rate in Test 3 was less stable than in Test 2; after an unintentional break in flow in the early part of the test, the flow rate dropped then rose again to 0.075 ml/minute, before falling again towards the end of the test, as occurred in Test 2 (Figure 9.3).

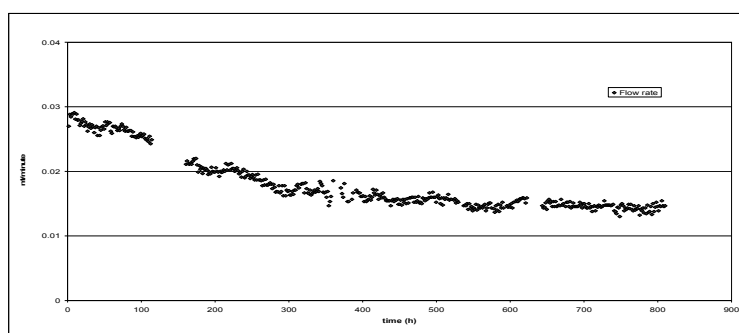


Figure 9.2 Flow rates through a sample of Mercia Mudstone in Test 2

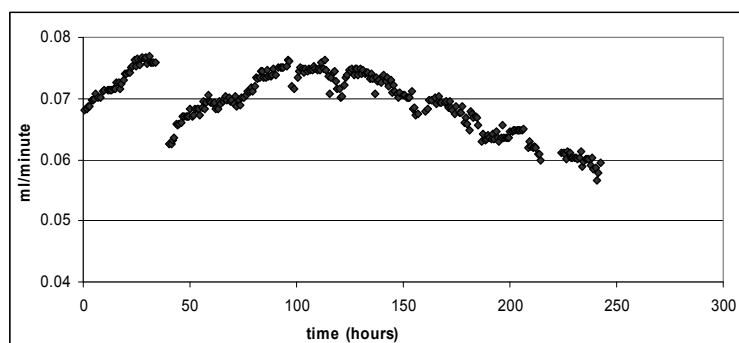


Figure 9.3 Flow rates through a sample of Mercia Mudstone in Test 3

The total masses of Mecoprop recovered were calculated by integrating the breakthrough curves and are given in Table 9.1. The lowest recovery of Mecoprop in Mercia Mudstone was 95.6 per cent (Test 5). This would suggest that any 'irreversible' sorption affected less than 4.4 per cent of the injected mass. This corroborates the results from batch sorption tests in synthetic leachate, in which reversible sorption was demonstrated and in which sorption reached a stable equilibrium value in less than five days.

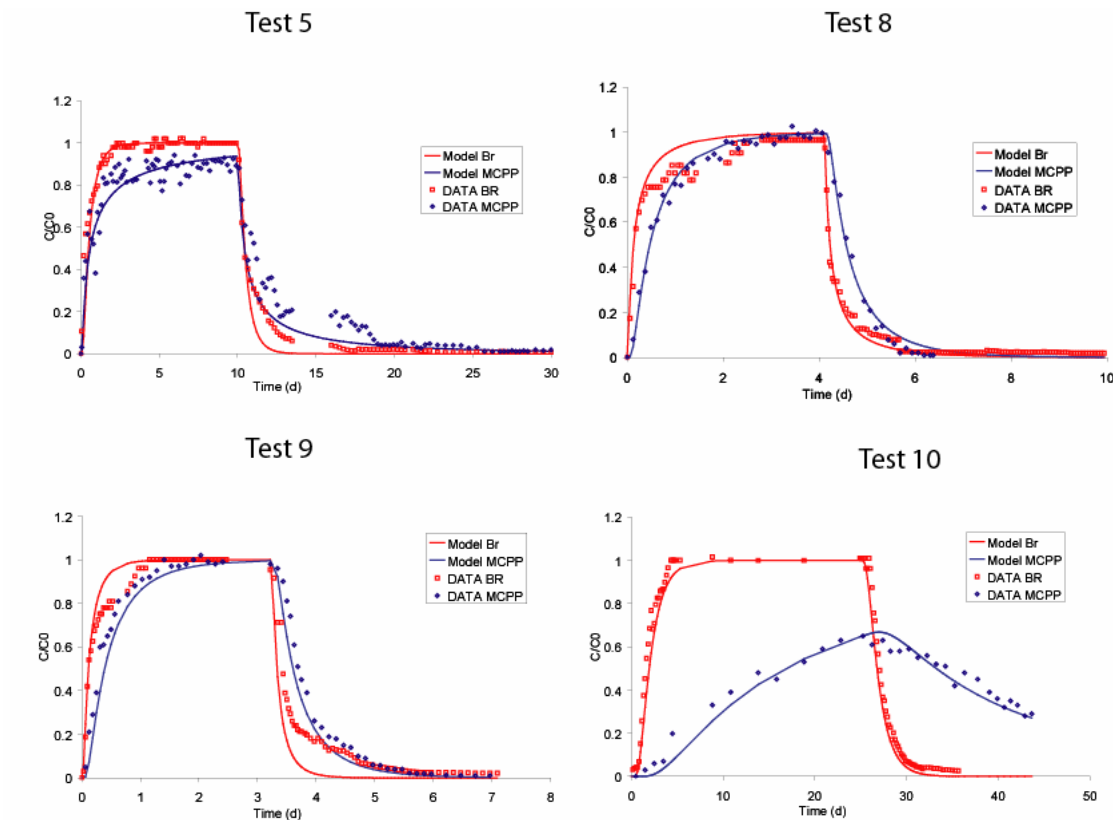


Figure 9.4 Bromide and MCPP breakthrough curves (points) and best fit curves (lines)

Figure 9.4 shows Tests 5, 8 and 9 (all in Mercia Mudstone) in which both bromide and Mecoprop were injected. Test 5 used a different sample from Tests 8 and 9. Test 8 had an increased flow rate relative to Test 9. By the end of the contaminant injection period, the mecoprop concentration in Test 5 had not yet reached $c=1$. To eliminate possible error in measurement of the input concentration, the effect on c was examined when corrected by a multiplicative factor until the mass recovered equalled 100 per cent. The correction required was only five per cent, but was insufficient to raise the maximum normalised concentration to one. The MCPP breakthrough curve in Test 5 is therefore less likely to be evidence of irreversible sorption than simply a reflection of the longer advection time in Test 5. Inclusion of the biocide sodium azide precludes decay as a possible explanation. The model provided a reasonable visual fit to the corrected test 5 data, although it did not flatten off at the end of injection as much as the data.

Retardation of Mecoprop in Mercia Mudstone was calculated from (1) the sorption coefficient according to Equation 9.1, and (2) by fitting to a simple transport model given by a basic 1D advection dispersion equation (Bear, 1972), Equation 9.2.

$$R = 1 + \frac{\rho_b K_d}{\theta} \quad (9.1)$$

where

- ρ_b = soil dry density (M/L^3)
- θ = effective porosity
- K_d = partition coefficient (L^3/M).

$$R \frac{\partial C_r}{\partial t} = D \frac{\partial^2 C_r}{\partial x^2} - v \frac{\partial C_r}{\partial x} \quad (9.2)$$

where

- R = retardation coefficient [-]
- C_r = (volume-averaged) concentration [ML^{-3}]
- x = distance along the column [L]
- D = hydrodynamic dispersion coefficient [L^2T^{-1}]
- v = linear velocity [LT^{-1}].

The retardation, R , in Mercia Mudstone estimated on the basis of the sorption isotherms was 9.95 (assuming the sorption coefficient of Mecoprop on Mercia Mudstone in tap water, $K_d = 1.9 \text{ ml/g}$ (Section 7.4.3), whereas R established by fitting the transport model was between 2.4 and 4.3 (equivalent to K_d ranging from 0.3 ml/g to 0.7 ml/g).

9.4 Oxford Clay column tests

Two tests were carried out with two samples of Oxford Clay, Tests 7 and 10. The samples were prepared as described in Section 8.2. Details of the samples and the conditions used in the triaxial cell apparatus are given in Table 9. 1.

The flow rate in Test 7 was much slower than in the Mercia Mudstone tests, with only around 3.5 ml collected each day (Figure 9.5) after some variation in flow at the start of the test. The bromide concentration rose steadily, reaching 97 per cent of the injection concentration after 30 days (Figure 9.5). Samples were taken for Mecoprop analysis but the concentration was below detection limits ($5 \mu\text{g/l}$) throughout the test.

The transport model (Equation 9.2) was applied to the data from Test 7, but a very poor fit was achieved with the porosity fixed at the measured value. The hydraulic conductivity of Test 7 ($2.3 \times 10^{-10} \text{ m/s}$), showed no sign of the sort of increase that might be expected with significant cell leakage. Some other form of experimental error is suspected and the fitting results are therefore not quoted. No MCPP breakthrough was observed in Test 7, requiring that the modelled retardation would have to exceed 12.

Test 10 provided a more reasonable fit for Oxford Clay than Test 7 and showed a more substantial retardation of MCPP than was observed for the Mercia Mudstone (Figure 9.4). Retardation on the basis of the sorption isotherms was 65.6 (assuming the sorption coefficient of Mecoprop on Oxford Clay in tap water, $K_d = 12.3 \text{ ml/g}$), whereas R established by fitting the transport model was 19.7, equivalent to $K_d = 3.6 \text{ ml/g}$.

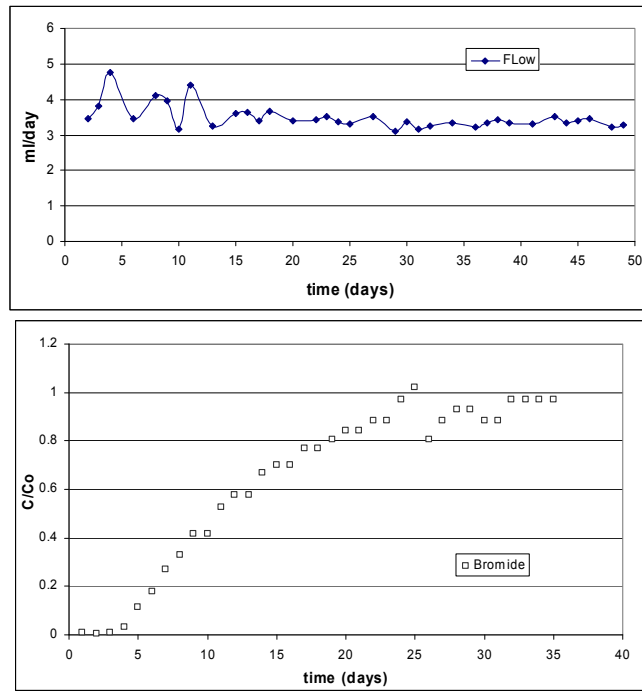


Figure 9.5 Flow rate and breakthrough curve for bromide through a sample of Oxford Clay in Test 7

10 Biodegradation tests

10.1 Introduction

The purpose of the biodegradation tests was to determine the potential for biodegradation of List I substances under conditions which simulated landfill liner environments. Tests were carried out in:

- (A) Synthetic MSW and MSWI leachates with a bacterial seed cultured from leachate from a UK landfill known to contain a range of List I substances (Sections 10.3 and 10.4).
- (B) Real landfill leachate with known potential for dechlorination of tetrachloroethene (Section 10.6).
- (C) Synthetic MSW and MSWI leachates seeded with leachate from Test (B) (Section 10.7).

Because of the large number of variables involved in test A (type of mineral liner material, bacterial seed sources, biological inhibitors, List I substances, leachate type and DOC characteristics), a number of additional control tests were carried out to enable a more comprehensive comparative interpretation of the biodegradation. These tests are discussed in Section 10.5.

10.2 Brief overview of methodology

10.2.1 Experimental methodology

The methodology for the synthetic leachate biodegradation tests (Test A) is given below; details of the control tests and tests using real leachate are given in the relevant sections.

In the synthetic leachate tests, the biodegradation of five List I substance was studied under two distinct metabolic microbial redox conditions (sulphate-reducing and methanogenic). For each condition studied, three different tests were carried out in duplicate:

- biodegradation of the List I substance(s) in the absence of mineral liner materials;
- biodegradation of the List I substance(s) in the presence of mineral liner materials;
- sorption of the List I substance(s) to the mineral liner material while biodegradation was inhibited.

Biodegradation was studied over a period of eight months of incubation using three mixtures of List I substances likely to occur in leachates: (1) Group I, including all five contaminants under investigation (toluene, TCE, TCB, naphthalene and Mecoprop); (2) Group II, including three contaminants (toluene, naphthalene and Mecoprop); and (3) Group III, naphthalene only.

Table 10.1 gives details of the experimental conditions used in the synthetic leachate biodegradation tests. The tests were carried out using 1,000 ml Duran type bottles with appropriate airtight OMNI fittings (Kinesis Ltd) for sampling (Figure 10.1). Each

bottle contained the synthetic leachate simulating methanogenic or sulphate-reducing conditions, bacterial seed, liner material and biological inhibitors as appropriate, and the List I substance or mixture of substances. Bacterial seeds (methanogenic and sulphate-reducing bacteria) for the biodegradation experiments were enriched from a leachate sample from a landfill site in S.E England known to contain List I substances (see Appendix 3 for enrichment procedure). A gas headspace of 80/15/5 (per cent nitrogen/carbon dioxide/hydrogen) was applied above the liquid level of the bottles. The bottles were sealed and stored in an anaerobic cabinet containing the same gas mixture.

Table 10.1 Experimental conditions for biodegradation tests using synthetic leachates

List I	Liner material	Bacterial seed	Biological inhibitors ^a	Test (from Figure 10.2)	Bottle ref (MSW synthetic leachate)	Bottle ref (MSWI synthetic leachate)
Group I (Toluene, TCE, TCB, naphthalene and mecoprop)	London Clay	-	+	3	1A, 1B	18A, 18B
		+	-	2	2A, 2B	19A, 19B
	Oxford Clay	-	+	3	3A, 3B	20A, 20B
		+	-	2	4A, 4B	21A, 21B
	Mercia Mudstone	-	+	3	5A, 5B	22A, 22B
		+	-	2	6A, 6B	23A, 23B
	-	+	-	1	7A, 7B	24A, 24B
Group II (Toluene, naphthalene and mecoprop)	London Clay	-	+	3	8A, 8B	25A, 25B
		+	-	2	9A, 9B	26A, 26B
	Oxford Clay	-	+	3	10A, 10B	27A, 27B
		+	-	2	11A, 11B	28A, 28B
	Mercia Mudstone	-	+	3	12A, 12B	29A, 29B
		+	-	2	13A, 13B	30A, 30B
	-	+	-	1	14A, 14B	31A, 31B
Group III (Naphthalene)	Oxford Clay	-	+	3	15A, 15B	32A, 32B
		+	-	2	16A, 16B	33A, 33B
	-	+	-	1	17A, 17B	34A, 34B

(+) = present, (-) = absent; ^a 20 mM molybdenum and 50 mM 2-bromoethanesulphonic acid

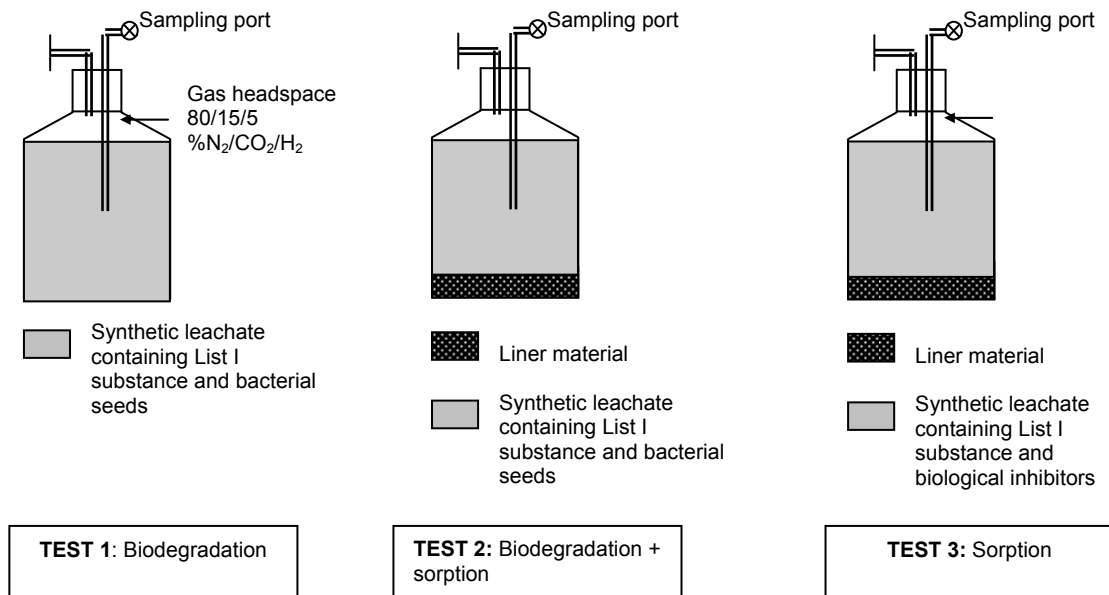


Figure 10.1 Experimental set-up of biodegradation tests using synthetic leachates

10.2.2 Starting conditions

The target concentrations of List I substances (individually or in a mixture) used in the synthetic leachate biodegradation study were within the range of the concentrations used for the batch sorption tests. The presence of the liner material, tannic acid and headspace in the bottles results in losses of the volatile List I substances from the aqueous phase by sorption and volatilisation. The amount of List I substances (which are no longer readily available for biodegradation) expected to be sorbed to the tannic acid and the mineral liners and lost by volatilisation, was calculated. The amount of substances added to the bottles was then adjusted in order to provide approximately the target concentrations (50 per cent more than the theoretical values was added to the bottles to allow for errors, Table 10.2).

The gas headspace present in the biodegradation bottles provides a partitioning phase for the volatile List I substances (TCE, TCB, toluene and naphthalene); once in the gas phase, the List I substances are no longer readily available for biodegradation. A theoretical calculation of the losses of the List I substances by volatilisation was made according to Henry's Law and the Ideal Gas Law (Equations 10.1 to 10.3: Schwarzenbach *et al.*, 1993). The variation with time of the concentration of List I substances during the incubation period is presented as the ratio of the total amount (aqueous + gas) at time t and that at the start of the test $M_{Total,t}/M_{Total,0}$ (see Equation 10.3).

$$P_t = H \times C_{aqueous,t} \quad (10.1)$$

where

- P_t = partial pressure of the List I substance at time t (atm)
- $C_{aqueous,t}$ = aqueous concentration of the List substance at time t (mol/m³)
- H = Henry's law constant for the List I substance (atm.m³/mol)

Toluene = 5.01×10^{-3} atm.m³/mol; TCB 2.20×10^{-3} atm.m³/mol; naphthalene 4.80×10^{-5} atm.m³/mol; TCE 1.61×10^{-2} atm.m³/mol; and Mecoprop 6.65×10^{-7} atm.m³/mol at 25°C (United States Environmental Protection Agency, 2000).

$$M_{gas,t} = P_t \times \frac{V_{headspace,t}}{24.5} \quad (10.2)$$

where

$M_{gas,t}$ = amount of List I substance in the bottle headspace at time t (mol)
 $V_{headspace,t}$ = volume of headspace in the bottle at time t (litres; this increases with time as liquid samples are collected)

One mole of an ideal gas occupies 24.5 litres at 25°C and at atmospheric pressure. P_t is as in Equation 10.1.

$$M_{Total,t} = M_{gas,t} + \frac{C_{aqueous,t}}{V_{leachate,t}} \quad (10.3)$$

where

$M_{Total,t}$ = total amount of List I substance in the bottle at time t (mol)
 $V_{leachate,t}$ = volume of leachate in the bottle at time t (m³; decreases with time as liquid samples are collected)

$M_{gas,t}$ is as in Equation 10.2; $C_{aqueous,t}$ is as in Equation 10.1.

Measured concentrations of the volatile List I substances at the start of the tests are listed in Tables 10.3 to 10.5 for both methanogenic and sulphate-reducing conditions. Concentrations were higher than target concentrations because they were measured before losses by sorption and volatilisation had reached equilibrium conditions.

Table 10.2 Concentration of List I substances for biodegradation tests

List I substance	Target aqueous conc. after sorption/volatilisation (µg/l)	Liner material	Concentration added (ug/l)	Calculated loss by sorption (%) ^a	Calculated loss by volatilisation (%) ^b
Mecoprop	10	London Clay	10.2	2.1	0
		Oxford Clay	15.1	0.8	
		Mercia Mudstone	15.0	0.2	
		-	12.5	-	
Naphthalene	10	London Clay	41.4	75.6	0.2
		Oxford Clay	19.6	23.2	
		Mercia Mudstone	16.0	6.1	
		-	12.5	-	
Toluene	70	London Clay	102.6	11.3	20.5
		Oxford Clay	139.5	4.2	
		Mercia Mudstone	133.7	0.9	
		-	110.1	-	
TCB	20	London Clay	32.8	30.0	9.0
		Oxford Clay	37.3	10.6	
		Mercia Mudstone	33.9	2.5	
		-	27.5	-	
TCE	30	London Clay	95.8	2.9	65.8
		Oxford Clay	136.1	1.1	
		Mercia Mudstone	132.7	0.2	
		-	109.8	-	

$${}^a \text{ \% sorbed} = \frac{C_i - C_{eq}}{C_i} 100$$

where

C_i is the initial aqueous concentration of the List I substance = concentration added to each bottle (ug/l)

C_{eq} is the equilibrium aqueous concentration of the List I substance (ug/l) given by:

$$C_{eq} = \frac{C_i}{K_{oc} f_{oc} M/V + 1}$$

where

K_{oc} is the soil sorption coefficient: toluene 268 ml/g; TCB 718 ml/g; TCE 68 ml/g; naphthalene 1,837 ml/g; mecoprop 49 ml/g (Estimation Programme Interface: SRC, 1988)

f_{oc} is the organic carbon content of the liners (dimensionless)

M is the dry mass of liner material in each bottle (2g)

V is the total volume of liquid in each bottle (1,000 ml)

$${}^b \text{ \% volatilisation} = \frac{C_{gas}}{C_{added}} 100$$

where

C_{added} is the initial aqueous concentration of the List I substance = concentration added to each bottle (ug/l)

C_{gas} is the concentration of List I substance in the gas phase at equilibrium conditions (ug/l), given by:

$$C_{gas} = \frac{C_{added} H}{TR}$$

where

H is Henry's constant (atm.m³mol⁻¹): toluene 5.01E-3; TCB 2.20E-3; TCE 1.61E-2; naphthalene 4.80E-5; Mecoprop 6.65E-7ml/g (Estimation Programme Interface: SRC, 1988)

T is the temperature at which the biodegradation tests are carried out (298K)

R is the universal gas constant (8.21E-5 m³atm.K⁻¹mol⁻¹)

Table 10.3 Concentration of Group I of volatile List I substances measured at start of biodegradation tests

Liner	Exp conditions	Methanogenic conditions				Sulphate-reducing conditions			
		Np ^a (µg/l)	Tol ^b (µg/l)	TCB (µg/l)	TCE (µg/l)	Np (µg/l)	Tol (µg/l)	TCB (µg/l)	TCE (µg/l)
<i>Target</i>		<i>10</i>	<i>70</i>	<i>20</i>	<i>30</i>	<i>10</i>	<i>70</i>	<i>20</i>	<i>30</i>
London Clay	Sorptions	34.2	123.6	29.7	114.8	42.2	73.5	26.3	62.7
		36.4	94.3	28.5	86.8	42.0	67.6	28.2	54.9
London Clay	Sorptions + biodegradation	54.6	96.7	28.3	65.9	48.5	79.5	27.1	74.9
		50.1	122.4	27.0	94.0	51.2	67.5	27.7	59.3
Mercia Mudstone	Sorptions	13.3	110.4	28.9	107.0	19.6	84.9	25.3	77.6
		14.2	108.6	29.9	105.2	18.2	80.3	24.3	71.3
Mercia Mudstone	Sorptions + biodegradation	18.2	120.2	24.6	102.0	18.3	73.1	24.7	79.4
		18.7	117.7	25.4	97.4	16.6	80.6	24.8	76.0
Oxford Clay	Sorptions	15.7	120.8	24.3	117.3	19.6	96.4	22.3	85.3
		16.2	120.3	23.6	117.3	18.1	93.8	20.4	80.5
Oxford Clay	Sorptions + biodegradation	16.9	132.5	20.5	116.4	15.0	98.6	18.0	98.4
		15.9	128.0	20.1	107.0	16.7	105.9	19.8	82.7
-	Biodegradation	15.7	101.4	22.9	77.2	14.9	66.3	17.8	65.8
		16.6	102.5	23.3	78.8	13.2	60.3	18.7	66.4

^a Np = Naphthalene; ^b Tol = Toluene

Table 10.4 Concentration of Group II of volatile List I substances at start of biodegradation tests

Liner	Exp conditions	Methanogenic conditions		Sulphate-reducing Conditions	
		Toluene (µg/l)	Naphthalene (µg/l)	Toluene (µg/l)	Naphthalene (µg/l)
<i>Target</i>		<i>70</i>	<i>10</i>	<i>70</i>	<i>10</i>
London Clay	Sorptions	83.0	34.3	102.5	52.3
		80.0	38.2	99.7	56.9
London Clay	Sorptions + biodegradation	90.8	43.5	97.3	42.6
		87.0	41.8	93.8	46.4
Mercia Mudstone	Sorptions	109.6	13.7	112.3	22.1
		102.4	13.7	112.3	22.1
Mercia Mudstone	Sorptions + biodegradation	106.7	21.7	128.4	18.7
		120.6	16.8	126.0	18.5
Oxford Clay	Sorptions	112.3	14.5	128.3	17.9
		128.0	15.8	126.7	18.1
Oxford Clay	Sorptions + biodegradation	100.1	15.0	132.8	16.7
		113.1	13.8	138.8	16.4
-	Biodegradation	80.4	14.8	110.4	14.8
		88.8	14.0	106.6	15.1

Table 10.5 Concentration of Group III of volatile List I substances at start of biodegradation tests

Liner	Experimental conditions	Methanogenic conditions	Sulphate-reducing conditions
		Naphthalene (µg/l)	Naphthalene (µg/l)
<i>Target</i>		<i>10</i>	<i>10</i>
Oxford Clay	Sorption	15.1	18.70
		15.7	17.45
	Sorption + biodegradation	15.4	17.04
		15.1	16.40
-	Biodegradation	17.4	27.41
		14.2	23.94

10.2.3 Analytical procedures

The volume of leachate required for analysis from each bottle at each sampling event was 24 ml. The number of sampling events was restricted to 10, so that no more than 25 per cent of the original leachate volume was removed. The samples taken were kept in the freezer (for cation, anion, Mecoprop and DOC analysis) or fridge (volatile List I substances analysis) until analysis. Samples were analysed for the List I substance(s) using GC-MS EI full scan to determine contaminant concentrations and identify biodegradation products. In addition to the analyses for the List I substances, the following were measured:

- major cations (NH₄-N; Ca²⁺; Mg²⁺; K⁺; Na⁺);
- major anions (NO₃⁻; NO₂⁻; PO₄³⁻; SO₄²⁻; Cl⁻);
- pH;
- dissolved inorganic carbon.

Anion and cation concentrations in the leachate were determined by liquid chromatography using a Dionex 500 anion/cation suppression chromatograph equipped with a AS14A (4x250 mm) column and an eluent (anions: 1 mM NaHCO₃, 8 mM Na₂CO₃, cations: 20 mM methanesulphonic acid) at a flow rate of 1 ml/min. The dissolved organic and inorganic carbon was determined by dry combustion using a Rosemount Analytical Dohrmann DC-190 Carbon Analyser.

VOC analyses were performed by headspace gas chromatography-mass spectroscopy (GC-MS) using a Thermo Finningan Polaris Q connected to a CombiPal Headspace Autosampler. The GC-MS was equipped with a Restek column Rtx-5MS, 30 m long, 0.25 mm ID, 1.0 µm film under the following conditions: injector temperature 110°C, column flow rate (helium) 1 ml/min and 45°C initial column oven temperature (ramped at 8°C/min to 190°C, hold time two minutes, and then ramped at 15°C/min to a final temperature of 260°C, hold time one minute).

The analysis of volatile List I substances by headspace GC-MS using an internal standard calibration method requires the combined measurement of List I substances and internal standards (1,4-dichlorobenzene; 1,4-dichlorobenzene-d₄ and 1,4-difluorobenzene). The matrix of the biodegradation samples (synthetic leachate or real leachate) is a complex of organic materials which includes DOC (tannic acid in synthetic leachate or natural DOC in real leachate), organic material released from the mineral liner materials during the tests, bacterial biomass and, in some of the

bottles, biological inhibitors. Interaction of the leachate components (matrix) with List I substances and internal standards may influence their behaviour in the headspace analysis due to alterations in their physico-chemical characteristics. This is known as a matrix effect and is an important consideration in sample to sample reproducibility, particularly in the preparation of standards (Kolb and Ettore, 1997). Due to the low stability of the tannic acid used in the synthetic leachates (precipitation occurs in the long term under anaerobic conditions) and the complex composition of real leachates, the preparation of GC-MS standards in a matrix that reproduces, as closely as possible, the matrix of the leachate samples is very difficult. To minimise the matrix effect, GC-MS standards were prepared in synthetic or real leachate with and without biological inhibitors. However, any liner material/DOC/bacterial seed interaction with the List I substances occurring during the incubation period cannot be totally reproduced in GC-MS standards. This is thought to be responsible for the considerable spread in the measured aqueous concentrations of List I substances in synthetic/real leachates (see Figure 10.3).

Mecoprop analysis was carried out at the Environment Agency laboratories in Leeds. In summary the method involved a solid phase extraction (ENV+ Cartridges, 3 ml bed-volume, Argonaut Ltd) to concentrate the sample from the liquid phase. The cartridges were initially conditioned using three washes with ethyl acetate then three with methanol and acidified with 0.5 per cent sulphuric acid (one bed volume). A volume of the sample was passed through the cartridge and the sample components were then eluted with dichloromethane (DCM 2 ml). The eluted DCM was treated with diazomethane (1-2 ml) for at least one hour, such that methyl esters of the components were formed. Diazomethane was prepared using a Diazald generator (Sigma-Aldrich). The DCM and diazomethane were then blown off and the sample taken up in ethyl acetate prior to GC-MS analysis.

Mecoprop analysis, carried out at the Environment Agency laboratories, of samples from the biodegradation tests in MSW synthetic leachate appeared to overestimate concentrations at the start of tests and showed poor repeatability over time for the same test bottle (see Figure 10.3). This was possibly due to:

- Poor preservation of samples: Although the samples were frozen during transport to the laboratory, they may have been affected by contact with oxygen (MSW leachate is unstable in aerobic conditions and precipitates).
- The effect of tannic acid on solid phase extraction: The Environment Agency method was replicated at Southampton University where the tannic acid was found to interfere with the solid/phase extraction of Mecoprop using ENV+ cartridges.

Tests carried out at the University of Southampton indicated that Chromabond Easy cartridges (polar modified polystyrene-divinylbenzene copolymer with a weak ion exchanger) provided a higher extraction rate of Mecoprop from the synthetic leachate. Recovery of mecoprop and dichlorprop by the Easy cartridges was enhanced by the presence of tannic acid; yield of mecoprop and dichlorprop from samples when tannic acid was present was 10 times that of samples from tannic-free leachate tests. Therefore, to improve the sensitivity of the technique, tannic acid was added (1 g/L) to samples taken from tannic-free leachate tests, and to standards prepared in tannic-free leachate.

10.3 Synthetic leachate tests

10.3.1 Synthetic MSW leachate – Group I

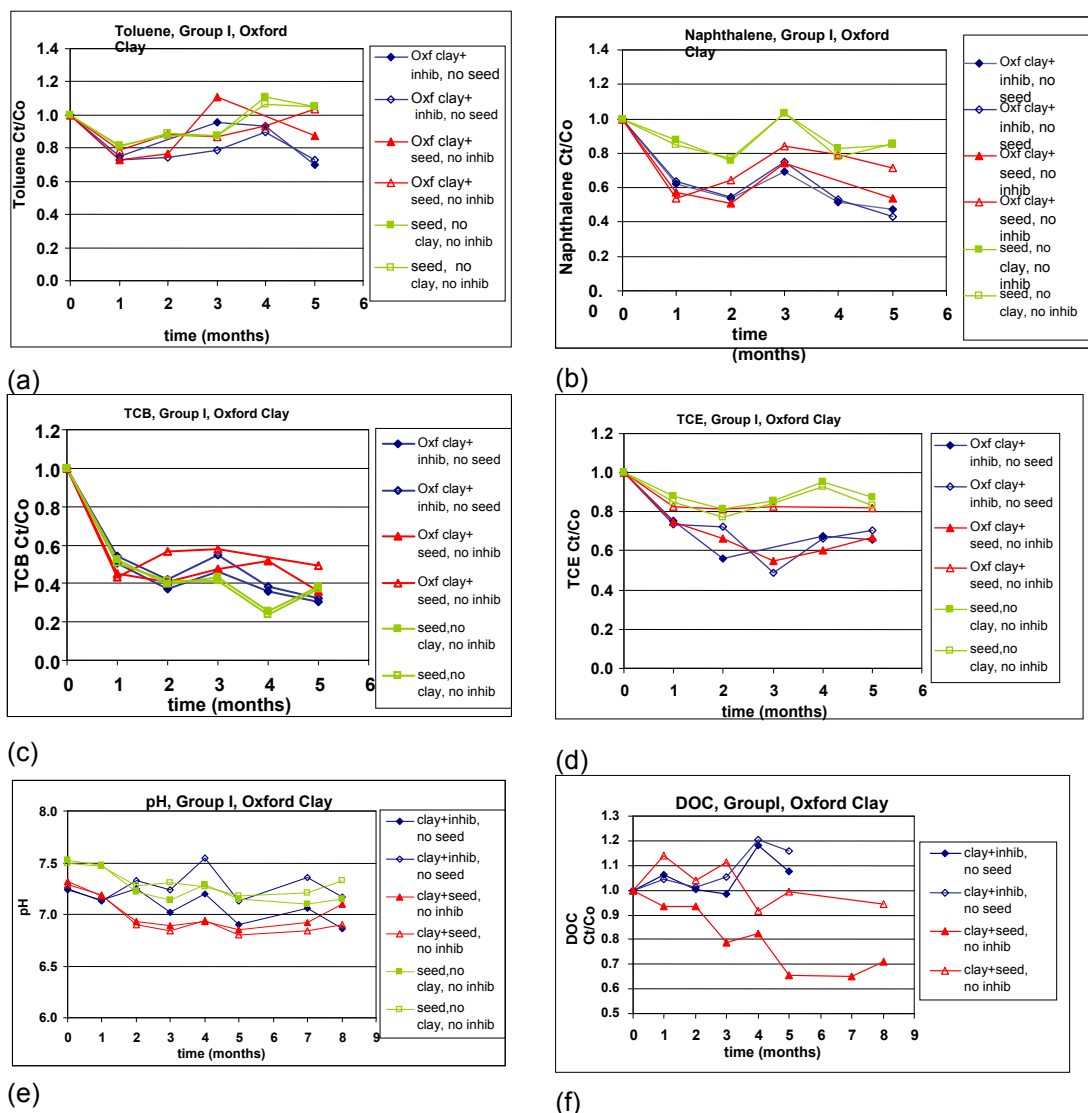
Aqueous concentrations of the five List I substances decreased (from their initial average concentrations of 99 µg/l TCE, 25 µg/l TCB, 114 µg/l toluene, 24 µg/l naphthalene and 35 µg/l Mecoprop) during the incubation period. This was observed in reactors both with and without biological inhibitors, suggesting that the decrease was primarily due to abiotic processes such as sorption to the liner material, bacterial seed or bottle (as seen in the control tests) and/or by deviation from theoretical calculations of losses by volatilisation. Figure 10.2 shows examples of the variation in contaminant concentration during the first five months of the biodegradation tests for reactors with Oxford Clay (where present); results for London Clay and Mercia Mudstone are given in Appendix 4. Common biodegradation products of TBC and TCE from reductive dechlorination processes (such as dichlorobenzenes and dichloroethene; Vogel and McCarty, 1985; and Middeldorp *et al.*, 1997) were not detected in the leachate (GC-MS detection limit one µg/l). Chloride concentration did not vary significantly over the first three months of incubation, although any increase, due to possible reductive dechlorination of TCB and TCE, would not be detectable due to the high chloride background levels in the MSW leachate (1,800-2,500 mg/l).

Measured Mecoprop aqueous concentrations (20-60 µg/l) at the start of the tests were higher than expected (each bottle was initially intended to be spiked with 15 ± 5 µg/l) (Figure 10.3.). Mecoprop aqueous concentrations decreased significantly (particularly in the first two months) in bottles both with and without biological inhibitors to levels of 10-15 µg/l after 10 months of incubation. This may be due to abiotic processes (sorption of Mecoprop to liner material, bacterial seed or bottle components), biodegradation of Mecoprop under redox conditions other than methanogenic or sulphate-reducing (which are theoretically totally inhibited by the specific biocides used) or due to errors/artifacts in the determination of initial Mecoprop concentrations (Section 10.2.3).

The pH in the bottles containing mineral liner material and bacterial seed and without inhibitors decreased slowly with time (Figure 10.2e). This may be due to CO₂ dissolution in the leachate as H₂CO₃, HCO₃⁻ and CO₃²⁻. Sources of CO₂ in the headspace include the trace concentration in the anaerobic gas mixture (five per cent) and biogas formed from biodegradation reactions. Biogas was found to be produced in the bottles containing mineral liner materials and seed and without inhibitors after five to ten months of incubation (detected by the increase in pressure inside the bottles during continuous sampling of leachate). To minimise the explosion hazard caused by the increasing pressure measured inside the bottles (see Table 10.6), venting of the bottles to atmospheric pressure was carried out (after 10 months of incubation) and the biogas composition determined (Table 10.6). The biogas was found to consist mainly of methane (above 40 per cent), carbon dioxide (above 15 per cent) and gases from the anaerobic gas mixture (nitrogen and traces of hydrogen). In the bottles containing mineral liner material and inhibitors but no seed, and in the bottles containing seed but no solid or inhibitors, biogas production was not observed (detected by negative pressure inside the bottles).

Production of biogas coincided with a 30 per cent decrease in DOC (Figure 10.6) suggesting that methanogenic bacteria converted DOC to methane and carbon dioxide. Biogas production occurred first, and in greater amounts, in the bottles containing London and Oxford Clays (after five months of incubation) followed by the bottles containing Mercia Mudstone (after 10 months of incubation) suggesting that

the mineral liner materials not only provide an attachment medium for the bacteria but may also act as a DOC source. Tannic acid (around 540 mg/l), methanol (added to the leachate as a solvent for Mecoprop and naphthalene) and 2-bromoethanesulphonic acid (biological inhibitor, where present) contributed to the DOC content of MSW synthetic leachate in the biodegradation bottles. DOC in the bottles containing clay and seed (especially Oxford and London Clays) and without biological inhibitors decreased with time, suggesting that biodegradation of the DOC might be occurring. This might depend on (among other factors) the release of organic material from the mineral liner materials, sorption/ desorption of tannic acid by the solid matrix, amount of biomass produced from endogenous metabolism, and the biogas production rate. Addition of 50 mM 2-bromoethane sulphonic acid to the leachate resulted in a change in the colour of the leachate (from yellow due to the presence of tannic acid to red) suggesting that the inhibitor interacted with the tannic acid. This interaction may have altered the properties of the tannic acid and its affinity for the mineral liner materials and the List substances.



Oxford Clay where indicated. Effect of volatilisation into headspace of bottles was taken into account in calculating relative concentrations of toluene, naphthalene, TCB, and TCE.

Figure 10.2 Variation in (a) toluene, (b) naphthalene, (c) TCB, (d) TCE, (e) pH concentration, and (f) DOC in Group I biodegradation tests.

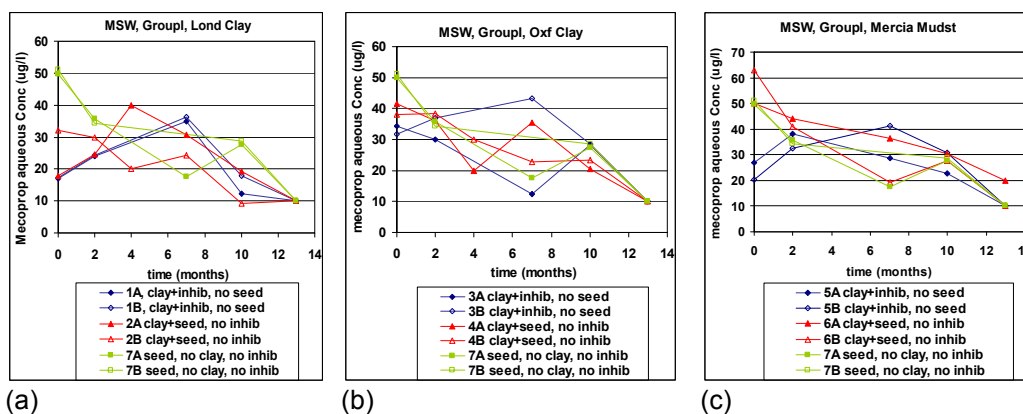


Figure 10.3 Variation with time of Mecoprop aqueous concentration in Group I biodegradation: (a) London Clay, (b) Oxford Clay and (c) Mercia Mudstone (where indicated)

Table 10.6 Biogas production in biodegradation tests of Group I of List I substances in synthetic MSW leachate

Group I	Biogas (ml) _{a,d}	Biogas composition ^d		Internal pressure (kPa) ^c
		CH ₄ (%) ^b	CO ₂ (%) ^b	
Liner material and inhibitors, no seed	-	-	-	Negative pressure
Seed, no liner material, no inhibitors	-	-	-	Negative pressure
Liner material and seed, no inhibitors				
London Clay	286	60.6	15.5	>200
London Clay	132	49.1	22.1	155.5
Mercia Mudstone	44	44.3	18.6	126.5
Mercia Mudstone	5	43.4	16.7	118.6
Oxford Clay	6	62.5	17.5	126.1
Oxford Clay	88	50.3	18.5	143.6

^a Measured by releasing the pressure inside each bottle into a 20 ml plastic syringe until the pressure inside the bottle was approximately atmospheric pressure.

^b Measured by gas chromatography using a Varian CP-3800 GC equipped with a TCD detector and two columns 1 m by 1/8 inches OD: Haysep C column (80-100 mesh) and a Porapak column (molecular sieve 13X, 60-80 mesh) under the following conditions: 50°C isothermal back-flush mode and argon carrier gas.

^c Measured using an Absolute Pressure Meter Digitron 2025P (measuring range 0-200 kPa).

^d After 10 months of incubation.

10.3.2 Synthetic MSW leachate – Group II

The average aqueous concentrations of the three List I substances at the start of the tests was measured at 100 µg/l toluene, 22 µg/l naphthalene and 29 µg/l Mecoprop). The variation with time of the concentration of toluene was not significant, suggesting that toluene was recalcitrant over the first eight months of incubation (Figure 10.4). Apart from the bottles containing Oxford Clay, the naphthalene concentration was found to be predominantly stable, suggesting that naphthalene was also recalcitrant over the first eight months of incubation (as observed in the Group I tests). The decrease in naphthalene concentration observed in the bottles containing Oxford Clay (both with and without biological inhibitors) suggests that abiotic processes may have been occurring, probably long-term sorption to Oxford Clay (Figure 10.4).

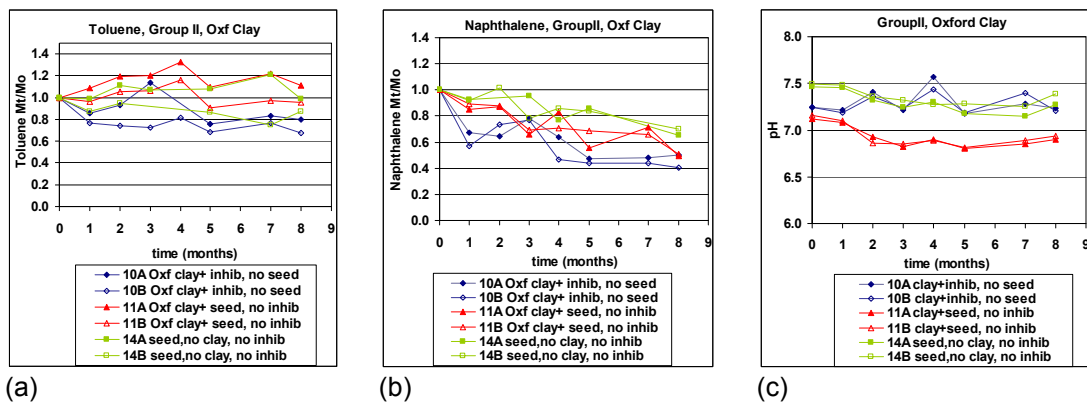


Figure 10.4 Variation with time of (a) toluene and (b) naphthalene relative concentrations and (c) pH in Group II biodegradation tests: Oxford Clay present where indicated

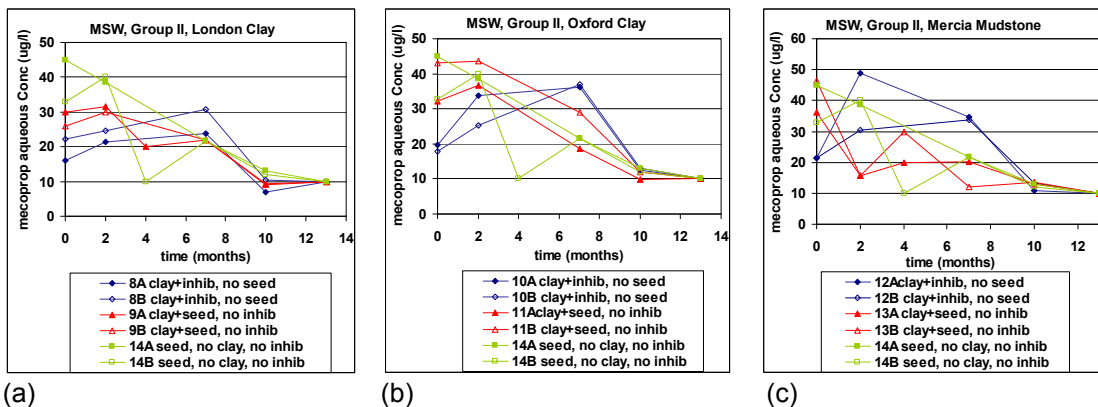


Figure 10.5 Variation with time of Mecoprop aqueous concentration in Group II biodegradation tests: (a) London Clay, (b) Oxford Clay and (c) Mercia Mudstone

As observed in the biodegradation tests of the Group I substances, measured Mecoprop aqueous concentrations at the start of the tests were again higher than the anticipated spike values ($15 \pm 5 \mu\text{g/l}$) and again were observed to decrease to $10\text{-}15 \mu\text{g/l}$ after 10 months of incubation in the bottles both with and without biological inhibitors (Figure 10.5). Possible causes for the decrease and variability in Mecoprop aqueous concentrations are discussed in Section 10.2.3.

As observed in the biodegradation of the Group I of List I substances, biogas was produced in the bottles containing mineral liner material and seed and without inhibitors after five to ten months of incubation (Table 10.7). The biogas consisted mainly of methane (above 40 per cent), carbon dioxide (above 15 per cent) and gases from the anaerobic gas mixture (nitrogen and traces of hydrogen).

Table 10.7 Biogas production in biodegradation tests of Group II substances in synthetic MSW leachate

Group II	Biogas (ml) ^a	Biogas composition		Internal pressure (kPa) ^c
		CH ₄ (%) ^b	CO ₂ (%) ^b	
Liner material and inhibitors, no seed	-	-	-	Negative pressure
Seed, no liner material, no inhibitors	-	-	-	Negative pressure
Liner material and seed, no inhibitors				
London Clay	330	60.2	16.5	>200
London Clay	372	59.3	15.8	>200
Oxford Clay	66	46.4	18.0	134.0
Oxford Clay	22	41.0	22.9	119.2
Mercia Mudstone	-	-	-	Negative pressure
Mercia Mudstone	12	39.9	24.5	101.4

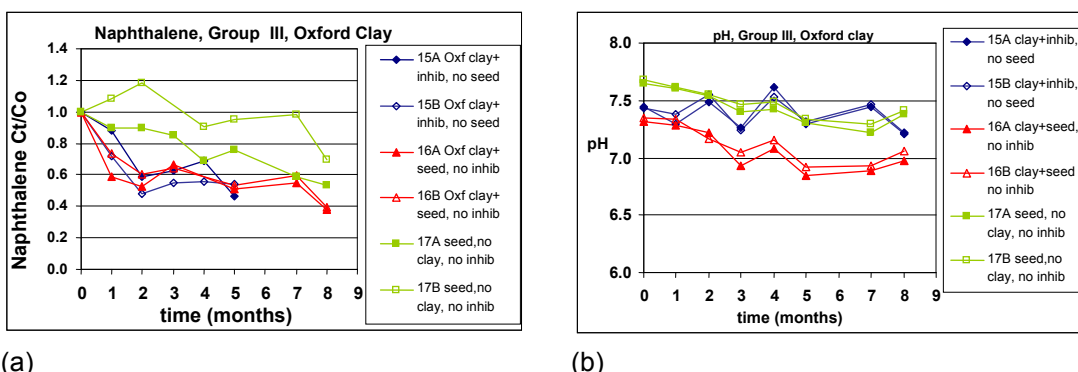
^a Measured by releasing the pressure inside each bottle into a 20 ml plastic syringe until the pressure inside the bottle was approximately atmospheric pressure.

^b Measured by gas chromatography using a Varian CP-3800 GC equipped with a TCD detector and two columns 1 m by 1/8 inches OD: Haysep C column (80-100 mesh) and a Porapak column (molecular sieve 13X, 60-80 mesh) under the following conditions: 50°C isothermal back-flush mode and argon carrier gas.

^c Measured using an Absolute Pressure Meter Digatron 2025P (measuring range 0-200 kPa).

10.3.3 Synthetic MSW leachate – Group III

Naphthalene concentration decreased slowly with time (from its initial average aqueous concentration of $15.5 \mu\text{g/l}$) in all of the bottles but more significantly in the ones containing Oxford Clay (both with and without biological inhibitors) (Figure 10.6). This could have been due to abiotic processes such as sorption to the solid matrix, bottle and bacterial seed. Potential losses to bottle components are discussed in Section 10.5.3. As observed for the Groups I and II of List I substances, the pH in the bottles containing liner material and seed and without inhibitors slowly decreased with time.



(a) (b)
Figure 10.6 Synthetic MSW leachate Group III biodegradation tests: variation in (a) naphthalene concentration, and (b) pH. The effect of volatilisation into the headspace of the bottles was taken into account in calculating relative concentrations of naphthalene. Oxford Clay where indicated.

As observed in the biodegradation of the Groups I and II of List I substances, biogas was produced in the bottles containing liner material and seed and without inhibitors after five to ten months of incubation (Table 10.8). The biogas consisted mainly of methane (above 50 per cent), carbon dioxide (above 20 per cent) and gases from the anaerobic gas mixture (nitrogen and traces of hydrogen).

Table 10.8 Biogas production in biodegradation tests of Group III substances in synthetic MSW leachate

Group III	Biogas (ml) ^a	Biogas composition		Internal pressure (kPa) ^c
		CH ₄ (%) ^b	CO ₂ (%) ^b	
Liner material and inhibitors, no seed	-	-	-	Negative pressure
Seed, no liner material, no inhibitors	-	-	-	Negative pressure
Liner material and seed, no inhibitors				
Oxford Clay	220	58.1	23.0	>200
Oxford Clay	66	52.3	23.9	138.7

^a Measured by releasing the pressure inside each bottle into a 20 ml plastic syringe until the pressure inside the bottle was approximately atmospheric pressure.

^b Measured by gas chromatography using a Varian CP-3800 GC equipped with a TCD detector and two columns 1 m by 1/8 inches OD: Haysep C column (80-100 mesh) and a Porapak column (molecular sieve 13X, 60-80 mesh) under the following conditions: 50°C isothermal back-flush mode and argon carrier gas.

^c Measured using an Absolute Pressure Meter Digitron 2025P (measuring range 0-200 kPa).

10.3.4 Synthetic MSW leachate – Summary of results

Results of the biodegradation tests of List I substances in MSW synthetic leachate indicate that:

- The five List I substances appear to be recalcitrant to biodegradation over an incubation period of eight months. Common biodegradation products of TBC and TCE from reductive dechlorination processes (such as dichlorobenzenes and dichloroethene; Vogel and McCarty, 1985; and Middeldorp *et al.*, 1997) were not detected in the leachate (less than one µg/l).
- The observed decrease in contaminant concentrations in synthetic leachate (particularly TCB, naphthalene and Mecoprop) is most likely associated with abiotic processes such as sorption to the liner material, the bacterial seed or bottle. Losses to bottle components are discussed in Section 10.5.3.
- Biogas, comprised mainly of methane and carbon dioxide, was produced in the bottles with liner material and seed but no inhibitors, suggesting that there is an active methanogenic population and that the liner materials provide an attachment medium for the bacteria.

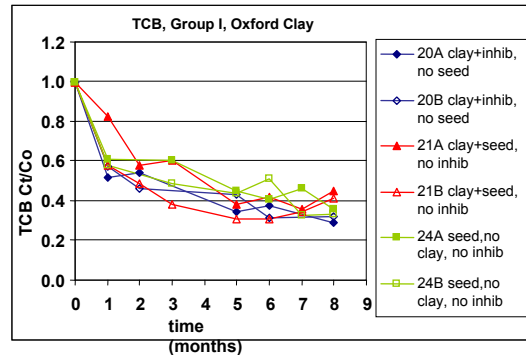
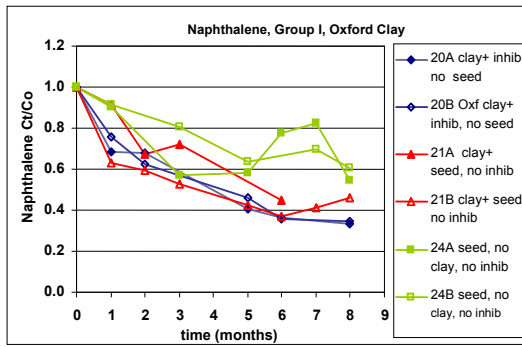
10.4 Synthetic MSWI leachate

10.4.1 Synthetic MSWI leachate – Group I

Figure 10.7 shows results for Group I tests with Oxford Clay; the results for the other London Clay and Mercia Mudstone are contained in Appendix 5. The average aqueous concentrations of the five List I substances at the start of the tests was measured at 74 µg/l TCE, 23 µg/l TCB, 81 µg/l toluene, 25 µg/l naphthalene and 12 µg/l Mecoprop. In the majority of the tests, there was no significant difference in concentrations for individual contaminants between the tests with and without inhibitors over the entire eight months of the incubation period. The decrease in concentrations of naphthalene and TCB (Figure 10.7) could be due to abiotic processes such as long-term sorption to the bacterial seed and/or losses to bottle structural components. Losses to bottle components are discussed in Section 10.5.3. Common biodegradation products of TCB from reductive dechlorination processes (dichlorobenzenes and chlorobenzene: see Middeldorp *et al.*, 1997) were not found in any bottles (GC-MS detection limit 0.1 µg/l).

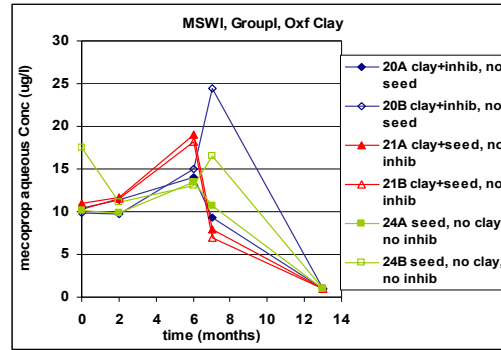
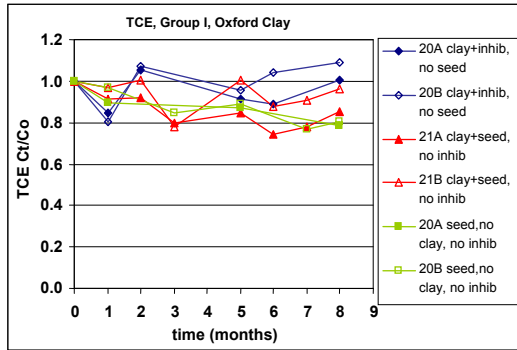
The TCE concentration did not vary significantly over the first eight months of incubation both with and without biological inhibitors (Figure 10.7). This suggests that attenuation of TCE is not occurring. Common biodegradation products of TCE from reductive dechlorination processes (dichloroethene and vinyl chloride: see Vogel and McCarty, 1985) were not found in any test bottles (GC-MS detection limit 0.1 µg/l).

Measured Mecoprop aqueous concentrations at the start of the tests were, in this instance, within the expected range (each bottle was initially spiked with 15 ± 5 µg/l). Mecoprop aqueous concentrations decreased to below the analytical detection limit (one µg/l) in the bottles both with and without biological inhibitors, suggesting that biodegradation processes were not involved or that biodegradation had occurred under redox conditions other than methanogenic or sulphate-reducing (which are theoretically totally inhibited by the specific biocides used).



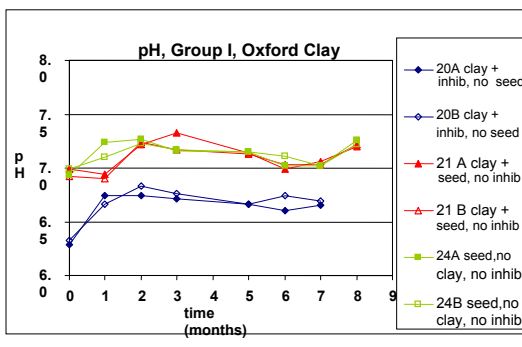
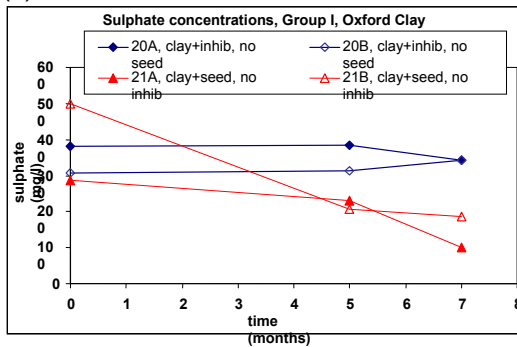
(a)

(b)



(c)

(d)

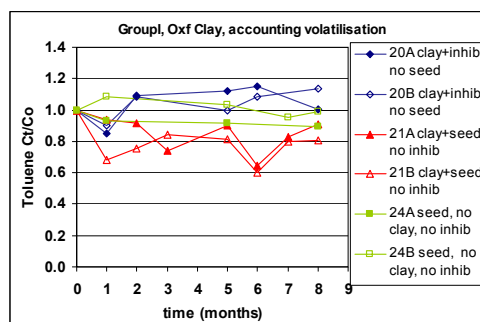
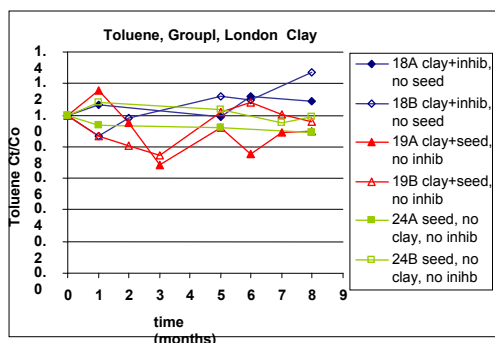


(e)

(f)

The effect of volatilisation into the headspace of the bottles was taken into account in calculating relative concentrations of naphthalene, TCB and TCE.

Figure 10.7 Synthetic MSWI leachate Group I biodegradations tests: (a) naphthalene, (b) TCB, (c) TCE, (d) Mecoprop, (e) sulphate, and (f) pH



(a) (b)
The effect of volatilisation into the headspace of the bottles was taken into account in calculating relative toluene concentrations.

Figure 10.8 Toluene concentrations in synthetic MSWI leachate Group I biodegradations tests on London and Oxford Clays

The exception to this general trend was toluene in the presence of London and Oxford Clays without inhibitors. In the bottles containing liner material and seed, but no inhibitors, toluene levels decreased to 10-20 per cent of initial concentrations after two months of incubation (Figure 10.8). This suggests that sorption of toluene to the solid matrix and/or biodegradation had occurred. A dark coat covering the London Clay was observed after five months of incubation (Figure 10.9). Darkening of the London Clay was thought to be due to precipitation of the iron present in the clay (six per cent Fe) as insoluble complexes by sulphate-reducing bacteria and/or iron-reducing bacteria. This dark coating might affect sorption of the List I substances to the clay.

In the tests containing Oxford Clay and seed but no inhibitors, sulphate levels in the synthetic leachate decreased by 75-80 per cent; in the tests without clay, sulphate concentrations decreased by around 10 per cent. No significant variation in sulphate concentration was observed in the presence of inhibitors (Figure 10.4). This suggests that sulphate in the synthetic leachate was used by sulphate-reducing bacteria. The pH of the MSWI leachate decreased from 7 to 6.5 in the bottles containing biological inhibitors due to the presence of bromoethane sulphonic acid (50 mM).



(a) (b)
(a) London Clay air dried and ground prior to use in the biodegradation tests; (b) dark coating after 10 months incubation

Figure 10.9 Dark coating covering London Clay in Synthetic MSWI leachate biodegradation tests

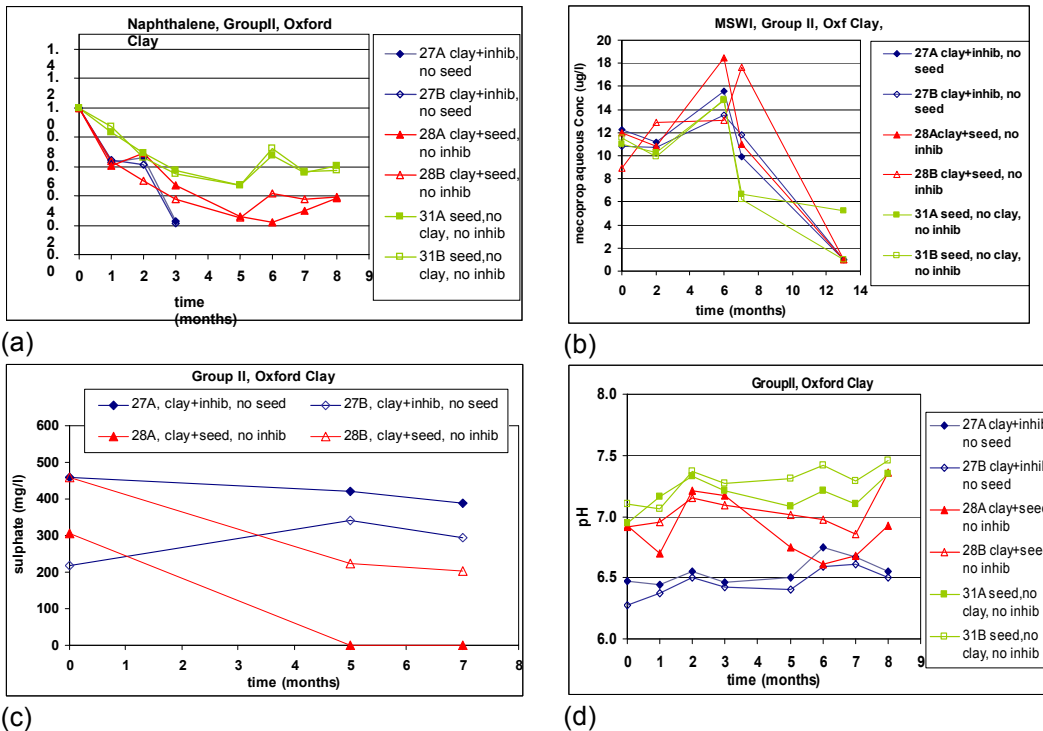
10.4.2 Synthetic MSWI leachate – Group II

The average aqueous concentrations of the three List I substances at the start of the tests was measured at 115 µg/l toluene, 27 µg/l naphthalene and 11 µg/l Mecoprop. There was no significant difference between the tests with and without inhibitors. The toluene aqueous concentration decreased to about 20 per cent of its initial concentration in the leachate both with and without biological inhibitors. This may have been due to abiotic processes (sorption to the liner material and bacterial seed), losses to the bottle and/or deviation from theoretical calculations of losses by volatilisation. Losses to bottle components are discussed in Section 10.5.3.

Apart from the bottles containing Oxford Clay, the naphthalene total concentration was found to decrease to about 60 per cent of its initial concentration. Given that this decrease was also found in the bottles containing biological inhibitors and in the bottles without liner material, it may be due to abiotic processes, such as long-term sorption to the bacterial seed and/or losses to the bottle components. In the bottles containing Oxford Clay (Figure 10.10) naphthalene was found to decrease to about 30 per cent of its initial concentration. Previous studies had shown that sorption to Oxford Clay should account for 86 per cent reduction in the naphthalene aqueous concentration.

As observed in the biodegradation of Group I of List I substances, Mecoprop aqueous concentrations decreased from around 15 µg/l to below the detection limit (one µg/l) in bottles with and without biological inhibitors (except bottle 31A), suggesting that biodegradation processes were not involved (sorption to the solid matrix, seed or bottle) or that biodegradation occurred under redox conditions other than methanogenic or sulphate reducing (which are theoretically totally inhibited by the specific biocides used).

Sulphate concentrations in the synthetic leachate decreased (by 55 to 99 per cent) in all the tests with and without mineral liner material, where no inhibitors were added. This decrease was more significant in the bottles with liner material present. The pH of the MSWI leachate was lower in the bottles containing biological inhibitors due to the presence of bromoethane sulphonic acid (50 mM).

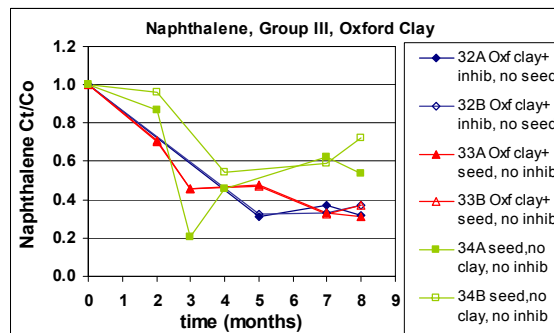


(a) (b) (c) (d)
The effect of volatilisation into the headspace of the bottles was taken into account in calculating relative concentrations of naphthalene. (a) Naphthalene, (b) Mecoprop, (c) sulphate and (d) pH.

Figure 10.10 Synthetic MSWI leachate Group II biodegradations tests

10.4.3 Synthetic MSWI leachate – Group III

The naphthalene concentration was observed to slowly decrease with time (from its initial average aqueous concentration of 20 µg/l) in all bottles but more significantly in the ones containing Oxford Clay (both with and without biological inhibitors) (Figure 10.11). This could be due to biodegradation and/or abiotic processes such as sorption to the liner material, bottle and bacterial seed. Losses to bottle components are discussed in Section 10.5.3. The pH of the MSWI leachate was lower in the bottles containing biological inhibitors due to the presence of bromoethane sulphonic acid (50 mM).



The effect of volatilisation into the headspace of the bottles was taken into account in calculating relative concentrations of Naphthalene.

Figure 10.11 Naphthalene concentration in Group III biodegradations tests in MSWI leachate

10.4.4 Synthetic MSWI leachate – Summary of results

The results of the biodegradation tests of List I substances in MSWI synthetic leachate indicate that:

- As observed in the biodegradation tests using MSW synthetic leachate, the five List I substances appear to be recalcitrant to biodegradation in synthetic MSWI leachate over an incubation period of eight months. Common biodegradation products of TBC and TCE from reductive dechlorination processes (such as dichlorobenzenes and dichloroethene; Vogel and McCarty, 1985; and Middeldorp *et al.*, 1997) were not detected in the leachate (under one µg/l).
- The observed decrease in contaminant concentrations in the synthetic leachate (particularly TCB, naphthalene and Mecoprop) is most likely associated with abiotic processes such as sorption to the liner material, the bacterial seed or bottle. Losses to bottle components are discussed in Section 10.5.3.
- Sulphate concentrations in the synthetic leachate decreased in the bottles where no biological inhibitors were added, but most significantly in the bottles containing liner materials. This suggests the presence of an active sulphate-reducing bacterial population and that the liner materials provide an attachment medium for the bacteria.

10.5 Biodegradation control tests

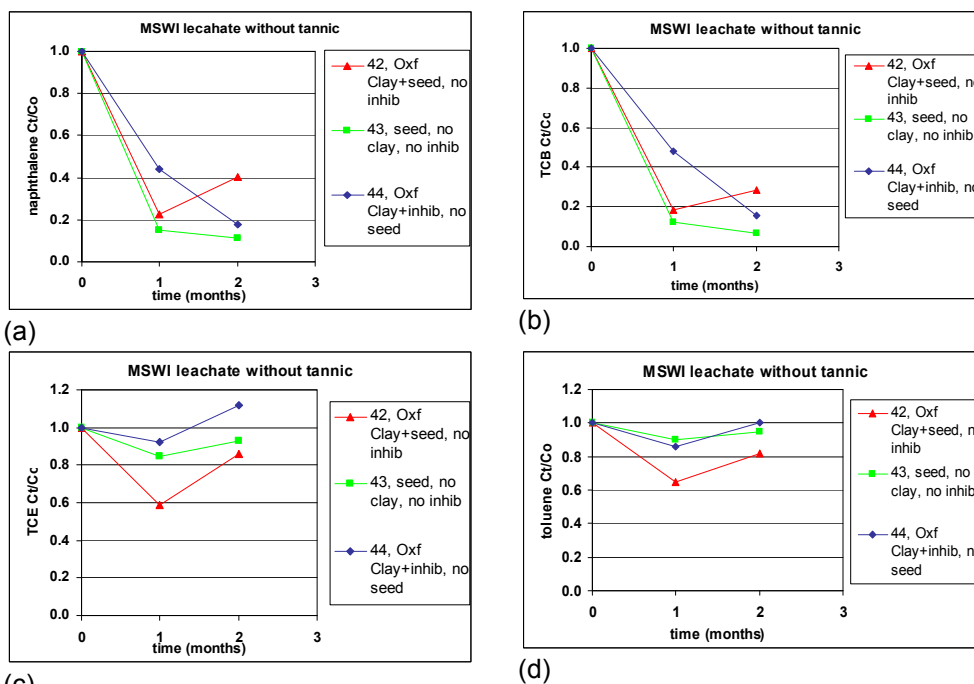
10.5.1 Introduction

The three types of biodegradation tests carried out in this study were designed by varying five parameters (the presence of tannic acid, List I substances, bacterial seed, liner materials and biological inhibitors). In some tests, variation in the concentration of List I substances could not be attributed to a single process due to the high number of parameters under investigation (such as biodegradation; sorption to solid matrix; sorption to the bacterial seed; sorption to the bottle components). Additional controls were set up to evaluate:

- the effect of the presence of tannic acid in synthetic leachate on the biodegradation/sorption of the List I substances;
- the sorption of List I substances to the bottle components (glass, PTFE tube and cap).

10.5.2 Biodegradation of List I substances in the absence of tannic acid

The results indicate that the variation with time of contaminant aqueous concentration is similar in MSWI leachate with and without tannic acid (Figure 10.12). This suggests that tannic acid at a concentration of 0.5 g/l did not affect contaminant sorption/biodegradation processes or contaminant losses to bottle components.



(a) Naphthalene, (b) TCB, (c) TCE, and (d) toluene. The effect of volatilisation into the headspace of the bottles was taken into account in calculating relative concentrations of naphthalene, TCB, TCE and toluene.

Figure 10.12 Biodegradation control tests in absence of tannic acid

10.5.3 Sorption of List I substances to the bottle components

Control tests were set up to investigate if the observed decrease in contaminant concentrations in the leachate could be attributed to sorption to the bottle components (glass and PTFE cap, sampling tube and valves). The tests were carried out in one-litre Duran type bottles, each containing Milli-Q water (one litre), biological inhibitors (20 mM molybdenum, bromoethane sulphonic acid 50 mM, HgCl_2 5 mg/l, NaN_3 100 mg/l) and the five List I substances. A gas headspace of 90/5/5 (per cent nitrogen/carbon dioxide/hydrogen) was applied above the liquid level of the bottles. The bottles were then sealed and stored in an anaerobic cabinet (Woflabs Model A Vinyl cabinet incorporating oxygen and hydrogen measurement and carbon dioxide controller) containing the same gas mixture. The bottles were sealed using three different types of caps: (i) PTFE cap with airtight OMNI fittings for sampling (the same as those used in the biodegradation tests with synthetic leachates); (ii) PTFE sheet; and (iii) aluminium sheet. A silylation reagent (dimethyldichlorosilane) was added to some of the bottles to deactivate the glass and therefore minimise the potential interaction between the glass and List I substances (Table 10.9).

Table 10.9 Control tests to assess sorption of List I substances to bottle components

Bottle	Cap	Silylation reagent	Aim of test	Average starting aqueous conc. (µg/l)
35A, 35B	PTFE with sampling valves	No	Evaluate losses to glass+PTFE cap+sampling valves	TCE (78.4), TCB (25.9), toluene (89.9) and naphthalene (13.2)
Ctr1	PTFE with sampling valves	Yes	Evaluate losses to sampling valves +PTFE cap	TCE (88.4), TCB (28.5), toluene (98.7) and naphthalene (11.3)
Ctr2	PTFE sheet	Yes	Evaluate losses to PTFE sheet	TCE (84.7), TCB (28.9), toluene (97.7) and naphthalene (12.7)
Ctr3	PTFE sheet	No	Evaluate losses to glass+PTFE sheet	TCE (72.7), TCB (31.2), toluene (86.7) and naphthalene (15.3)
Ctr4	Aluminium sheet	No	Evaluate losses to glass+aluminium sheet	TCE (61.2), TCB (29.4), toluene (76.6) and naphthalene (14.1)

The results indicate a decrease in total contaminant concentration of one to 38 per cent over a two-month incubation period (for starting aqueous contaminant concentrations given in Table 10.9). This decrease was in general more significant in the bottles with the PTFE cap and airtight OMNI fittings (Bottles 35A, 35B and Ctr1), suggesting that the contaminants sorbed to the PTFE cap and/or sampling tube (Figure 10.13 and Table 10.10). TCB and naphthalene appear to be the contaminants most affected by losses to bottle components. This is consistent with the observed decrease in total naphthalene and TCB concentrations in the bottles with and without biological inhibitors (see Figure 10.2).

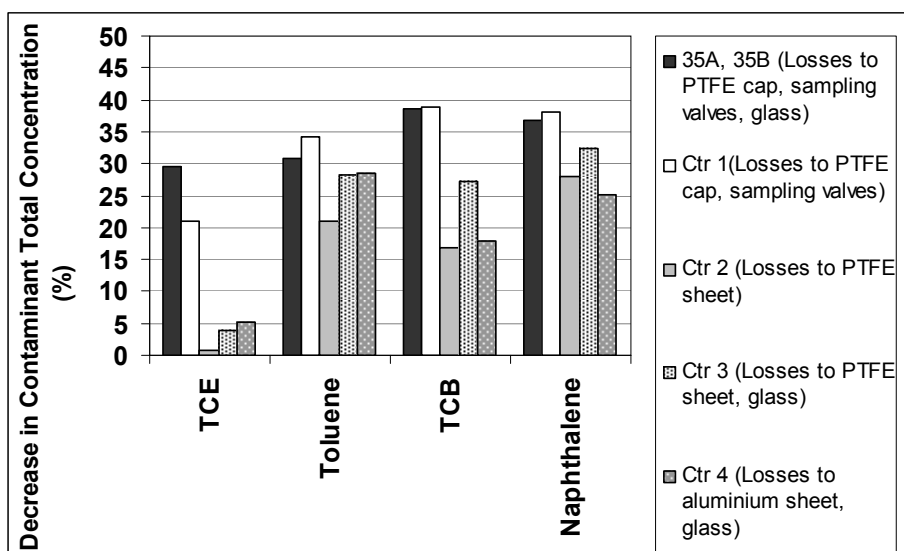


Figure 10.13 Loss of List I substances from aqueous solution in biodegradation control tests

Table 10.10 Loss of List I substances from aqueous solution in biodegradation control tests

Bottle	List I	Initial concentration Ci (ug/l)	Final conc. Cf (µg/l)^a	% List I lost from aqueous solution
35A	TCE	80.70	49.47	38.7
35B		82.82	51.04	38.4
Ctr1		88.36	70.33	20.4
Ctr2		84.68	84.58	0.12
Ctr3		72.73	70.41	3.19
Ctr4		61.19	58.47	4.4
35A		Toluene	88.95	48.25
35B	90.54		52.75	41.7
Ctr1	98.66		66.22	32.9
Ctr2	97.67		78.51	19.6
Ctr3	86.75		63.44	26.9
Ctr4	76.55		55.69	27.2
35A	TCB		16.0	8.31
35B		15.5	8.99	41.8
Ctr1		28.49	17.63	38.1
Ctr2		28.88	24.36	15.7
Ctr3		31.21	22.98	26.4
Ctr4		29.40	24.47	16.8
35A		Naphthalene	13.0	7.06
35B	12.7		7.12	44.1
Ctr1	11.76		7.11	39.5
Ctr2	12.66		9.25	26.9
Ctr3	15.86		9.16	42.3
Ctr4	14.05		10.65	24.2

a- After eight months for bottles 35A and 35B and two months for control bottles 1, 2, 3 and 4 (TCB, TCE, toluene and naphthalene)

10.6 Biodegradation tests with real landfill leachate

10.6.1 Introduction

As the tests with synthetic leachate demonstrated no firm evidence of biodegradation of List I substances over eight months of the test period, a decision was taken to set up a test to evaluate biodegradation in real landfill leachate instead of synthetic leachates. Leachate from a landfill site in the UK previously shown to support biodegradation of tetrachloroethene (research carried out at Newcastle University by Dr Hossain and Dr Sallis) was used.

10.6.2 Experimental methodology

Prior to setting up the biodegradation tests, the leachate was characterised with respect to carbon content and the major anions (Table 10.11). The leachate was dark brown, frothy and with no strong smell. Tests were set up to replicate experimental conditions previously used at Newcastle University, that is, one-litre Duran type bottles with appropriate airtight OMNI fittings for sampling. Each bottle contained the leachate, the liner material (Oxford Clay or Mercia Mudstone) and the List I substance or a mixture of substances (Table 10.12.). A mixture of biological inhibitors was added to some of the bottles, including 50 mM 2-bromoethane sulphonic acid (specific inhibitor for methanogenic bacteria), 20 mM ammonium molybdate (specific inhibitor for sulphate-reducing bacteria) and 5 mg/l mercuric chloride (non-specific inhibitor). In addition, bottles were set up with sand, instead of the liner material, to replicate the tests carried out at Newcastle University. Prior to use, the sand (1.18 to 0.6 mm grain size; David Ball Group PLC) was thoroughly washed in distilled water and dried at 70°C. A gas headspace of 90/5/5 (per cent nitrogen/carbon dioxide/hydrogen) was applied above the liquid level of the bottles. The bottles were then sealed and stored in an anaerobic cabinet (Wolflabs Model A Vinyl cabinet incorporating oxygen and hydrogen measurement and carbon dioxide controller) containing the same gas mixture at an incubation temperature of 20°C. Samples were collected every 10-15 days of incubation and analysed for the List I substances being investigated, using GC-MS EI full scan to identify biodegradation products. In addition to List I substance analysis, cations, anions, pH and DOC were also measured.

To minimise addition of methanol to the leachate, TCE, TCB and toluene were added as neat solutions to the leachate (one µl neat solution/litre leachate; also mimicking the procedure used at Newcastle University). Due to the very low spiking volumes of the neat TCB, TCE and toluene solutions (0.5-1 µl), some variation in the resulting concentration was expected (see Table 10.13). Because of the low aqueous solubility of Mecoprop and naphthalene, stock solutions were first prepared in methanol (100 mg/2 ml) and diluted in the leachate (50 mg/l). This stock solution was then used to spike the biodegradation bottles to a final concentration of 0.5 mg/l (10 ml stock/one litre leachate).

Table 10.11 Characterisation of real landfill leachate used in biodegradation tests

Parameter	Parameter value
DTC (mg/l)	2,249
DOC (mg/l)	792
Sulphate (mg/l)	14
Nitrate (mg/l)	15
Nitrite (mg/l)	12
Chloride (mg/l)	2,243
pH	7.62

Table 10.12 Experimental conditions of biodegradation tests using real landfill leachate

List I substances	Solid phase	Leachate (l)	Biological inhibitors ^b	Bottle ref.
Mecoprop ^c	Sand (500ml=790g)	0.5	no	H1A, H1B
Mecoprop	Sand (500ml=790g)	0.5	yes	H2
Mecoprop	Oxford Clay (2g)	1	no	H3
Mecoprop	Oxford Clay (2g)	1	yes	H4
Mecoprop	Mercia Mudstone (2g)	1	no	H5
Mecoprop	Mercia Mudstone (2g)	1	yes	H6
Group I ^{a,c}	Sand (500ml=790mg)	0.5	no	H7A, H7B
Group I ^a	Sand (500ml=790mg)	0.5	yes	H8
Group I ^a	Oxford Clay (2g)	1	no	H9
Group I ^a	Oxford Clay (2g)	1	yes	H10
Group I ^a	Mercia Mudstone (2g)	1	no	H11
Group I ^a	Mercia Mudstone (2g)	1	yes	H12

a- Mecoprop, toluene, naphthalene, TCE, TCB.

b- 20 mM ammonium molybdate; 50 mM 2-bromoethanesulphonic acid (Oremland and Capone, 1998); and HgCl₂ 5 mg/l (as used at Newcastle University).

c- Tests carried out in duplicate.

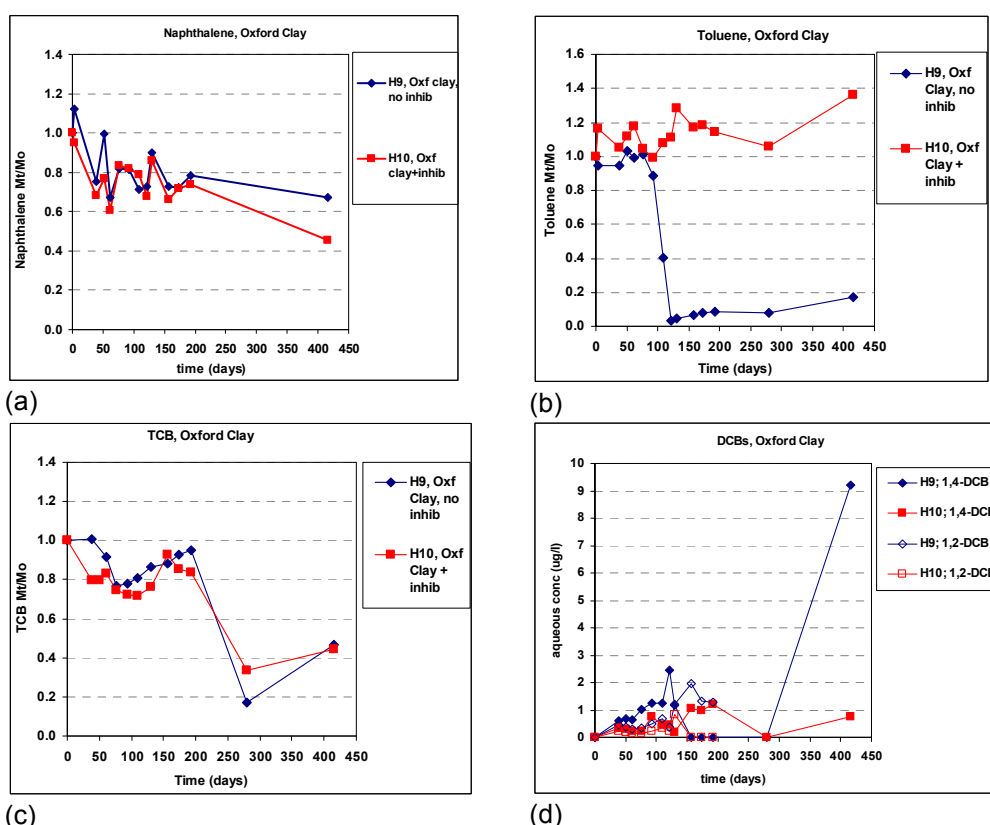
Table 10.13 Aqueous concentration of List I substances at start of biodegradation tests

Solid phase	Bottle ref.	Toluene (µg/l)	TCB (µg/l)	Naphthalene (µg/l)	TCE (µg/l)
Sand (500ml=790mg)	H7A, H7B	1,598 - 842	988 - 941	432 - 402	1,478 - 1,365
Sand (500ml=790mg)	H8	803	259	392	1,275
Oxford Clay (2g)	H9	662	529	388	1,043
Oxford Clay (2g)	H10	355	258	400	573
Mercia Mudstone (2g)	H11	678	703	398	1,032
Mercia Mudstone (2g)	H12	360	396	402	786

10.6.3 Results – Real leachate Group I

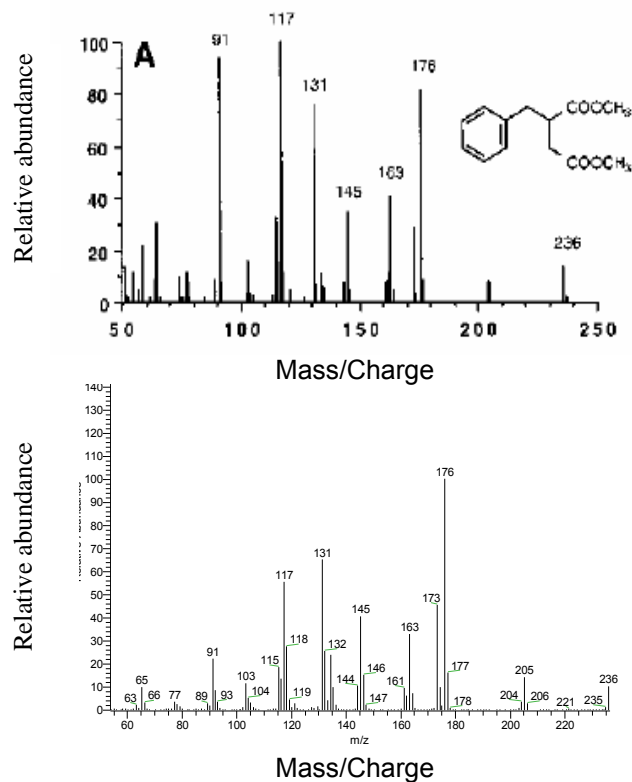
Naphthalene total concentrations did not change significantly over a period of 416 days of incubation both in the presence and absence of biological inhibitors in the bottles containing Mercia Mudstone and sand (see results in Appendix 6). A 20-30 per cent decrease in naphthalene total concentration was observed in the bottles containing Oxford Clay with and without inhibitors. This was most likely associated with sorption to the solid matrix (Figure 10.6). Because of problems with the analysis of Mecoprop in this test, the results were discounted.

Toluene total concentration did not change significantly in the presence or absence of biological inhibitors over a period of 416 days of incubation in the bottles containing Mercia Mudstone and London Clay (see results in Appendix 6). In the bottle containing Oxford Clay (without biological inhibitors) (Figure 10.6), toluene levels decreased from 600 µg/l to less than 20 µg/l between 80 and 109 days of incubation. Given that this variation was not observed in the presence of biological inhibitors, it suggests that biodegradation processes may be responsible for toluene depletion from the aqueous phase. This was confirmed by detection of benzy succinate in solution (a common anaerobic biodegradation product of toluene; Beller and Edwards, 2000, Figure 10.6) after 160 of incubation which was not initially present in the leachate. Following a lag phase of around 72 days, toluene was degraded with an estimated half-life of 12 days. The lag phase may be associated with the observed dechlorination of TCE to DCEs during the same period which may involve the same bacterial population.



(a) Variation with time of (a) toluene, (b) TCE, (c) TCB, and (d) DCBs concentrations

Figure 10.14 Biodegradation tests in real landfill leachate



(a) Mass Spectra of benzy succinate standard (from Beller and Spormann, 1997);
 (b) benzy succinate produced from toluene in bottle containing real landfill leachate and Oxford Clay after 160 days of incubation

Figure 10.15 Mass spectra of benzy succinate from real leachate biodegradation tests

The TCB total concentration did not change significantly over 416 days of incubation in the bottles containing Mercia Mudstone both in the presence and absence of biological inhibitors (see results in Appendix 6). A 20-30 per cent decrease in TCB total concentration was observed in the bottles containing Oxford Clay and sand with and without inhibitors. This is most likely associated with sorption to the mineral liner material or sand (Figure 10.14). Common biodegradation products of TCB from reductive dechlorination processes, that is dichlorobenzenes and chlorobenzene (Middeldorp *et al.*, 1997) were detected in all bottles at very low concentrations (under 7 µg/l) over the incubation period and found to slowly increase with time (Figure 10.14). This suggests that reductive dechlorination may be contributing to TCB depletion.

TCE aqueous concentration was found to decrease to 0.02 per cent of its initial concentration after only 40 days of incubation in all of the test bottles with an estimated half-life of four to six days (Figure 10.16). Common reductive dechlorination products of TCE (1,1-DCE, trans-1,2-DCE, cis-1,2-DCE and vinyl chloride, VC (Figure 10.17; see Vogel and McCarty) were not present in the leachate at the start of the tests. DCEs were found in the leachate after 40 days of incubation, suggesting that TCE was converted to DCE. Conversion of DCE to VC was observed after 110 days of incubation which indicates that it was either at a slower rate or that a bacterial population to enable the conversion took longer to establish. TCE degradation was observed with and without biological inhibitors, suggesting that abiotic processes may be contributing to TCE degradation and/or that the biocides did not completely inhibit TCE biodegradation. Freedman and Gossett (1989) have reported that the complete

inhibition of PCE biodegradation under methanogenic conditions required successive additions of bromoethane sulphonic acid.

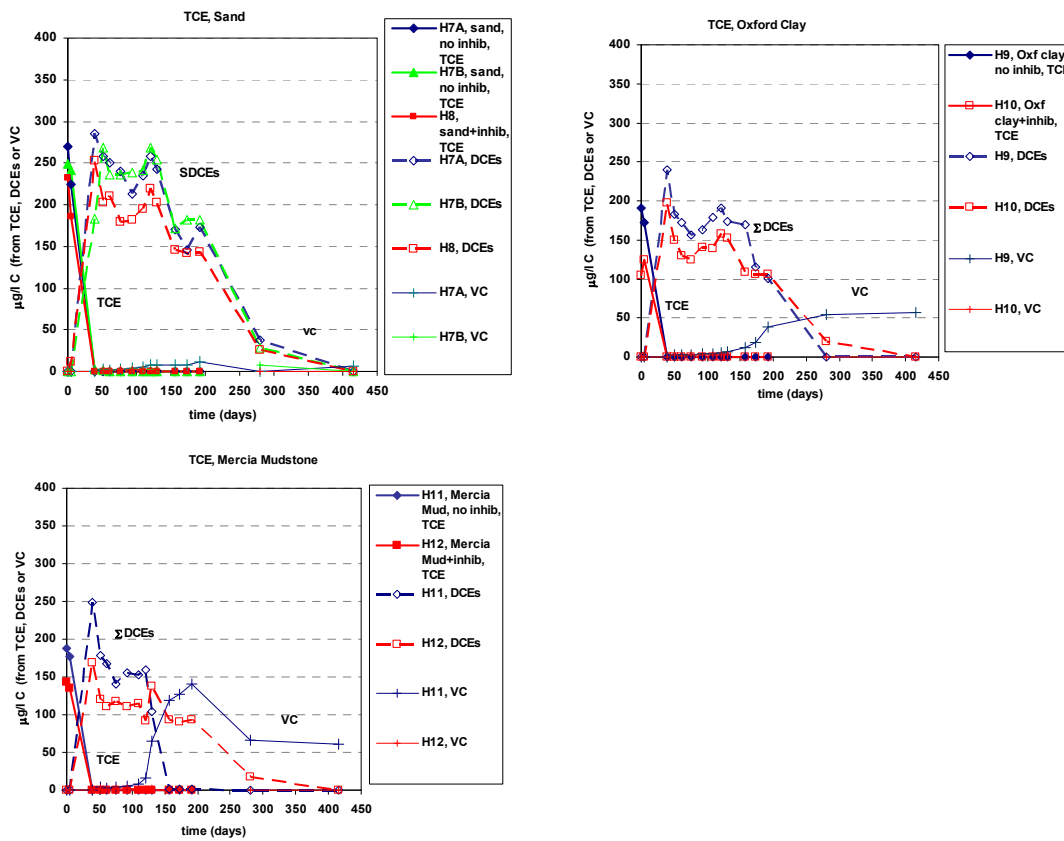


Figure 10.16 Variation with time of aqueous TCE concentration in bottles containing real landfill leachate and mineral liner materials (Σ DCEs is the sum of 1,1-DCE, trans-1,2-DCE, cis-1,2-DCE)

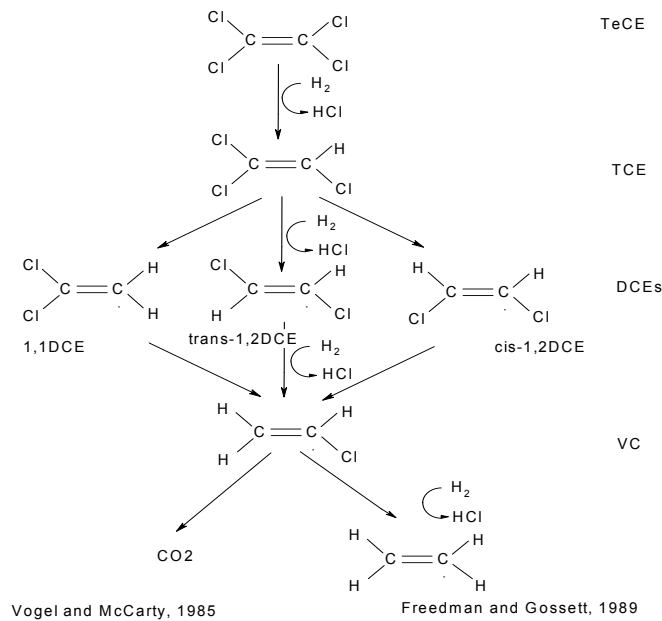


Figure 10.17 Reductive dechlorination of PCE and TCE under anaerobic conditions

Further control tests were set up (Section 10.6.4) to investigate whether abiotic processes contributed to TCE conversion to less chlorinated forms; additional biodegradation tests to evaluate TCE biodegradation in greater detail were also carried out (Section 10.6.5). Reductive dechlorination of TCE has been reported under methanogenic, sulphate-reducing and iron-reducing conditions (see Skubal *et al.*, 2001). Low concentrations of methane (under eight per cent) were detected in the headspace of the biodegradation bottles, suggesting the presence of an active methanogenic bacterial population which may have been involved in the reductive dechlorination of TCE and/or degradation of toluene (Table 10.6.4).

Table 10.14 Methane and carbon dioxide concentration in headspace of biodegradation reactors at different incubation times

Experimental conditions	Inhibitors	CH ₄ (%) ^a			CO ₂ (%) ^a		
		Start ^b	52 days	121 days	Start ^b	52 days	121 days
Sand Bottle 1	x	0	1.86;	4.84;	5	2.29;	2.75;
Sand: Bottle 2			1.44	1.60		2.06	2.41
Sand	✓	0	0.32	0.32	5	5.73	6.30
Oxford Clay	x	0	7.59	7.00	5	3.12	3.98
Oxford Clay	✓	0	1.54	1.31	5	10.50	9.81
Mercia Mudstone	x	0	c	c	5	c	c
Mercia Mudstone	✓	0	1.21	1.08	5	10.04	9.63

^a Measured by gas chromatography using a Varian CP-3800 GC equipped with a TCD detector and two columns 1 m by 1/8 inches OD: Haysep C column (80-100 mesh) and a Porapak column (molecular sieve 13X, 60-80 mesh) under the following conditions: 50°C isothermal back-flush mode and argon carrier gas.

^b Gas mixture initially applied above liquid level of bottles consisted of 90/5/5 (per cent nitrogen/carbon dioxide/hydrogen; Wolf labs Model A Vinyl cabinet incorporating oxygen and hydrogen).

^c Headspace sample not collected due to sampling tube being in contact with liquid phase.

The variation in Fe (II) and Fe (III) aqueous concentration over time in the real leachate tests was determined by standard colorimetric analysis. The Fe total concentration was found to increase with time in the bottles containing sand, suggesting that the sand may have released Fe into solution (Figures 10.18 and 10.19); the increase is particularly evident between Days 93 and 192 of the incubation. The majority of Fe produced in solution during the incubation was in Fe (II) form (an increase from 1.9 mg/l to 7.8 mg/l after 192 days) which may be indicative of microbially mediated iron-reducing activity on solid phase Fe (III) constituent of the sand. An abiotic mediated conversion cannot be ruled out, but the conversion to Fe (II) is less in the presence of biological inhibitors. Fe transformation in the presence of Oxford Clay and Mercia Mudstone was not evident.

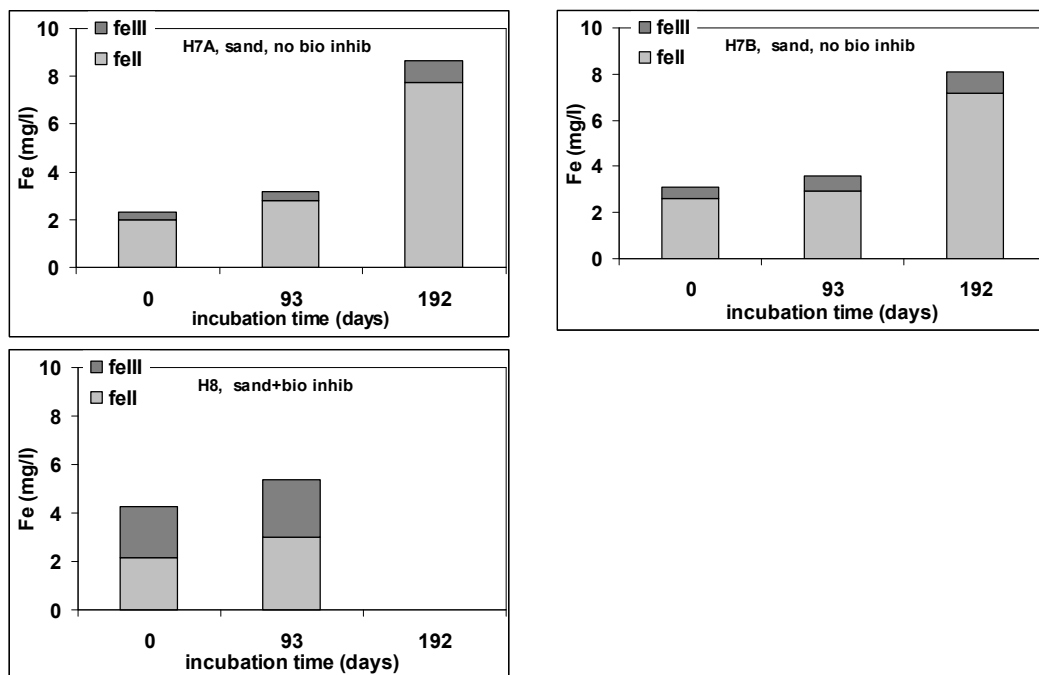


Figure 10.18 Variation of aqueous iron concentration in bottles containing real landfill leachate and sand

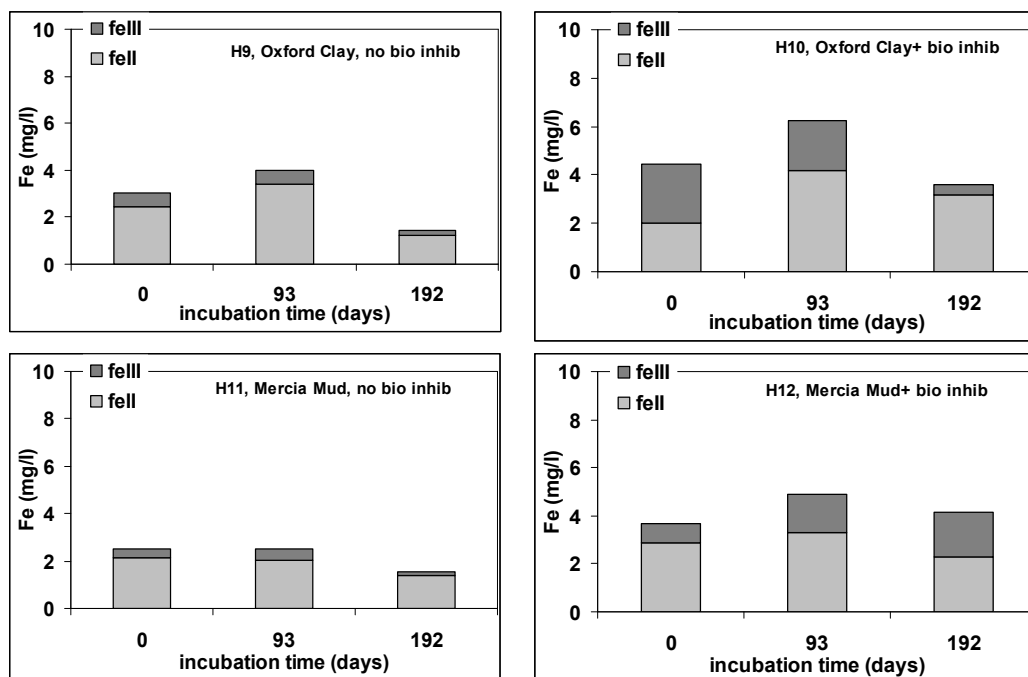


Figure 10.19 Variation of aqueous iron concentration in bottles containing real landfill leachate and Oxford Clay and Mercia Mudstone

10.6.4 Additional control tests with real leachate

Additional biologically inhibited tests were set up (Table 10.15) to evaluate whether abiotic processes contributed to the observed degradation of List I substances in real leachate. A new batch of leachate was collected from the same UK landfill site (as used in previous tests (Section 10.6.2)) and kept under anaerobic conditions until use. Tests were prepared following the same experimental procedure used for the biodegradation of the five List I substances except that inhibition of biological processes was achieved by autoclaving the leachate three times (120°C for 15 minutes (Kroman *et al.*, 1998)) and then adding a range of biological inhibitors (20 mM ammonium molybdate, 50 mM 2-bromoethane sulphonic acid, HgCl₂ 5 mg/l, NaN₃ 100 mg/l).

Table 10.15 Experimental conditions of biologically inhibited biodegradation tests using real landfill leachate

Bottle ref	Solid phase	Leachate (l)	Average starting aqueous concentration (µg/l)
HCtr1	Sand (500ml=790g)	0.5	TCE (835), TCB (477), toluene (582) and naphthalene (570)
HCtr2	Oxford Clay (2g)	1	
HCtr3	Mercia Mudstone (2g)	1	
HCtr4	No liner material -	1	

The variation in TCE, TCB, toluene and naphthalene aqueous concentrations over 40 days of incubation was not significant, suggesting that abiotic processes did not contribute to the degradation of List I substances in real leachate. This also indicated that autoclaving of the leachate was required for complete inhibition of biological activity (Figure 10.20).

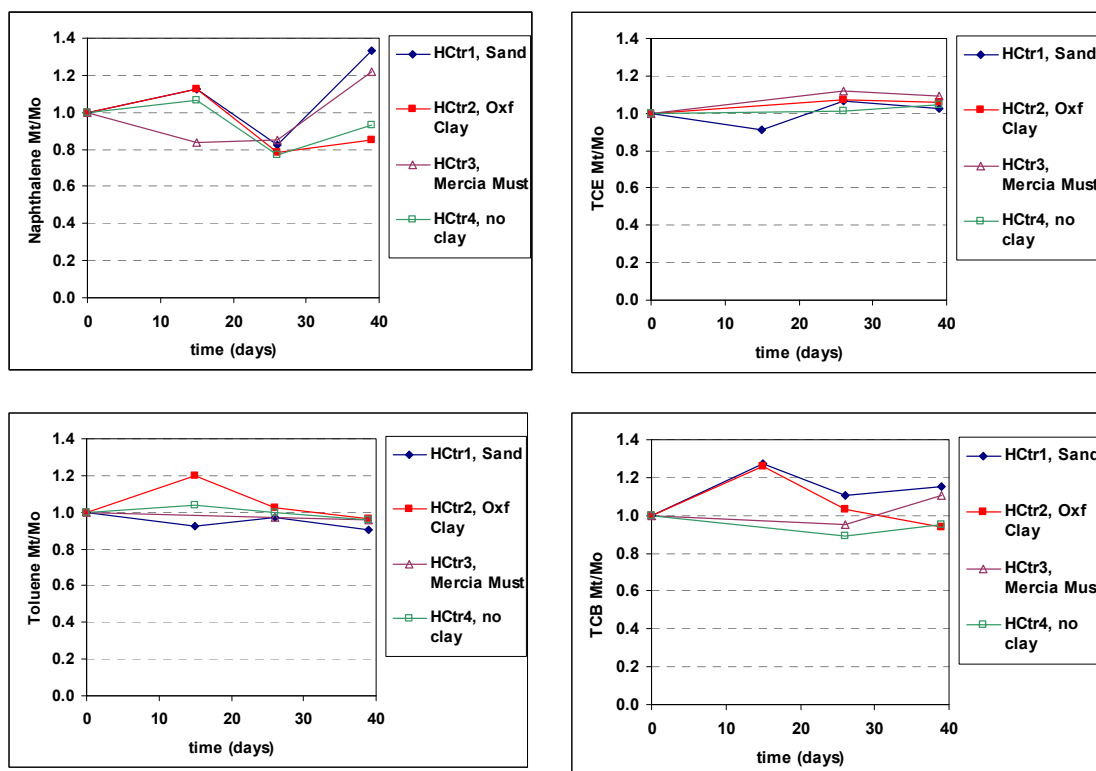


Figure 10.20 Variation with time of List I substances aqueous concentration in biologically inhibited biodegradation tests using real landfill leachate

10.6.5 Additional TCE biodegradation tests

Additional biodegradation tests were set up to evaluate TCE biodegradation in real leachate in greater detail. The tests were set up following the same experimental procedure used for biodegradation of the five List I substances (described in Section 10.6.2) with the same batch of leachate used in the control tests. Biodegradation of TCE was evaluated in the presence of Oxford Clay, Mercia Mudstone and without solid material (Table 10.16). Biologically inhibited control tests were prepared using the autoclave method described in Section 10.6.4 which was shown to completely inhibit biodegradation.

Table 10.16 Experimental conditions of TCE biodegradation tests using real landfill leachate

Bottle ref	Solid phase	Leachate (l)	Biological inhibitors	Starting TCE aqueous concentration (µg/l)
TCE1	Oxford Clay (2g)	1	x	1,679
TCE2	Oxford Clay (2g)	1	✓	1,739
TCE3	Mercia Mudstone (2g)	1	x	1,582
TCE4	Mercia Mudstone (2g)	1	✓	1,528
TCE5	No liner material	1	x	1,030

TCE aqueous concentration was found to decrease to 0.07 per cent of its initial concentration after 20 days of incubation in all samples (in the absence of biological inhibitors), with an estimated half-life of approximately three days (Figure 10.21). Common reductive dechlorination products of TCE (1,1-DCE, trans-1,2-DCE, cis-1,2-DCE and vinyl chloride, VC; see Vogel and McCarty, 1985) were not present in the leachate at the start of tests. As TCE aqueous concentration decreased, increasing concentrations of DCEs were detected in the leachate suggesting that TCE was converted to DCEs. Low concentrations of methane were detected in the headspace of the bottles without inhibitors, suggesting the presence of an active methanogenic bacterial population which may be involved in the dechlorination process (Table 10.17). Conversion of TCE to VC does not appear to require the presence of liner material and is slower in the presence of Oxford Clay.

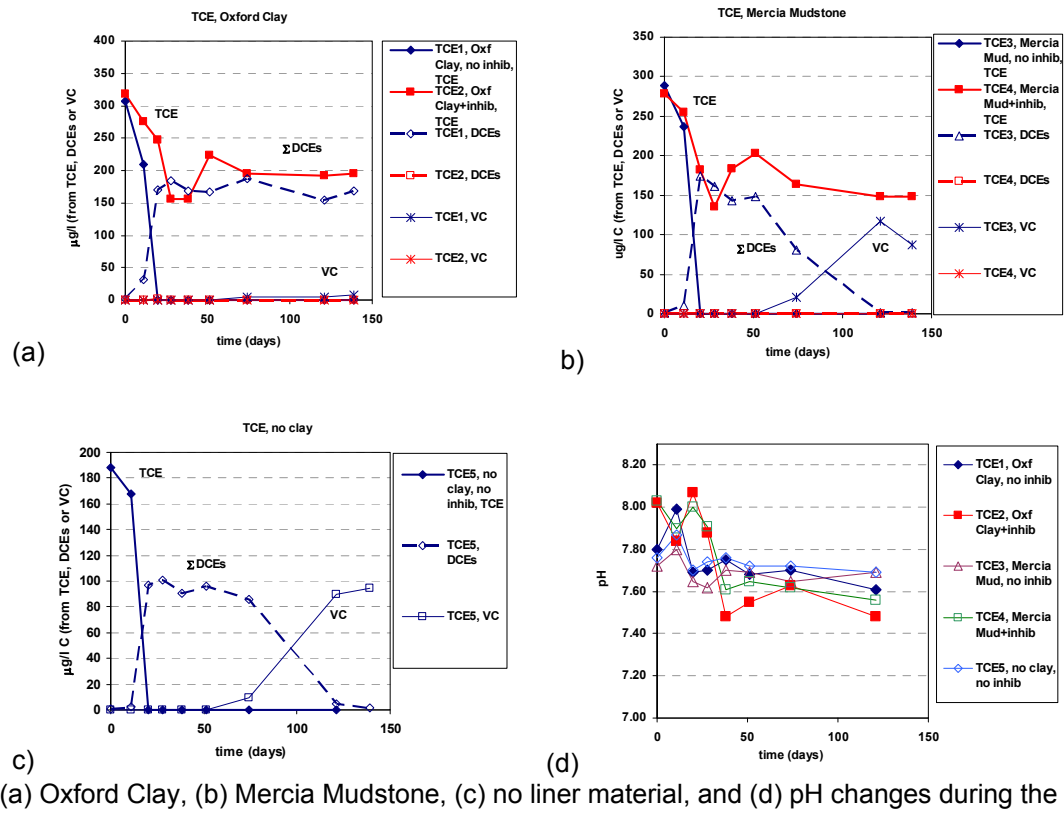
Variation in Fe (II) and Fe (III) aqueous concentration over time was determined by colorimetric analysis. In the bottles with liner materials, the Fe total concentration was found to increase with time suggesting that the clays may have released Fe into solution. As observed in previous biodegradation tests of the five List I substances, most of the Fe in solution was in Fe (II) form; Fe (II) concentration was not found to increase over time in relation to Fe (III) which would indicate iron-reducing conditions (Figure 10.22).

Table 10.17 Methane and carbon dioxide concentration in headspace of biodegradation bottles at different times incubation

Experimental conditions	Inhibitors	CH ₄ (%) ^a		CO ₂ (%) ^a	
		start ^b	39 days	start ^b	39 days
Oxford Clay	x	0	4.87	5	3.51
Oxford Clay	✓	0	0.11	5	0.46
Mercia Mudstone	x	0	6.43	5	3.94
Mercia Mudstone	✓	0	0.12	5	0.46
No liner material	x	0	5.65	5	3.36

^a Measured by gas chromatography using Varian CP-3800 GC equipped with a TCD detector and two columns 1 m by 1/8 inches OD: Haysep C column (80-100 mesh) and Porapak column (molecular sieve 13X, 60-80 mesh) under the following conditions: 50°C isothermal back-flush mode & argon carrier gas.

^b Gas mixture initially applied above the liquid level of the bottles consisted of 90/5/5 (per cent nitrogen/carbon dioxide/hydrogen; Wolfabs Model A Vinyl cabinet incorporating oxygen and hydrogen).



(a) Oxford Clay, (b) Mercia Mudstone, (c) no liner material, and (d) pH changes during the test.

Figure 10.21 Variation with time of TCE aqueous concentration in bottles containing real landfill leachate

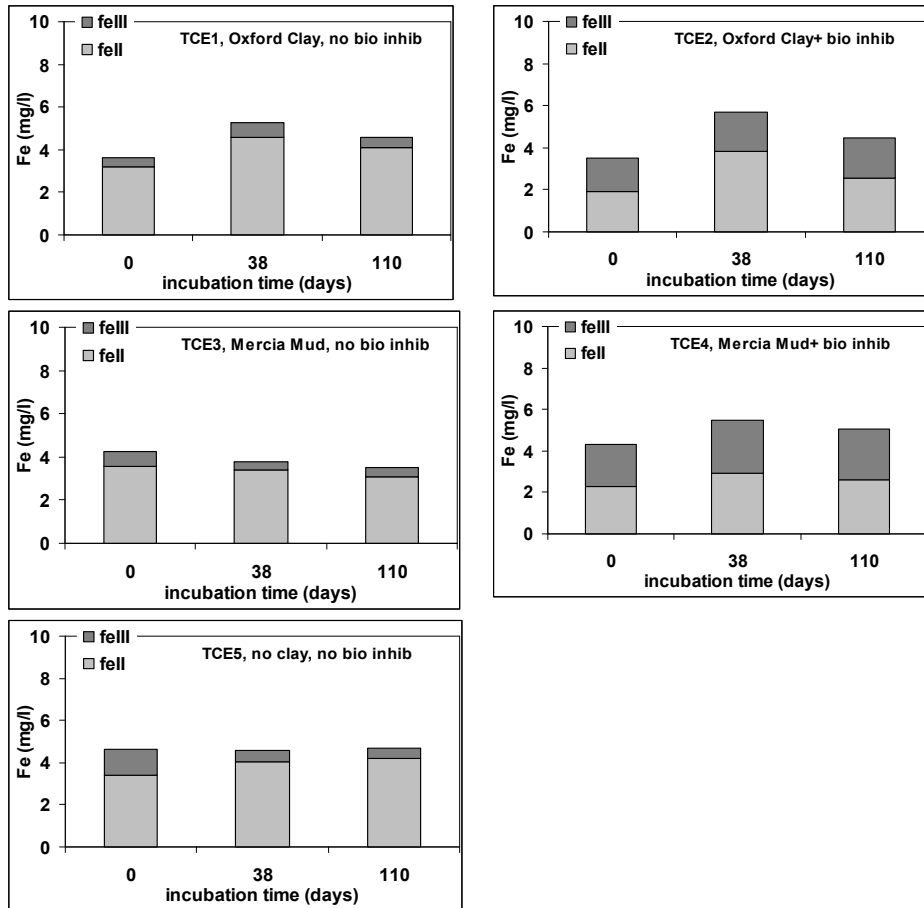


Figure 10.22 Variation with time of aqueous iron concentration in bottles containing real landfill leachate and mineral liner materials

10.7 Biodegradation tests with synthetic leachate containing active bacterial seed

10.7.1 Introduction

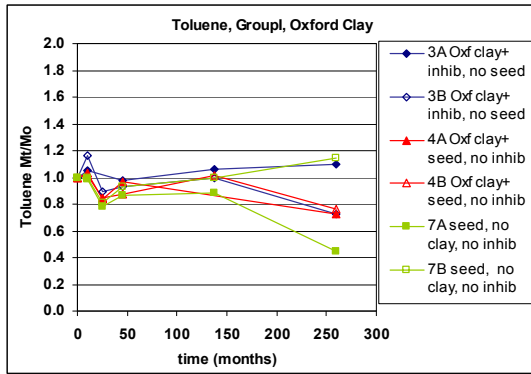
Additional tests (C) were set up to evaluate biodegradation of the five List I substances in MSW and MSWI synthetic leachates from previous tests (A) using as a bacterial seed the UK landfill leachate previously shown to support biodegradation of TCE and toluene (as used in Test B).

10.7.2 Experimental methodology

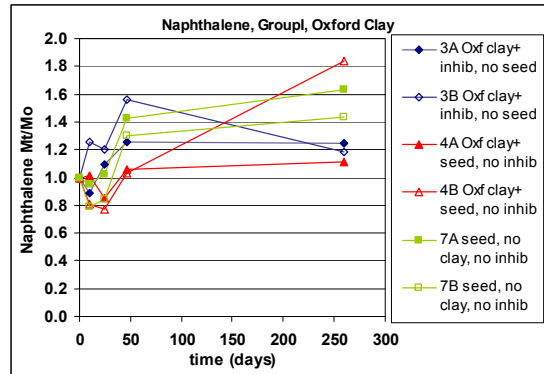
A new batch of leachate was collected from the same UK landfill site. Bottles from the biodegradation tests in MSW and MSWI synthetic leachates containing the five List I substances (Group I) were spiked with 50 ml of the UK landfill leachate used in previous tests (eight per cent of total volume in bottle) using the liquid sampling port. The bottles were kept sealed and stored in an anaerobic cabinet (Wolflabs Model A Vinyl cabinet incorporating oxygen and hydrogen measurement and carbon dioxide controller) at an incubation temperature of 20°C. Samples were collected (initially every 10-15 days of incubation, then after several months) and analysed for the List I substances, using GC-MS EI full scan to identify biodegradation products.

10.7.3 Results – synthetic leachate with active bacterial seed

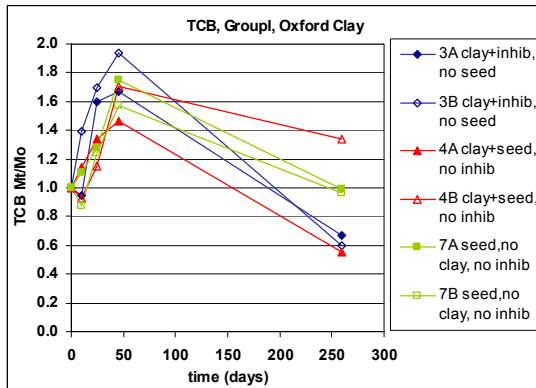
The results indicated that the addition of bacterial seed to the synthetic MSW and MSWI leachates did not have a significant effect on the aqueous concentration of toluene, TCB and naphthalene over 260 days of incubation (Figure 10.23). TCE aqueous concentration was found to decrease from 50 µg/l to under 10 µg/l of its initial concentration after 260 days of incubation in all of the test bottles containing MSW synthetic leachate but not MSWI synthetic leachate (Figure 10.24). Common reductive dechlorination products of TCE (1,1-DCE, trans-1,2-DCE, cis-1,2-DCE not present in the leachate at the start of the tests) were found in the MSW leachate after 91 days of incubation suggesting that TCE was converted to DCEs. Conversion of DCEs to VC was not observed over 260 days of incubation. Dechlorination of TCE observed with and without biological inhibitors is consistent with results from the tests in real leachate which indicated that autoclaving of the leachate, in addition to biological inhibitors, was required for complete biological inhibition (Section 10.6.4). TCE dechlorination occurred at a slower rate (half-life above 50 days following a lag phase of 46 days) than in the bottles containing real leachate. This is consistent with diluting of the active bacterial seed from the real leachate in synthetic leachate (eight per cent of total volume in bottle). TCE dechlorination was generally faster in bottles without biological inhibitors suggesting that the bacterial population responsible for dechlorination may include methanogenic bacteria. Dechlorination was faster in the presence of the mineral liner materials, particularly Mercia Mudstone (half-life 48-61 days).



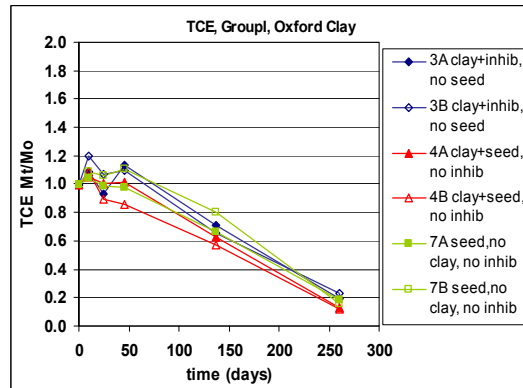
(a)



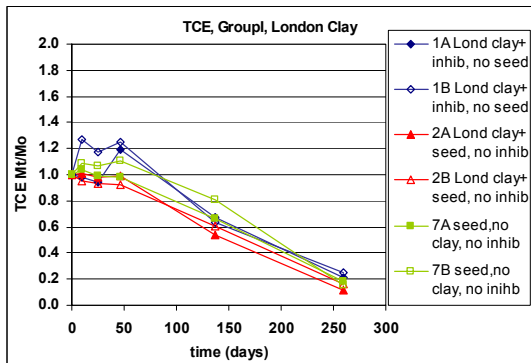
(b)



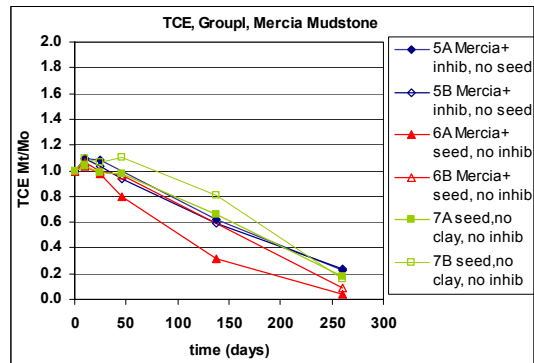
(c)



(d)



(e)



(f)

Figure 10.23 Variation with time of List I substances aqueous concentration in MSW synthetic leachate spiked with real landfill leachate seed

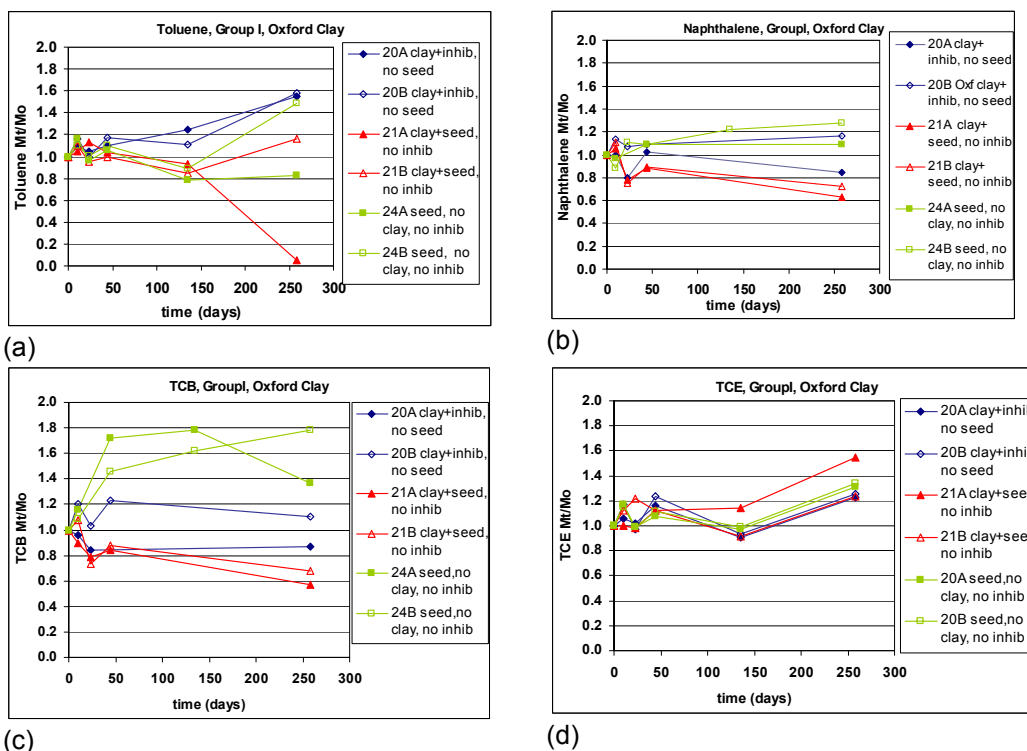


Figure 10.24 Variation with time of List I substances aqueous concentration in MSWI synthetic leachate spiked with real landfill leachate seed

10.8 Summary of results from biodegradation tests

Biodegradation of five List I substances (TCE, TCB, naphthalene, toluene and Mecoprop) was studied under anaerobic conditions using bacterial seeds from leachates of two landfill sites in the UK and different mineral liner materials. Two sets of tests were carried out in batch reactors. In one set of tests, biodegradation was studied in synthetic MSW and MSWI leachates containing a bacterial seed enriched from leachate of landfill site I. In the other tests, biodegradation was studied in leachate from landfill site II which contained a natural bacterial seed known to support reductive dechlorination of tetrachloroethene.

All List I substances were found to be recalcitrant to biodegradation in the synthetic leachates over a period of eight months of incubation. The observed decrease in contaminant concentrations (particularly TCB, naphthalene and Mecoprop) in the leachates was attributed to sorption to the liner material, bacterial seed and losses to bottle components. Although the List I substances were not degraded, active methanogenic and sulphate-reducing bacterial populations were identified in the MSW and MSWI synthetic leachates, respectively, particularly in the reactors containing liner materials. This suggests that the liner materials provide an attachment medium for the bacteria and that the bacteria were using another source of carbon other than the List I substances.

The landfill leachate from site II showed fast biodegradation of TCE and toluene, while TCB and naphthalene were recalcitrant to biodegradation over four months of incubation. TCE was biodegraded by reductive dechlorination to DCE within 20 days (half-life four to six days) with and without liner materials. Conversion to vinyl chloride was observed in all reactors but at a slower rate, particularly in the presence of

Oxford Clay. The highest dechlorination rate occurred in the reactors without mineral liner material or with Mercia Mudstone within 120 days (half-life four days). Toluene was biodegraded within four months and benzylsuccinate, a common intermediate in the anaerobic toluene degradation, was found in the leachate (half-life of 12 days following a lag phase of 72 days). The lag phase may be associated with observed dechlorination of TCE to DCE during the same period suggesting that the same bacterial population(s) may be involved. An active methanogenic bacterial population was identified in the reactors which may be involved in the dechlorination process. Conversion of TCE to VC does not appear to require the presence of mineral liner materials and is in general slower in the presence of Oxford Clay.

Addition of the active bacterial seed in the real leachate to the synthetic MSW and MSWI leachates (eight per cent of total volume in bottle) did not have a significant effect on the aqueous concentration of toluene, TCB and naphthalene over 260 days of incubation. After a lag phase of 46 days TCE dechlorination was observed in all bottles containing MSW synthetic leachate (with added bacterial seed from landfill leachate II; half-life 48-61 days) but not in those bottle containing MSWI leachate. TCE dechlorination occurred even in the presence of biological inhibitors, albeit at slower rates than in the bottles without biological inhibitors, suggesting that the bacterial population(s) responsible for the dechlorination process include methanogenic bacteria.

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

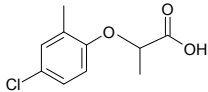

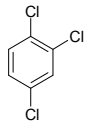
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List of abbreviations

AOM	Amorphous organic matter
BTEX	Benzene, toluene, ethyl benzene and xylene.
CEC	Cation exchange capacity
DCE	Dichloroethene
DOC	Dissolved organic carbon
HOCs	Hydrophobic organic compounds
MCPP	Mecoprop ((R,S)2-(2-methyl-4-chlorophenoxy)-propionic acid)
MSW	Municipal solid waste
MSWI	Landfill containing bottom ash from incineration of MSW
OC	Organic carbon
TCE	Trichloroethene
TCB	1,2,4 Trichlorobenzene
TOC	Total organic carbon
VOC	Volatile organic contaminant
VC	Vinyl chloride
GC-MS	Gas chromatography-mass spectroscopy
SPE	Solid phase extraction
PTFE	Polytetrafluoroethene
PCE	Tetrachloroethene
2,4-D	2,4-dichlorophenoxyacetic acid
2,4,5-T	2,4,5-trichlorophenoxyacetic acid
K_{oc}	K_d normalised to the fraction of organic carbon in a matrix
K_{ow}	Octanol-water partition coefficient (ratio of the concentration of a contaminant in n-octanol to its concentration in water at equilibrium under defined test conditions)
K_d	Partition coefficient (ml/g)
f_{oc}	Fraction of organic carbon
K_f	Freundlich equilibrium coefficient for the sorption reaction ($\mu\text{g}^{1-n} \text{ml}^n/\text{g}$)
K_L	Langmuir adsorption or affinity constant (dimensionless)
M	Total number of sorption sites (a constant related to the area occupied by a monolayer of sorbate, $\mu\text{g}/\text{g}$).
R	Retardation coefficient
SSA	Specific surface area (m^2/kg)

Appendix 1 – List I contaminants

Parameters for List I organic compounds used in experimental work

List I substance	Structure	log K_{ow} (-)	H (atm.m ³ /mol) ^a	S (mg/l) ^a
Trichloroethylene		2.47	1.6 x 10 ⁻²	778.7
Toluene (BTEX)		2.54	5.0 x 10 ⁻³	573.1
Mecoprop		2.94 ^b (0.1) ^c	6.7 x 10 ⁻⁷	193.7
Naphthalene		3.17	4.8 x 10 ⁻⁵	142.1
1,2,4-trichlorobenzene		3.93	2.2 x 10 ⁻³	20.0

K_{ow} - octanol-water partition coefficients, H - Henry's constant, and S - water solubility (SRC, 1988)

^a Measured at 25°C

^b Log K_{ow} = 2.94 for Mecoprop in undissociated form (Tomlin, 1997).

^c Log K_{ow} = 0.1 for Mecoprop in dissociated form present at pH 7-9 typical of MSW methanogenic leachate (Tomlin, 1997).

Appendix 2 – Literature review

A2.1. Introduction

More than 30 trace organic substances were identified in leachates in the UK PI study (Environment Agency, 2001). There was a need to restrict the number of substances that would be reviewed in detail prior to the start of experimental work in the programme. Substances were grouped according to their status as a List I substance under the Groundwater Regulations 1998, and their occurrence and concentration in UK leachates. Substances being investigated in other natural attenuation projects and that the Environment Agency were particularly interested in (such as from foot and mouth disposal sites) were also included in the initial review.

Substances subject to initial screening are shown in Table A2.1, along with criteria used for prioritisation. The table also shows substances excluded from the literature review for this project. The review itself provides brief descriptions of the physical properties of compounds, their likely concentration and occurrence in leachates (where known) and the potential for attenuation through biodegradation and sorption processes. There were few examples in the literature of sorption or biodegradation studies on landfill liners, so much of the data was derived from soils and sediments. Where possible, examples of biodegradation rates under methanogenic or sulphate-reducing conditions, such as might be found in a landfill environment, are given. Although not likely to occur under anaerobic conditions in a landfill liner, aerobic biodegradation of organic contaminants is also discussed briefly for completeness.

The literature review was originated in 2003 and has been subject to only minimal revision. Numerous publications and reviews have become available since the review was completed. For example, biodegradative pathways for many of the contaminants found in landfill leachate, under many different environmental conditions, are available, including PAH anaerobic biodegradation (Meckenstock *et al.*, 2004), anaerobic biodegradation of aromatic hydrocarbons (Foght, 2008), biodegradability of chlorinated aliphatic compounds (Field and Sierra-Alvarez, 2004), microbial degradation of chlorinated benzenes (Field and Sierra-Alvarez, 2008) and Mecoprop degradation (Buss *et al.*, 2006).

Table A2.1 Summary of substances to be included in the study or rejected

Priority for literature review	Priority for literature review	Possible inclusion in literature review	Not included in the study
Substances that are List I and widely present in UK landfill leachates	Requested by Environment Agency but not widely present in UK landfill leachates	Either, List I but not widely found, Or, not List I but widely found	Substances that will not be investigated because not List I, or no evidence for presence in leachate
Benzene, toluene, ethylbenzene, xylenes (BTEX compounds)	Trichlorobenzenes	1,1-Dichloroethane	Tetrachloroethene
Polycyclic aromatic hydrocarbons (PAH), e.g. phenanthrene	Trichloroethene	Mineral oils	MCPA ((4-chloro-2-methyl phenoxy) acetic acid)
Naphthalene (bicyclic aromatic hydrocarbon)	Atrazine		Nonylphenols
Mecoprop (MCP)	Diazinon	2,4-D or 2,4,5-T	Pentachlorophenol
Organotin compounds	Phthalates		Aniline
	Bisphenol A		Methyl tertiary butyl ether (MTBE)
	Propetamphos		Dichloprop
			Diuron
			Formaldehyde
			Brominated diphenyl ethers
			Short-chain chlorinated paraffins, SCCPs
			Medium-chain chlorinated paraffins, MCCPs
			Long-chain chlorinated paraffins, LCCPs
			Biphenyl

A2.2. Aromatic hydrocarbons

A2.2.1. Introduction

Benzene, toluene, ethylbenzene and isomers of xylene (known as the BTEX compounds) are aromatic hydrocarbons commonly found together in crude petroleum and petroleum products. They are considered to be one of the major causes of environmental pollution because of widespread occurrences of leakage from petroleum storage tanks and spills at production refineries, wells and pipelines. BTEX compounds are also found in relatively high concentrations in landfill leachate. Toluene and the xylenes occur more frequently than ethylbenzene and benzene in

UK leachates (Environment Agency, 2001, 2003). Toluene, thought to originate from detergent residues in landfill, is found in the highest concentrations of individual BTEX compounds (Environment Agency, 2003). BTEX compounds are relatively water soluble, have low polarity and are volatile (Table A2.2).

Table A2.2 Physical properties of the BTEX compounds.

	Water solubility (mg/l, 25°C)	Vapour pressure (mmHg at 25°C)	Log K _{ow}	Log K _{oc} (ml/g) ^d	Median UK leachate concentrations (µg/l)
Benzene	1790	94.8	2.13	1.2-2.5	
Toluene	526	28.4	2.54	1.7-3.0	21 ^a
Ethylbenzene	169	9.6	3.15	1.6-3.2	<10 ^b
Xylenes	106 ^c	7.99 ^c	3.16 ^c	1.8-3.2	35 ^a

^a Toluene and total xylenes (Environment Agency, 2001).

^b Ethylbenzene (Environment Agency, 2003).

^c Physical properties for m-xylene.

^d Adapted from Delle Site, 2001.

A2.2.2. Aerobic degradation of aromatic hydrocarbons

Under aerobic conditions, benzene is broken down microbially and catechol is formed (Colberg and Young, 1995). Toluene has a number of separate biodegradation pathways, some of which include 3-methylcatechol, which is also the end product of m-xylene degradation. Ethylbenzene biodegrades to 3-ethylcatechol. The aromatic ring of the catechols produced during biodegradation can then undergo ring cleavage prior to further degradation.

Aerobic, single substrate, column tests indicate that the mineralisation of benzene, toluene, and xylene (equimolar mixture of the isomers) occurred at rates of 1.32, 1.42 and 0.833 mmol/l/hour (Kelly *et al.*, 1996). In tests containing all BTEX compounds, xylene is the fastest removed and benzene the slowest. There may be a short lag period (100 hours) before degradation of xylene starts in the mixed substrate tests. Benzene and toluene degradation also show a lag period in both the mixed and sole substrate tests. In general, the mean first-order rate constants from field values and in situ microcosms are lower than laboratory values. In addition, higher rate constants are found in laboratory experiments when the BTEX compounds are sole carbon sources, than when additional carbon compounds are present.

A2.2.3. Anaerobic degradation

Benzene

Up to recently, benzene was regarded as resistant to biodegradation under strictly anaerobic conditions. However, anaerobic degradation of benzene has now been demonstrated in both laboratory and field aquifer studies (Kazumi *et al.*, 1997; Edwards and Grbic-Gali, 1992; Anderson and Lovley, 1999). The anaerobic degradation pathway for benzene is currently unknown, but while no single microorganism has been shown to degrade benzene under anaerobic conditions, the compound has been mineralised by an enriched consortium of microorganisms in laboratory microcosm studies. Anaerobic degradation of benzene is generally demonstrated when it is the sole carbon source. It is suggested that biodegradation of benzene only occurs after toluene, ethylbenzene, xylene and other carbon sources have been degraded.

First-order rate constants (k_1) from aquifer and in situ microcosm studies for benzene degradation average 0.0046/day for the range of most commonly found concentrations (1-1,630 $\mu\text{g/l}$) in landfill leachates (Christensen *et al.*, 2001). However, as benzene is rapidly degraded in aerobic conditions, these rates may indicate the presence of dissolved oxygen in the aquifer. Results from aquifer and in situ microcosm studies are variable, some sites reporting biodegradation and others not (Aronson and Howard, 1997). Long incubation periods may be necessary to enable the microbial population to become acclimated to benzene. In one study, biodegradation rates of zero to 0.0048/day were found under methanogenic and sulphate reduction conditions in laboratory experiments that ran for 320 to 520 days (Kazumi *et al.*, 1997). However, it has been suggested that although long-term experiments show the potential for biodegradation, they are not representative of conditions in aquifers (Lovley, 1997). In a number of field studies no biodegradation of benzene was reported and it was thought that the short residence time at the sites did not allow biodegradation to occur (Wilson, *et al.*, 1991). Average laboratory degradation rate constants (0.0099/day) tend to be much higher than field results (0.0014/day); there appears to be no correlation between the rate constants for benzene and initial concentration from either field or laboratory studies (Figure A2.1).

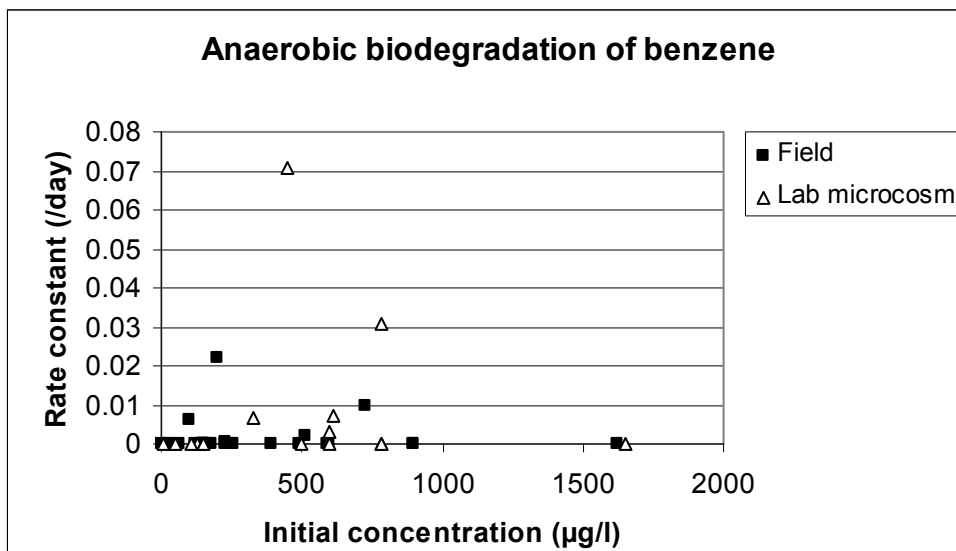


Figure A2.1 Anaerobic biodegradation rates for benzene from field and laboratory microcosm studies in aquifers (from Aronson & Howard 1997)

Toluene

Toluene biodegrades readily under anaerobic conditions in aquifers with methanogenic, denitrifying, sulphate-reducing and iron-reducing environments (Aronson and Howard, 1997). The UK Pollution Inventory study reports a median value for toluene concentration of 21 $\mu\text{g/l}$ in UK landfill leachate (Environment Agency, 2001), but other studies have observed concentrations up to 12,300 $\mu\text{g/l}$ (Christensen *et al.*, 2001). No reference to degradation in mineral liner materials was found in the literature, but examples from aquifer environments, ranging from one to 12,500 $\mu\text{g/l}$ are shown in Figure A2.2 (adapted from Aronson and Howard, 1997). First-order rate constants for toluene from aquifer field and in situ microcosm studies, range from zero to 0.3/day with an average of 0.072/day. The rate of anaerobic degradation of toluene appears to be related to redox conditions: mean first-order rate constants for denitrifying, sulphate-reducing, methanogenic and iron-reducing studies are 0.23/day, 0.042/day, 0.021/day and 0.023/day, respectively. Only five of the studies in Aronson and Howard's review (1997) reported no biodegradation of toluene, but four of these

were in situ studies carried out in aquifers. Only a few studies report lag periods prior to the start of biodegradation of toluene. The average lag time for field and in situ microcosms was 31 days, whereas for laboratory microcosms, an average of 70 days was found. The average biodegradation rate for laboratory microcosms was 0.13/day, rather higher than that found in aquifer studies. As with benzene, there is no correlation between initial concentration and degradation rate in either the field or laboratory studies (Figure A2.2).

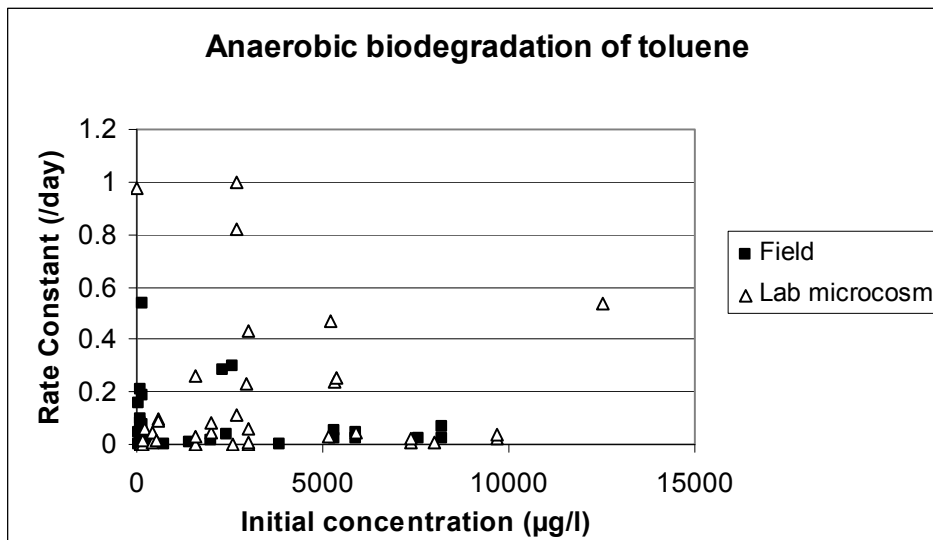


Figure A2.2 Anaerobic biodegradation rates for toluene from field and laboratory microcosm studies in aquifers (from Aronson & Howard 1997)

Ethylbenzene

Ethylbenzene biodegrades in anaerobic environments at a similar rate to xylenes, but not as rapidly as toluene. No references to ethylbenzene biodegradation in mineral liner materials were found in the literature search. Results from 50 aquifer studies for the range of ethylbenzene concentrations under consideration (zero to 1,300 µg/l), show first-order rate constants in aquifers range from zero to 0.029 per day with an average value of 0.018/day and median of 0.0015/day (Aronson and Howard, 1997). Only sixteen of the fifty studies reported showed no degradation. No correlation between initial ethylbenzene concentration and rate could be discerned for the field data (Figure A2.3). There was some correlation from the laboratory microcosm data ($R^2 = 0.5$) but this was from a small number of studies. Like toluene, ethylbenzene and xylenes are most readily degraded under nitrate-reducing conditions. Mean first-order rate constant values for ethylbenzene under nitrate-reducing, methanogenic, and iron-reducing environments are 0.027/day, 0.005/day and 0.001/day, respectively. There was insufficient data to calculate a mean rate constant for sulphate-reducing conditions.

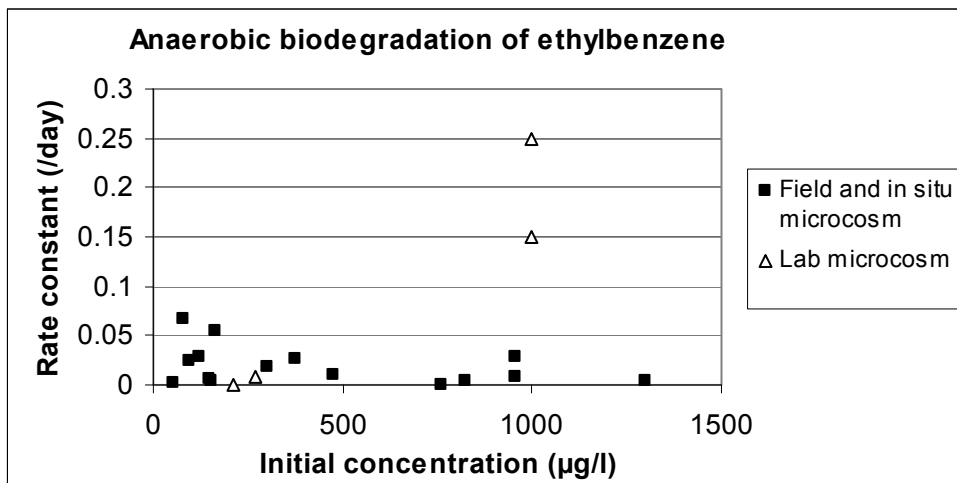


Figure A2.3 Anaerobic biodegradation of ethylbenzene from field and laboratory aquifer studies (adapted from Aronson & Howard 1997)

Xylene

Xylene isomers may biodegrade in nitrate-reducing, sulphate-reducing, methanogenic and iron-reducing environments. They are generally not as readily degraded as toluene but at a similar rate to ethylbenzene. Rate constants for total xylene isomers from field, in situ and laboratory aquifer studies range from zero to 0.12/day for the range of xylene concentrations most commonly found in landfill leachates, with mean values ranging from 0.004 to 0.031 per day for the three isomers (Aronson and Howard, 1997). Again, there is no correlation between the rate constants and xylene concentration (Figure A2.4).

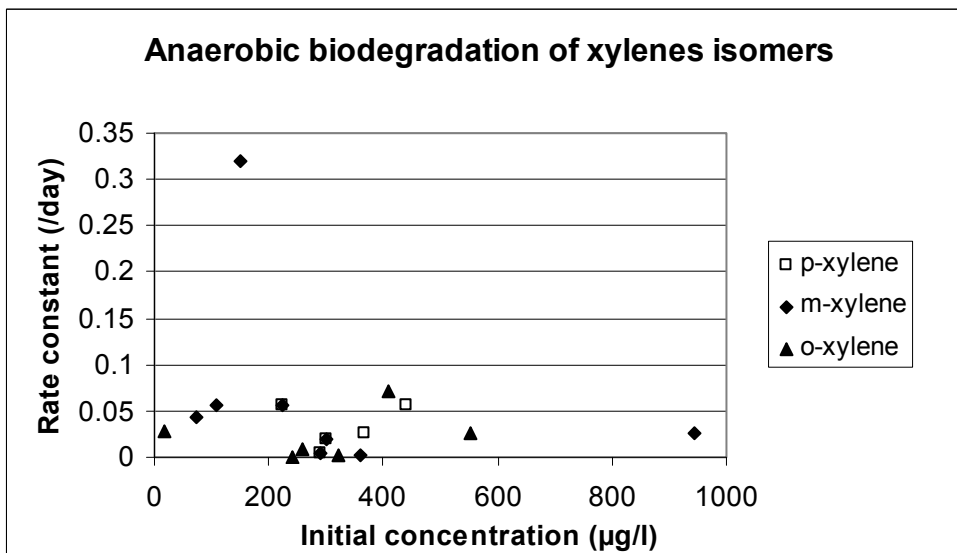


Figure A2.4 Anaerobic biodegradation of the xylene isomers from aquifer studies (adapted from Aronson & Howard 1997)

A2.2.4. Sorption

BTEX compounds are relatively hydrophobic and therefore sorb readily to sediments with a high concentration of organic matter. Transport through low organic matter sandy aquifers is relatively unimpeded. For benzene and toluene, Bright *et al.* (2000) reported partition coefficients (K_d) of 0.14 and 0.13 respectively, in column

experiments with quartz sand. At higher clay and organic carbon content (five per cent Oxford Clay), the sorption coefficients for benzene and toluene were 0.67 and 1.15 respectively, compared to the calculated values of 0.19 and 0.47 (Bright *et al.*, 2000). It was thought that sorption to dissolved organic matter and mineral surfaces could explain the higher experimental values. With 10 per cent Oxford Clay, K_d values for benzene and toluene were 0.58, and 1.1 respectively (Thornton *et al.*, 1999). Kim *et al.* (2001) reported that a log K_{oc} value for toluene of 1.98 ml/g using Kirby Lake Till, a low plasticity clay with one per cent organic carbon. Table A2.3 gives average sorption coefficients and K_{oc} values for BTEX compounds in soils (Delle Site, 2001).

In the clay liner at the Sarnia (Ontario) hazardous waste landfill, observed log K_{oc} values for benzene, toluene, and ethylbenzene were 3.0, 3.27, and 3.79 ml/g, respectively (Johnston *et al.*, 1989); these exceeded expected log K_{oc} values (1.8, 2.5, 2.9 for benzene, toluene, and ethylbenzene from Mabey *et al.*, 1982) by approximately an order of magnitude. Myrand *et al.* (1992), performing laboratory tests on the same substrate, found similar values at low BTEX concentrations but at concentrations greater than one mg/l, measured K_d values approached the calculated K_d values. The observed values were explained by interactions between the HOCs and the kerogen-rich organic carbon and clay minerals in the deposit (an unweathered glaciolacustrine clay with 40 per cent clay particles (illite and smectite) and one per cent organic carbon content) (Allen-King *et al.*, 1997).

In one long-term laboratory study carried out over twelve years, permeation rates of organic compounds through different clay materials in test cells were assessed. The proportion of toluene retained in kaolinite/illite clay with montmorillonite was much greater than in kaolinite/illite clays with one or two per cent bentonite added (Kalbe *et al.*, 2002).

Adsorption/desorption of a mixture of five hydrocarbons (benzene, toluene, p-xylene, m-xylene, and o-xylene) on montmorillonite, illite and kaolinite was studied using the batch equilibrium method (Li and Gupta, 1993). The sorption coefficients (K_d) ranged from 0.01 to 0.85 and were relatively lower than reported K_d values for soils high in organic matter. The adsorption of these hydrocarbons on montmorillonite and illite was higher than on kaolinite. The adsorption reactions were reversible for toluene and illite. A smaller amount of toluene was adsorbed from mixtures of BTEX compounds ($K_d = 0.83$) compared to the adsorption from single hydrocarbon studies ($K_d = 2.42$) (Li and Gupta, 1993).

To enhance the sorption of organic contaminants, modified clays were developed for use as barrier materials. Organoclay BB-40, for example, is produced by the exchange of dicetyldimethylammonium ions for sodium ions on the internal and external mineral surfaces of bentonite. Lo *et al.* (1997) examined the ability of organoclay BB-40 to retard contaminants, including aqueous solutions of benzene, toluene, ethylbenzene and o-xylene. They found that BB-40 has a high sorption capacity for BTEX compounds, whereas the sorption capacity of unmodified bentonite clays is insignificant. The BTEX isotherms were linear and sorption decreased in the order o-xylene, ethylbenzene, toluene, benzene; sorption was higher at pH 5 than at pH 9. The increased retention of BTEX by modified clays is also reported by Gitipour *et al.* (1997) and Smith and Galan (1995).

Table A2.3 Average sorption coefficients (K_d) and K_{oc} values for BTEX compounds in soils; figures in brackets indicate number of samples

f_{oc}	K_d (ml/g)				All fractions	K_{oc} (ml/g)
	<0.01	>0.01 to <0.06	>0.06 to <0.11	>0.11		
Benzene	0.16 (25)	1.1 (5)	Insufficient data	23.7 (5)	3.66 (35) $r^2=0.19$	1.2-2.5
Toluene	0.47 (12)	3.37 (5)	11.4 (2)	41.4 (7)	13.3 (26) $r^2=0.75$	1.7-3.0
Ethyl benzene	0.44 (3)	5.3 (3)	Insufficient data	213 (3)	73.1 (9) $r^2=0.76$	1.6-3.2
p-xylene	0.62 (9)	5.9 (4)	Insufficient data	Insufficient data	2.25 (13) $r^2=0.59$	1.8-3.2

A2.2.5. Conclusions

BTEX compounds degrade readily under aerobic conditions, but less easily under anaerobic conditions. Monitoring of anaerobic plumes has demonstrated degradation of toluene, ethylbenzene and xylenes, albeit at lower rates than under aerobic conditions. Benzene was generally believed to be recalcitrant to degradation under anaerobic conditions, although recent evidence shows that benzene does degrade in the absence of oxygen. Being hydrophobic, BTEX compounds are readily sorbed by organic matter, but are easily transported through low carbon sediments.

A2.3. Chlorinated aromatic hydrocarbons

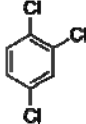
A2.3.1. Introduction

Trichlorobenzenes have been found only occasionally in UK leachates; in the 2001 PI study, none of the trichlorobenzene isomers were found (Environment Agency, 2001). 1,2,4-Trichlorobenzene (TCB) was chosen as a representative compound for the chlorinated aromatic hydrocarbon group (Table A2.4). TCB has various uses in industry such as a carrier to apply dyes to polyester materials, a heat transfer medium, a degreaser and a lubricant. It also functions as a pesticide and an aquatic herbicide.

A2.3.2. Aerobic degradation

Aerobic biodegradation of 1,2,4-trichlorobenzene generally involves conversion to trichlorocatechol via dioxygenase and dehydrogenase reactions. From trichlorocatechol the compound may be degraded to straight chain organic acids through ring cleavage (UMBBD, 2003).

Table A2.4 Physical properties of 1,2,4-trichlorobenzene (TCB)

Structure	Solubility (mg/l at 25 °C)	Vapour pressure (mm Hg at 20°C)	Log K _{ow}	K _{oc} (ml/g)
TCB 	Negligible	36	3.9-4.2	3.3-3.5

The biodegradation of 1,2,4-trichlorobenzene has been observed under aerobic conditions in laboratory and field studies (Nishino *et al.*, 1992; Nielsen *et al.*, 1996; Van der Meer *et al.*, 1998; Kao and Prosser, 1999; and Dermietzel and Vieth, 2002). Studies suggest that aerobic biodegradation is relatively rapid, with faster kinetics obtained for soil or aquifer sediments which have previously been exposed to chlorinated benzene contamination. A lag period is often observed before the onset of biodegradation, indicating that chlorinated benzenes are not readily degradable by most microorganisms (Bouwer and McCarty, 1984; Nielsen *et al.*, 1996; Van der Meer *et al.*, 1998).

Resistance of chlorinated benzenes to aerobic attack seems to rise as the number of chlorine atoms attached to the benzene molecule increases. Several studies have reported faster degradation rates for chlorobenzene and dichlorobenzenes than for trichlorobenzenes. The degradability under aerobic conditions of chlorobenzene, 1,4-dichlorobenzene and 1,2,4-trichlorobenzene was observed in laboratory experiments by indigenous microorganisms from a contaminated aquifer (Dermietzel and Vieth, 2002). Complete mineralisation of the added chlorobenzene (15.5 to 0.002 mg/l) occurred with a half-life of three to seven days. Seventy-five per cent of 1,4-dichlorobenzene in a concentration range up to 20 mg/l was mineralised to carbon dioxide but 1,2,4-trichlorobenzene was only incompletely degraded.

A2.3.3. Anaerobic biodegradation

Biodegradation of chlorinated benzenes under anaerobic conditions appears to involve two stages. The chlorine atoms are first eliminated from the benzene ring by a process known as reductive dechlorination, followed by cleavage of the aromatic ring.

A number of studies reporting anaerobic biodegradation of 1,2,4-trichlorobenzene are shown in Table A2.5. Reductive dechlorination of 1,2,4-trichlorobenzene has been observed under methanogenic conditions, whereas sulphate-reducing and nitrifying conditions have been reported to inhibit dechlorination (Bosma *et al.*, 1988; Bosma *et al.*, 1996; and Adrian *et al.*, 1998). A lag period is often observed before the onset of dechlorination, indicating the need for acclimatisation of bacteria to the chlorinated aromatic hydrocarbon. Low in situ temperatures might be a major obstruction to 1,2,4-

trichlorobenzene dechlorination under natural conditions. In the laboratory, dechlorination ceased at temperatures below 10°C (Middeldorp *et al.*, 1997).

It is still questionable whether the dichlorobenzenes and chlorobenzene resulting from reductive dechlorination of trichlorobenzenes will undergo further biodegradation under anaerobic conditions. Grbic-Galic (1990) reported that chlorobenzene was anaerobically transformed in the laboratory and eventually mineralised in acclimatised methanogenic cultures. To date there has been no published evidence on the biodegradation of chlorinated benzenes under other redox conditions. Anaerobic biodegradation of chlorinated benzenes is not widespread and several authors have found these compounds to be recalcitrant to biodegradation (Bouwer and McCarty, 1983; and Acton and Barker, 1992). This seems to indicate that molecular oxygen may be required for ring cleavage of the benzene molecule (Grbic-Galic, 1990; and Christensen *et al.*, 1994).

A2.3.4. Sorption

Sorption of 1,2,4-trichlorobenzene on soils and sediments has been reported to occur rapidly. Published equilibration times include less than 18 hours on river, lake and aquifer sediments (Schwarzenbach and Westall, 1981), and less than 24 hours on silt loam soil (Chiou *et al.*, 1983). Similar to other hydrophobic organic contaminants, the degree of sorption of 1,2,4-trichlorobenzene on natural sorbents was reported to be strongly correlated to the organic carbon content of the sorbents (Schwarzenbach and Westall, 1981; Southworth and Keller, 1989; Lee *et al.*, 1989; Paya-Perez *et al.*, 1991) (Figure A2.5).

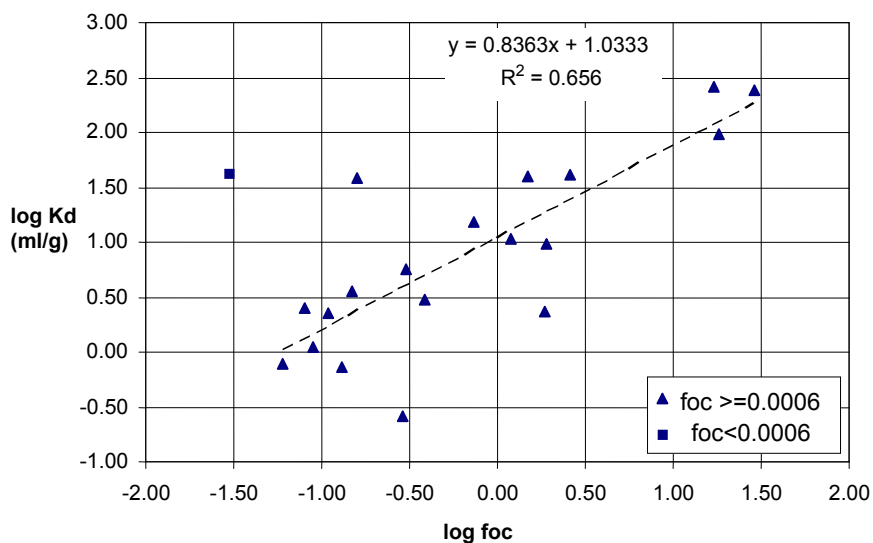


Figure A2.5 Sorption coefficient values (K_d) for 1,2,4-trichlorobenzene as a function of the organic carbon content of the sorbents (f_{oc}).
(Data referenced in Table A2.6).

A2.3.5. Conclusions

Both aerobic and anaerobic biodegradation of 1,2,4-trichlorobenzene have been reported. Dechlorination of the compound is favoured by methanogenic conditions and may not occur in sulphate-reducing or nitrifying conditions. Research is therefore needed to understand the potential for anaerobic biodegradation of 1,2,4-trichlorobenzene in sulphate-rich leachates. Sorption of 1,2,4-trichlorobenzene correlates positively with organic carbon and is therefore likely to be retarded by high organic mineral liners.

Table A2.5 Anaerobic biodegradation studies of 1,2,4-trichlorobenzene on soil and sediments

Initial conc.	Study type	Redox conditions	Lag phase (days)	Observed dechlorination	Ref
5.4-9.1 µg/l	Columns packed with river sediments (Rhine, Holland)	Methanogenic	120 days	Total dechlorination to chlorobenzene via 1,4-dichlorobenzene over 520 days	[1]
		Denitrifying	-	No dechlorination observed	
3.9mg/l	Batch tests using mixture of river sediments and sludges from wastewater treatment plant (Holland). Stable microbial methanogenic consortium.	Methanogenic	-	Up to 80 per cent converted to chlorobenzene via 1,4-dichlorobenzene over 40 days.	[2]
0.5-20 µg/l	Column packed with river sediment	Methanogenic	60 days (river sediment) 15 days (dune sediments)	Total dechlorination to chlorobenzene via 1,4-dichlorobenzene (>99%)	[3]
		Denitrifying	-	No dechlorination observed	
3.6mg/l	Batch tests (sediment-free mixed microbial consortium)	Methanogenic	-	Total dechlorination to chlorobenzene via 1,4-dichlorobenzene in 14 days	[4]
		Sulphate-reducing	-	No dechlorination observed	

[1] Bosma *et al.*, 1988; [2] Middeldorp *et al.*, 1997;

[3] Bosma *et al.*, 1996; [4] Adrian *et al.*, 1998.

Table A2.6 Sorption coefficients for 1,2,4-trichlorobenzene on soil and sediments

K_d (ml/g)	K_F (μg^{1-n} ml ⁿ /g)	K_{oc} (ml/g)	soil/sediments	Exp. method	Ref.
9.55	-	3.7	Woodburn silt loam soil, $f_{oc}=0.0019$ CEC 14 meq/100g	Batch	[1]
1.12	-	3.1	Lincoln fine sandy soil $f_{oc}=0.0009$, CEC 3.5 meq/100g	MD	[2]
0.26	-	2.0	Borden soil, $f_{oc}=0.0029$	MD	[3]
3.55	-	3.4	Aquifer material KB1H, 63-125 μm , $f_{oc}=0.0015$	Batch and MD	[4]
14.45	-	3.3	Aquifer material KS1, <125 μm , $f_{oc}=0.0073$		
2.51	-	3.5	Aquifer material KB1H, <125 μm , $f_{oc}=0.0008$		
2.40	-	-	Kaolin (inorganic mineral surface, China clay)		
95.50	-	2.7	Muck <1mm, $f_{oc}=0.18$	MD	[5]
3.02	-	2.9	Eustis soil <1mm, $f_{oc}=0.0039$		
0.72	-	2.7	Sandy aquifer material (Tampa, Florida) $f_{oc}=0.0013$	MD	[6]
2.29	-	3.3	Apison soil (<2mm), $f_{oc}=0.0011$, CEC 76 meq/100g	Batch	[7]
0.78	-	3.1	Fullerton soil (<2mm), $f_{oc}=0.0006$, CEC 64 meq/100g		
10.72	-	3.0	Durmont soil (<2mm), $f_{oc}=0.012$. CEC 129 meq/100g		
-	2.57 (n=0.84)		Augusta soil (Spinks), $f_{oc}=0.0003$	Batch	[8]
-	4.90 (n=0.85)		Delta soil (Ottookee), $f_{oc}=0.0016$		
-	9.55 (n=0.89)		Ann Arbor II soil (Brookston), $f_{oc}=0.0058$		
-	46.67 (n=0.77)		Wagner soil (Miami), $f_{oc}=0.0249$		
-	52.48 (n=0.75)		Ypsilanti soil (Wasapi), $f_{oc}=0.0124$		
-	109.65 (n=0.68)		Ann Arbor I soil (Brookston), $f_{oc}=0.0129$		
263.03	-	3.2	Charles river sediment, $f_{oc}=0.17$	Batch	[10]
646.7	-	-	Aldrich humic acid	Dialysis	[11]
40.74	-	5.1	Ispra soil (C2 horizon), $f_{oc}=0.0003$, sand	Batch	[12]
38.90	-	3.4	99.3%		
223.87	-	3.1	Ispra soil (C4 horizon), $f_{oc}=0.0016$, sand		
			95.5%		
			Ispra soil (A2 horizon), $f_{oc}=0.0187$, sand		
			91.8%		

5.62	-	3.3	Marlette soil (Bt horizon), $f_{oc} = 0.0030$, CEC 14.6meq/100g	Batch	[13]
40.74	-	3.2	Marlette soil (A horizon), $f_{oc} = 0.0259$, CEC 16.4meq/100g		
39.5	-	3.4	Dickinson aquifer sediments $f_{oc} = 0.015$	Batch	[14]
239.9	-	2.9	Peaty soil, $f_{oc} = 0.29$	Batch	[15]
2041.7	-	4.7	Lake Ontario sediment trap material, $f_{oc} = 0.041$	Field measurements	[9]

MD = Miscible displacement; f_{oc} = organic carbon content of the sorbent; CEC = cation exchange capacity. References: [1] Chiou *et al.* (1983); [2] Wilson *et al.* (1981); [3] Hu *et al.* (1995); [4] Schwarzenbach and Westall (1981); [5] Brusseau *et al.* (1990); [6] Brusseau and Rao (1991); [7] Southworth and Keller (1986); [8] Weber *et al.* (1992); [9] Oliver and Charlton (1984); [10] Wu and Gschwend (1986); [11] Chin and Weber (1989); [12] Paya-Perez *et al.* (1991); [13] Lee *et al.* (1989) [14] Chen *et al.* (2000); [15] Friesel *et al.*, 1984.



A2.4. Chlorinated aliphatic hydrocarbons

A2.4.1. Introduction

The chlorinated aliphatic hydrocarbons include compounds such as carbon tetrachloride, 1,2-dichloroethane, tetrachloroethene (also known as perchloroethylene or PCE), trichloroethene (TCE), dichloroethene (DCE) and vinyl chloride (VC). PCE, TCE, (Table A2.7) carbon tetrachloride and other chlorinated solvents are degreasing agents once commonly used in manufacturing, maintenance and service industries throughout the world, and are frequently found in contaminated groundwater.

Among the chlorinated aliphatic hydrocarbons, the solvents TCE and PCE are suspected carcinogens and are categorised as List I substances. Both TCE and PCE are reported in leachates from a number of landfill sites. In the 2001 UK PI study (Environment Agency, 2001) TCE and PCE were found in less than five per cent of the leachates studied. TCE is generally found in the highest concentrations in leachates, ranging from 0.05 to 750 $\mu\text{g/l}$ (Christensen *et al.*, 2001). TCE can be present in samples either as an original component or as a reductive dechlorination product of PCE. Chlorinated solvents can exist in multiple phases depending on how they were released and the site conditions: in the vapour phase in unsaturated sediments, or dissolved in the saturated zone. Chlorinated solvents may also be present as non-aqueous phase liquids (NAPLs) as droplets or coatings which do not mix with water.

Table A2.7 Physical properties of PCE and TCE.

	Structure	Solubility (mg/l at 25 °C)	Vapour pressure (mm Hg at 25°C)	Log K _{ow}	K _{oc} (ml/g)
PCE		206	18.5	3.4	
TCE		1280	69	2.47	2.09-3.43

A2.4.2. Biodegradation of chlorinated aliphatic hydrocarbons

Chlorinated aliphatic hydrocarbons undergo biodegradation by a number of processes, some of which are common to both aerobic and anaerobic conditions:

- as a primary substrate
- by reductive dechlorination
- by co-metabolism.

In addition, abiotic hydrolysis reactions are known to be involved in some of the degradative pathways.

Only the less oxidised chlorinated aliphatics, such as vinyl chloride, dichloroethene and dichloromethane, are known to biodegrade as primary substrates, aerobically and in some cases anaerobically. In this type of reaction, the facilitating microorganism obtains energy and organic carbon from the degraded chlorinated aliphatic hydrocarbon. Most chlorinated solvents degrade by co-metabolism, where the chlorinated compound is converted to another substance during microbial metabolism of another compound, which is the primary growth substrate. Degradation is catalyzed by an enzyme or cofactor that is produced by the microorganisms for other purposes.

Chlorinated solvents can also act as electron acceptors in a process known as reductive dechlorination in which hydrogen replaces chlorine atoms. Reduction dechlorination does not result in the production of energy for these microorganisms because the chlorinated compounds are used as electron acceptors. Therefore an electron donor or carbon source is required to produce energy for the microbes. Electron donors may be present in the form of co-contaminants or organic carbon in landfill leachate. In general, reductive dechlorination occurs by sequential dechlorination from PCE to TCE to DCE to VC to ethene. Reductive dechlorination has been demonstrated under nitrate- and iron-reducing conditions, but the most rapid biodegradation rates, affecting the widest range of chlorinated aliphatic hydrocarbons, occur under sulfate-reducing and methanogenic conditions (Bouwer, 1994).

A2.4.3. Aerobic degradation

Of the chlorinated ethenes, vinyl chloride is the most susceptible to aerobic biodegradation and PCE the least. PCE is not known to undergo co-metabolic

biodegradation under aerobic conditions; however, TCE is biodegraded aerobically and may be co-metabolically degraded by several microorganisms which use other substrates such as methane, ammonia, toluene, propylene, propane, dichlorophenoxyacetate and isopropylbenzene. It is difficult to define the specific degradation rates for the aerobic biodegradation of TCE because there are many different microbial systems/primary substrate combinations. In microcosm studies, aerobic degradation of TCE, with phenol used as the primary substrate, occurred at a rate of 16 µg/l/day (Kao and Prosser, 1999).

A2.4.4. Anaerobic degradation

A number of bacteria have been isolated which dechlorinate PCE to TCE under anaerobic conditions. It is thought that a mixed population of bacteria are required to biodegrade PCE in natural environments in the absence of oxygen and nitrate (Ellis *et al.*, 2000). TCE undergoes reductive dechlorination to form dichloroethene isomers, followed by vinyl chloride, then ethene, and finally, ethane. Daughter compounds such as chloroform, 1,1-dichloroethene or vinyl chlorides may be more toxic than the parent compounds.

During reductive dechlorination, hydrogen replaces each chlorine atom, and each stage becomes progressively more difficult and reaction rates decrease. Thus dechlorination is relatively easy for TCE but more difficult for vinyl chloride; its conversion to ethene appears to be the rate-limiting step. There is evidence that the stronger reducing environments such as methanogenic or sulphate-reducing environments are needed to enable the reductive dechlorination of highly chlorinated compounds such as TCE through to ethane (Freedman and Gossett, 1989). Less chlorinated compounds and the daughter products of reductive dechlorination can be biodegraded in less reducing environments (Vogel, 1995).

The determination of rate constants for biodegradation of chlorinated compounds such as PCE and TCE during field studies is difficult. Chloride is generated during biodegradation and must be separately accounted for if chloride is used as a conservative tracer by calculating a mass balance for chloride including both organic and ionic species (Wiedemeier *et al.*, 1996). Another method is to measure daughter products, but these must be chosen with care since degradation products such as vinyl chloride are often present as co-contaminants. Products from reductive dechlorination initially increase in concentration as they are produced, then decrease as they are degraded further down gradient.

No data was found in the literature for the degradation of PCE, TCE in mineral landfill liners. However, some reports cover the attenuation of chlorinated aliphatics in leachate and in groundwater studies. In leachate microcosm studies, Leahy and Shreve (2000) demonstrated that PCE biodegraded at a rate of 23.8 µg/day. When the microcosms were supplemented with organic carbon, biodegradation was quicker (61 µg/day). The authors concluded that biodegradation of PCE would proceed more quickly in young landfills, and that as landfills aged biodegradation might be limited by the availability of degradable organic matter (Leahy and Shreve, 2000).

There are relatively few groundwater studies reporting PCE rate constants. Aronson and Howard (1997) reported rate constants ranging from 0.00019 to 0.0046 per day for PCE but concluded that there was insufficient evidence to determine a rate constant for particular redox environments. For the range of concentrations found in leachate (0.05 to 750 µg/l (Christensen *et al.*, 2001)), the average rate constant for TCE is 0.003/day (range = 0.00017 to 0.0056/day) (Aronson and Howard (1997)). From groundwater studies, there appears to be no correlation between TCE

concentrations and rate constant (Figure A2.6), and again, the paucity of data from different sites means that rate constants for different redox conditions cannot be determined.

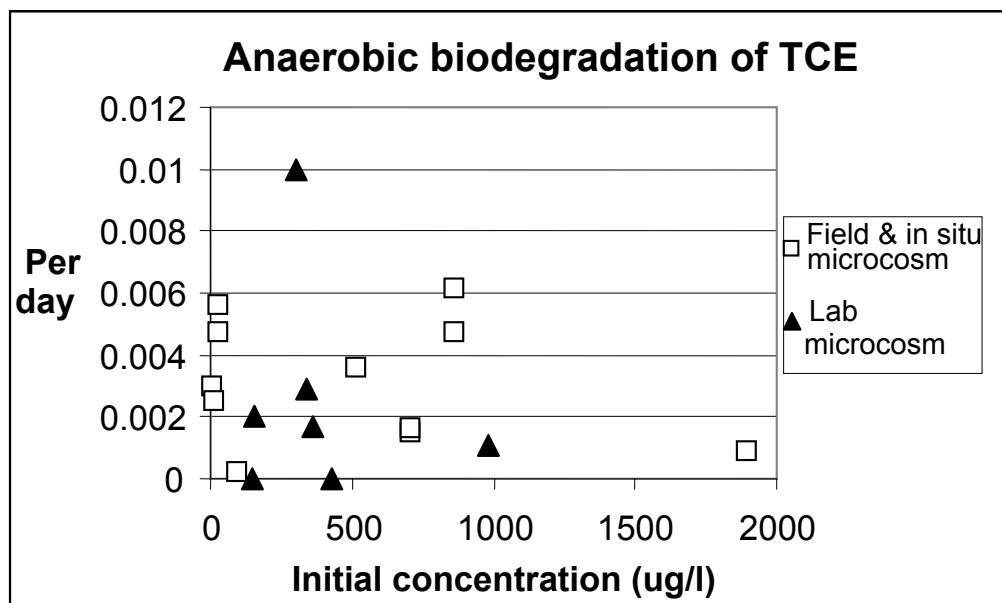


Figure A2.6 Anaerobic biodegradation rates for TCE from field and laboratory microcosm studies in aquifers (adapted from Aronson & Howard 1997)

A2.4.5. Sorption

The number of reports on the sorption of chlorinated solvents in mineral landfill liners is limited, but there are studies for soils and containment sites from which information can be derived. There is a good correlation between the organic carbon content of a range of soils (f_{oc} ranging from 0.00007 to around 0.65) and the sorption coefficients (K_d) of PCE (Figure A2. 7) and TCE (Figure A2.8), but correlation is poor for less humified soils ($f_{oc} < 0.001$; $R^2=0.23$ for PCE and $R^2=0.18$ for TCE). Sorption coefficients (K_d) for PCE and TCE, determined from a range of soil types, are 0.41 and 0.47 respectively (Table A2.8).

The addition of natural humus considerably improved the sorption capacity of a bentonite soil barrier. The sorption coefficient (K_d) with five per cent humus increased to 2.43, compared to 0.53 for the soil bentonite mixture alone, which contained six per cent bentonite and one per cent organic matter (Kandewhal and Rabideau, 2000). As TCE is relatively polar, sorption is influenced by surface interactions, as well as the organic matter content of a soil or sediment. In a typical landfill liner soil (clay 13 per cent, silt 50 per cent and sand 37 per cent) mixing with coal slurry to improve the organic content to approximately 32 per cent resulted in a sorption coefficient (K_f) of 387; increasing the organic content to 50 per cent did not result in a corresponding increase in sorption coefficient ($K_f = 401.2$) (Malone *et al.*, 1994). The authors concluded that the surface area and polarity of the coal slurry particles had a significant influence on the sorption coefficient of TCE, but it is also possible that the type of organic carbon in the coal slurry was strongly sorptive.

Gullick and Weber (2001) found that different sorption processes were occurring between TCE and modified organoclays and shale. TCE tended to adsorb to the organic part of an organoclay modified with a 16-carbon aliphatic chain such as HDTMA-bentonite, but on TMPA-bentonite (triphenyl ammonium bentonite) or natural shale, adsorption onto the mineral surface was the principal sorption mechanism. Sorption coefficients were greatest for TMPA-bentonite ($K_d=303$) and shale ($K_d=62.2$), compared to the long-chain modified organoclay ($K_d=14.2$).

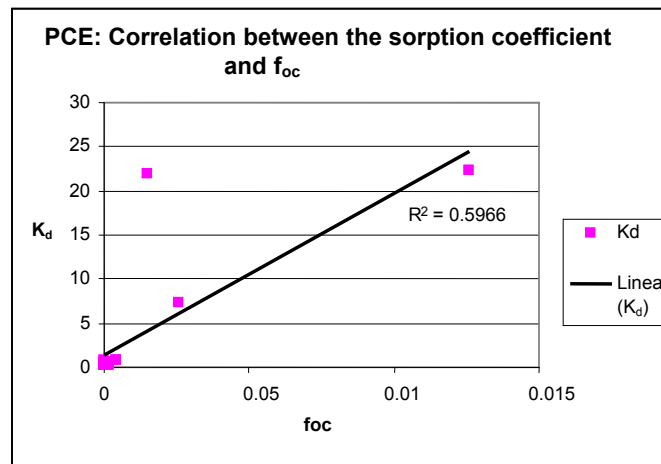


Figure A2.7 Correlation between tetrachloroethene sorption coefficients (K_d) and organic carbon in a range of soils (adapted from Delle Site, 2001)

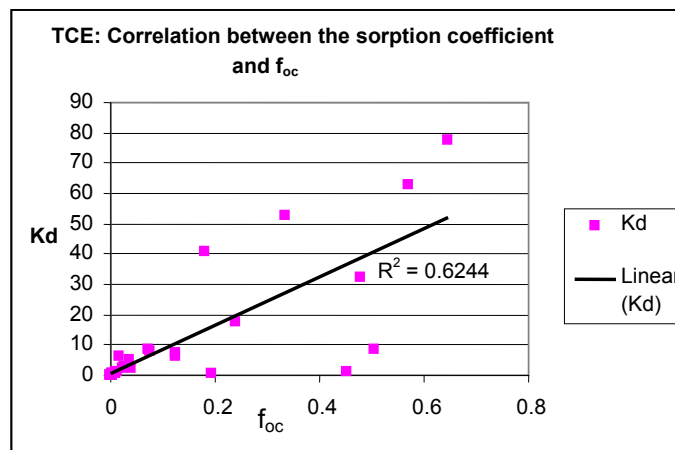


Figure A2.8 Correlation between trichloroethene sorption coefficients (K_d) and organic carbon in a range of soils (adapted from Delle Site, 2001)

Table A2.8 Average sorption coefficients (K_d) for PCE and TCE in soils

f_{oc}	K_d (ml/g)				All fractions
	<0.01	>0.01 to <0.0600	>0.06 to <0.11	>0.11	
PCE	-0.41 (16)	Insufficient data	Insufficient data	Insufficient data	0.41 (16) $r^2 = 0.6$
TCE	-0.63 (18)	0.42 (8)	0.92 (8)	1.39 (11)	0.47 (39) $r^2 = 0.62$

Figures in brackets indicate number of samples (adapted from Delle Site, 2001)

A2.4.6. Conclusions


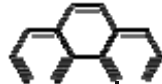
There is good potential for biodegradation of PCE and TCE in anaerobic environments provided that a supplementary organic carbon source is available. This is likely to be the case in landfills, but as the landfill ages and easily available sources of organic matter are used up, biodegradation of chlorinated aliphatics will decline. Further research is needed to determine degradation rates in different redox environments for PCE and TCE. Both PCE and TCE sorption coefficients increase in organic soils, therefore it is likely that sorption of these compounds will occur in the type of soils used for mineral liners.

A2.5. Polycyclic aromatic hydrocarbons

A2.5.1. Introduction

Polycyclic aromatic hydrocarbons are fused ring compounds including naphthalene, acenaphthalene, fluorene, methyl-naphthalene, pyrene and phenanthrene. The polycyclic aromatic hydrocarbons (PAHs) and naphthalene (BAH) are all List I substances. Values for key physical properties are given in Table A2.9.

Table A2.9 Physical properties of naphthalene and phenanthrene

	Chemical structure	Solubility (mg/l at 25°C)	Vapour pressure (mm Hg at 25°C)	Log K _{ow}	K _{oc} (ml/g)
Naphthalene		31.7	36.8	3.17	2.71-3.92
Phenanthrene		1.15	0.113	4.35	3.95-4.92

A2.5.2. Naphthalene

Naphthalene (C₁₀H₈) and its substituted derivatives are found in crude oil and oil products. It is common in landfill leachate, with a concentration range of 0.1 to 260 µg/l (Christensen *et al.*, 2001). Median values in UK leachates are 0.46 µg/l. Only one study involving a UK aquifer was found during the literature search (Thornton *et al.*, 2000), and no studies on landfill liners were found. However, the biodegradation of naphthalene in US and European aquifers and other sediments has been studied, and a number of reports explore sorption in sediments with different proportions of organic material.

A2.5.3. Aerobic degradation of Naphthalene

Biodegradation rates for naphthalene in the sandy aquifer close to the Vejen landfill site, Denmark, were determined from in situ microcosms (0.2 to 0.8 per day) and

laboratory microcosms (0.4 to 0.9 per day) (Nielsen *et al.*, 1996). Lag times of six to twelve days were reported.

A2.5.4. Anaerobic degradation of Naphthalene

Until recently, naphthalene was generally considered recalcitrant to biodegradation under anaerobic conditions. However, anaerobic biodegradation has now been demonstrated, and the pathway for anaerobic biodegradation of naphthalene in sulphate-reducing environments has been elucidated (Annweiler *et al.*, 2002). The primary intermediate is 2-naphthoic acid, which is reduced prior to ring cleavage to saturated intermediates with a cyclohexane ring structure and two carboxylic acid groups.

Naphthalene degradation has been demonstrated in laboratory experiments using iron-reducing, denitrifying and sulphate-reducing environments. For example, naphthalene was biodegraded in anaerobic petroleum-contaminated harbor sediments amended with iron oxide (Coates *et al.*, 1996). Naphthalene biodegradation was also found in anaerobic studies with PAH-contaminated sediments under denitrifying and sulphate-reducing conditions (Rockne and Strand, 1998; Johnson and Ghosh, 1998; Langenhoff *et al.*, 1996). In anaerobic fixed bed reactors fed with a mixture of PAHs (with no additional carbon source), naphthalene removal rates in the denitrifying environment (approximately 200 µg/l/day) were faster than under sulphate-reducing conditions (approximately 50 µg/l/day) (Rockne and Strand, 1998). Eriksson *et al.* (2003) demonstrated complete degradation of naphthalene at 7°C and 20°C in sandy soils enriched with microbial cultures specially adapted to PAHs and nitrate-reducing conditions. Thornton *et al.* (2000) demonstrated anaerobic biodegradation of naphthalene-spiked leachate in column experiments; with an initial concentration of 120 µg/l, a mean half-life of 82.5 days was determined.

In field and in situ studies, anaerobic biodegradation of naphthalene is more open to question. In the 21 anaerobic field and in situ aquifer studies collated by Aronson and Howard (1997), only 12 studies report biodegradation of naphthalene, with a mean rate of 0.0072/day. The authors questioned whether the aquifers were truly anaerobic and suggest that naphthalene should be regarded as recalcitrant to degradation under these conditions. Naphthalene mineralization was not found in the anaerobic leachate plume downgradient of the Grinsted landfill site which is dominated by iron-reducing conditions (Bjerg *et al.*, 1999; Ruge *et al.*, 1999). In situ microcosm studies in the early 1990s at Vejen landfill, where methanogenic, sulphate-reducing and iron-reducing conditions prevail in the leachate plume, did not demonstrate biodegradation of naphthalene (Nielsen *et al.*, 1995). However, more recent studies at the Vejen landfill appear to support naphthalene biodegradation (Baun *et al.*, 2003).

A2.5.5. Sorption of Naphthalene

As a hydrophobic compound, sorption of naphthalene is strongly influenced by the proportion of organic matter in a soil or sediment. King and Barker (1999) found that naphthalene was retarded by 2.6 to 3.5 times relative to chloride (a conservative tracer) in the Borden aquifer. In this low carbon aquifer, batch tests suggested a K_d value of 1.66 (King *et al.*, 1999). Similarly, a low sorption coefficient ($K_d = 1.16$) was determined in the Bemidji aquifer, which has the same organic carbon content, and approximately five per cent clay (Piatt *et al.*, 1996). In highly organic soils, sorption increases significantly, Tables A2.10 and A2.11. Xing (1997) found that the quality of soil organic matter may also affect the sorption rate of naphthalene. For example, a Cretaceous soft coal mixed with weathered shale, which has a high concentration of

aromatic compounds, has a greater sorption capacity than a relatively young sedge peat soil which is more aliphatic in nature (Xing, 1997).

Table A2.10 Sorption coefficients for naphthalene

Soil type	f_{oc}	Clay %	K_d (ml/g)	K_{oc} (ml/g)	K_f ($\mu\text{g}^{1-n} \text{l}^n/\text{g}$)	Reference
Cretaceous soft coal, mixed with weathered shale	0.534		781	3.17	775	Xing (1997)
Well humified young sedge peat	0.322		158	2.7	164	Xing (1997)
White clay, Quaternary sediment	0.074		45.4	2.79	56.5	Xing (1997)
Glacial till, Black Chermozenic	0.025		39.9	3.2	35.7	Xing (1997)
Glacial till, Brown Chermozenic	0.026		13.4	2.7	16.5	Xing (1997)
Dark grey silt loam (Dover AFB, DE)	0.0149	18			18.3	Xia & Ball (1999)
Cretaceous weathered shale (Devon, Alberta)	0.016	43	38	3.37		Sawatsky <i>et al.</i> (1997)
Borden aquifer	0.0002		1.66	3.91		King <i>et al.</i> (1999)
Bemidji aquifer (MN)	0.0002	<5%	1.6	3.9		Piatt <i>et al.</i> (1996)
Well mixed sandy loam, Massachusetts	0.0108				343	Gunesakara <i>et al.</i> (2003)
West Midlands sandstone aquifer	0.00026		0.56	3.3		Thornton <i>et al.</i> (2000)
Silty loam	0.0149	17.7	4.23	2.45		Bayard <i>et al.</i> (2000)
Sandy river sediment	0.0027	2.0	2.2	2.91		Kan <i>et al.</i> (1994)

Table A2.11 Average sorption coefficients (K_d) and K_{oc} values for naphthalene and phenanthrene in soils

f_{oc}	K_d (ml/g)				All fractions	K_{oc} (ml/g)
	<0.01	>0.01 to <0.06	>0.06 to <0.11	>0.11		
Naphthalene	11.8 (38)	34.5 (10)	Insufficient data	1,100 (5)	119 (53) $r^2 = 0.84$	3.0
Phenanthrene	50.8 (4)	170 (4)	Insufficient data	Insufficient data	419 (8) $r^2 = 0.69$	3.7

Figures in brackets indicate number of samples (adapted from Delle Site, 2001)

A2.5.6. Phenanthrene

Phenanthrene, ($C_{14}H_{10}$) a tricyclic aromatic hydrocarbon, is often found at sites contaminated with creosote. It is one of the most commonly detected PAHs in landfill leachates. Phenanthrene is the smallest PAH and it is often used as a model substrate for degradation studies.

A2.5.7. Aerobic degradation of phenanthrene

PAHs with less than five rings are readily degraded by microorganisms under aerobic conditions. Aerobic biodegradation involves dioxygenase attack on the terminal ring to form catechol, followed by further oxygenolytic cleavage of catechol, and then further ring cleavage to metabolically useful substrates (Rockne and Strand, 1998).

Phenanthrene is degraded aerobically by some soil bacteria through one of two different routes. In one route, 1-hydroxy-2-naphthoic acid is oxidized to 1,2-dihydroxynaphthalene, which is further degraded to salicylate which can be further metabolized. In the other pathway, the ring of 1-hydroxy-2-naphthoic acid is cleaved and further metabolized via the phthalate pathway. It has been demonstrated that naphthalene and phenanthrene share a common upper metabolic pathway (Kiyohara H, *et al.* 1994).

Aerobic biodegradation of phenanthrene has been demonstrated in batch experiments with contaminated soil (Richnow *et al.*, 2000). A lag period of five days was found as the microbiota adapted to the ring-labeled ^{13}C -phenanthrene, this was followed by rapid mineralization to $^{13}CO_2$ over the next fourteen days. After this, $^{13}CO_2$ evolved more slowly as ^{13}C -phenanthrene became more strongly sorbed to the soil. With an initial concentration of 354.3 $\mu g/g$ phenanthrene, 73 per cent was evolved as carbon dioxide, at an average of 5.4/day.

A2.5.8. Anaerobic degradation of phenanthrene

There is little information about the anaerobic biodegradation of phenanthrene in anaerobic aquifers. In the few studies in which degradation has been reported, this is likely due to the presence of low levels of dissolved oxygen (Aronson and Howard, 1997). However, King *et al.* (1999) observed degradation of phenanthrene, from a creosote plume at the Borden AFB, under anaerobic conditions (mean dissolved oxygen = 0.13 mg/l) with an estimated half-life of 49 days. Biodegradation in

phenanthrene-contaminated marine sediments has also been demonstrated (Hayes *et al.*, 1999; Coates *et al.*, 1996). In anaerobic fixed bed reactors, with an adapted microbiota and a mixture of PAHs (with no additional carbon source), phenanthrene removal rates in the sulphate-reducing environment (approximately 6 µg/l/day) were slower than under denitrifying conditions (130 µg/l/day)(Rockne and Strand, 1998).

A2.5.9. Sorption of phenanthrene

As with naphthalene, the sorption of phenanthrene is influenced by the percentage of organic carbon in the sediment (Table A2.12).

A2.5.10. Conclusions

While studies have demonstrated that both naphthalene and phenanthrene can be degraded without oxygen, further research is needed to confirm the degradation rates and sorption coefficients of these compounds under different redox conditions and in environments applicable to landfill liners.

Table A2.12 Sorption coefficients for phenanthrene.

Soil type	f_{oc}	Clay %	K_d (ml/g)	$\log K_{oc}$ (ml/g)	Reference
Dark grey silt loam (Dover AFB, DE)	0.0149	18			Xia & Ball (1999)
Borden aquifer	0.0002		1.8	2.93	King <i>et al.</i> (1999)
Bemidji aquifer (MN)	0.0002	<5	2.7	3.13	Piatt <i>et al.</i> (1996)
Sandy river sediment	0.0027	2.0	32.2	4.08	Kan <i>et al.</i> (1994)
Pond sediments	0.028–0.033			4.36 ^a	Karickhoff <i>et al.</i> (1979)
Soils from Michigan, Minnesota, and Ohio	0.011–0.029			4.19 ^b	Chiou <i>et al.</i> (1998)
River, lake and coastal sediments	0.004–0.052			4.55 ^c	Chiou <i>et al.</i> (1998)
Borden aquifer, bulk sand	0.0002			4.27	Ran <i>et al.</i> (2003)
Borden aquifer, isolated organic fraction (kerogen)				5.04	Ran <i>et al.</i> (2003)

^a Average from coarse silt fraction of two pond sediments.

^b Average value for five soils.

^c Average value for seven sediments.

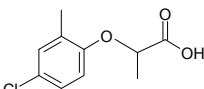
A2.6. Mecoprop

A2.6.1. Introduction

Mecoprop ((R,S)2-(2-methyl-4-chlorophenoxy)-propionic acid), abbreviated as MCPP, is one of a group of phenoxyalkanoic herbicides which include 2,4-D (2,4 dichlorophenoxyacetic acid), 2,4,5-T (2,4,5- trichlorophenoxyacetic acid), and MCPA (2-methyl-4-chlorophenoxyacetic acid) among others. Mecoprop was introduced as selective, systemic hormone-type herbicide in 1956 for post-emergence control of broadleaved weeds (such as cleavers, chickweed, clovers and plantains) in wheat, barley, oats and grassland. Mecoprop comprises equal proportions of R- and S-isomers (a racemic mixture); Mecoprop-P contains only the R-isomer.

Mecoprop is water soluble (Table A2.13) and easily leaches from soils with the result that it is one of the most commonly detected herbicides in groundwater (Environment Agency, 2004). In the UK Pollution Inventory (PI) studies of landfill leachate, Mecoprop was found in 98 per cent of samples (Environment Agency, 2001). The average concentration of Mecoprop in leachates is generally low. For example, in the PI study, the median concentration of Mecoprop was 11 µg/l (range = 0.1 to 140 µg/l); concentrations in European and US leachates are in a similar range (Christensen *et al.*, 2001; Gintautus *et al.*, (1992). However, high concentrations of Mecoprop have been recorded downgradient of some landfills, such as 3,000 µg/l at Helpston, UK (Williams *et al.*, 2003), 600 µg/l at Vejen, Denmark (Baun *et al.*, 2003) and 300 µg/l at Sjoelund (Tuxen *et al.*, 2003).

Table A2.13 Physical properties of Mecoprop

Structure	Solubility (mg/l)	Vapour pressure (mm Hg)	pKa	Log K _{ow}
	734	7.5x10 ⁻⁷	3.1 - 3.78 ^a	0.1 ^b - 2.94 ^c

Vapour pressure measured at 20°C; K_{ow}-octanol-water partition coefficients and S-water solubility (SRC, 1988); *measured at 25°C; Ref: ^apKa = 3.1 (Dept of the Environment, 1994); pKa = 3.78 (Tomlin, 1997); ^bMecoprop in anionic dissociated form; ^cMecoprop in neutral (non-ionised) form at pH2 (Tomlin, 1997).

A2.6.2. Degradation of Mecoprop

There is no evidence of chemical degradation of Mecoprop in soils but photochemical degradation in aqueous solution has been found (Smith, 1989). Mecoprop readily biodegrades in aerobic soils (Smith, 1989) and aquifers (Agertved *et al.*, 1992; Heron and Christensen, 1992; Ruge *et al.*, 1995) to 4-chloro-2-methyl-phenol followed by ring hydroxylation and ring opening. 4-Chloro-2-methyl-phenol (4-CMP, also known as chlorocresol or PCOC) is highly toxic to aquatic organisms and is designated a List I substance under the Groundwater Regulations (JAGDAG, 2001); it tends not to accumulate because further degradation is rapid. 4-CMP may be found as an impurity

in phenoxyalkanoic herbicides, and therefore its presence in the environment may not be evidence of biodegradation of Mecoprop (Reitzel *et al.*, 2004).

In aerobic conditions, both enantiomers of Mecoprop degrade, with S-Mecoprop being more rapidly transformed than R-Mecoprop (Harrison *et al.*, 2003; Williams *et al.*, 2003). Several authors note that pre-exposure to Mecoprop reduces lag periods and leads to rapid degradation (Smith, 1989; Torang *et al.*, 2003). In microcosm studies using sediments collected from an unpolluted aquifer at Vejen, Denmark, a lag period of 20 to 110 days was found before degradation of Mecoprop commenced (Heron and Christensen, 1992). Field trials at Vejen resulted in degradation of Mecoprop after a lag period of 80 to 120 days (Broholm *et al.*, 2001; Ruge *et al.*, 2002). Degradation of Mecoprop was found in some boreholes in the Triassic Sherwood Sandstone aquifer, but not in the unpolluted Lincolnshire Limestone or Chalk (Johnson *et al.*, 2000).

There have been few reports of anaerobic degradation of Mecoprop and the degradative pathway is unknown. However, initial transformation by reductive dechlorination and dealkylation has been observed for other phenoxyalkanoic acid herbicides (2,4-D and 2,4,5-T) in anaerobic aquifer sediments (Gibson and Suflita, 1990; Mikesell and Boyd, 1985). Limited anaerobic biodegradation of Mecoprop may occur under nitrate-reducing conditions. Larsen and Armand (2001) reported reduction of Mecoprop concentrations after 312 days from anaerobic microcosms which were amended with nitrate. In flasks containing anaerobic sediments from a wetland ecosystem (with added nitrate), eight per cent of Mecoprop biodegraded in 478 days, 10 per cent under sulphate-reducing conditions, and 13 per cent under methanogenic conditions (Larsen *et al.*, 2001). Williams *et al.* (2001, 2003) reported Mecoprop degradation in laboratory microcosms using limestone and groundwater extracted downstream of the Helpston landfills. Degradation of Mecoprop at 0.65 mg/l/day was found under nitrate-reducing conditions (Williams *et al.*, 2001); in later microcosm experiments, biodegradation was not demonstrated with iron-reducing, methanogenic or sulphate-reducing conditions (Harrison *et al.*, 2003). S-Mecoprop did not degrade but R-Mecoprop was transformed to 4-CMP, which itself degraded after R-Mecoprop concentrations fell to zero.

Degradation of Mecoprop was assessed in a landfill leachate plume at Grinstead Landfill site, Denmark (Ruge *et al.*, 1999); complete mineralisation was not found during field injection tests, in situ microcosm or laboratory experiments, although dechlorination did occur (Ruge *et al.*, 1995). In this aquifer, anaerobic conditions were dominated by iron reduction, but methanogenic and sulphate reduction also occurred close to the landfill (Ruge *et al.*, 1999). Tuxen *et al.* (2003) reported Mecoprop degradation at Sjoelund, Denmark, in the nitrate- and iron-reducing zones of the landfill plume.

Degradation in aerobic topsoils has been widely studied, with Mecoprop biodegradation half-lives reported to be 1.3 to 100 days, Table A.2.14. There are few data on degradation rates in unsaturated subsoils and groundwater in the UK, and because of this, the Environment Agency (England and Wales) states that it may be inappropriate to apply biodegradation as an attenuation mechanism for Mecoprop in these environments unless site-specific evidence is available to support it (Environment Agency, 2004). In laboratory studies, degradation rates in aerobic and

nitrate-reducing microcosms have been measured, but it may not be appropriate to scale the results of laboratory tests to the field.

Table A2.14 Literature biodegradation values ($t_{1/2}$) for Mecoprop

Aerobic	Soil/Lithology	Author
1.3-20		Helweg, 1993
20	Sandy soils	Larsen <i>et al.</i> , 2000
8-77	Calcareous soils, Spain	Romero <i>et al.</i> , 2000
62-100	Various soils and aquifer sediments	Johnson <i>et al.</i> , 2003
7-19	Various soils	Dept of the Environment, 1994
7-9	Various soils	Smith, 1989
3.3	UK soils	Brooke and Matthiessen, 1991

A2.6.3. Sorption of Mecoprop

Sorption processes may contribute to the attenuation of this compound in the landfill liner environment. Mecoprop has a polar carboxylic group and a lipophilic phenyl group. Sorption of Mecoprop might therefore occur by interactions between the carboxylic group and charged surfaces, or by partitioning via the lipophilic group and organic matter. The Mecoprop carboxylic group is principally found in the dissociated form at pH levels (7-9) likely to be found in methanogenic leachate. Because of its negative charge, Mecoprop would not be expected to sorb to clay minerals that are themselves predominantly negatively charged. Acetogenic landfill leachate tends not to reach the pKa of Mecoprop, therefore, it is likely to remain ionized. However, there is some evidence that Mecoprop sorbs more strongly at lower pH than it at higher pH (Madsen *et al.*, 2000). MCPP may interact with clays through surface complexation with electrolyte cations (Clausen *et al.*, 2001). In addition, sediments coated in iron oxyhydroxides, which have positively charged surfaces in neutral to acid environments, may sorb Mecoprop (Clausen and Fabricius, 2001). Mecoprop is only weakly hydrophobic ($\log K_{ow} = 0.1$; Tomlin 1997), therefore the organic carbon content is not likely to be important for sorption of this compound. However, in some cases a positive correlation of Mecoprop sorption with humus content has been observed (Fomsgard, 1997). Table 2.15 gives some sorption coefficient values for Mecoprop.

Table A2.15 Literature sorption values for Mecoprop

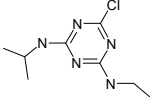
K_d (ml/g)	Clay %	f_{oc}	Soil/Lithology	Author
0.61		0.033		Harris <i>et al.</i> , 2000
0.07-0.2		0.024- 0.026		Helweg, 1993
0-0.07		0.002-0.01		Fomsgaard, 1997
0.4-0.8		0.02-0.04		Fomsgaard, 1997
2.6-2.8		0.047- 0.051		Fomsgaard, 1997
0-0.04		0.0002	Sand and gravel	Tuxen <i>et al.</i> , 2000
0.003- 0.11		0.0105	Siltstone	Env. Agency, 2004
0.26	<1	0.0005	Sandy sediments, Drengsted, Denmark	Madsen <i>et al.</i> , 2000
0.15	<1	0.0003	Sandy sediments, Fladerne Bæk, Denmark	Madsen <i>et al.</i> , 2000
0.18	<1	0.0002	Sandy sediments, Grinsted, Denmark	Madsen <i>et al.</i> , 2000
0.07	<1	0.0002	Sandy sediments, Vejen, Denmark	Madsen <i>et al.</i> , 2000
0.09	3	0.0007	Esker sediments, Spanager, Denmark	Madsen <i>et al.</i> , 2000
0.09- 0.16	3-9	0.0006- 0.0012	Till deposits Vestskoven, Denmark	Madsen <i>et al.</i> , 2000
				Clausen and Fabricius, 2001
0-0.04		0.0002	Sand and gravel	Tuxen <i>et al.</i> , 2000
0.003- 0.11		0.0105	Siltstone	Environment Agency, 2004
<1			Sandstone and marl	Zipper <i>et al.</i> , 1998

A2.7. Atrazine

A2.7.1. Introduction

Atrazine (2-chloro-4-ethylamino-6-isopropylamino-1,3,5-triazine) is the leading member of a class of triazine ring-containing herbicides that includes simazine and terbuthylazine. Atrazine is a selective herbicide used to control broadleaf and grassy weeds in corn, sorghum, sugarcane, pineapple, and other crops, and in conifer reforestation plantings. It is also used as a nonselective herbicide on non-cropped industrial lands and on fallow lands. Atrazine is widely used in the US, but its application is banned in the European Union where terbuthylazine is used instead. Atrazine is moderately soluble in water (Table A2.17).

Table A2.16 Physical properties of Atrazine.

Structure	Solubility (mg/l)	Vapour pressure (mm Hg)	pKa	Log K _{ow}	Log K _{oc} (ml/g)
	33	2.36 E-009	1.7	2.5	2.1-2.9

Vapour pressure measured at 20°C; K_{ow}-octanol-water partition coefficients and S-water solubility (SRC, 1988) *measured at 25°C.

A2.7.2. Biodegradation of atrazine

Aerobic biodegradation is considered to be the main mechanism for loss of atrazine from the surface soils. The biodegradation of atrazine and other chloro-s-triazine herbicides generally involves a series of hydrolytic reactions catalyzed by amidohydrolase enzymes yielding cyanuric acid which can be used as a carbon and nitrogen source (Helweg, 1989; Radosevich *et al.*, 1997; Wackett *et al.*, 2002).

The half-life for aerobic biodegradation of atrazine in surface soils is 50 days, compared to 114 days in sterilised soils (Accinelli *et al.*, 2001). In anaerobic soils, atrazine degradation has been attributed to abiotic hydrolysis catalysed by minerals and organic matter, but biodegradation also occurs and the degradative pathway via hydroxyatrazine formation and ring cleavage has been elucidated (Crawford *et al.*, 1998). The major metabolite, hydroxyatrazine, tends to accumulate in soil. The half-life of atrazine in anaerobic soils is 124 days, compared to 700 days in sterile soils.

A2.7.3. Sorption of atrazine

The sorption of atrazine appears to depend on the organic carbon content and the pH of the soil (Xing *et al.*, 1996; Herwig *et al.*, 2001; Boivin *et al.*, 2005). Depending on the pH, atrazine may be present as a protonated or a neutral species (pKa = 1.7; Table A2.17). The neutral form of atrazine has functional groups capable of sorption to clay surfaces via H-bonding, van der Waals bonding and ligand exchange,

whereas under acid conditions, cation exchange may be involved (Herwig *et al.*, 2001). Helwig *et al.* (2001) calculated the sorption coefficients (K_d) of 0.72, 2.08 and 3.27 ml/g for atrazine on pure sodium kaolinite, illite and montmorillonite, respectively. Some sorption coefficients for atrazine on soils, sediments and model sorbents are given in Table A2.18. Log K_{oc} values range from vary low values (-0.18 ml/g) to high values (3.8 ml/g).

Table A2.17 Literature sorption values for atrazine

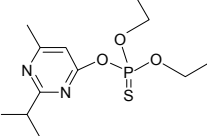
K_d (ml/g)	K_{oc} (ml/g)	log K_{oc} (ml/g)	Clay %	f_{oc}	Soil/Lithology	Author
0.46 to 2.2	0.37 to 0.68	-0.42 - -0.17		0.0125 to 0.0325	Sandy loam soil	Spark and Swift, 2002
2.2	0.69	-0.18		0.063	Loamy clay soil	Spark and Swift, 2002
No sorption found	No sorption found			0.001-0.003	Med/coarse grained sandy sediments (Grinsted Landfill, Denmark)	Rugge <i>et al.</i> , 1999
0.72				<0.0001	Na ⁺ kaolinite	Herwig <i>et al.</i> , 2001
2.08				<0.0001	Na ⁺ illite	Herwig <i>et al.</i> , 2001
3.27				<0.0001	Na ⁺ montmorillonite	Herwig <i>et al.</i> , 2001
13.7				0.06	Fine, loamy soil	Laird <i>et al.</i> , 1994
0.19 to 2.54	64 to 238	1.81 to 2.38		0.0014 to 0.067	Sandy loam	Ben-Hur <i>et al.</i> , 2003
0.31			7.1	0.0043	Hanford sandy loam	Singh <i>et al.</i> , 1996
3.1	6,200	3.79	<1	0.0005	Sandy sediments, Drenghed, Denmark	Madsen <i>et al.</i> , 2000
0.68	2,267	3.36	<1	0.0003	Sandy sediments, Fladerne Baek, Denmark	Madsen <i>et al.</i> , 2000
1.1	5,500	3.74	<1	0.0002	Sandy sediments, Grinsted, Denmark	Madsen <i>et al.</i> , 2000
0.16	800	2.90	<1	0.0002	Sandy sediments, Vejen, Denmark	Madsen <i>et al.</i> , 2000
0.54	771	2.89	3	0.0007	Esker sediments, Spanager, Denmark	Madsen <i>et al.</i> , 2000
0.33-0.97	550-808	2.74 to 2.91	3-9	0.0006-0.0012	Till deposits Vestskoven, Denmark	Madsen <i>et al.</i> , 2000

A2.8. Diazinon

A2.8.1. Introduction

Diazinon (O,O-diethyl 0-2-isopropyl-6-methyl(pyrimidine-4-yl) phosphorothioate, also known as phosphorodithioic acid, O,O-diethyl O-(2-isopropyl-6-methyl-4-pyrimidinyl) ester) is a non-systemic organophosphate insecticide used to control cockroaches, silverfish, ants and fleas in residential buildings, and on gardens and farms to control a wide variety of sucking and leaf-eating insects (Kidd and James, 1991). It also has veterinary uses against fleas and ticks. Diazinon may be found in formulations with a variety of other pesticides such as pyrethrins, lindane, and disulfoton. Trade names of Diazinon include Basudin, Dazzel, Gardentox, Kayazol, Knox Out, Nucidol, and Spectracide. The use of Diazinon on sheep prior to the foot-and-mouth outbreak in the UK in 2001 led to concern that Diazinon may reach groundwater from landfills which received large numbers of sheep treated with this insecticide. Table A2.18 gives some of the physical properties of Diazinon.

Table A2.18 Physical properties of diazinon

Structure	Solubility (mg/l, 20°C)	Vapour pressure (mPa, 20°C)	pKa	Log K _{ow}	Log K _{oc} (ml/g)
	40 ^a	0.093 ^a	<2.5 ^c	3.81 to 3.86 ^b	2.28 ^c

^aKidd and James (1991).

^bNemeth-Konda *et al.* (2002).

^cClemson University Organophosphate fact sheet.

<http://entweb.clemson.edu/pesticide/document/leeorg1/leeorg3.htm>

A2.8.2. Degradation of Diazinon

Diazinon degrades by hydrolysis, photolysis and microbial metabolism. In water, it degrades by hydrolysis to 2-isopropyl-4-methyl-6-hydroxypyrimidine, with a half-life of 12 days at pH 5, but is more stable under neutral conditions with a half-life of 138 days at pH 7 (Howard, 1991). The major microbial degradation product of Diazinon is Di-ethyl-2-isopropyl-4-methyl-6-hydroxy-pyrimidine, formed by hydrolysis at the P-O bond (Ragnarsdottir, 2000).

Biodegradation is expected to be a major fate process in soils with reported half-lives of two to four weeks in non-sterile soils (Wauchope *et al.*, 1992). Overall persistence in soils has been reported to be three to 14 weeks. Diazinon may be degraded in soil in anaerobic environments under certain conditions; half-lives of 17 and 34 days were reported when soil samples were amended with glucose (Arienzo *et al.*, 1994).

A2.8.3. Sorption of Diazinon

In an examination of 25 different soils, Arienzo *et al.* (1994) found that sorption (K_d) was highly correlated with organic matter content in soils in which organic carbon was greater than two per cent (Table A2.20). In soils with less than two per cent organic carbon, K_d was significantly correlated with silt and clay content. The average sorption coefficient for low organic soils ($K_d = 3.8$; range 0.8 to 18.1) was lower compared to soils with higher organic carbon content ($K_d = 9.9$; range = 3.6 to 19.7). Cooke *et al.* (2004) found that sorption of Diazinon was related to the presence of soil organic carbon and humic substances, and only weak correlated with cation species (Na, Al, Mn and Fe), despite the potential for ion-dipole reactions between cations and the phosphate part of the compound.

Table A2.19 Literature sorption values for Diazinon

K_d (ml/g)	$\log K_{oc}$ (ml/g)	f_{oc}	Soil/Lithology	Author
0.84 – 19.7	1.8-3.15	0.0008- 0.05	Clay loam and sandy loam	Arienzo, <i>et al.</i> , 1994
	3.18	0.0068	Forest soil with clay alluvium	Nemeth-Konda <i>et al.</i> , 2002
12.4- 35.4	2.93	0.0175- 0.035	Loamy sand	Cooke <i>et al.</i> , 2004

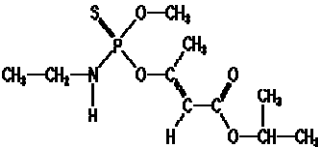
A2.9. Propetamphos

A2.9.1. Introduction

Propetamphos (E)-1-methylethyl 3-[[[(ethylamino) methoxyphosphinothioyl]oxy]-2-butenate (Table A2.21) is an organophosphate insecticide (Wellmark International, 2000). Propetamphos acts by inhibition of cholinesterase and is designed to control cockroaches, flies, ants, ticks, moths, fleas and mosquitoes in households, and where vector eradication is necessary to protect public health. Propetamphos is also used in veterinary applications to combat parasites such as ticks, lice and mites in livestock. Its use in sheep dips led to contamination of a number of UK water courses (Virtue and Clayton, 1997; Defra, 2002).

Propetamphos is highly toxic to fish: LC_{50} values range from 0.13 mg/L in bluegill and 0.36 mg/L in rainbow trout to 3.7 to 8.8 mg/L in carp. It may also be highly toxic to aquatic invertebrates, with reported LC_{50} values ranging between 0.68 μ g/L and 14.5 μ g/L in *Daphnia magna* (Extoxnet, 1996).

Table A2.20 Physical properties of Propetamphos

Structure	Solubility (mg/l, 20°C)	Vapour pressure (mPa, 24°C)	pKa	Log K _{ow}
	110 ^a	1.9 ^a	13.6 ^b	3.82 ^a

^aKid and James (1991).

^bYokar Chemical Ltd (www.yokar.cn/en/products).

A2.9.2. Degradation of Propetamphos

Propetamphos degrades by hydrolysis (one year at pH 6) and photolysis (two years) (Wellmark International, 2000), and degrades more rapidly under acidic (pH 3) or alkaline (pH 9) conditions (half-life 11 and 41 days respectively). At pH 7 the half-life was 17 days in aqueous solution maintained at an elevated temperature of 45°C. Isopropyl acetoacetate is an intermediate degradation product of hydrolysis, which will further degrade to isopropanol, acetone and carbon dioxide. Only limited data is available on the potential for biodegradation of propetamphos in soils and sediments. The experimentally determined half-life for Propetamphos in river and estuarine sediments was 15 days in aerobic conditions and 19 days under anaerobic conditions (Garcia-Ortega *et al.*, 2006).

A2.9.3. Sorption of Propetamphos

The sorption of Propetamphos to a range of sandy loam soils (with organic carbon contents ranging from 1.75 to 3.5 per cent) was investigated by Cooke *et al.* (2004). No strong correlation with organic carbon content was found. In sorption studies with activated carbon, Fullers earth, activated bauxite and synthetic clay, activated carbon was the best sorbent of Propetamphos, whereas the three inorganic adsorbents showed negligible sorption (Lambert *et al.*, 1997). The formulation of Propetamphos appears to affect sorption; the presence on an organic solvent may increase sorption (Garcia-Ortega *et al.*, 2006).

Appendix 3 - Methodology

A3.1. Characterisation of the mineral liner materials

A3.1.1. Collection of material

Samples of London Clay (50 kg), Oxford Clay (160 kg) and Mercia Mudstone (200 kg) were obtained from Ockendon landfill in Essex, Bletchley landfill and Waresley Quarry at Hartlebury, respectively. The liner materials were stored in air-tight plastic containers.

A3.1.2. Preparation of liner materials for laboratory work

The London Clay, Bletchley Oxford Clay and Mercia Mudstone were prepared for the experimental work according to the following procedure (BS1377: Part 1: 1990):

- a) Six to eight subsamples were collected from each air-tight container for water content determinations. The moisture content of the liner materials was determined and a description of their appearance is given in Table A3.1.
- b) Subsamples (500 g) of each liner material were collected for Fe and Mn oxides determination. The subsamples were stored in the anaerobic cabinet to prevent oxidation.
- c) Further subsamples were taken for the experimental study. Aggregations of particles were broken down in such a way as to avoid crushing of the individual particles.
- d) The broken-down material was air-dried.
- e) The dried sample was then mixed thoroughly and subdivided by quartering to obtain eight representative samples for particle size distribution.
- f) The remaining sample was ground into 3 mm granules using a soil grinder.
- g) The sample was again mixed thoroughly and subdivided by quartering to obtain representative subsamples for use during the period of experimental study (Figure A3.1). Subsamples were stored in five-litre air-tight containers.

Table A3.1 Description and moisture content of freshly dug samples of the liner materials

Liner material	Moisture content (%)	Sample description
London Clay	28.7	Firm brown clay
Mercia Mudstone	6.7	Firm red clay
Bletchley Oxford Clay	33.0	Soft, moist, dark grey clay with carbonaceous shells and rootlets

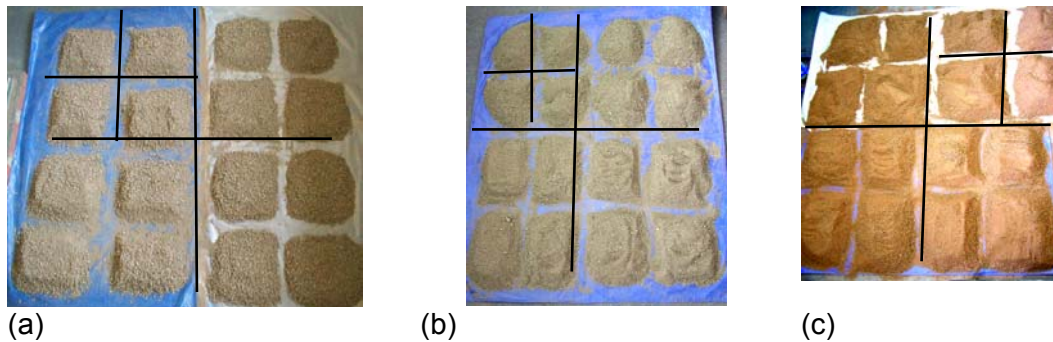


Figure A3.1 Quartering to obtain representative subsamples of the mineral liner materials.

a) London Clay; b) Bletchley Oxford Clay and; c) Mercia Mudstone.

A3.1.3. Density

In the British Standard Methods of testing for soils for civil engineering purposes (BS Part 2: classification tests), density is expressed in terms of mass density. The bulk density of a soil, ρ , is the mass per unit volume of the soil deposit including any water it contains, and dry density, ρ_d , is the mass of dry soil contained in a unit volume. In this study the small pycnometer method was used to determine the landfill liners density. This method is suitable for soils consisting of particles smaller than two mm, so before testing, large particles were ground to pass through a two-mm sieve. The mineral liner materials were oven-dried at 105°C overnight and transferred to a desiccator to cool down.

Two density bottles were used for each landfill liner. The bottles were washed with methanol and dried completely before each use. The mass of density bottles and stoppers was recorded. Five grams of liner materials were weighed (dried materials) and transferred to the bottles, and the weight of bottle plus its contents was recorded. Sufficient air-free distilled water was added to the bottles to cover the materials. The stoppers were removed from bottles, and bottles were placed in a vacuum desiccator. The air was evacuated gradually, and the pressure reduced to approximately 20 mm Hg with a hand pump. The bottles and contents were left in the desiccator for one hour, then removed and the soil was stirred with a spatula very gently to remove any trapped air. The bottles were returned to the desiccator and the pressure reduced to 20 mm Hg. This process was repeated twice, and then the bottles and their contents were left overnight in the evacuated desiccator. The bottles were removed from the desiccator and filled completely with air-free water and stoppers were placed in the top of the bottles. The density bottles were transferred to a constant-temperature bath (27 °C). The bottles were checked every hour and filled with air-free water if there was any decrease in the volume of water. This process was repeated until the liquid volume was constant, then the stoppered bottles were taken out of the bath and carefully wiped and weighed.

The density bottles were emptied, washed with methanol and filled with air-free distilled water. The bottles were placed in the constant-temperature bath with the same temperature (27 °C). The bottles were checked every one hour and filled with air-free water until the volume was constant. The bottles were removed from the bath, wiped carefully and the weight recorded.

The landfill liner material densities, ρ_s , (in g/cm³) were calculated from the equation:

$$\rho_s = \frac{m_2 - m_1}{(m_4 - m_1) - (m_3 - m_2)} \quad (A3.1)$$

where

m1 = mass of density bottle (g)

m2 = mass of density bottle and dry liner materials (g)

m3 = mass of density bottle, liner materials and water (g)

m4 = mass of density bottle full of water only (g).

Table A3.2 Dry density of the landfill liner materials

	Sample 1	Sample 2	Average density (g/cm ³)
London Clay	2.72	2.72	2.72
Mercia Mudstone	2.8	2.79	2.8
Oxford Clay	2.51	2.482	2.496

A3.1.4. Particle size distribution

Particle size distribution (PSD) measurements of the mineral liner materials were obtained by wet sieving and laser diffraction. The samples were initially sieved down to 63 μ m (British Standard Method BS1377: Part 2, 1990) (Table A3.3). The fraction passing through the 63 μ m sieve was subsequently analysed by laser diffraction at the Southampton Oceanography Centre using a Coulter LS 130 (Beckman Coulter®) equipped with a Micro Volume Module (laser power and wavelength: 4 mW and 750 nm, respectively) and related software (Table A3.4).

Table A3.3 Particle size distribution of mineral liner materials by wet sieving

Liner materials	% Particle size			
	Coarse silt-sand	Medium silt	Fine silt	Clay
London Clay	16.8	28.4	30.9	24.3
Mercia Mudstone	7.1	26.6	33.9	29.6
Oxford Clay	13.4	35.6	31.1	20.0

Table A3.4 Laser diffraction analysis of below 63 µm fraction of Mercia Mudstone, London Clay and Oxford Clay

Particle size (%)	London Clay	Mercia Mudstone	Oxford Clay
Clay	24.3	29.6	20.0
Fine silt	30.9	33.9	31.1
Medium silt	28.4	26.6	35.6
Coarse silt & fine sand	16.8	7.1	13.4

A3.1.5. Specific surface area

The specific surface area of the mineral liner materials was determined by three methods: i) BET nitrogen gas adsorption (carried out at the Chemistry Department of Southampton University); ii) ethylene glycol monoethyl ether (EGME) sorption method, and iii) polyvinylpyrrolidone (PVP) sorption method (according to Blum and Eberl, 2004).

i) BET (Brunauer-Emmett-Teller) surface area

Adsorption and desorption of nitrogen on the surface of solids can provide information about the surface area of the materials. Routine surface area analysis is carried out by using commercially available instruments that record the adsorption and desorption of nitrogen before calculating a surface area from the collected data.

The BET surface area technique has been widely used as the standard procedure to determine the surface area of solids, porous as well as non-porous. This technique is based on gas adsorption and carried out by exposing a solid (the adsorbent) to an adsorptive gas (the adsorbate) at different relative pressures and at the liquid temperature of the adsorptive gas. For BET surface area measurement nitrogen is the preferred gas, as it is relatively insensitive to the chemical nature of the surface. The surface area of a sample can be obtained by applying the BET model to the adsorption data. The BET method is based on the hypothesis of monolayer coverage on the solid. The rate of adsorption onto the adsorptive sites of the solid is assumed to be equal to the desorption rate of the gas from the occupied sites. The BET surface area method was carried out using a Micrometrics Gemini III 2375 Surface Area Analyser in the Chemistry Department of Southampton University.

The sample tube was cleaned by washing it in an ultrasound bath of deionised water for one minute and rinsed with acetone before drying in oven at 60 °C overnight. A 20 mg of sample was weighed accurately into the analysis tube.

The instrument was set up according to the following method:

- Forty adsorption points between P/P° 0.01-0.95 and 32 desorption points.
- Saturation pressure $P^\circ=760$ mm Hg.
- Evacuation rate = 500 mm Hg/min.
- Evacuation time = 30 minutes.

ii) Ethylene glycol monoethyl ether (EGME) sorption method

In this method the surface area of a sample is measured by sorption of ethylene glycol monoethyl ether EGME. In theory, as EMGE can access the internal surface of the sample the results are more accurate.

The mineral liner materials were ground down and duplicate samples weighed (200 mg) into clean aluminium dishes. The samples and a blank aluminium dish were transferred to an oven at 105 °C overnight. Samples were placed in a desiccator to cool down. The samples were then weighed to a constant weigh (± 0.5 mg between successive weighs). Two ml of EMGE was added to each dish and placed into the desiccator. After about 30 minutes, the desiccator was evacuated for 30 minutes and the samples left under vacuum for two hours. Air was then allowed to enter to the desiccator very slowly. Samples were weighed immediately then returned to the desiccator and the process repeated again for three days until the weights of the dishes were constant.

The surface area (SA) of the mineral liner materials was calculated as follows:

$$SA = \frac{\text{massEMGE}}{\text{massSample}} \times 3496.5 \text{ m}^2 / \text{g} \quad (\text{A3.2})$$

iii) Polyvinylpyrrolidone (PVP) sorption method

The BET and EMGE methods tend to underestimate surface area (Blum and Eberl, 2004). Measurement of surface area by polyvinylpyrrolidone (PVP) sorption is a new method which does not involve gaseous sorption. Polyvinylpyrrolidone (PVP, CA#9003-39-8) (Figure A3.2) is a widely used industrial surfactant, emulsifier and adhesive, with applications including hair spray, textile dye stripping, extender for blood plasma, ink-jet printing, tablet binder in pharmaceuticals, and the adhesive at both ends of toilet paper rolls. It available in variety of chain lengths with molecular weights (MW) ranging from 10 K to 1,200 K, which corresponds chains of around 90 to 11,000 monomers. In this experiment, PVP 55 K is used.

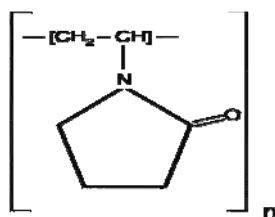


Figure A3. 2 Chemical structure of the polyvinylpyrrolidone (PVP) monomer

In the PVP sorption method samples should typically be saturated with Na^+ or Li^+ . About 20 g of the liner material was transferred to a centrifuge bottle and 100 ml of 1M NaCl added. It was left on the agitator for one hour and then centrifuged for 30 minutes at 1,400 rpm. The supernatant liquid was discarded. Fifty ml of distilled water was added to each of the bottles. These were left on a bottle roller over night and then centrifuged for 30 minutes at 1,400 rpm, after which the supernatant liquid was discarded. The washing process was repeated to ensure that all soluble salts were removed and that they would not interfere with the measurement of the surface area. Then 100 ml of distilled water was added to each of the bottles and the content transferred to dialysis bags and left overnight in the bucket of distilled water. The dialysis bag is effective for removing any residual NaCl and other low-molecular weigh-soluble materials which might be present in the samples, while retaining all the

solid particles. The dialysis bag contents were emptied in a container and transferred to an oven at 75°C. Samples were weighed every day until the weights were constant.

Subsamples (200 mg) were transferred to a pre-weighed 50 ml capacity centrifuge tube. About 20 ml of distilled water were added to the tube and left in the ultrasonic bath for about 30 minutes. About 8 ml of 10 per cent PVP 55 K was added to the centrifuge tube and weighed. Samples were left on a bottle roller overnight, then centrifuged for four hours at 10,000 rpm. The supernatant liquid was decanted from the centrifuge tube into a weighed bottle and both the bottle and solid sample (in the centrifuge tube) were placed in the oven at 75°C overnight. The sample and supernatant were weighed regularly until constant weight and the mass of PVP sorbed on the sample calculated. The surface area of the solid sample was calculated according to the following equation.

$$SA(m^2 / g) = \frac{\text{mass of PVP uptake}(g / g)}{0.99(g / m^2)} \times 1000 \quad (A3.3)$$

Gravimetric calibration of PVP was also carried out. Twelve empty bottles were washed and left over night in the oven at 105 °C to dry completely. Samples of one, two, four, six, eight and 10 ml of a 10 per cent PVP solution were added to the pre-weighed bottles (in duplicate) and these left in the oven at 75 °C overnight, then weighed. The surface area of the samples is given in Table A3.5.

Table A3.5 Surface area of liner materials using BET, EGME and PVP methods

Liner material	Average surface area (m ² /g)		
	BET method	EGME method	PVP method
London Clay	35.8	54.0	29.5
Mercia Mudstone	Not available	45.0	31.6
Oxford Clay	Not available	50.2	55.5

A3.1.6. Bulk and clay mineral composition

The bulk and clay mineral composition of the mineral liner materials was established by X-ray diffraction (XRD) carried out at the Southampton Oceanography Centre using a Philips PW 3040/60 X-ray Diffractometer and related X'Pert software.

For the whole liner material (bulk) analysis, an unoriented mount was prepared by packing a finely ground powder of the material into a holder. For the clay mineral analysis, the clay fraction of the samples (particle size less than two µm) was first separated by centrifugation at 750 rpm for 3.5 minutes and then smeared on to a glass slide for X-ray diffraction analysis. An X-ray diffraction trace was run off the powder, and four trace runs run off the oriented aggregate in the following order: (1) Mg-saturated air dried sample, (2) Mg-saturated glycolated sample, (3) Mg-saturated heated sample (375°C), and (4) Mg-saturated heated sample (550°C). Traces were run using iron-filtered CoK α radiation at a scanning speed of 1.2° 2 θ per minute.

In liner samples with significant organic carbon content, it may be difficult or even impossible to disperse and separate the clay fraction of the samples as a result of the aggregation action of the organic matter. For such samples, removal of organic matter may be required before mineralogical analysis can take place. Hydrogen peroxide can be used to oxidise the organic matter according to the British Standard Method, *Soils for civil engineers purposes. Part 2: Classification Tests*, Section 9.4.6.1. (BS13377: Part 2, 1990). The results for bulk and clay mineral composition of the liner materials are summarised in Table A3.6.

A3.1.7. Major and trace elements

The major and trace elements present in the mineral liner materials were determined by X-ray fluorescence at the Southampton Oceanography Centre using a Philips Magix-Pro wavelength XRF spectrometer (4 kW Rh end-window X-Ray tube). Prior to analysis, the samples were mixed with lithium-tetraborate/metaborate (20:80) flux in a platinum-gold dish and fused at 1200°C for 15 minutes before casting as a glass disk in a Pt-Au dish. The results are summarised in Table A3.7.

Table A3.6 Mineral composition of the liner materials (%)

Mineral	London Clay	Mercia Mudstone	Oxford Clay
Quartz	19	15	18
Calcite	0	1	9
Aragonite	0	0	2
Pyrite	0.5	0	1
Plagioclase	2	3	2
K-Feldspar	3	3	2
Dolomite	2	17	0
Gypsum	0	0	2
Hematite	0	2	0
Total non-clay	26.5	41	36
Smectite+illite/smectite+chlorite/smectite	31	18	32
Illite	29	36	15
Kaolinite	11	0	9
Chlorite	2	3	0.5
Total clay	73	57	56.5

A3.1.8. Cation exchange capacity

In this study, the standard method recommended by the Environment Agency for determining CEC in geological materials was used: the BaCl₂-triethanolamine method. This method is already widely used and has been shown to provide consistent results and to be suited to a wide range of geological materials (Environment Agency, 2000).

In the BaCl₂-triethanolamine method, classified as a compulsive displacement method, the sample is saturated initially with Ba in the form of BaCl₂, then exchanged by Mg by reaction with MgSO₄, forming a precipitate of BaSO₄. The quantity of Mg (which corresponds to the CEC) is estimated by loss from the MgSO₄ solution added. The use of triethanolamine results in the formation of a protective coat of BaCO₃ around reactive calcium-rich minerals, making them insoluble and eliminating the problem of interference by calcium release from dissolved gypsum and calcite.

Reagents

- Triethanolamine solution ([HOCH₂CH₂]₃N), pH 8.1: dilute 90 ml of triethanolamine with water to about one litre and adjust the pH to 8.1 with 2M HCl solution. Dilute with water to two litres and mix.
- Barium chloride solution (BaCl₂), 1 M.
- Buffered BaCl₂ reagent: mix equal volumes of triethanolamine solution and barium chloride solution.
- Magnesium sulphate solution (MgSO₄.7H₂O), 0.025 M.
- EDTA (ethylenediamine-tetra-acetic acid disodium salt: dihydrate) solution, (C₁₀H₁₆N₂O₈), 0.01 M.
- Ammonia buffer: dissolve seven grams of ammonium chloride in 57 ml of ammonia solution, sp. gr. 0.88, and dilute to 100 ml with water.
- Indicator: dissolve 0.25 g of Solochrome Black 6B in 50 ml ethanol.

Table A3.7 Major and trace elements present in the clay liners

		London Clay	Mercia Mudstone	Oxford Clay
SiO ₂	(%)	54.02	44.79	42.56
TiO ₂	(%)	1.01	0.64	0.81
Al ₂ O ₃	(%)	17.55	13.26	15.90
Fe ₂ O ₃	(%)	8.33	6.30	4.45
MnO	(%)	0.04	0.09	0.03
MgO	(%)	3.41	9.75	1.49
CaO	(%)	1.10	6.52	9.59
K ₂ O	(%)	3.43	4.00	2.93
Na ₂ O	(%)	0.34	0.42	0.29
P ₂ O ₅	(%)	0.18	0.13	0.21
Cl	(%)	0.03	0.03	0.01
S	(%)	0.16	0.03	0.11
Sum	(%)	89.39	85.90	78.25
Ba	(ppm)	258	232	319
Cr	(ppm)	116	75	106
Rb	(ppm)	115	117	128
Sr	(ppm)	155	79	373
Zn	(ppm)	102	68	100
Zr	(ppm)	179	157	138

Procedure

A five gram sample of liner material is weighed into a 250 ml centrifuge bottle (weight of bottle and its contents, M_1) and 100 ml of buffered BaCl_2 reagent are added. The mixture is agitated on a shaker for one hour and then centrifuged. The supernatant liquid is discarded. Around 200 ml of buffered BaCl_2 reagent is added to the sample and the mixture agitated for one hour on a shaker and then left overnight. After centrifuging the mixture, the supernatant liquid is discarded and the solid residue is washed with 200 ml of distilled water under agitation on a shaker for a few minutes. The mixture is then centrifuged and the supernatant liquid discarded.

Before saturating the solid residue with Mg, the weight of the bottle plus contents is noted (M_2). Around 100 ml of MgSO_4 0.025 M solution is added to the bottle and left for two hours, agitating on a shaker occasionally. The mixture is then centrifuged and the supernatant liquid decanted into a stoppered bottle. The quantity of Mg in this supernatant liquid and in the MgSO_4 0.025 M solution is determined by titration with standard EDTA 0.01 M solution (titre A_1 and titre B, respectively). Five ml of each Mg solution are added into a 100 ml conical beaker together with five ml of ammonia buffer and six drops of indicator and then titrated.

Calculation

The sample titre (A_1) is corrected for the effect of the volume of liquid retained by the centrifuged sample after the water wash using the equation below.

$$A_2 = \frac{A_1(100 + M_2 - M_1)}{100} \quad (\text{A3.4})$$

where

A_1 = volume of EDTA standard 0.01M solution used to titrate 5 ml of the supernatant liquid obtained after saturating the solid residue with Mg, in ml

A_2 = A_1 after correction for the effect of the volume of liquid retained by the centrifuged sample after the water wash, in ml

M_1 = weight of the 250 ml centrifuge bottle plus sample of liner material, in g

M_2 = weight of the 250 ml centrifuge bottle plus sample of liner material after the water wash, in g.

The CEC of the liner material is estimated by loss of Mg from the MgSO_4 0.025 M solution added to the sample initially saturated with Ba using the equation below.

$$CEC = (B - A_2) \times C_{EDTA} \times \frac{100}{5} \times \frac{100}{W} \quad (\text{A3.5})$$

where

CEC = cation exchange capacity of the sample of liner material, in meq/100g

B = volume of EDTA standard 0.01 M solution used to titrate 5 ml of the MgSO_4 0.025M solution, in ml

C_{EDTA} = concentration of standard EDTA solution used for titrating samples, in N

W = dry mass (g); A_2 (ml) as in first equation

If the CEC of the liner material exceeded 50 meq/100 g, the determination was repeated using less sample and the calculation adjusted accordingly. CEC values for the liner materials are given in Table A3.8.

Table A3.8 CEC values for the mineral liner materials

	CEC (meq/100g)		
	London Clay	Mercia Mudstone	Oxford Clay
Sample 1	23.6	20.3	27.7
Sample 2	28.0	21.5	32.5
Sample 3	21.8	24.5	31.7
Sample 4	30.5	29.3	24.99
Sample 5	28.8	27.5	25.34
Average	26.54	24.6	28.45
St.dev	3.68	3.83	3.51

Samples 1 to 3 by operator A, samples 4 and 5 by operator B

A3.1.9. Organic carbon content

Subsamples of the liner materials were ground to a fine powder for carbon analysis using a Knifetec 1095 Sample Mill (Foss). The total carbon content of the liners was determined by dry combustion at 900°C in oxygen atmosphere with 140 ml/min helium carrier gas and TCD detection of the gases produced using a CE Instruments 1112 Flash Elemental Analyser (Thermo Finnigan).

Determination of the inorganic carbon was carried out by treating the liner materials with 10 ml of H₃PO₄ (50 per cent) and sparging with air to drive off any inorganic constituents (Figure A3.3). The evolved carbon dioxide was measured by infrared spectroscopy (Rosemount Analytical Dohrmann DC-190 Carbon Analyser) where the resulting peak height of the carbon dioxide is proportional to the inorganic carbon in the sample. The method was calibrated using inorganic carbon standards (NaHCO₃) at different concentrations. The amount of liner material used in the analysis was adjusted to provide a clear carbon dioxide peak (0.01-1 g). The organic carbon of the material was then determined by calculation, assuming that total carbon equals the sum of organic and inorganic carbon.

To confirm that all the inorganic carbon was removed from the liner material by acid digestion, the remaining carbon in the digested sample was quantified for a limited number of samples (mass balance). The digested sample consisted of two fractions: (i) liquid fraction containing dissolved organic carbon that may have leached from the solid sample, and (ii) the solid fraction (a third fraction consisting of volatile organic carbon was not considered). The two fractions were separated by filtration and the solid fraction washed with distilled water. Water from the washings was collected and mixed with the liquid fraction of the digested sample (Figure 3.4). Both the liquid and solid fractions were analysed for total carbon. If removal of inorganic carbon was complete, the carbon remaining in the digested sample (liquid fraction + solid fraction) should be roughly the same as the organic carbon determined by the difference total carbon - inorganic carbon (differences may be due to the volatile organic carbon fraction not accounted for in this method or differences in carbon content between the sample analysed for total carbon and that analysed for inorganic carbon).

Subsamples of each mineral liner material were collected for preliminary carbon analysis (Table A3.9). Additional subsamples were analysed for total and inorganic

carbon. Due to the slow release of carbon dioxide by Mercia Mudstone during acid treatment with H_3PO_4 , inorganic carbon analysis was repeated using a stronger acid such as HCl.

Table A3.9 Organic carbon content of the liner materials

Liner material	TC (%) ^a	IC (%) ^a	OC (%)	Literature OC (%)
London Clay	0.64 (0.62-0.66) [20]	0.04 (0.032-0.046) [8]	0.60	1.2-2.3
Mercia Mudstone	2.02 (1.81-2.29) [6]	0.26 (0.22-0.33) [8]	1.76	0-0.5
Oxford Clay	7.22 (6.21-8.05) [6]	1.73 (1.28-1.98) [13]	5.49	4-8

^a Average (measured range) [no. replicates]
 TC-total carbon; IC-inorganic carbon, OC-organic carbon

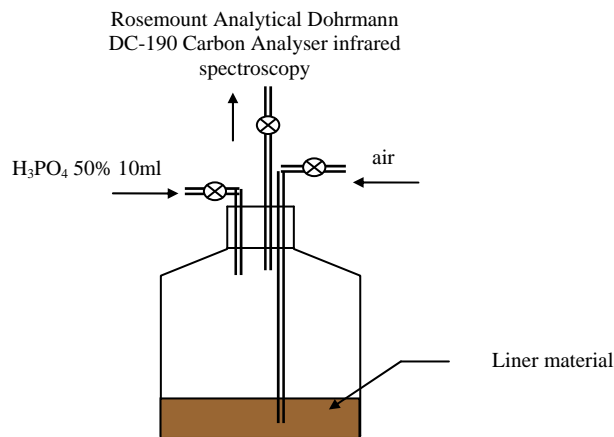


Figure A3.3 Determination of inorganic carbon content of the liner materials

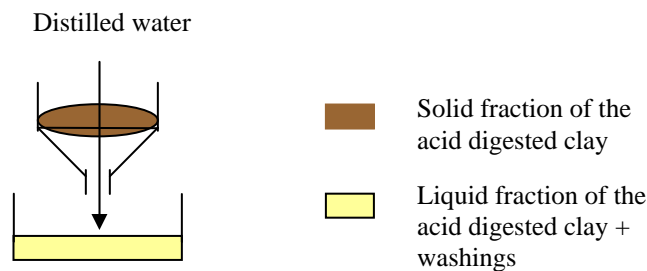


Figure A3.4 Separation of liquid and solid fractions of digested sample

A3.1.10. Organic matter characterisation

Because of the importance of organic matter in sorption of hydrophobic organic contaminants, a further investigation was undertaken to characterise the organic carbon (OC) in the mineral liner materials. Because of the low OC of Mercia Mudstone, and difficulty in extraction of this small carbon fraction, OC characterisation was only carried for the Oxford Clay.

The OC in the Oxford Clay sample was isolated using a decarbonation-demineralisation (HF/HCl) procedure. Prior to isolation of the organic matter, subsamples were ground to a fine powder using a Knifetec 1095 Sample Mill (Foss). Removal of carbonates was achieved by treating a 70 g subsample at 60°C for 20 hours in 300 ml of 6M HCl contained in Teflon centrifuge bottles. After digestion, the contents were centrifuged at 1,500 rpm for 30 minutes (WIFUG 4000E), the supernatant was decanted, and the solid residue rinsed three times with 2M HCl. The residue was then treated with 60 per cent HF for three days to remove the silicates. After digestion, the residue was rinsed with Milli-Q water until the aqueous phase became neutral. Polished thin sections (slides) of the organic matter isolates were prepared for microscopic examination following the method described in Hillier and Marshall (1988).

In coal petrography, three main types of kerogen are usually distinguished within the same sample by different reflectances: (a) liptinite, (b) vitrinite and (c) fusinite. These were identified and quantified by optical microscopy in reflected and transmitted white light and incident UV light (wavelength 450-490 nm; long pass above 520 nm) using a Zeiss UMSP 50 Universal Microspectrometer. Vitrinite and inertinite reflectance values were measured in monochromatic green light (wavelength 546 nm) using diamond as a reflectance standard (reflectance = 5.227 per cent). The classification scheme used in this study was based on commonly used classifications in organic petrography for kerogen (see Taylor *et al.*, 1998) as follows.

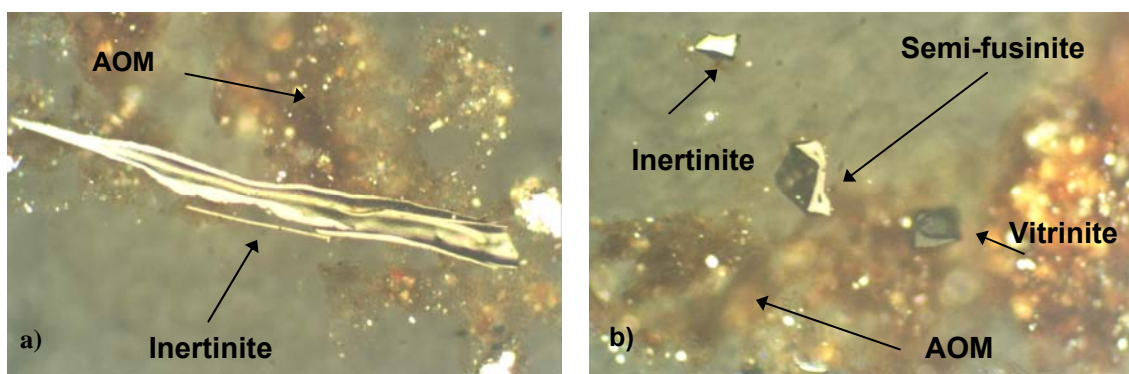
- Liptinites are derived from hydrogen-rich plant remains such as resins, waxes, fats and spores. These include amorphous organic matter (AOM), sporinite, cutinite and alginite. They have low reflectance and are transparent in white light. Under UV incident light, the degree of fluorescence of liptinite depends on its maturity (intense fluorescence for immature liptinite and no fluorescence for mature liptinite).
- Vitrinite and inertinite are typically derived from cell wall materials and woody tissues of plants but have undergone different modes of degradation and preservation. Inertinite is more reflective and opaque than vitrinite in white light. Both inertinite and vitrinite are non-fluorescent under UV light.

Vitrinite and inertinite can be distinguished from liptinite under transmitted white light as only liptinite is transparent. Distinction of inertinite from vitrinite is possible in reflected white light, where inertinite is more reflective than vitrinite. The percentages of each type of kerogen in the polished slide were determined using the point counting method (Taylor *et al.*, 1998). At completion of the analysis, counts were converted to a percentage on a mineral free-basis. $\text{volume mineral-free (\%)} = \text{number opaque} + \text{number translucent} = 100$ per cent and the standard deviation of each estimate was determined using Equation A3.6

$$\sigma = \sqrt{\frac{P * 100 - 100}{N}} \quad (\text{A3.6})$$

where P is the percentage of each organic matter component; σ is the standard deviation of the point-count estimate P; and N is the total number of points counted.

Kerogen components present in isolated organic matter from the Oxford Clay were found to comprise liptinite (amorphous organic matter AOM, spores, pollen and algae), vitrinite, semi-fusinite and inertinite (Figure A3.5). An estimate of the relative volume fraction of the organic matter components was obtained by the point counting method in transmitted light. Observations made for 393 particles showed that liptinite (mainly AOM) was the dominant type of organic matter (92 per cent) and that inertinite+semi-fusinite+vitrinite were minor components of the organic material (eight per cent). This is in accordance with previous petrographic studies of the Oxford Clay Formation which reported amorphous organic matter of phytoplanktonic origin as the dominant organic matter (85 to 95 per cent of total organic matter) in the Peterborough Member with lignitic debris and well-preserved plant fragments comprising the remaining five to 15 per cent (Belin and Kenig, 1994).



(a) Inertinite with well-preserved cellular structure and high reflectance and AOM containing highly reflective pyrite; reflected light; and (b) inertinite with high reflectance, semi-fusinite with median reflectance, and vitrinite with low reflectance; reflected light (field of view 260 μm by 170 μm).

Figure A3.5 Photomicrographs of the different organic matter components present in Oxford Clay

A3.1.11. Elemental analysis

The carbon, hydrogen, nitrogen and sulphur (CHNS) contents of the mineral liner materials were determined using a CE Instruments 1112 Flash Elemental Analyser (Thermo Finnigan). Prior to analysis, dried samples were ground to a fine powder using a Knifetec 1095 Sample Mill (Foss) and then weighed in tin containers. CHNS of the samples was determined by dry combustion at 900°C in oxygen atmosphere with 140 ml/min helium carrier gas and TCD detection of the gases produced (Table A3.10).

Table A3.10 CHNS content of the liner materials

Liner material	C (%) ^a	H (%) ^a	N (%) ^a	S (%) ^a
London Clay	0.64 (0.62-0.66) [20]	0.82 (0.67-0.95) [20]	0.05 (0.04-0.08) [20]	0.06 (0-0.11) [20]
Mercia Mudstone	2.02 (1.81-2.29) [6]	0.50 (0.46-0.53) [6]	ND [6]	ND [6]
Bletchley Oxford Clay	7.22 (6.21-8.05) [6]	1.24 (1.08-1.37) [6]	0.56 (0.51-0.60) [6]	0.43 (0-0.79) [6]

^a Average (measured range) [no. replicates]

ND Not detected

A3.2. Batch tests

A3.2.1. Sorption tests

A typical data set for sorption isotherms developed in this study is comprised of 16 to 20 points (eight to 10 sorption tests in duplicate) spanning about two orders of magnitude in aqueous-phase solute concentrations. Each point represents an individual batch sorption experiment carried out at a constant solid/solution ratio but at different initial aqueous phase solute concentrations. Preliminary sorption tests were carried out to select a solid/liquid ratio to establish the sorption isotherm (Section 3.2.1) and to establish the contact time required for the system to reach sorption equilibrium (Section 3.2.2). Sorption tests were then carried out over a range of aqueous concentrations to establish a sorption isotherm (Section 3.2.3).

The sorption tests were carried out according to the procedure described in the Environment Agency P1-500/5 Experimental Methodology Report. For the substances with low aqueous solubility (under 779 mg/l), stock solutions were prepared prior to the batch tests by adding the appropriate amount of each compound to methanol. Sodium azide (100 mg/l) and mercuric chloride (0.05 mg/l) were added to the leachate to inhibit biological activity during the tests (Nielsen *et al.*, 1996). The batch tests were carried out in glass crimp-top bottles (122 ml internal volume, Sigma Aldrich, UK) which were cleaned prior to use (acid wash in 0.1M HCl, followed by rinsing in Milli-Q Plus and oven drying). The mineral liner material was weighed into the bottles and these were filled with leachate in an anaerobic glovebox (Wolflabs Model A Vinyl cabinet). The contaminants under investigation were then added to the bottles, further leachate added to leave no headspace, and the bottles sealed immediately with aluminium caps with Teflon®-coated septa to avoid volatilisation of the compound. The bottles containing the liner material and leachate were mixed by horizontal rotary agitation, at 20 ± 2°C. Bottles containing leachate and the List I compounds, but no liner material, were also prepared to assess losses of contaminant by volatilisation or sorption to the bottle or septa. Losses of contaminant from the aqueous solution other than by sorption to the solid matrix (such as sorption to glass or septa, or biodegradation) were found to be negligible. At the end of the contact time, the solid and liquid phases were separated by centrifugation (1,400 rpm for 10-30 minutes). Duplicate samples of the supernatant liquid (10 ml) were then

collected from each bottle in a 20 ml headspace vial (Sigma-Aldrich, UK) for determination of the contaminant aqueous concentration.

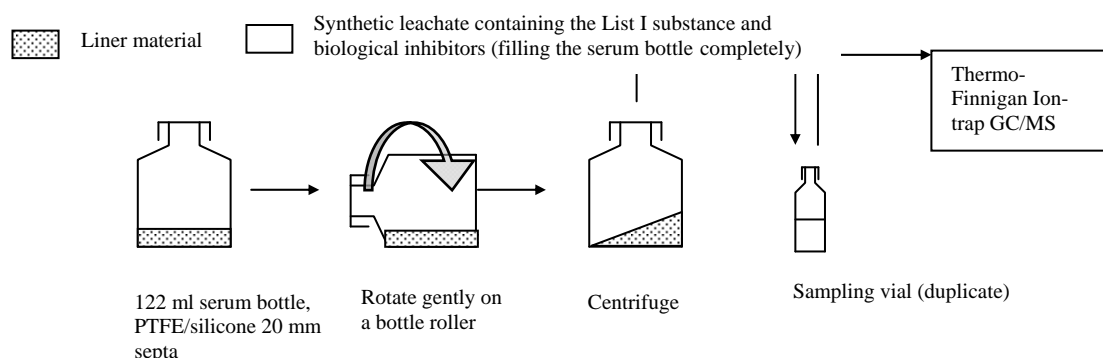
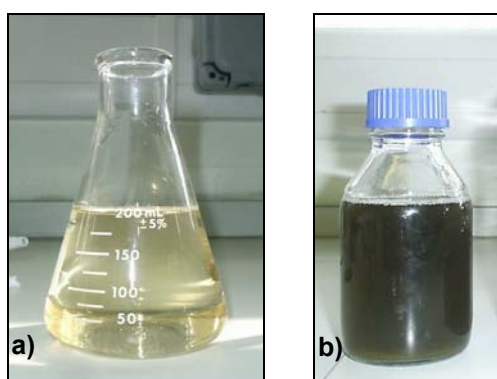


Figure A3.6 Experimental set-up of the sorption batch tests

Preliminary sorption tests showed that the synthetic MSW leachate was unstable in the presence of oxygen. Darkening and precipitation of the leachate was observed together with a loss of 38 per cent of the dissolved organic carbon (DOC) to the precipitate (Figure A3.7, Table A3.11).



a) MSW leachate on the day of preparation; b) MSW leachate two days after preparation

Figure A3.7 Darkening and precipitation of synthetic MWS leachate with time

Table A3.11 Reduction in DOC in MSW synthetic leachate on exposure to air

Synthetic MSW leachate	DOC (mg/l)
Theoretical	540
Fresh leachate	536
Five-day filtered leachate	357
Thirteen-day filtered leachate	332

Reaction of the leachate with oxygen from the air is thought to be due to the presence of tannic acid in the synthetic leachate. The tannic acid has five or more gallic acid residues attached to the glucose core. The larger structures contain the encircled ester bond (Figure A3.8). In alkaline solutions, the gallic acid rapidly absorbs oxygen from the air and becomes brown in colour (Digital Library of India, 2004). This change in composition of the leachate by reaction with oxygen may not be representative of the conditions within landfill liners, which are expected to be anaerobic. Therefore,

preparation of the sorption tests was carried out in the anaerobic cabinet (Woflabs Model A Vinyl cabinet incorporating oxygen and hydrogen measurement and carbon dioxide controller).

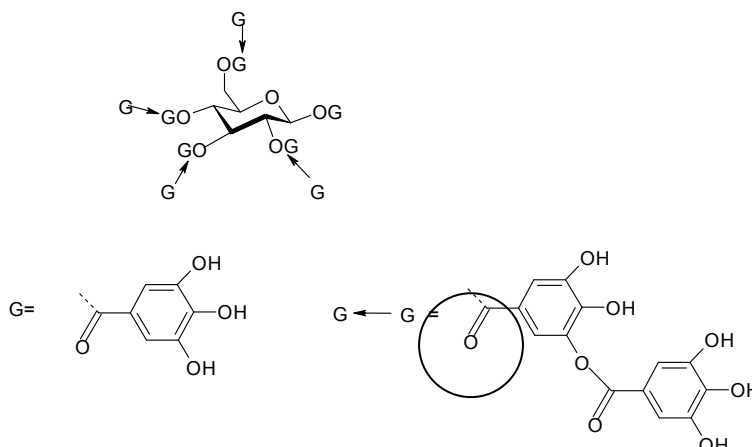


Figure A3.8 General structural representation of tannic acid (after Halkes *et al.*, 2002)

Preliminary sorption tests were carried out over seven days at different solid/liquid ratios to select a ratio that would result in 20 to 80 per cent sorption of contaminant (tests carried out within this ratio have been shown to reduce experimental errors; Delle Site, 2001). A non-linear regression model (exponential rise to maximum model, Sigma Plot 8.0) was used to fit the sorption data as a function of the solid/liquid ratio (Figure A3.9). Parameters of the non-linear regression fit of TCB on London Clay are listed in Table A3.2. A solid/liquid ratio of 2.05 per cent was selected for the sorption isotherm tests to provide 50 per cent sorption of TCB. As seen from Figure A3.9, sorption of TCB in MSW leachate is slightly higher than in distilled water. This is likely due to the tannic acid in the MSW leachate behaving as an additional sorbent for TCB; the complex of tannic acid-TCB may also be sorbed by the liner material. Uptake of tannic acid by London Clay was observed and was found to increase with the London Clay/liquid ratio, as indicated by the decrease in DOC of the leachate (Figure A3.10).

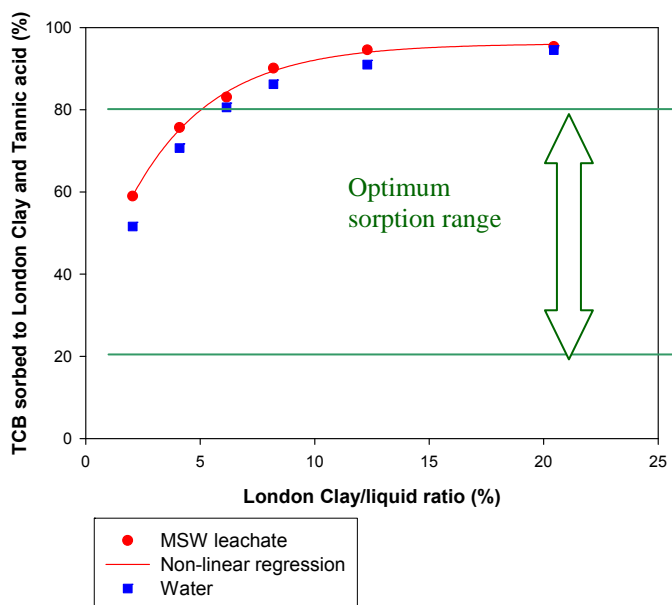


Figure A3.9 Variation of TCB sorption onto London Clay and tannic acid with London Clay/liquid ratio

Table A3.12 Non-linear regression model fit to experimental sorption data

Regression model	Coefficient a [#]	Coefficient b [#]	Coefficient c [#]	Correlation coefficient R ²
$y = a + b(1 - e^{-cx})$	30.41 (3.50)	65.71 (3.17)	0.28 (0.02)	0.997

[#] Standard error given in parenthesis

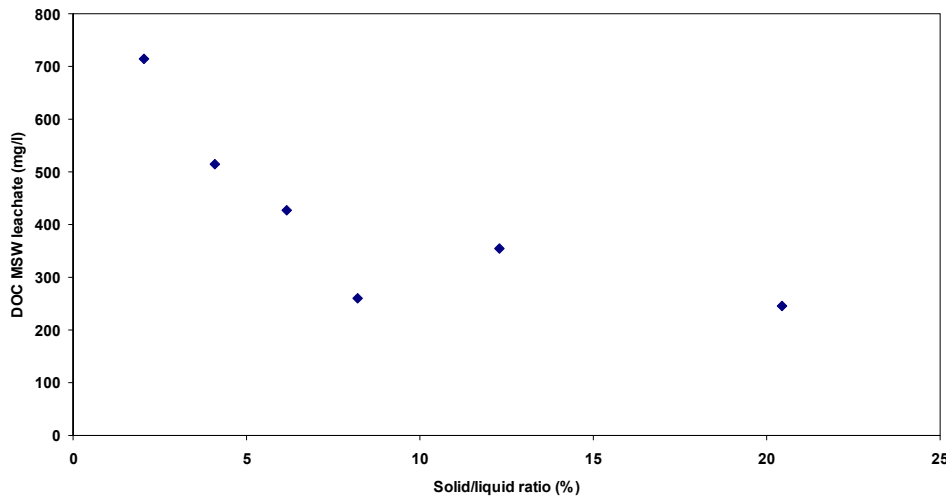


Figure A3.10 DOC content of MSW leachate as a function of solid/liquid ratio

A3.2.2. Desorption tests

Desorption equilibria are generally measured by the batch sorption, decant and refill method (Bowman, 1979). In this technique, the supernatant solution is removed after equilibration with the solid in the batch sorption test and replaced with a solute-free solution. This allows the solute sorbed to the solid phase to desorb into the solute-free aqueous phase until a new equilibrium condition is reached. After determination of the contact time to reach equilibrium in the desorption phase, sorption and desorption isotherm tests can be carried out and the sorption and desorption distribution coefficients established.

The solute-free leachate used in the desorption tests was produced by mixing the liner material and fresh synthetic leachate, in the same ratio as the sorption tests and for the same contact time. This was done so that the solute-free solution was as similar as possible, in terms of dissolved organic carbon and colloidal material, to the supernatant solution removed at the end of the sorption step. In this way, sorption of the contaminant to a third phase (DOC and/or colloids) could be reduced (Huang *et al.*, 1998). However, it was not possible to be certain that the solute free leachate and the leachate used in the sorption step would be identical because of the variation in both the content and nature of the organic carbon present in the mineral liner materials which might leach into solution during the batch tests.

In the sorption batch tests, preliminary tests were carried out to establish the best ratio of sorbent to solution to obtain measureable changes in aqueous contaminant concentration during sorption (30-60 per cent sorption). If sorption was reversible, the same ratio of sorbent to solution should be suitable for the desorption tests.

Desorption tests were carried out using the batch method similar to the sorption tests described in Appendix 3, Section 1. After the initial sorption step (using the contact times given in Table A3.13), samples were collected for analysis of the equilibrium concentration, where the supernatant was removed and the bottles refilled with solute-free leachate. The bottles were agitated and samples were taken at intervals over a 30-day period to determine the time required to reach desorption equilibrium for each of the liner material/contaminant combinations. Desorption equilibrium was considered to be attained when the contaminant concentration change was too small to measure over a number of days. Desorption isotherm tests were carried out by taking the samples from the sorption tests, replacing the supernatant with fresh equilibrated leachate (as described above) and agitating for the given contact time. At the end of the contact time, the bottles were centrifuged and duplicate samples taken for analysis.

Table A3.13 Contact times for sorption and desorption used in isotherm tests

	Contact time (days)					
	London Clay		Mercia Mudstone		Oxford Clay	
	sorption	desorption	sorption	desorption	sorption	desorption
Mecoprop	5	10	5	10	5	10
Naphthalene	n/c	n/c	7	10	7	10
Toluene	7	12	2	10	7	12
TCB	5	15	4	10	7	10
TCE	n/c	n/c	5	n/c	5	n/c

n/c= not carried out

A3.3. Analysis of List I substances

A3.3.1. VOC analysis

VOC analysis was performed by headspace GC-MS using a Thermo Finnigan Polaris Q connected to a CombiPal Headspace Autosampler. The GC-MS was equipped with a Restek column Rtx-5MS, 30 m long, 0.25 mm ID, 1.0 µm film under the following conditions: injector temperature 110°C, column flow rate (helium) one ml per minute and 45°C initial temperature (ramped at 8°C/minute to 190°C, hold time two minutes, and then ramped at 15°C/minute to a final temperature of 260°C, hold time one minute). In these conditions, retention times of VOCs, quantification ions and respective internal standards are listed in Table A3.14.

Table A3. 14 Analysis of VOCs by Headspace GC-MS

VOC	Retention time (min)	Quant. ion	Internal standard
1,4-difluorobenzene	7.29	114	-
1,4-dichlorobenzene	16.50	146	-
Naphthalene	20.16	128	1,4-dichlorobenzene
Toluene	9.99	91	1,4-difluorobenzene
TCB	19.93	182	1,4-dichlorobenzene
TCE	7.96	130	1,4-difluorobenzene

A3.3.2. Analysis of Mecoprop

Samples were taken from the biodegradation tests and the sorption and desorption tests for analysis of Mecoprop. Samples from the biodegradation tests were sent to the Environment Agency laboratories, Leeds, UK. In summary, the Environment Agency method for analysis of Mecoprop involved a solid phase extraction (ENV+ Cartridges, three ml bed-volume, Argonaut Ltd) to concentrate the sample from the liquid phase. The cartridges were initially conditioned using three washes with ethyl acetate then three with methanol and acidified with 0.5 per cent sulphuric acid (one bed volume). A volume of the sample was passed through the cartridge and the sample components were eluted with dichloromethane (DCM two ml). The eluted sample was treated with diazomethane (one to two ml) for at least one hour, such that methyl esters of the components were formed. Diazomethane was prepared using a Diazald generator (Sigma-Aldrich). The DCM and diazomethane were then blown off and the sample taken up in ethyl acetate prior to GC-MS analysis.

This method was found to be insufficiently sensitive for the small volume injector on the GC-MS used at the University of Southampton. Accordingly, the Environment Agency method was modified. The samples were acidified to pH 2 and concentrated by solid phase extraction using Chromabond Easy cartridges (Machery-Nagel) according to the method for removal of phenoxycarboxylic acids from water (Machery-Nagel Application No:302860). In summary, the cartridges are preconditioned with acetone and Milli-Q water, the sample is applied then the cartridges are thoroughly dried. The sample is eluted with a 1:1 mixture of acetone and ethyl acetate. Eluted samples were derivatised using diazomethane (freshly prepared using a Diazald generator) before analysis.

Recovery of Mecoprop and the internal standard, Dichlorprop, by the Easy cartridges was enhanced by the presence of tannic acid in the synthetic leachate; yield of MCPP and Dichlorprop in samples when tannic acid was present was 10 times that in samples from the tap water and tannic-free leachate tests. Therefore, to improve the sensitivity of the technique, tannic acid was added (one g/l) to samples taken from the tap water and tannic-free leachate tests, and to the standards prepared in tap water and tannic-free leachate.

Quantitative analysis was carried out by gas chromatography-mass spectroscopy (GC-MS) using a Thermo Finnigan Polaris Q connected to a CombiPal Autosampler. The GC-MS was equipped with a Rtx-5MS column 0.25 mm ID, 30 m long and one µm film thickness (Restek, UK) under the following conditions: helium flow rate one

ml/minute; injector temperature 250°C, volume injected 5 µl; 100°C initial oven temperature, ramped at 10°C/minute to 300°C, hold for four minutes.

A3.4. Column tests

Soil column tests employing inert (PTFE) triaxial cells were used to determine the scalability of the sorption parameters derived from the batch tests for Mecoprop on Mercia Mudstone and Oxford Clay. Preparation of the samples for the triaxial cell included grinding, mixing and consolidation. The standard triaxial cell apparatus was modified to minimise interaction between Mecoprop and the apparatus. All parts of the apparatus contacting with the landfill leachate were substituted by PTFE due to the high resistance of this material to most known chemical agents.

A3.4.1. Sample preparation

The mineral liner material (150g) was ground by hand to produce particles of fine silt size or below. Disaggregation was achieved by grinding the dried liner material in small quantities using a pestle and mortar, and sieving until the sample passed a 63 µm sieve; a dispersant solution was not used due to the likelihood of contaminating the sample with chemicals. The ground sample was mixed with freshly deaired tap water. Mixing was done by hand to achieve a smooth slurry consistency. A moisture content of 85 per cent should be achieved by this method (a moisture content of about 100 per cent is too easily extruded from around the edge of the consolidation tube).

A3.4.2. Sample consolidation

The reconstituted sample was consolidated in a clear acrylic tube of approximately 39 mm internal diameter mounted in an oedometer loading device (BS 1377: 5, 1990), Figure A3.11. The loading device was used to apply several increments of stress in order to produce a normally consolidated sample. It was modified with a taller loading yoke to allow a greater range of consolidation.

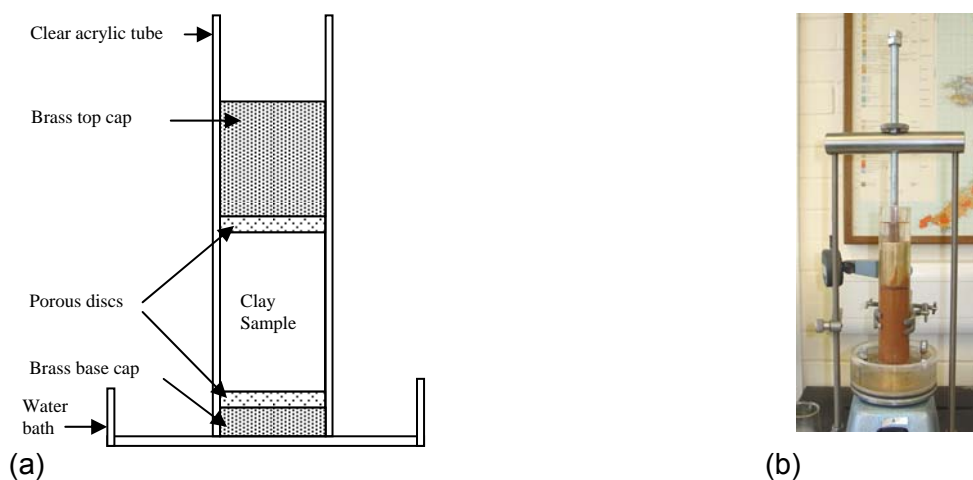


Figure A3.11 Consolidation of Murcia Mudstone sample: (a) consolidation tube and water bath, (b) consolidation tube mounted in oedometer loading device

When the maximum consolidation stress was reached (400 kPa), the sample was unloaded in stages, and kept at the effective stress used in the column test (90 kPa) until required. The tube and contents were lifted from the bath, and the sample pushed out. A small slice was taken from the sample in order to measure its moisture content. The prepared sample was weighed to determine its bulk density, and measurements of its diameter and height are recorded. The remaining sample was sealed in a plastic bag to prevent moisture loss if not immediately used.

A3.4.3. Preparation of the sample in the triaxial cell

The triaxial cell consisted of a transparent cylinder enclosed by corrosion-proof metal top and base plates (Figures A3.12 and A3.13). The cylindrical consolidated sample was wrapped in PTFE tape (RS Thread Seal Tape), followed by PTFE sheet (Polyflon PTFE sheet 0.25 mm thick) and a thin latex membrane, and surrounded by tap water within the cell. The soil sample was subjected to an all-round isotropic stress obtained by pressurising the cell fluid (confining pressure).

Two clean porous discs were de-aired in a vacuum desiccator. The de-aired discs were placed on either end of the sample and the sample positioned on the cell base cap. Thin PTFE tape was wrapped around the base cap and then up around the sample until the top was reached. The top cap was placed on top of the uppermost porous disc and the tape wrapped around to secure it in place. The PTFE tape needed to be applied quite tightly, but without disturbing the sample, in order to prevent leakages. The PTFE sheet was placed around the PTFE tape. The sheet overlapped at the sides and the height of the sheet was such that it fitted over the base and up to the top of the uppermost porous disc. Thin PTFE tape was wrapped around the PTFE sheet to hold it in place. Again, the PTFE tape was applied quite tightly to ensure that leaks were prevented. The tape was followed by a latex membrane which was held in position at the bottom of the sample with two rubber rings. The latex membrane was rolled up to cover the cell top cap and again this was held in position with two rubber rings. The cell was then closed and filled with de-aired tap water. When ready, the data monitor spreadsheet was opened, the time period set (such as 300 seconds) and the controllers for the top and base pressure (for example, 140 kPa) and cell pressure (for example, 160 kPa) set as required and started. The data monitor was started and the sample left to equilibrate overnight.

A3.4.4. Permeameter test

When the sample had equilibrated, the permeameter test was started. The top pressure controller was set at atmospheric pressure, the base set to 140 kPa and the cell pressure to 160 kPa, producing an effective stress of 90 kPa.

A3.4.5. Running the tracer test

The base pressure controller was filled with the de-aired tracer solution (potassium bromide, 50 mg/l) and the contaminant (Mecoprop, 300 or 500 µ/l) at room temperature. Sodium azide (100 mg/l) was added to the solution to prevent biodegradation of the contaminant during the test. The cell outlet tubing was positioned so that the solution could be collected in a fraction collector. The fraction collector timer was set such that it would enable collection of a sample of sufficient

volume for analysis. The data logger was started. The top pressure was set to zero, and the base pressure applied (for example, 140 kPa).

A3.4.6. Sorption tests of Mecoprop on PTFE and latex

In the modified triaxial cell used in this study, the consolidated sample was wrapped in PTFE sheet material and placed in a latex sleeve inside the triaxial cell. To assess whether Mecoprop was sorbed by the PTFE or latex, sorption experiments were carried out. The PTFE sheet was cut into one-cm square pieces and around six grams was added to a 122 ml glass serum bottle. Similarly, the latex was cut up and 2.5 g added to a serum bottle. The bottles were filled with tap water and Mecoprop added such that the concentration in the bottles was 100 µg/l. Samples were taken after seven days. The results showed that there was no sorption of Mecoprop by PTFE, but 20 per cent of Mecoprop was sorbed by the latex sleeve material.



Figure A3.12 Triaxial cell apparatus containing a sample wrapped in PTFE and latex

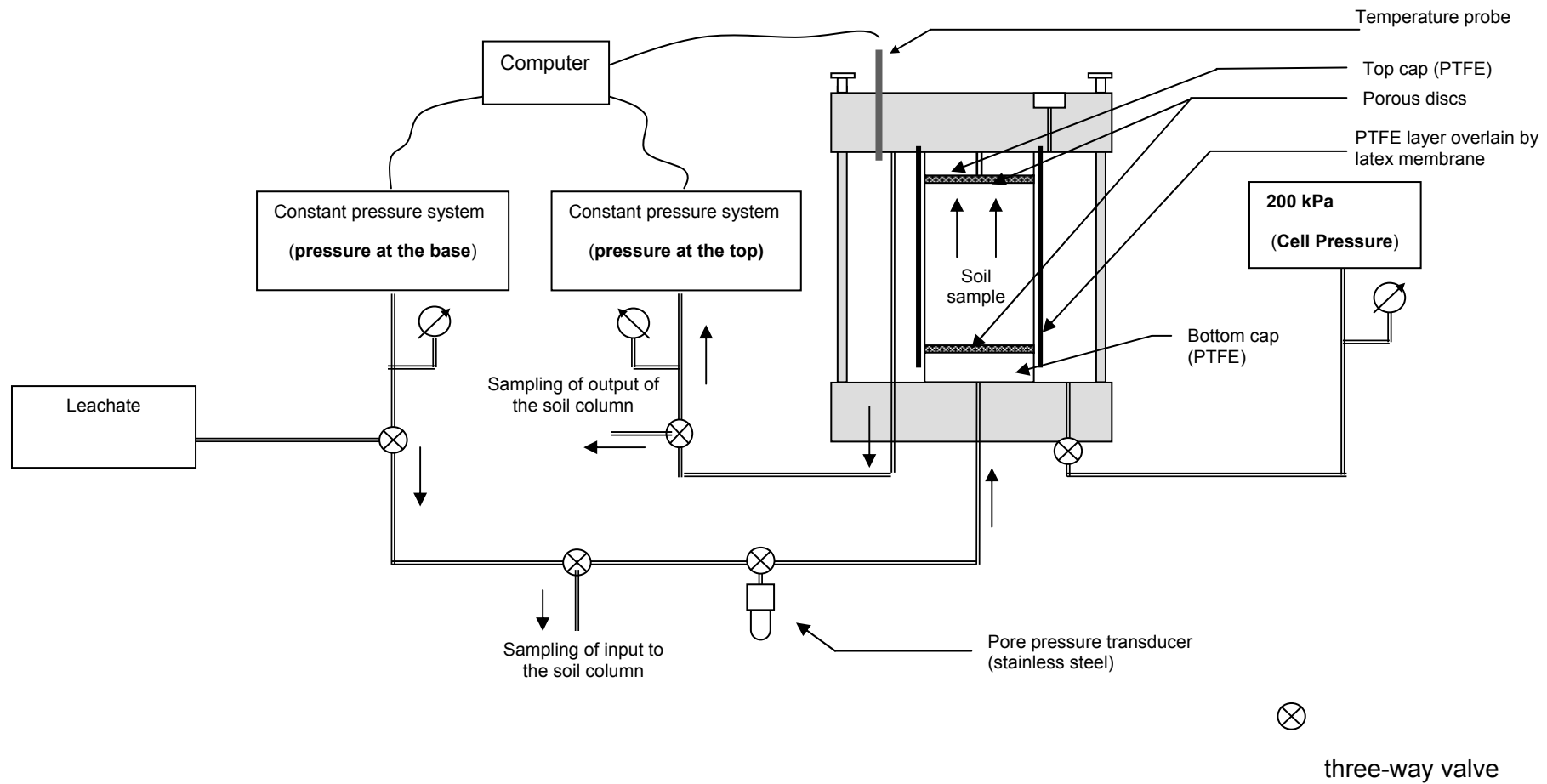


Figure A3.13 Diagram of the modified triaxial cell used for the soil column test

A3.5. Biodegradation tests

A3.5.1. Preparation of MSW and MSWI leachates

The MSWI leachate was prepared according to the Environment Agency P1-500/5 Experimental Methodology Report. The composition of the MSWI leachate was found to be above the solubility limit of one or more of the leachate components at the resulting pH of 7.8 (Figure A3.14). Due to the difficulty in filtering and heating the large amount of leachate required for the biodegradation tests (34 litres), an alternative recipe was investigated which used CaCl₂ and H₂SO₄ as the sources of calcium and sulphate, respectively, instead of CaSO₄ (Table A3.15). This resulted in a 21 per cent increase in Cl⁻ concentration in solution and a pH of 6.15. The pH of the leachate was then adjusted using NaOH to pH 6.8, resulting in eight per cent increase of sodium in solution. No precipitation was observed in the leachate.

Table A3.15 Composition of the MSWI leachate

Leachate component	Literature review composition (mg/l)	Alternative composition (mg/l)
Tannic acid (C ₇₆ H ₅₂ O ₄₆)	500	500
Ammonium chloride, NH ₄ Cl	150	150
Sodium chloride, NaCl	4,000	4,000
Sodium bicarbonate, NaHCO ₃	2,000	2,000
Calcium sulphate, CaSO ₄	1,000	-
Sodium hydroxide, NaOH	50	297
Calcium chloride, CaCl ₂	-	816
Sulphuric acid, H ₂ SO ₄	-	721
TOC	270	270
Cl ⁻	2,527	3,049
Na ⁺	2,149	2,322
NH ₄ -N	39	39
Ca ²⁺	294	294
SO ₄ ²⁻	706	706
pH	7.80	6.80

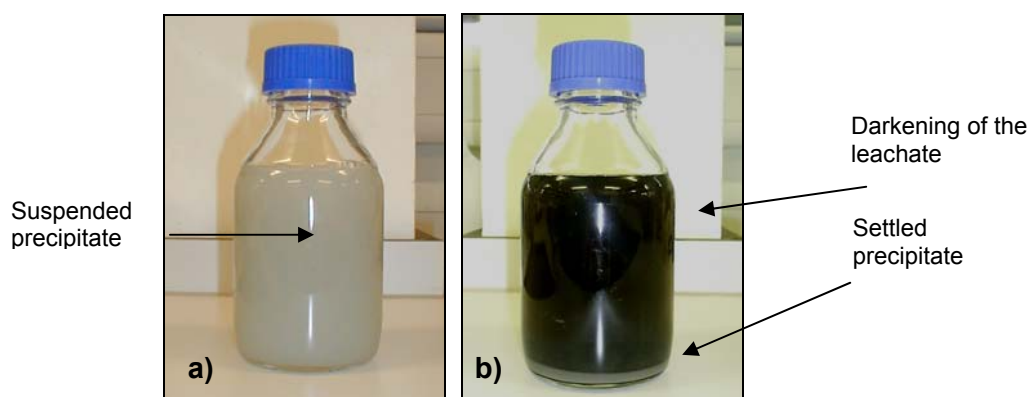


Figure A3.14 Darkening and precipitation of MSWI leachate
 a) MSWI leachate on the day of preparation; b) MSWI leachate four days after preparation

A3.5.2. Enrichment of bacterial seeds

Bacterial seeds for the biodegradation experiments were enriched in one-litre Duran type bottles (with airtight OMNI fittings for sampling) from two types of sludge: Sludge 1 collected at a landfill leachate treatment plant and Sludge 2 from a sewage works (Figure A3.15). MSW and MSWI synthetic leachates were used to provide electron donors for methanogenic and sulphate-reducing bacteria, respectively. A small amount of leachate from the landfill, which was expected to contain List I organic contaminants, was also added to the synthetic leachates. Sodium acetate and sodium formate were added as carbon sources.

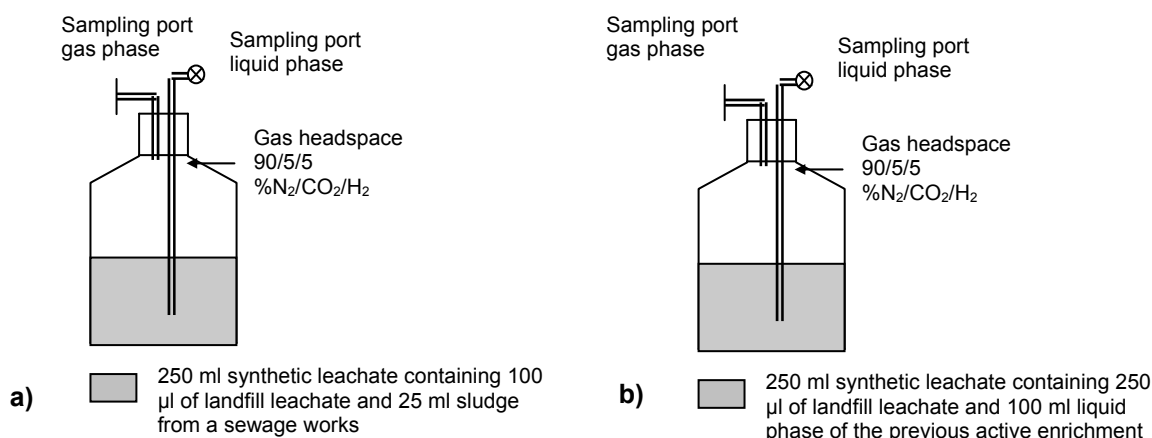


Figure A3.15 Enrichment of bacterial seeds for biodegradation experiments
 a) first active enrichment; b) subculture of first active enrichment into fresh medium

Methane concentration in the gas phase was determined by gas chromatography using a Varian CP-3800 GC equipped with a TCD detector and two columns 1 m by 1/8 inches OD: Haysep C column (80-100 mesh) and a Porapak column (molecular sieve 13X, 60-80 mesh). The following conditions were used: 50°C isothermal back-flush mode and argon carrier gas. Sulphate concentration in the aqueous phase was determined by liquid chromatography using a Dionex 500 anion suppression

Chromatograph equipped with a AS14A (4x250 mm) column and an eluent (1mM NaHCO₃, 8mM Na₂CO₃) at a flow rate of one ml/minute.

Methane production was detected in both synthetic leachates while a decrease in sulphate was detected in the MSWI leachate, indicative of active methanogenic and sulphate-reducing populations, respectively (Tables A3.5 and A3.6). Although sulphate is available as an electron acceptor in the MSWI synthetic leachate, some methanogenic activity is co-occurring.

To generate an active microbial consortium in the absence of the sludge, a subculture was obtained by transferring about 10 per cent of the active enrichments into fresh medium. Methane production and sulphate reduction was still detected in the subcultures (in smaller rates than the enrichments due to the dilution of the bacterial populations), indicating that the bacterial seeds were still active at lower concentrations of the sludges (Tables A3.16 and A3.17).

Table A3.16 Methane production and sulphate reduction in the synthetic leachates containing bacterial seeds enriched from sewage plant sludge

Incubation time (days)	Methane production (%)		Sulphate reduction (%) ^a
	MSW leachate	MSWI leachate	MSWI leachate
11	8.4	29.0	-
17	16.3	30.5	-
51	40.8	33.6	71 to 96 (30-233 mg/l SO ₄ ²⁻)
109	48.4	51.7	-
124	20.2	13.4	-
137	27.6	17.2	-
151	30.6	21.3	-
176	-	-	SO ₄ ²⁻ added (270-302 mg/l SO ₄ ²⁻)
185	28.0	18.4	-
7	5.3	1.3	155% (813 mg/l SO ₄ ²⁻)
19	2.6	0.8	-
64	36.0	43.6	-
75	-	-	>93 (56 mg/l SO ₄ ²⁻)
79	33.7	34.4	-
92	47.2	42.6	-
106	57.5	51.8	-
131	-	-	SO ₄ ²⁻ added (296-340 mg/l SO ₄ ²⁻)
140	28.6	36.6	-

^a Sulphate reduction = 100*Ct/Cc, where Ct is measured sulphate concentration at time t and Cc is conservative sulphate concentration at time t (no reduction occurring).

Table A3.17 Methane production and sulphate reduction in synthetic leachates containing bacterial seeds enriched from Leachate Treatment Plant sludge

Incubation time (days)	Methane production (%)		Sulphate reduction (%) ^a
	MSW leachate	MSWI leachate	MSWI leachate
20	31.2	47.1	-
36	29.2	20.3	99 (7.56 mg/l SO ₄ ²⁻)
92	31.7	42.4	-
107	50.5	53.2	-
120	51.2	53.3	-
134	55.8	53.3	-
159	-	-	SO ₄ ²⁻ added (336-360 mg/l SO ₄ ²⁻)
168	39.2	34.6	-
7	4.5	1.7	37% (594 mg/l SO ₄ ²⁻)
19	10.2	2.8	-
64	45.7	43.7	-
75	-	-	>98 (<20 mg/l SO ₄ ²⁻)
79	30.8	31.0	-
92	42.6	35.4	-
106	42.0	40.6	-
131	-	-	SO ₄ ²⁻ added (272-326 mg/l SO ₄ ²⁻)
140	34.6	26.9	-

^a Sulphate reduction = 100*Ct/Cc, where Ct is measured sulphate concentration at time t and Cc is conservative sulphate concentration at time t (no reduction occurring),

A3.5.3. Acclimatisation of bacterial seeds to List I substances

The methanogenic and sulphate-reducing bacterial seeds enriched from sewage sludge and the leachate treatment plant sludge were acclimatised to the List I substances (Figure A3.16). The List I substances were added to the subcultures at increments of 25 per cent of target concentrations for the biodegradation tests (toluene 17.5 µg/l, TCE 7.5 µg/l, TCB 5 µg/l, mecoprop 10 µg/l and naphthalene 10 µg/l). Sodium formate and sodium acetate were added as carbon sources. Additional sulphate was added whenever it was depleted from solution as a result of sulphate reduction. Acclimatisation of the bacterial seeds was initially carried out in 0.3 litres of each synthetic leachate (Table A3.18) and then in a further 1.2 litres of leachate (Table A3.19). Methane production and sulphate reduction were observed at the target concentrations for the biodegradation tests, indicating that the microorganisms were still active in the presence of List I substances.

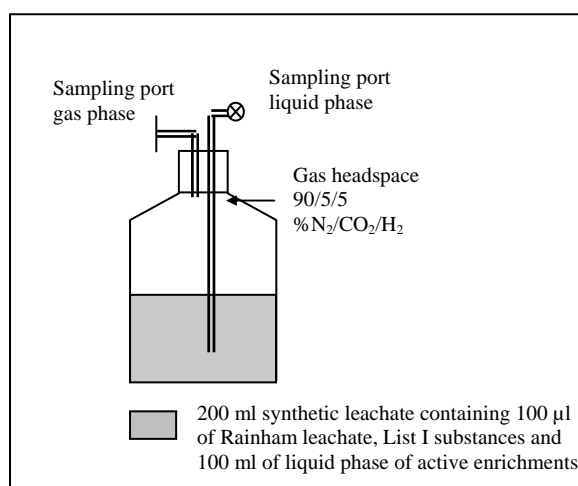


Figure A3.16 Acclimatisation of enriched bacterial seeds to List I substances

Table A3.18 Methane production and sulphate reduction by bacterial seeds during acclimatisation to List I substances in 0.3 litres of MSW and MSWI leachates

Incubation time (days)	Methane production (%)		Sulphate reduction (%) ^a
	MSW leachate	MSWI leachate	MSWI leachate
8	4.9	3.7	-
13	-	-	25 (587 mg/l SO ₄ ²⁻)
21	7.3	8.4	-
45	-	-	97 (<20 mg/l SO ₄ ²⁻)
56	100% target concentrations List I		
59	-	-	SO ₄ ²⁻ added (464 mg/l SO ₄ ²⁻)
68	22.5	7.5	
73	-	-	53 (216 mg/l SO ₄ ²⁻)
97	45.8	16.6	-
109	46.8	19.4	-
111	-	-	>97 (<20 mg/l SO ₄ ²⁻)

^a = 100 * Ct/Cc, where Ct is the measured sulphate concentration at time t and Cc is the conservative sulphate concentration at time t (no reduction occurring)

Table A3. 19 Methane production and sulphate reduction by bacterial seeds during acclimatisation to List I substances in 1.2 litres of MSW and MSWI leachates

Incubation time (days)	Methane production (%)		Sulphate reduction (%) ^a
	MSW leachate	MSWI leachate	MSWI leachate
0	50% target concentrations List I		
10	4.4 (bottle 1) 22.1 (bottle 2)	14.6 (bottle 1) 19.4 (bottle 2)	-
14	100% target concentrations List I		
22	22.7 (bottle 1) 35.1 (bottle 2)	8.9 (bottle 1) 9.6 (bottle 2)	-
24	-	-	88 (55 mg/l bottle 1 SO ₄ ²⁻) 85 (70 mg/l bottle 2 SO ₄ ²⁻)

A3.5.4. Biodegradation tests

Biodegradation tests were carried out in one-litre Duran type bottles with appropriate airtight OMNI fittings for sampling. Each bottle contained MSW (methanogenic) or MSWI (sulphate-reducing) synthetic leachate, active methanogenic or sulphate-reducing bacterial seeds acclimatised to the List I substances, two grams of liner material (only in the bottles where sorption effects were being studied) and the List I substance or a mixture of substances. A gas headspace of 80/15/5 (per cent nitrogen/carbon dioxide/hydrogen) was applied above the liquid level of the bottles. The bottles were then sealed and stored in an anaerobic cabinet (Woflabs Model A Vinyl cabinet incorporating oxygen and hydrogen measurement and carbon dioxide controller) containing the same gas mixture. Three different tests were carried out in duplicate (Figure A3.17):

- In the first test, biodegradation of the List I substance(s) was evaluated in the absence of the liner material. The test was prepared by adding synthetic leachate containing the List I substance(s) and bacterial seeds to the bottles.
- In the second test, both the effects of biodegradation of the List I substance(s) and sorption to the liner material were evaluated. Synthetic leachate containing the List I substance(s) and bacterial seeds were added to the bottle together with the liner material.
- In the third test, biodegradation was inhibited with bacteriological inhibitors (20 mM molybdenum and 50 mM 2-bromoethanesulphonic acid) and sorption of the List I substance(s) to the liner material evaluated. The test were prepared by adding to the bottles the liner material and synthetic leachate containing the List I substance(s) and biological inhibitors.

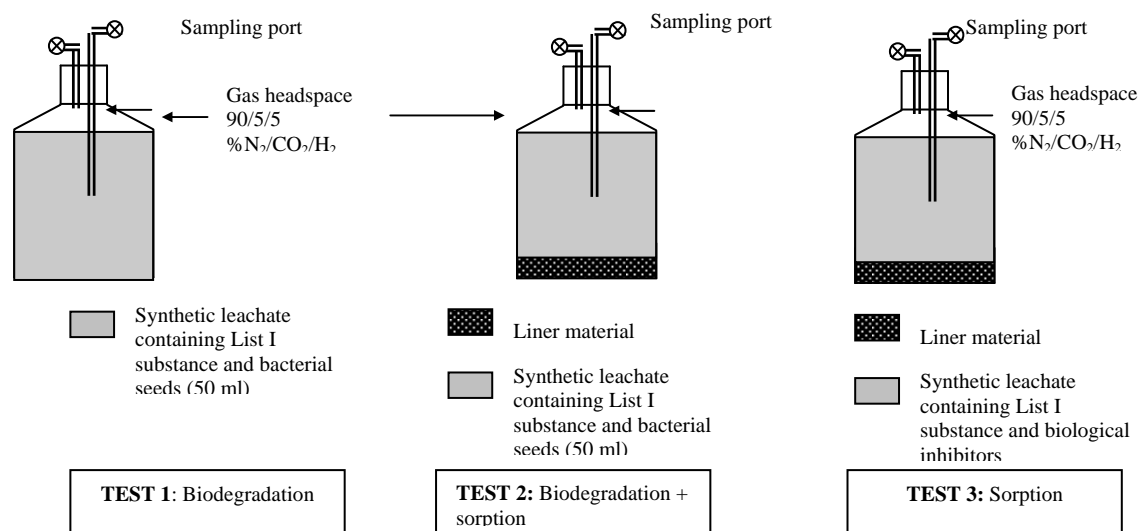


Figure A3.17 Experimental set-up of the biodegradation tests

Biodegradation was studied using three mixtures of List I substances which are likely to occur in leachates (Table A3.20). The target concentrations of List I substances (either individually or in a mixture) used in the biodegradation study were within the range of concentrations used for the sorption tests. The presence of the mineral liner material, tannic acid and headspace in the bottles resulted in losses of the List I substances from the aqueous phase by sorption and volatilisation, which were no longer readily available for biodegradation. A theoretical calculation of losses of List I substances by sorption to the tannic acid and liner materials and losses by volatilisation was made. The amount of substances added to the bottles was then adjusted to provide target concentrations (50 per cent more than the theoretical values was added to the bottles to allow for errors, Table A3.21). Further details of the biodegradation tests are given in Section 10 and Appendix 4, 5 and 6.

Table A3.20 Groups of List I substances studied in the biodegradation tests

Group I	Group II	Group III
Mecoprop	Mecoprop	Naphthalene
Toluene	Naphthalene	
Naphthalene	Toluene	
1,2,4-trichlorobenzene		
Trichloroethylene		

Appendix 4 – Biodegradation: MSW synthetic leachate (additional results)

A4.1. Introduction

Section 10.3 of the main report contains the results from the MSW synthetic leachate biodegradation tests mainly relating to Oxford Clay; this appendix contains data from tests involving London Clay and Mercia Mudstone, together with additional Oxford Clay data.

Biodegradation of the five List I substances was evaluated under methanogenic conditions (in MSW synthetic leachate) according to the procedure described in Section 10 and Appendix 3. Biodegradation was studied using three mixtures of List I substances which are likely to occur in leachates (Table A4.1).

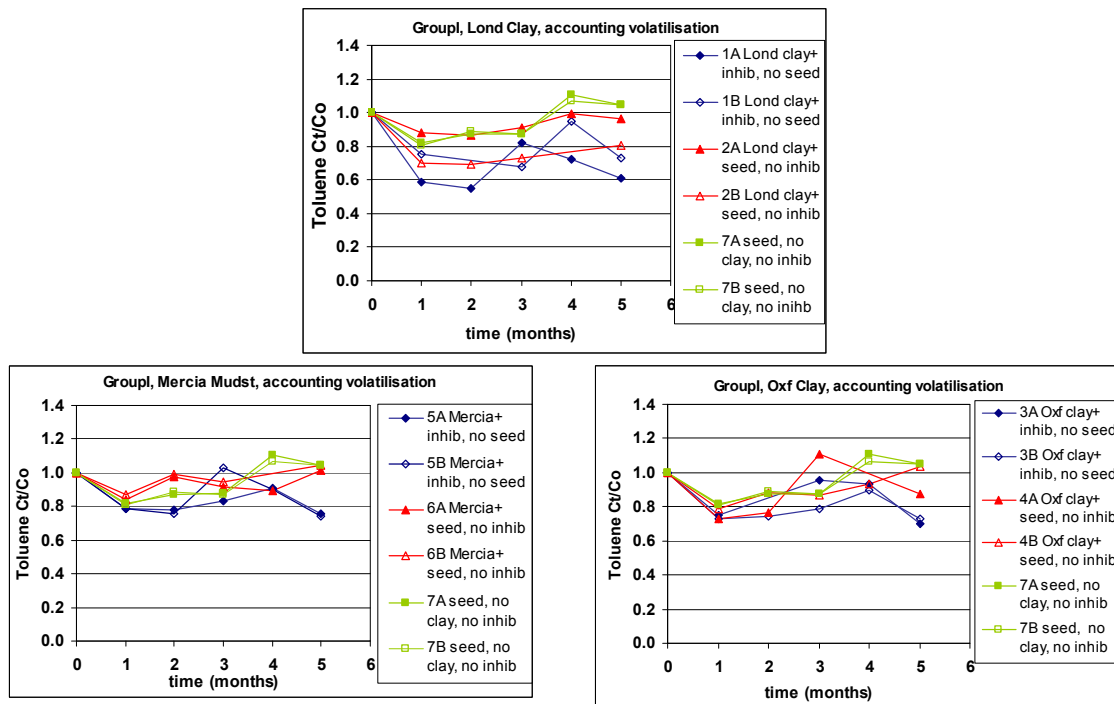
Table A4.1 Experimental conditions for the biodegradation tests under methanogenic conditions

List I	Liner	Bacterial seed	Biological inhibitors ^a	Bottle	Bottle
Group I (Toluene, TCE, TCB, naphthalene and Mecoprop)	London Clay	-	+	1A	1B
		+	-	2A	2B
	Oxford Clay	-	+	3A	3B
		+	-	4A	4B
		Mercia Mudstone	-	+	5A
	-	+	-	6A	6B
	-	+	-	7A	7B
Group II (Toluene, naphthalene and Mecoprop)	London Clay	-	+	8A	8B
		+	-	9A	9B
	Oxford Clay	-	+	10A	10B
		+	-	11A	11B
		Mercia Mudstone	-	+	12A
	-	+	-	13A	13B
	-	+	-	14A	14B
Group III (Naphthalene)	Oxford Clay	-	+	15A	15B
		+	-	16A	16B
	-	+	-	17A	17B

^a 20 mM molybdenum and 50 mM 2-bromoethane sulphonic acid; + (added); - (not added)

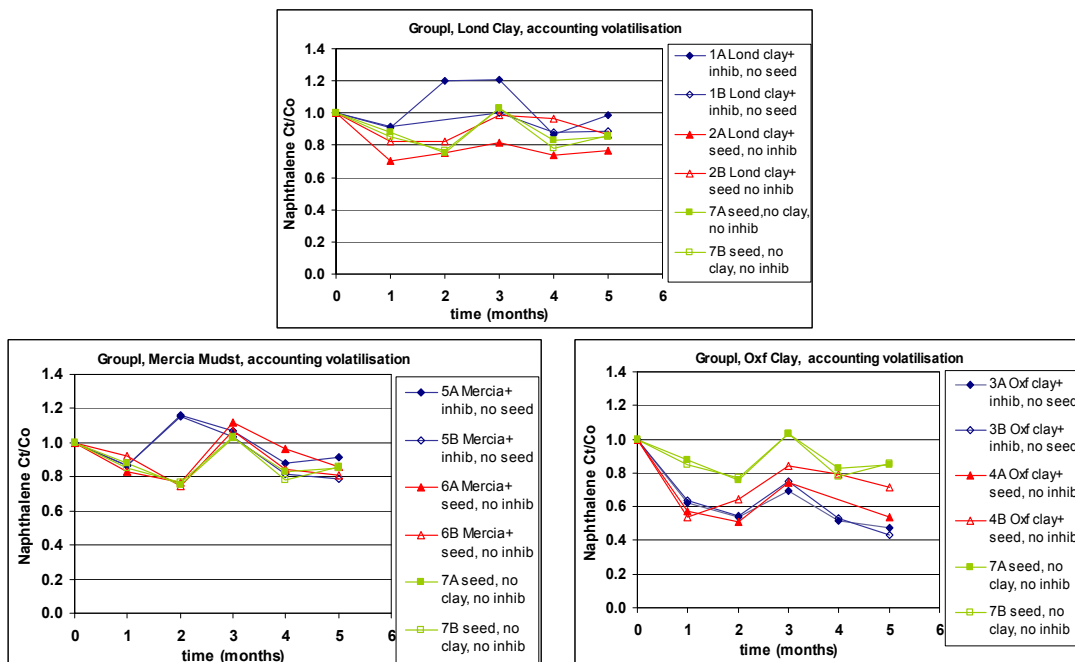
- In the first test, biodegradation of the List I substance(s) was evaluated in the absence of the liner material. The test was prepared by adding synthetic leachate containing the List I substance(s) and bacterial seeds to the bottles.
- In the second test, both the effects of biodegradation of the List I substance(s) and sorption to the liner material were evaluated. Synthetic leachate containing the List I substance(s) and bacterial seeds were added to the bottle together with the liner material.
- In the third test, biodegradation was inhibited with bacteriological inhibitors (50 mM 2-bromoethanesulphonic acid for inhibition of methanogenic bacteria; Oremland and Capone, 1998) and sorption of the List I substance(s) to the liner material evaluated. The test was prepared by adding to the bottles the liner material and synthetic leachate containing the List I substance(s) and biological inhibitors.

A4.2. Group I List I substances



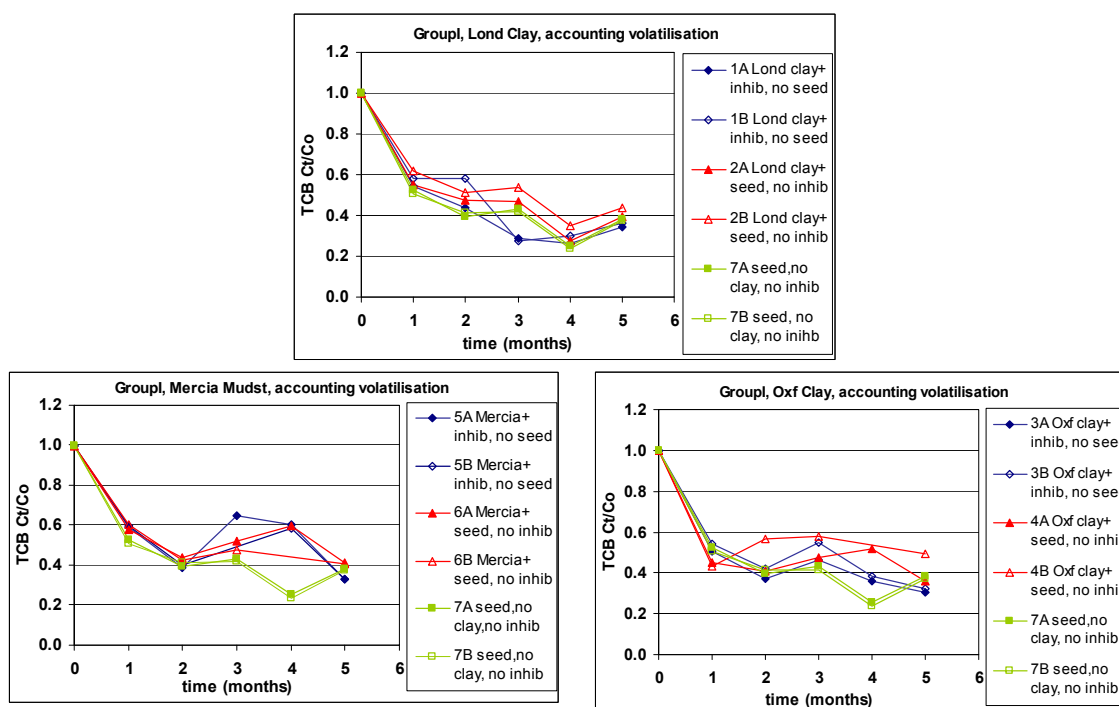
The decrease in toluene concentration over the first month of incubation was probably due to sorption to the liner material/bacterial seed and/or deviation from theoretical calculations of losses by volatilisation. No significant decrease in toluene aqueous concentration was observed, suggesting that toluene is recalcitrant over the first five months of incubation.

Figure A4.1 Toluene in MSW synthetic leachate containing Group I List I substances



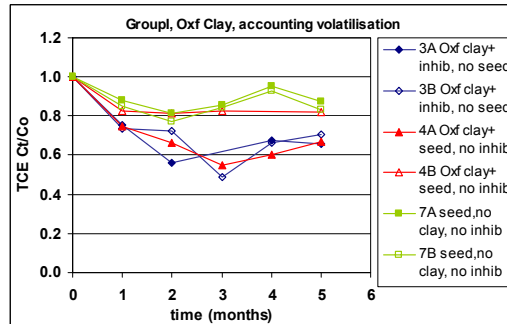
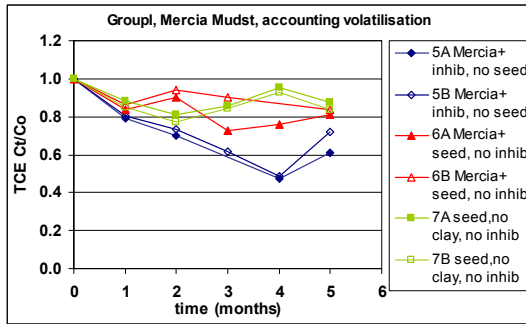
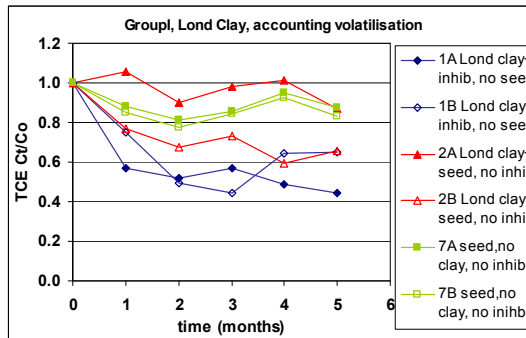
Apart from the bottles containing Oxford Clay, no significant decrease in naphthalene aqueous concentration was observed, suggesting that naphthalene is recalcitrant over the first five months of incubation. In the bottles containing Oxford Clay (Bottles 3 and 4) naphthalene concentration was found to decrease to 40% of the initial concentration. Given that this decrease was also found in the bottles containing biological inhibitors (Bottles 3A, 3B), it may be due to abiotic processes, such as long-term sorption to the liner material and bacterial seed.

Figure A4.2 Naphthalene in MSW synthetic leachate containing Group I List I substances



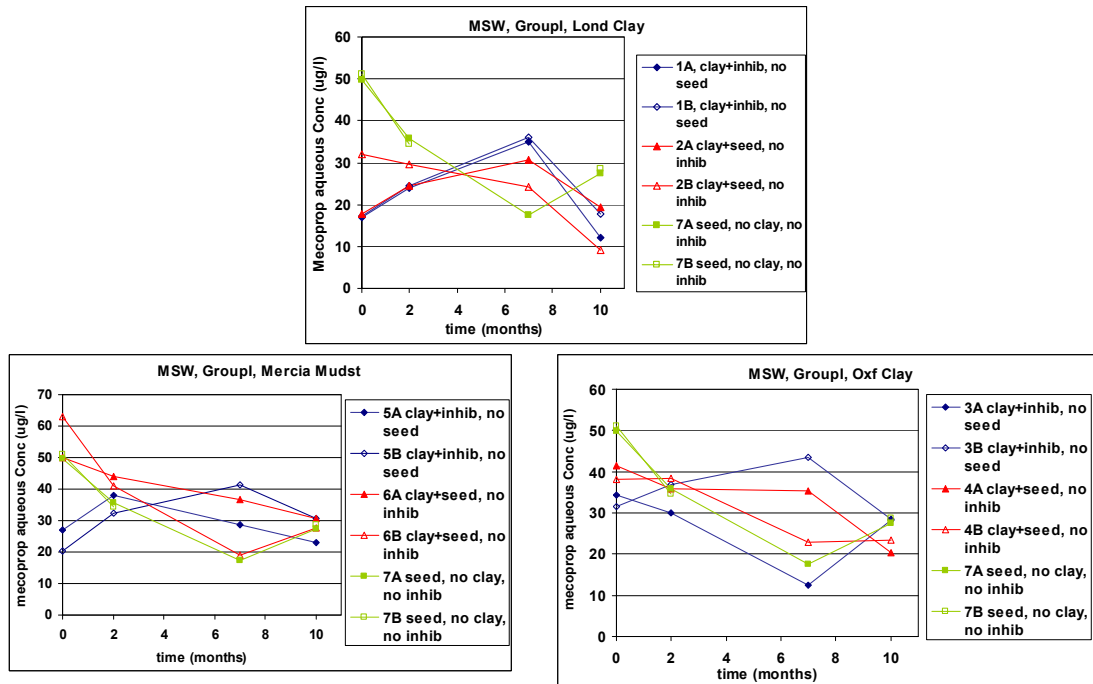
TCB concentration was found to decrease in the first two months of incubation to about 0.3-0.4Co in all bottles. Given that this reduction in concentration was also observed in the presence of biological inhibitors, it may be due to abiotic processes (sorption to the liner material and bacterial seed), losses to the bottle and/or deviation from theoretical calculations of losses by volatilisation. Common biodegradation products of TCB from reductive dechlorination processes (dichlorobenzenes and chlorobenzene) were not found in any of the bottles (GC-MS detection limit 0.1 ug/l).

Figure A4.3 TCB in MSW synthetic leachate containing Group I List I substances



TCE concentration was found to decrease in the first two months of incubation to about 0.6-0.8Co, after which no significant changes were observed. Apart from Bottle 2A (containing London Clay + seed and without biological inhibitors), TCE concentration was lower in the presence of liner material, both with and without biological inhibitors. This suggests that TCE may be sorbing to the liner material or bacterial seed. Common biodegradation products of TCE from reductive dechlorination processes (dichloroethene and vinyl chloride) were not found in any of the bottles (GC-MS detection limit 0.1ug/l).

Figure A4.4 Trichloroethene in MSW synthetic leachate containing Group I List I substances



- Measured Mecoprop aqueous concentration at the start of the tests was higher than expected (each bottle was initially spiked with $15 \pm 5 \mu\text{g/l}$).
- Mecoprop aqueous concentration in the bottles containing London and Oxford Clays was similar with or without biological inhibitors suggesting that biodegradation did not occur.
- Mecoprop aqueous concentration in the bottles containing Mercia Mudstone decreased only when biological inhibitors were not present.
- Mecoprop aqueous concentration in the bottles without mineral liner material and biological inhibitors decreased to about 50 per cent of its initial concentration.

Figure A4.5 Mecoprop aqueous concentration in MSW leachate containing Group I of List I substances

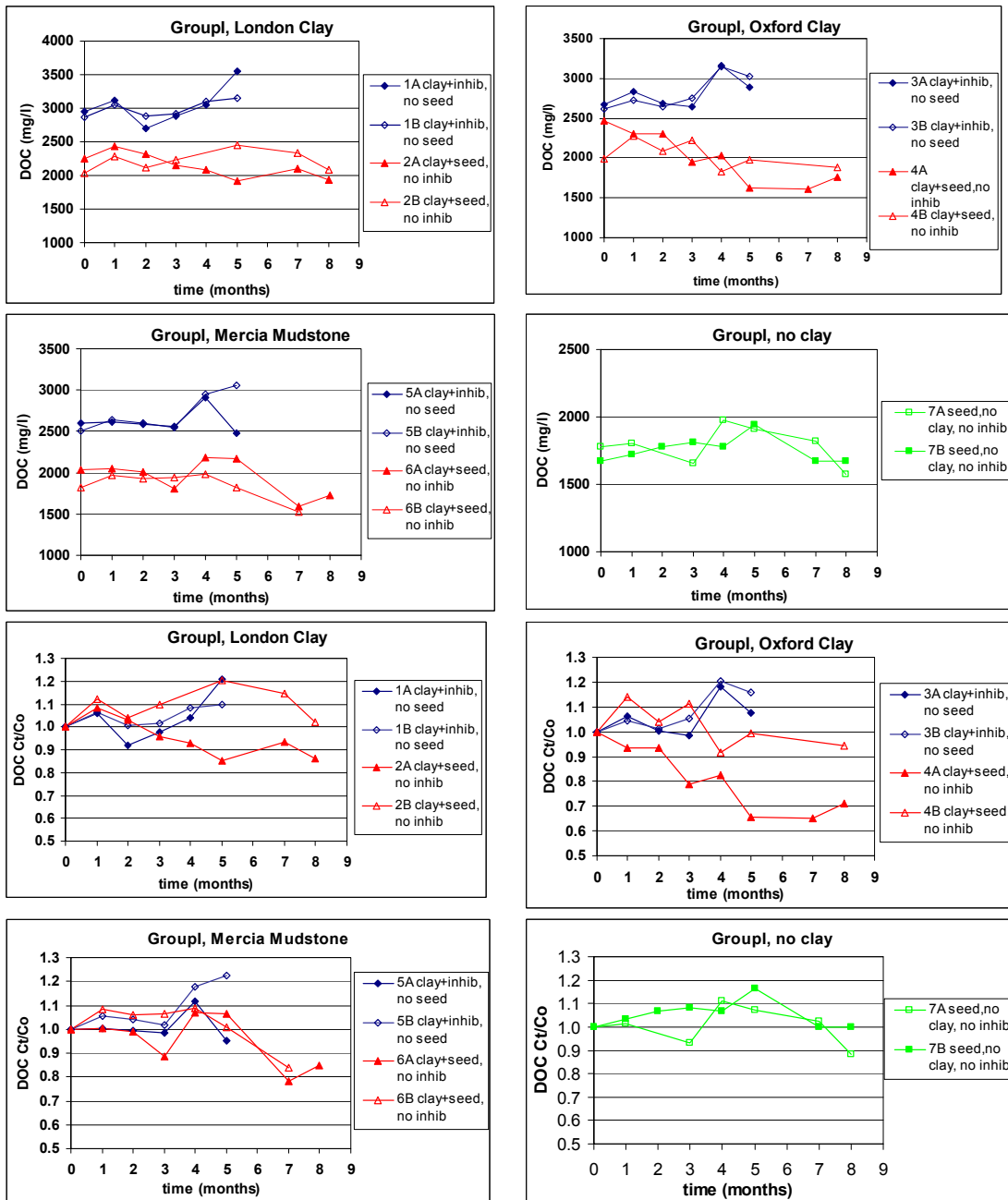


Figure A4.6 Variation in DOC with time for MSW leachate containing Group I List I substances

The DOC content of the MSW leachate in the biodegradation bottles (1,700 to 3,000 mg/l) was higher than the theoretical content based on the tannic acid content (540 mg/l). Potential sources of DOC in the leachate are discussed below. The MSW leachate for the biodegradation tests was prepared in two batches - the first was used for the bottles without biological inhibitors and the second was used for the bottles containing biological inhibitors.

Leachate batch for bottles without biological inhibitors

The methanol added to the leachate as a solvent for Mecoprop and naphthalene contributed to the high DOC values measured. Theoretical calculations based on the amount of methanol added indicate that initial DOC values should be approximately:

- 1,668 mg/l for the bottles without liner material (Bottle 7; experimental DOC 700 mg/l).;
- 2,025mg/l for the bottles containing Oxford Clay (Bottle 4 A and B experimental DOC 2,000-2,500mg/l);
- 2,351mg/l for the bottles containing London Clay (Bottle 2A and B; experimental DOC 2,000-2,200mg/l);
- 1,906 mg/l for the bottles containing Mercia Mudstone (Bottle 6A and B; experimental DOC 1,800-2,000mg/l).

Leachate batch for bottles containing biological inhibitors

The DOC in the bottles containing mineral liner materials and inhibitors and no seed (2,500-2,900 mg/l; Bottles 1, 3 and 5) was higher than the theoretical values based on the amount of methanol added (2,025, 2,351 and 1,906 mg/l for the bottles containing Oxford Clay, London Clay and Mercia Mudstone, respectively). In addition to the DOC contribution by methanol, differences in the preparation of the second batch of MSW leachate may also have contributed to a higher DOC. Furthermore, it was observed that the addition of 50 mM 2-bromoethanesulphonic acid (biological inhibitor) to the leachate resulted in the change of colour (from yellow to red) and pH of the leachate suggesting that the inhibitors interacted with the tannic acid (Figure A4.7). This interaction may have altered the properties of the tannic acid and its affinity for the liner materials and List substances.

During the biodegradation tests, the DOC content of the leachate changes with time depending on (among other factors) the release of organic material from the liner materials, sorption/desorption of tannic acid by the liner material, amount of biomass produced from endogenous metabolism, and biogas production rate (Figure A4.8). The DOC in the bottles containing liner material+seed (especially Oxford and London Clays) and without biological inhibitors appeared to be slowly decreasing with time (Bottles 2A, 4A, 4B, 6A), suggesting that biodegradation of the DOC might be occurring (leading to biogas production, see Table A4.2).

Biogas was found to be produced in the bottles containing liner material+seed and without inhibitors (Bottles 2, 4 and 6) after five to 10 months of incubation (detected by the increase in pressure inside the bottles). In the bottles containing liner material+inhibitors, no seed (Bottles 1, 3 and 5) and the bottles containing seed, no liner material, no inhibitors (Bottle 7), biogas production was not observed (detected by negative pressure inside the bottles resulting from continuous sampling of leachate). To minimise the explosion hazard caused by increasing pressure inside the bottles, venting of the bottles to atmospheric pressure was carried out and the biogas volume, composition and pressure were determined. The biogas was found to consist mainly of methane (above 43 per cent), carbon dioxide (above 15 per cent) and gases from the anaerobic gas mixture (nitrogen and traces of hydrogen). Production of biogas coincided with a decrease in DOC suggesting that methanogenic bacteria were converting DOC to methane and carbon dioxide. Biogas production occurred first and in higher amounts in the bottles containing London and Oxford Clays (after five months of incubation) followed by the bottles containing Mercia Mudstone (after 10 months of incubation), suggesting that the liner materials were not only providing an attachment medium for the bacteria but may also have been acting as a DOC source, which might depend on the type of organic matter (Figure A4.9).

Table A4.2 Biogas production in biodegradation bottles containing Group I of List I substances

Bottle	Biogas (ml) ^a	Biogas composition		Internal pressure (kPa) ^c
		CH ₄ (%) ^b	CO ₂ (%) ^b	
Liner material+inhibitors, no seed (Bottles 1, 3 and 5)	-	-	-	Negative pressure
Seed, no liner material, no inhibitors (Bottle 7)	-	-	-	Negative pressure
Liner material+seed, no inhibitors				
2A (London Clay)	286	60.6	15.5	>200
2B (London Clay)	132	49.1	22.1	155.5
4A (Oxford Clay)	6	62.5	17.5	126.1
4B (Oxford Clay)	88	50.3	18.5	143.6
6A (Mercia Mudstone)	44	44.3	18.6	126.5
6B (Mercia Mudstone)	5	43.4	16.7	118.6

^a Measured by releasing the pressure inside each bottle into a 20 ml plastic syringe until the pressure inside the bottle was approximately atmospheric pressure.

^b Measured by gas chromatography using a Varian CP-3800 GC equipped with a TCD detector and two columns 1 m by 1/8 inches OD: Haysep C column (80-100 mesh) and a Porapak column (molecular sieve 13X, 60-80 mesh) under the following conditions: 50°C isothermal back-flush mode and argon carrier gas.

^c Measured using an Absolute Pressure Meter Digitron 2025P (measuring range 0-200 kPa).



Figure A4.7 Colour of biodegradation bottles

MSW leachate containing bacterial seed, Oxford Clay and without biological inhibitors (yellow colour, bottle on the left); MSW leachate containing Oxford Clay and biological inhibitors and without bacterial seed (red colour, bottle on the right)



Figure A4.8 Change of DOC content of the MSW leachate during the biodegradation tests

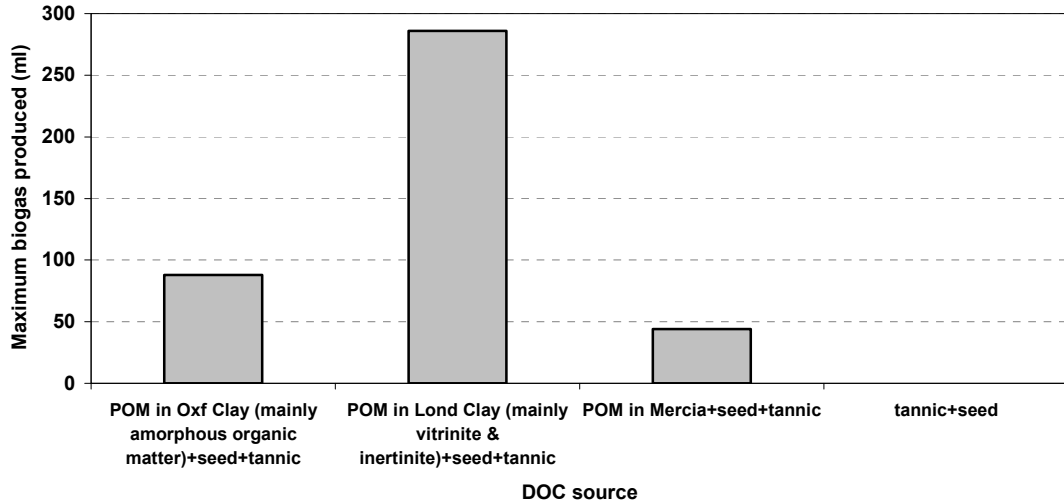
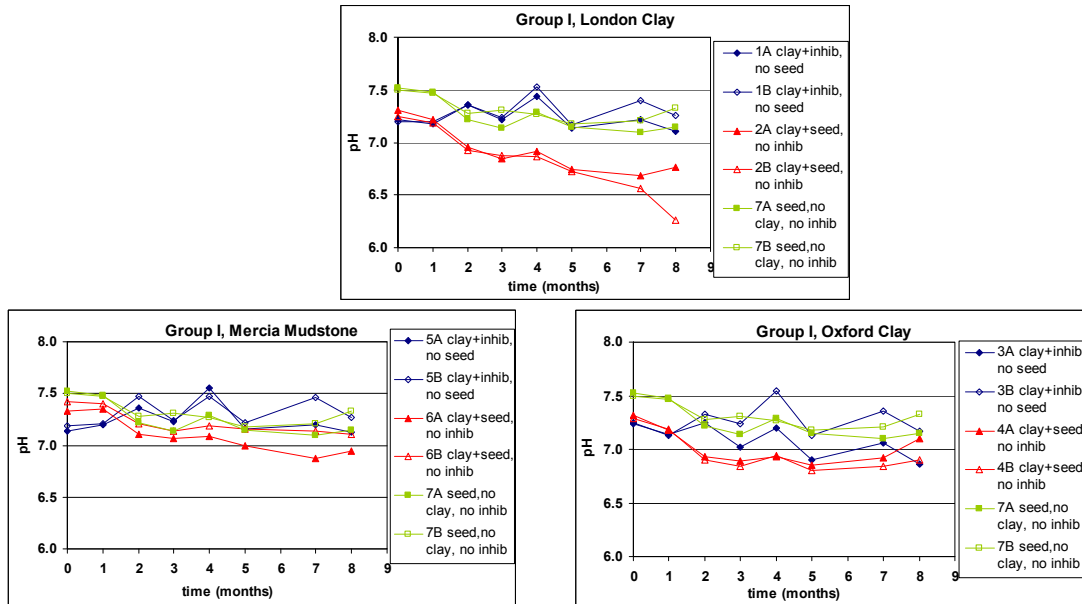
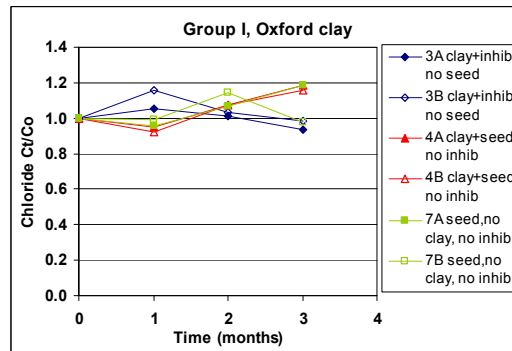
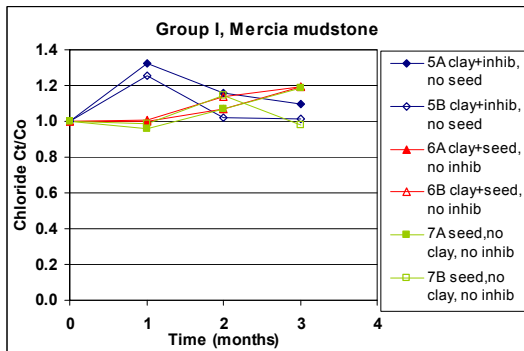
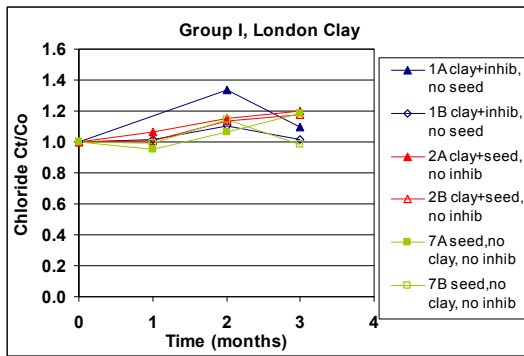


Figure A4.9 Biogas production after 10 months of incubation as a function of the DOC source in the leachate (POM = particulate organic matter)



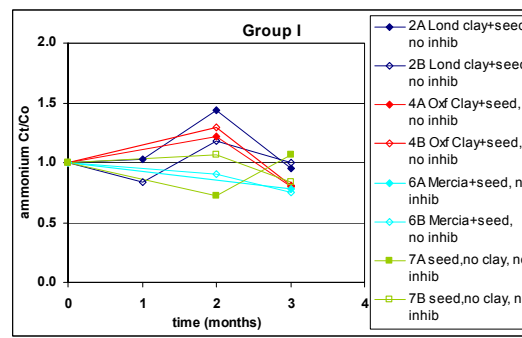
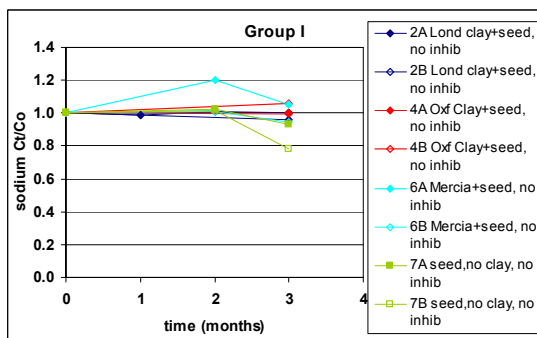
The pH in the bottles containing liner material+seed and without inhibitors (Bottles 2, 4 and 6) slowly decreases with time. This may be due to CO₂ dissolution in the leachate as H₂CO₃, HCO₃⁻ and CO₃²⁻. Sources of CO₂ in the headspace include the trace concentration in the anaerobic gas mixture (five per cent) and biogas formed from biodegradation reactions.

Figure A4. 10 Variation with time of pH of MSW leachate containing Group I List I substances



Chloride concentration did not vary significantly over the first three months of incubation. An increase in chloride concentration due to possible reductive dechlorination of TCB and TCE (see Vogel and McCarty, 1985; and Middeldorp *et al.*, 1997) was probably not detectable due to the high chloride background levels in the MSW leachate (1,800-2,500 mg/l).

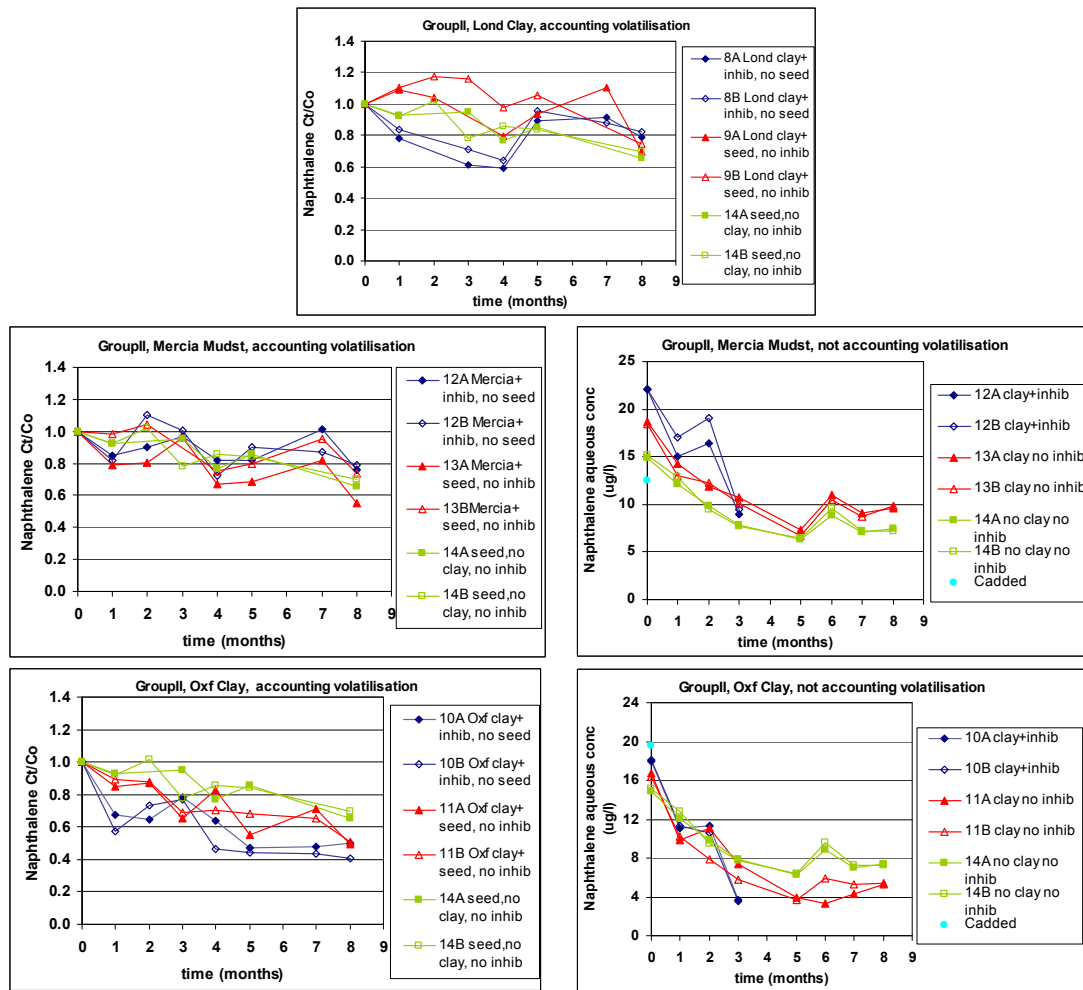
Figure A4.11 Variation with time of chloride of MSW leachate containing Group I List I substances



Variation in the sodium content of the MSW leachate was not significant over three months of incubation. Ammonium concentration in the MSW leachate was found to vary between 0.7-1.5Co (290-1,893 mg/l) without a clear trend in concentration versus time. Variability in the measured ammonium concentrations was probably related to the sample preservation technique which consisted of freezing.

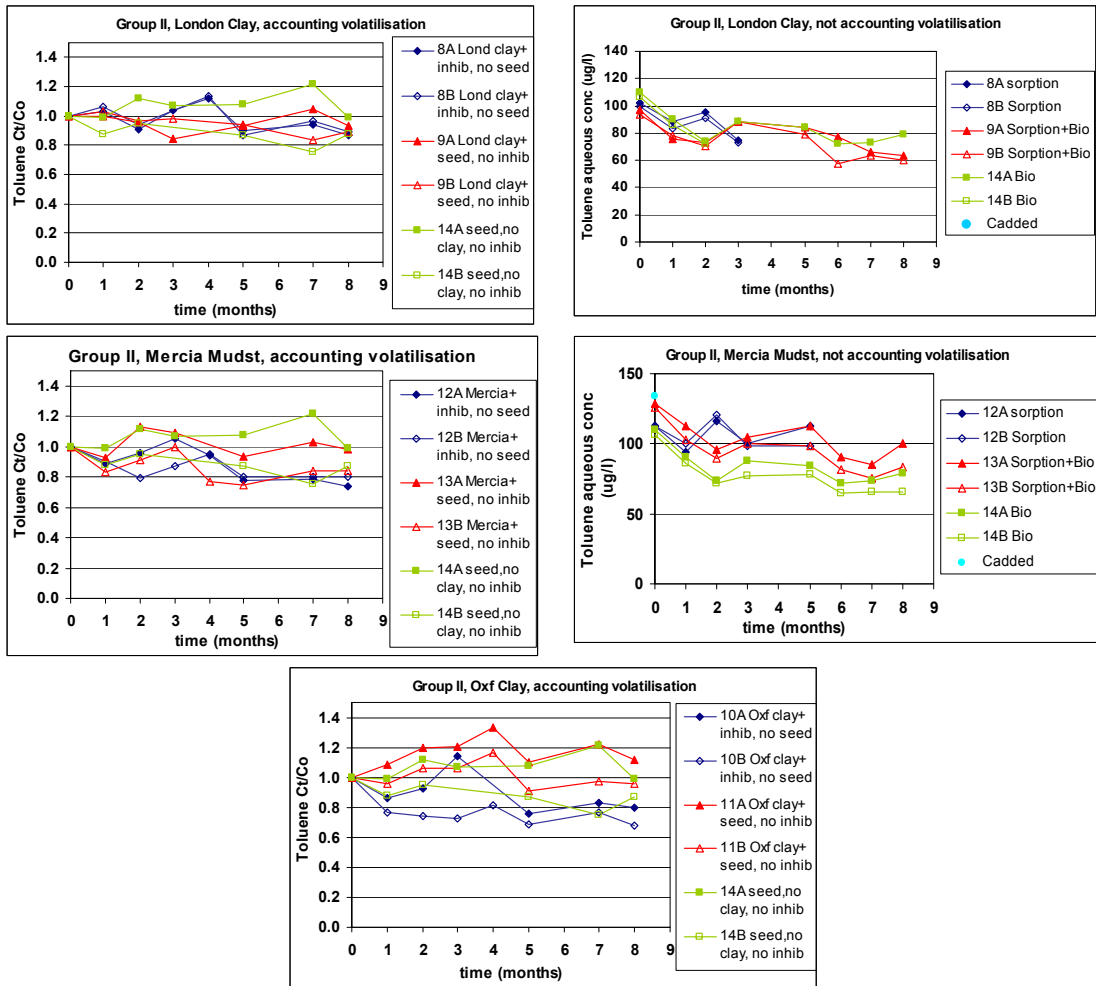
Figure A4.12 Variation with time of sodium and ammonium ions of MSW leachate containing Group I List I substances

A4.3. Group II List I substances



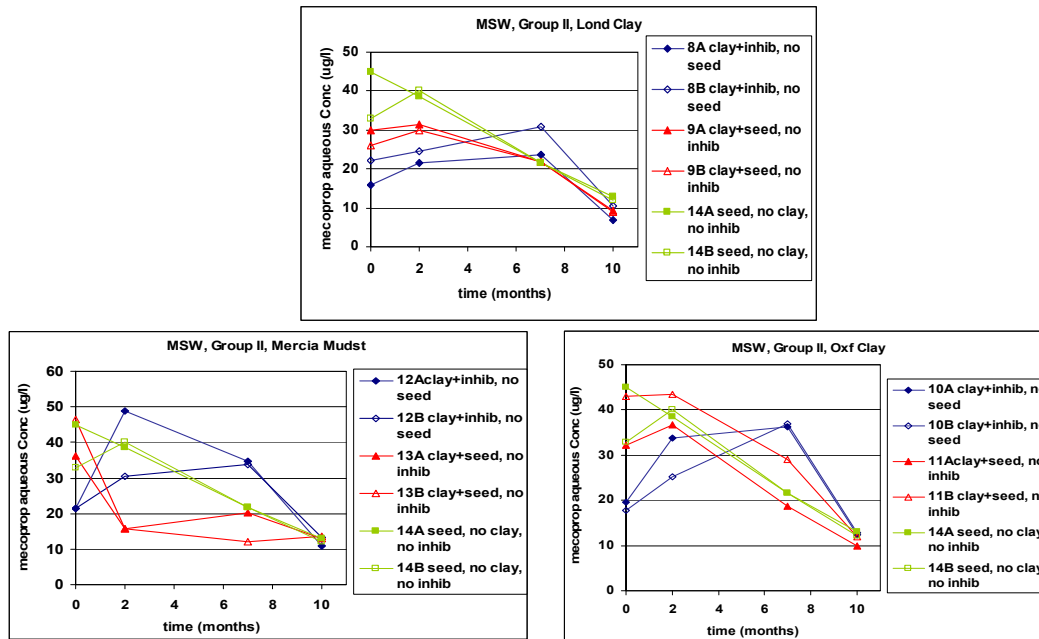
Apart from bottles containing Oxford Clay, naphthalene concentration was found to be roughly constant suggesting that naphthalene was recalcitrant over the first eight months of incubation. The decrease observed in the bottles containing Oxford Clay (both with and without biological inhibitors) suggests that abiotic processes may be occurring, such as long-term sorption to Oxford Clay/bacterial seed.

Figure A4.13 Naphthalene aqueous concentration in MSW leachate containing Group II of List I substances



Variation with time in toluene concentration was not significant, suggesting that toluene is recalcitrant over the first eight months of incubation.

Figure A4.14 Variation with time of toluene aqueous concentration in MSW leachate containing Group II of List I substances.



- Measured mecoprop aqueous concentration at the start of the tests was higher than expected (each bottle was initially spiked with $15 \pm 5 \mu\text{g/l}$).
- Mecoprop aqueous concentration in the bottles containing London Clay was similar with or without biological inhibitors, suggesting that biodegradation did not occur.
- Mecoprop aqueous concentration in the bottles containing Oxford Clay and Mercia Mudstone decreased more significantly when biological inhibitors were not present.
- Mecoprop aqueous concentration in the bottles without liner material and biological inhibitors decreased to about 20 per cent of its initial concentration, suggesting that biodegradation processes and/or losses to bottle components may have occurred

Figure A4.15 Mecoprop aqueous concentration in MSW leachate containing Group II of List I substances

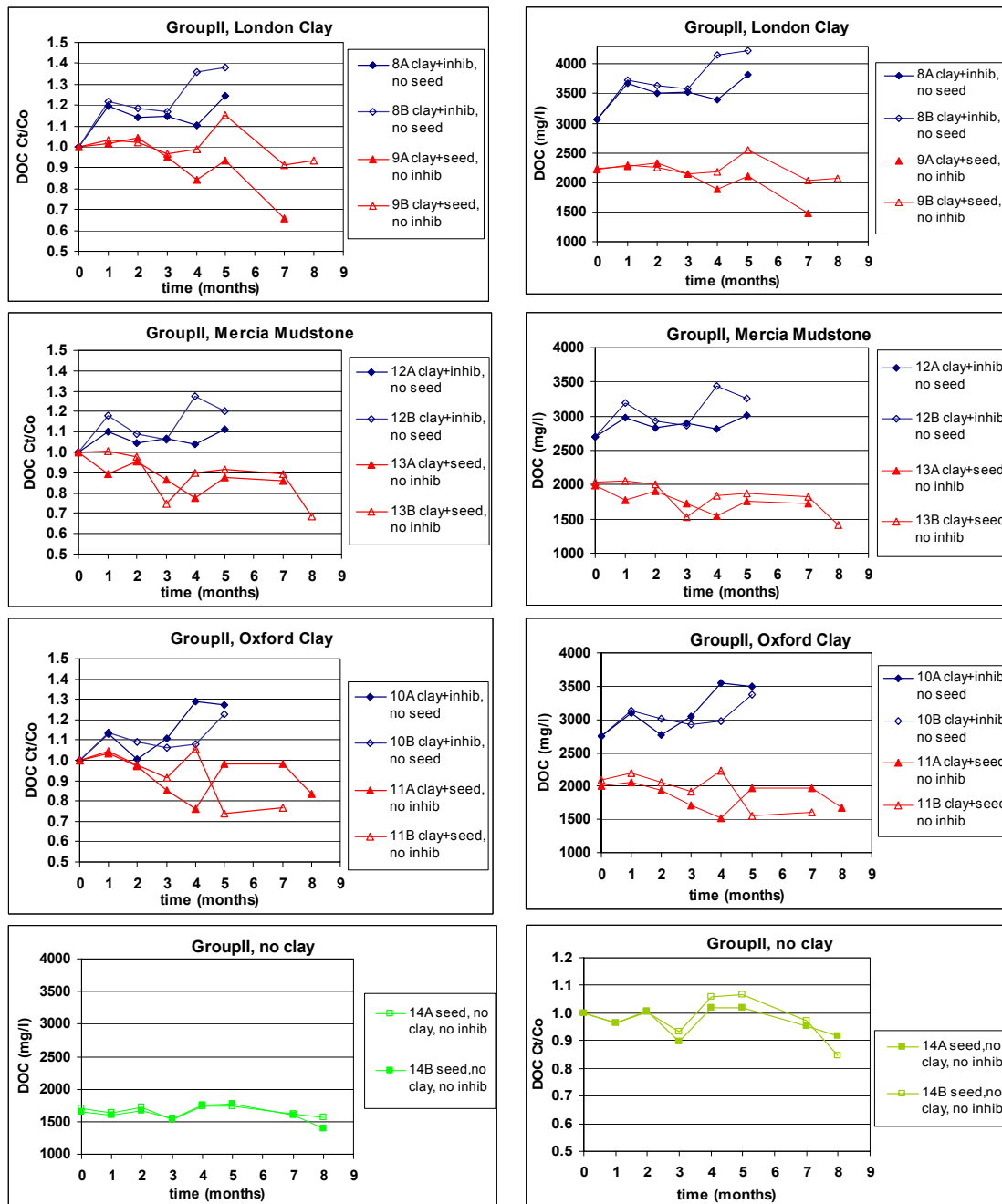


Figure A4.16 Variation in DOC with time for MSW leachate containing Group I List II substances

As observed for the Group I of List I substances, the DOC content of MSW leachate in the biodegradation bottles (1,700-3,000 mg/l) was higher than the theoretical content based on the tannic acid content (540 mg/l). The high DOC values measured were due to the methanol added to the leachate as a solvent for mecoprop and naphthalene and differences in the preparation of the batch of MSW leachate containing biological inhibitors.

DOC content of the leachate may change during biodegradation tests according to (among other factors): release of organic material from the liner materials, sorption/desorption of tannic acid by liner materials, amount of biomass produced from endogenous metabolism, and biogas production rate. DOC in the bottles containing liner material+seed (especially Oxford and London Clays) and without

biological inhibitors slowly decreased with time (Bottles 9B, 11A, 11B, 13A and 13B), suggesting that biodegradation of the DOC may be occurring (leading to biogas production, see Table A4.3).

As observed for the Group I of List I substances, biogas was produced in the bottles containing liner material+seed and without inhibitors (Bottles 9, 11 and 13) after five to 10 months of incubation (detected by the increase in pressure inside the bottles). In the bottles containing liner material+inhibitors, no seed (Bottles 8, 10 and 12) and the bottles containing seed, no liner material, no inhibitors (Bottles 14), biogas production was not observed (detected by negative pressure inside the bottles resulting from continuous sampling of leachate). To minimise the explosion hazard caused by increasing pressure inside the bottles, venting of the bottles to atmospheric pressure was carried out on 25 August 2005 and the biogas volume, composition and pressure were determined (Table A4.3). The biogas was found to consist mainly of methane (above 40 per cent), carbon dioxide (above 16 per cent) and gases from the anaerobic gas mixture (nitrogen and traces of hydrogen). As observed for the Group I of List I substances, production of biogas coincided with a decrease in DOC suggesting that methanogenic bacteria were converting DOC to methane and carbon dioxide. Biogas production occurred first and in higher amounts in the bottles containing London and Oxford Clays (after five months of incubation) followed by the bottles containing Mercia Mudstone (after 10 months of incubation), suggesting that the liner materials were not only providing an attachment medium for the bacteria but may also have been acting as a DOC source, which may depend on the type of organic matter.

Table A4.3 Biogas production in biodegradation bottles containing the Group II of List I substances

Bottle	Biogas (ml) ^a	Biogas composition		Internal pressure (kPa) ^c
		CH ₄ (%) ^b	CO ₂ (%) ^b	
Liner material+inhibitors, no seed (Bottles 8, 10 and 12)	-	-	-	Negative pressure
Seed, no liner material, no inhibitors (Bottle 14)	-	-	-	Negative pressure
Liner material+seed, no inhibitors				
9A (London Clay)	330	60.2	16.5	>200
9B (London Clay)	372	59.3	15.8	>200
11A (Oxford Clay)	66	46.4	18.0	134.0
11B (Oxford Clay)	22	41.0	22.9	119.2
13A (Mercia Mudstone)	-	-	-	Negative pressure
13B (Mercia Mudstone)	12	39.9	24.5	101.4

^a Measured by releasing the pressure inside each biodegradation bottle into a 20 ml plastic syringe until the pressure inside the bottle was approximately atmospheric pressure.

^b Measured by gas chromatography using a Varian CP-3800 GC equipped with a TCD detector and two columns 1 m by 1/8 inches OD: Haysep C column (80-100 mesh) and a Porapak column (molecular sieve 13X, 60-80 mesh) under the following conditions: 50°C isothermal back-flush mode and argon carrier gas.

^c Measured using an Absolute Pressure Meter Digitron 2025P (measuring range 0-200 kPa).

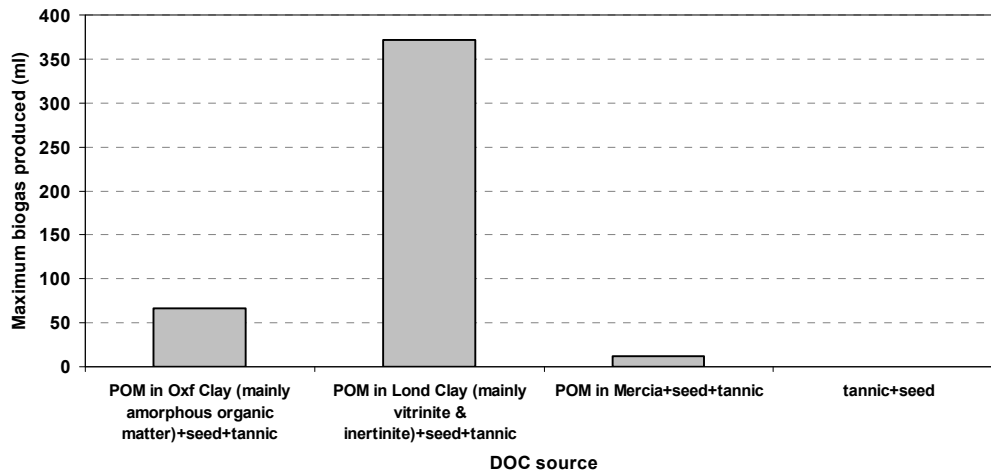
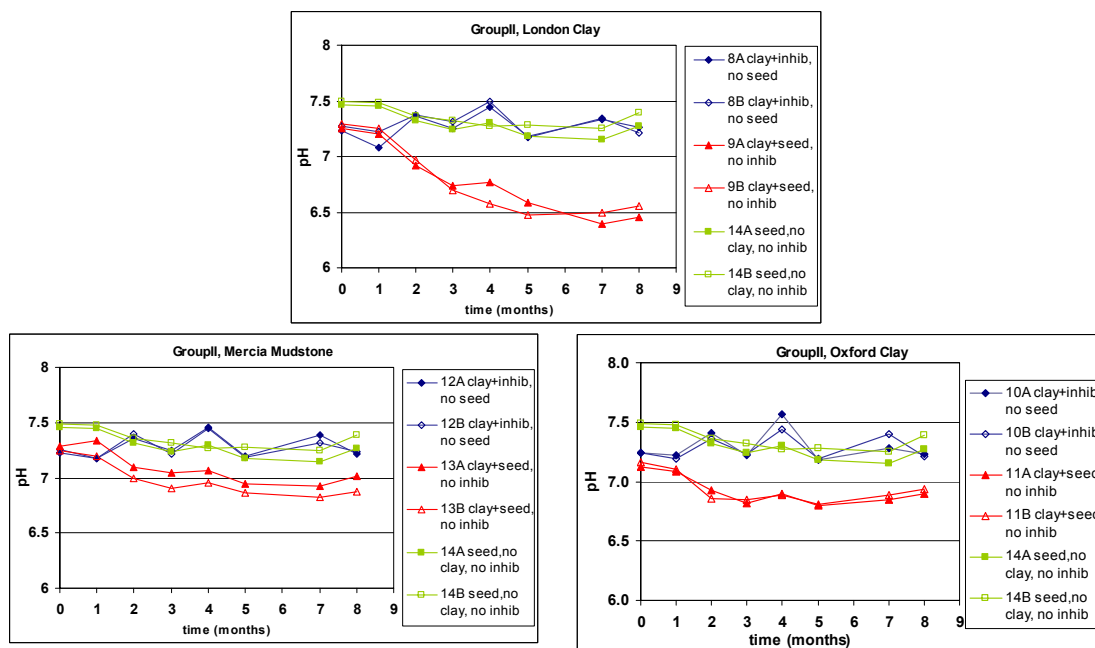


Figure A4.17 Biogas production after 10 months of incubation as a function of the DOC source in the leachate (POM is the particulate organic matter)



As observed for Group I of List I substances, pH in bottles containing liner material+seed and without inhibitors (Bottles 9, 11 and 13) slowly decreased with time. This may be due to CO₂ dissolution in the leachate as H₂CO₃, HCO₃⁻ and CO₃²⁻. Sources of CO₂ in the headspace included the trace concentration in the anaerobic gas mixture (five per cent) and biogas formed from biodegradation reactions (Table A4.3).

Figure A4.18 Variation with time of pH of MSW leachate containing Group II List I substances

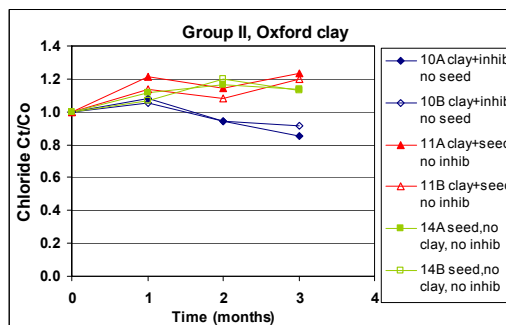
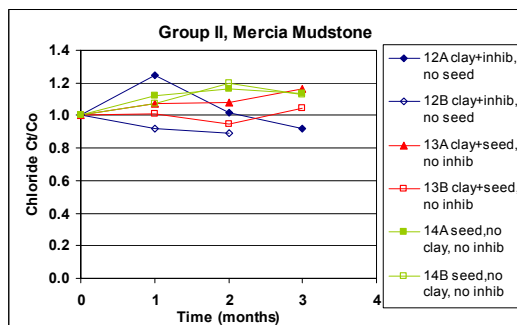
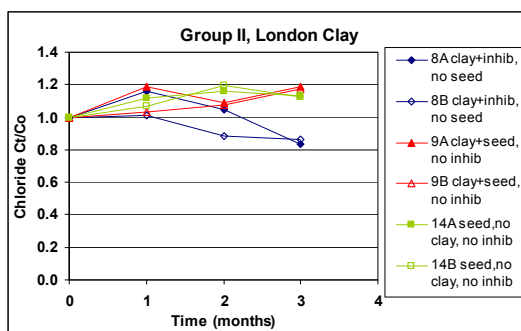
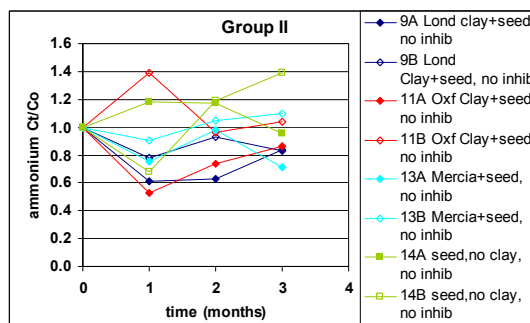
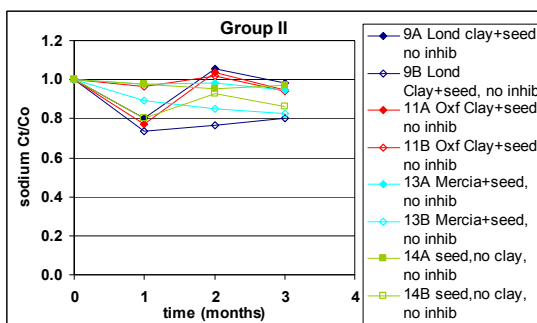


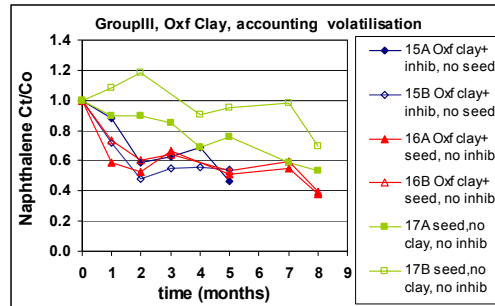
Figure A4.19 Chloride concentration in MSW leachate containing Group II List I substances



Variation in the sodium content of the MSW leachate was not significant over three months of incubation. Ammonium concentration in the MSW leachate was found to vary between 0.5-1.4Co (574-1,843 mg/l) without a clear trend in concentration versus time. Variability in the measured ammonium concentrations was probably related to the sample preservation technique which consisted of freezing.

Figure A4.20 Sodium and ammonium concentration in MSW leachate containing Group II List I substances

A4.4. Group III List I substance



Naphthalene concentration appears to be slowly decreasing with time in all bottles but more significantly in the ones containing Oxford Clay (with and without biological inhibitors). This could be due to biodegradation and abiotic processes such as sorption to the liner material and bacterial seed.

Figure A4.21 Naphthalene in MSW leachate containing Group III List I substance

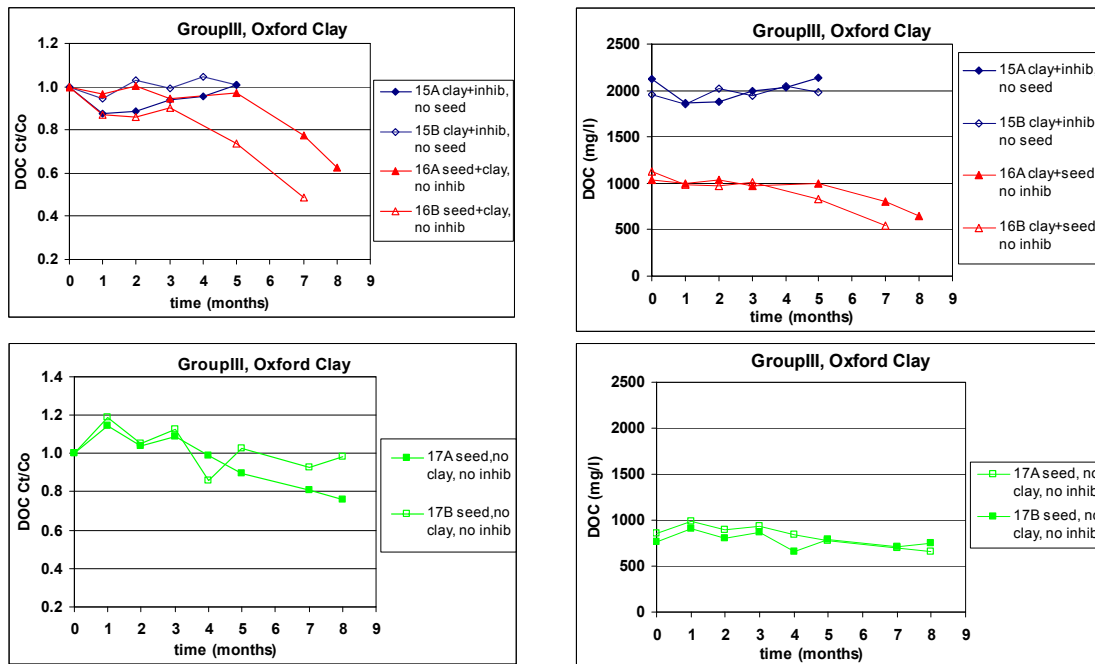


Figure A4.22 DOC in MSW leachate containing Group III List I substances

As observed for the Groups I and II of List I substances, the DOC content of the MSW leachate in the Group III biodegradation bottles (770-2,130 mg/l) is higher than the theoretical content based on the tannic acid content (540 mg/l). As discussed above, the high DOC values measured are due to the methanol added to the leachate as a solvent for naphthalene and differences in the preparation of the batch of MSW leachate containing biological inhibitors.

As discussed above, the DOC content of the leachate will change during the biodegradation tests according to (among other factors): the release of organic material from the solid matrix, sorption/desorption of tannic acid by the liner material,

amount of biomass produced from endogenous metabolism, and biogas production rate. The DOC in the bottles containing liner material+seed and without biological inhibitors appears to be slowly decreasing with time (Bottle 16), suggesting that biodegradation of the DOC may be occurring (leading to biogas production, see Table A4.4).

As observed for Groups I and II of List I substances, biogas was produced in bottles containing mineral liner material+seed and without inhibitors (Bottle 16) after five to 10 months of incubation (detected by the increase in pressure inside the bottles). In the bottles containing liner material+inhibitors, no seed (Bottle 15) and bottles containing seed, no liner material, no inhibitors (Bottle 17), biogas production was not observed (detected by negative pressure inside the bottles resulting from continuous sampling of leachate). To minimise the explosion hazard caused by increasing pressure inside the bottles, venting of the bottles to atmospheric pressure was carried out and biogas volume, composition and pressure were determined (Table A4.4). The biogas was found to consist mainly of methane (above 52 per cent), carbon dioxide (above 23 per cent) and gases from the anaerobic gas mixture (nitrogen and traces of hydrogen). Production of biogas coincided with a decrease in DOC suggesting that methanogenic bacteria were converting DOC to methane and carbon dioxide. Lack of biogas production in the bottles without liner material suggest that the solid matrix may have provided an attachment medium for the bacteria and may have acted as a DOC source.

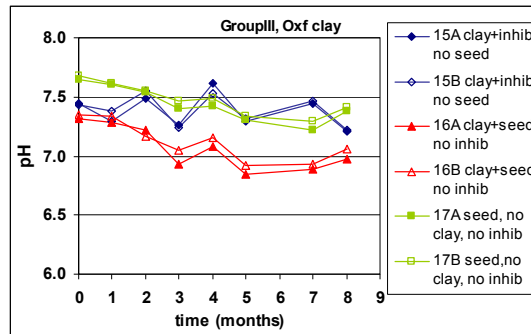
Table A4.4 Biogas production in biodegradation bottles containing Group III of List I substances

Bottle	Biogas (ml) ^a	Biogas composition		Internal pressure (kPa) ^c
		CH ₄ (%) ^b	CO ₂ (%) ^b	
Liner material+inhibitors, no seed (Bottle 15)	-	-	-	Negative pressure
Seed, no liner material, no inhibitors (Bottle 17)	-	-	-	Negative pressure
Liner material+seed, no inhibitors				
16A (Oxford Clay)	220	58.1	23.0	>200
16B (Oxford Clay)	66	52.3	23.9	138.7

^a Measured by releasing the pressure inside each bottle into a 20 ml plastic syringe until the pressure inside the bottle was approximately atmospheric pressure.

^b Measured by gas chromatography using a Varian CP-3800 GC equipped with a TCD detector and two columns 1 m by 1/8 inches OD: Haysep C column (80-100 mesh) and a Porapak column (molecular sieve 13X, 60-80 mesh) under the following conditions: 50°C isothermal back-flush mode and argon carrier gas.

^c Measured using an Absolute Pressure Meter Digitron 2025P (measuring range 0-200 kPa).



As observed for Groups I and II of List I substances, the pH in bottles containing liner material+seed and without inhibitors slowly decreased with time (Bottles 16A and 16B). This may be due to CO₂ dissolution in the leachate as H₂CO₃, HCO₃⁻ and CO₃²⁻. Sources of CO₂ in the headspace include the trace concentration in the anaerobic gas mixture (5%) and biogas formed from biodegradation reactions (see Table A4.4).

Figure A4.23 Variation with time of pH of MSW leachate containing Group III of List I substances

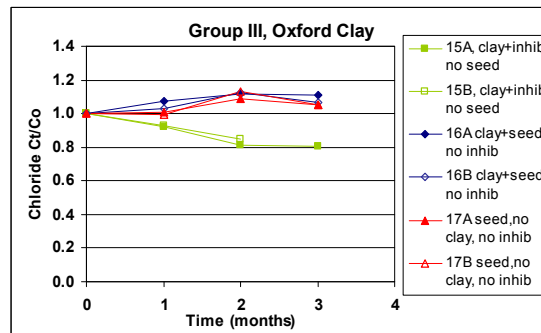
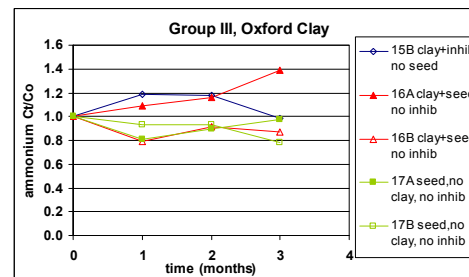
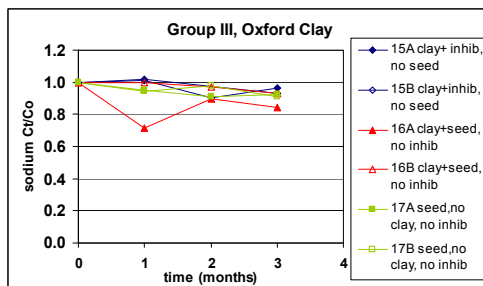


Figure A4.24 Variation with time of chloride in MSW leachate containing Group III of List I substances



Variation in sodium content of MSW leachate was not significant over first three months of incubation. Ammonium concentration in MSW leachate was found to vary between 0.8-1.4Co (760-3,675 mg/l) without a clear trend in concentration versus time. The variability in the measured ammonium concentrations is probably related to the sample preservation technique which consisted of freezing.

Figure A4.25 Sodium and ammonium in MSW leachate containing Group III of List I substances

Appendix 5 – Biodegradation: MSWI synthetic leachate (additional results)

A5.1. Introduction

Section 10.4 of the main report contains the results from the MSWI synthetic leachate biodegradation tests mainly relating to Oxford Clay; this appendix contains data from tests involving London Clay and Mercia Mudstone, together with additional Oxford Clay data.

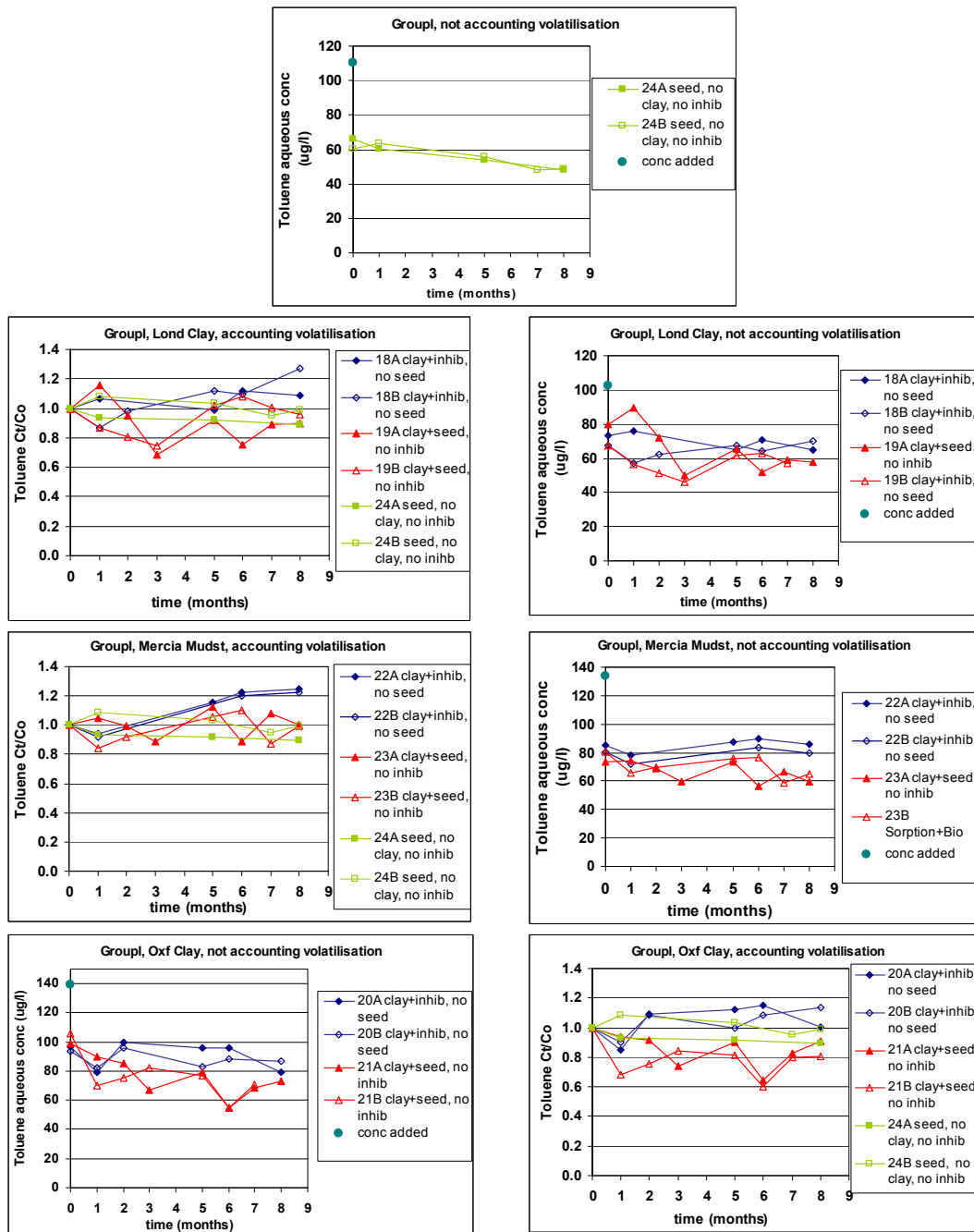
Biodegradation of the five List I substances was evaluated under sulphate-reducing conditions in MSWI synthetic leachate, according to the procedure described in Section 10 and Appendix 3. Three different tests were carried out in duplicate (Table A5.1):

- In the first test, biodegradation of the List I substance(s) was evaluated in the absence of the liner material. The test was prepared by adding synthetic leachate containing the List I substance(s) and bacterial seeds to the bottles.
- In the second test, both the effects of biodegradation of the List I substance(s) and sorption to the liner material were evaluated. Synthetic leachate containing the List I substance(s) and bacterial seeds were added to the bottle together with the liner material.
- In the third test, biodegradation was inhibited with bacteriological inhibitors (20 mM ammonium molybdate for sulphate-reducing bacteria and 50 mM 2-bromoethanesulphonic acid for methanogenic bacteria; Oremland and Capone, 1998) and sorption of the List I substance(s) to the liner material evaluated. The test was prepared by adding to the bottles the liner material and synthetic leachate containing the List I substance(s) and biological inhibitors.

Table A5.1 Experimental conditions for biodegradation tests under sulphate-reducing conditions

List I	Liner	Bacterial seed	Biological inhibitors^a	Bottle	Bottle
Group I (Toluene, TCE, TCB, naphthalene and Mecoprop)	London Clay	-	+	18A	18B
		+	-	19A	19B
	Oxford Clay	-	+	20A	20B
		+	-	21A	21B
	Mercia Mudstone	-	+	22A	22B
		+	-	23A	23B
	-	+	-	24A	24B
	Group II (Toluene, naphthalene and Mecoprop)	London Clay	-	+	25A
+			-	26A	26B
Oxford Clay		-	+	27A	27B
		+	-	28A	28B
Mercia Mudstone		-	+	29A	29B
		+	-	30A	30B
-		+	-	31A	31B
Group III (Naphthalene)		Oxford Clay	-	+	32A
	+		-	33A	33B
	-	+	-	34A	34B

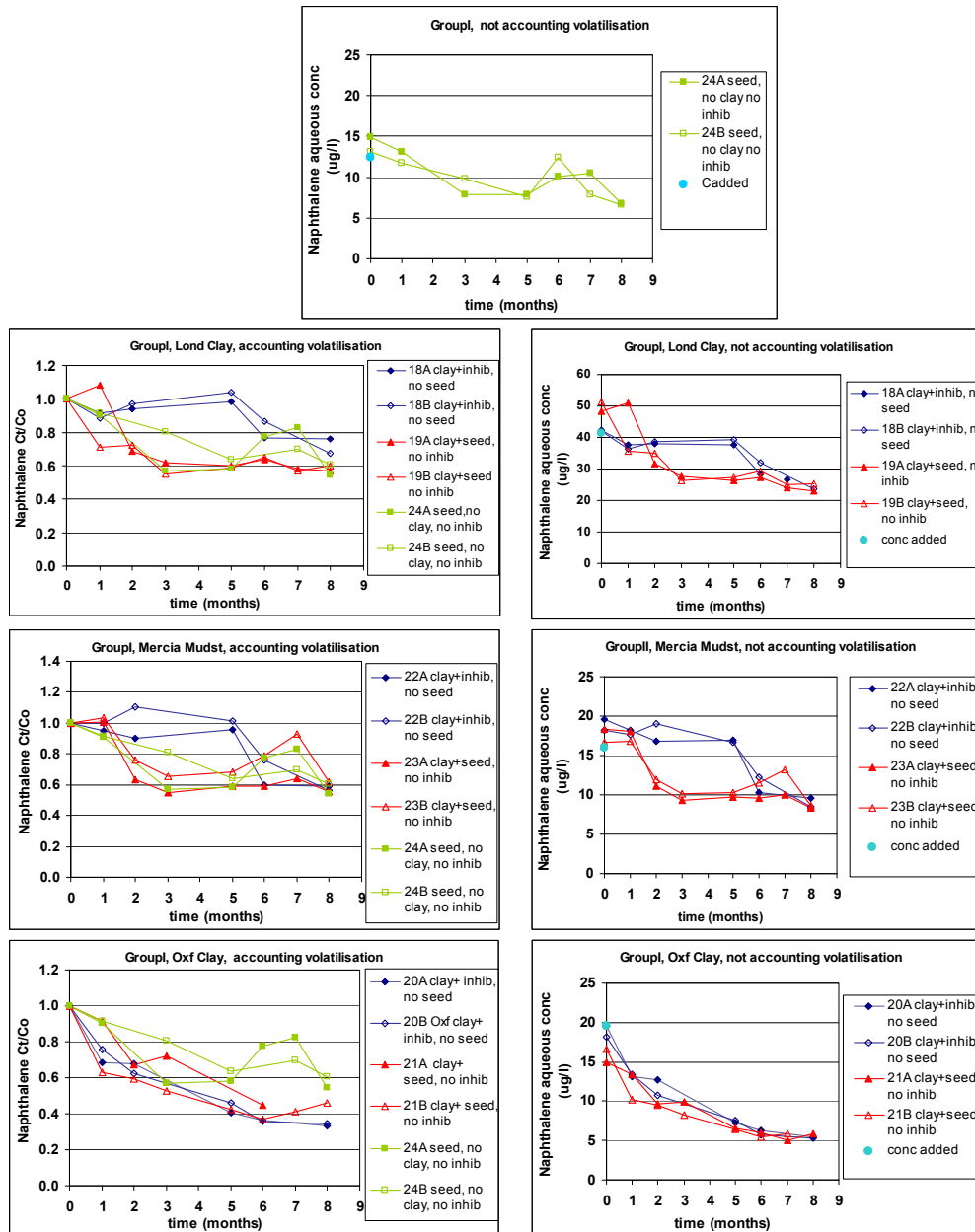
A5.2. Group I List I substances



Toluene concentration in the bottles containing mineral liner materials and biological inhibitors (18, 20 and 22) did not vary significantly with time. In the bottles containing seed and no inhibitors and liner material (24), toluene concentration was found to be constant over time suggesting that biodegradation was not occurring.

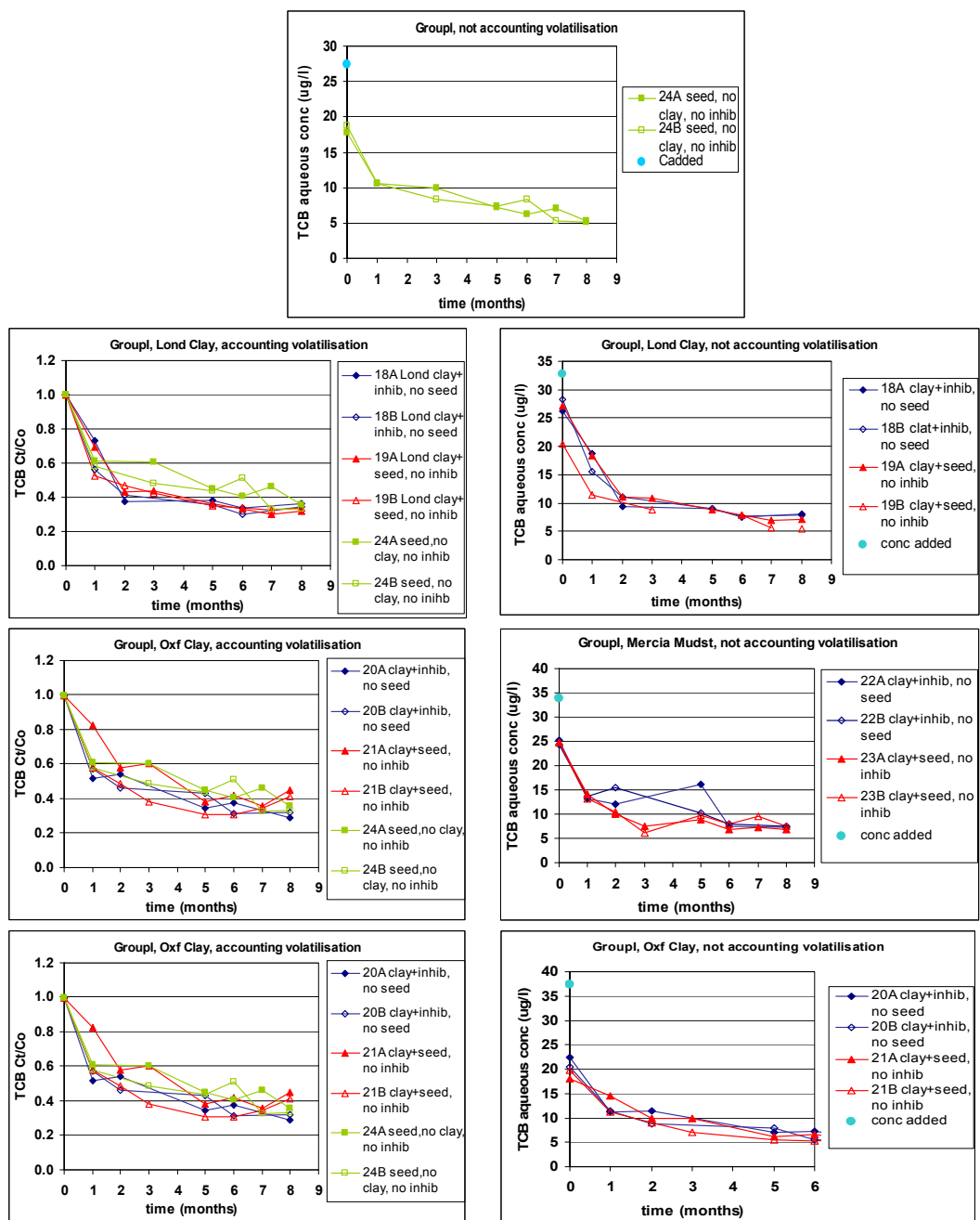
In the bottles containing mineral liner materials+seed and no inhibitors (19 and 21), toluene concentration decreased to about 10-20 per cent of its initial concentration. This suggests that sorption and/or biodegradation was occurring. If sorption was the main attenuation process, the higher sorption levels observed without inhibitors may have been due to sorption to the dark coat covering the liner material.

Figure A5.1 Variation with time of toluene aqueous concentration and Ct/Co in the biodegradation reactors



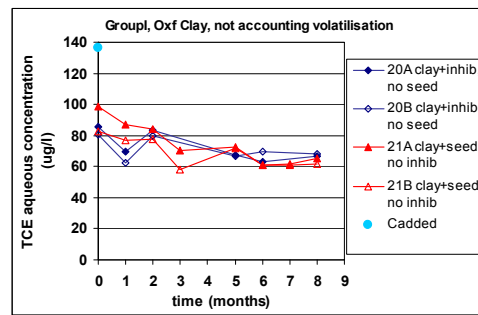
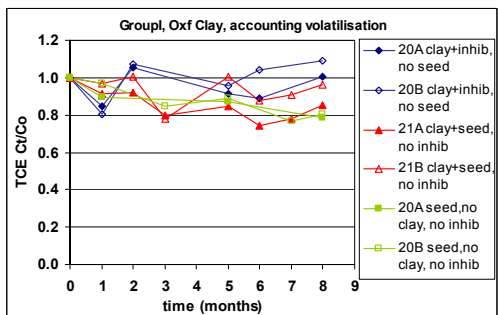
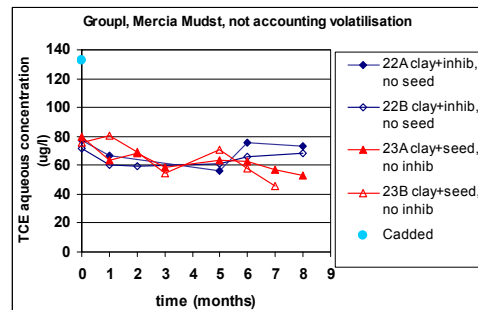
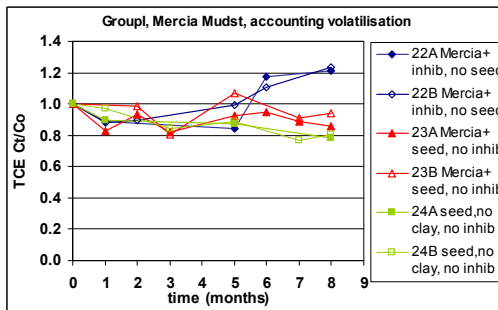
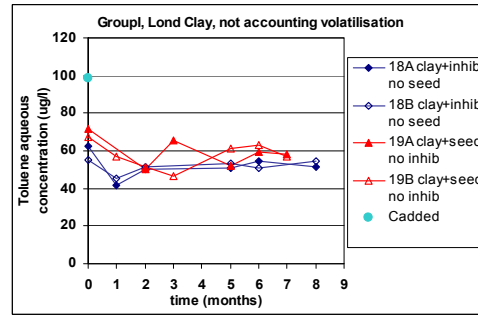
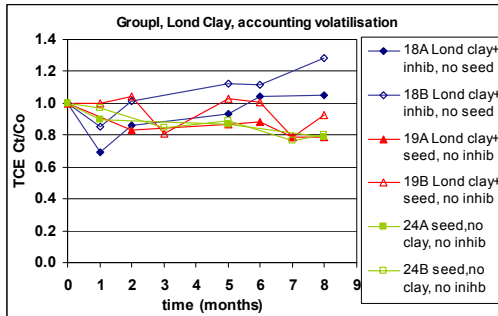
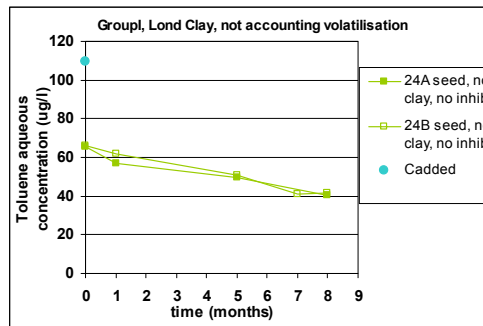
Apart from bottles containing Oxford Clay, naphthalene total concentration was found to decrease to about 60 per cent of its initial concentration. Given that this decrease was also found in bottles with biological inhibitors (18 and 22) and in bottles without liner material (24), it may be due to abiotic processes, such as long-term sorption to the bacterial seed and/or losses to the bottle components. In the bottles containing Oxford Clay (Bottles 20 and 21) naphthalene concentration was found to decrease to about 40 per cent of its initial concentration. Sorption to Oxford Clay should account for 86 per cent reduction in naphthalene aqueous concentration.

Figure A5.2 Variation with time of naphthalene aqueous concentration and Ct/Co in the biodegradation reactors



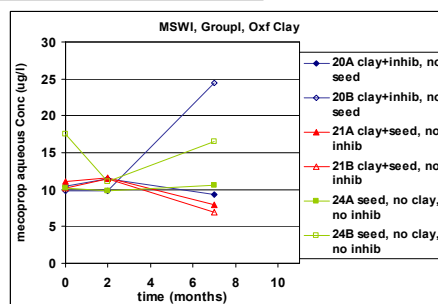
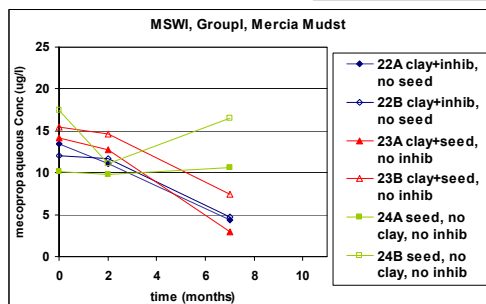
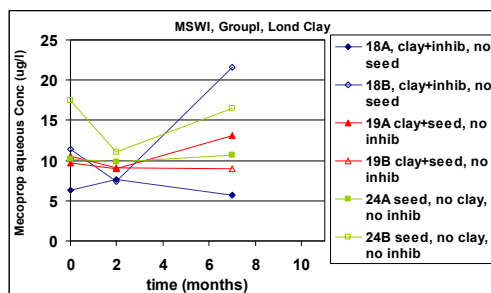
TCB concentration was found to decrease in the first two months of incubation to about 30-40 per cent of its initial concentration. Given that this reduction in concentration was also observed in the presence of biological inhibitors, it may be due to abiotic processes (sorption to liner material and bacterial seed), losses to the bottle an/or deviation from theoretical calculations of losses by volatilisation. Theoretical sorption: 14 per cent London Clay; 88 per cent Oxford Clay and no significant sorption for Mercia Mudstone. Common biodegradation products of TCB from reductive dechlorination processes (dichlorobenzenes and chlorobenzene: e.g. Middeldorp *et al.*, 1997) were not found in any of the bottles (GC-MS detection limit 0.1 ug/l).

Figure A5.3 Variation with time of TCB aqueous concentration and Ct/Co in the biodegradation reactors



TCE concentration did not vary significantly over the first eight months of incubation both with and without biological inhibitors. This suggests that attenuation of TCE was not occurring. Common biodegradation products of TCE from reductive dechlorination processes (dichloroethene and vinyl chloride: e.g. Vogel and McCarty, 1985) were not found in any of the bottles (GC-MS detection limit 0.1 ug/l).

Figure A5.4 Variation with time of TCE aqueous concentration and Ct/Co in the biodegradation reactors



Measured mecoprop aqueous concentrations at start of tests were within expected range (each bottle was initially spiked with $15 \pm 5 \mu\text{g/l}$). Mecoprop aqueous concentration in bottles containing mineral liner materials was similar with or without biological inhibitors suggesting that biodegradation did not occur. Mecoprop aqueous concentration in bottles without liner materials and biological inhibitors did not change significantly.

Figure A5.5 Mecoprop aqueous concentration in MSWI leachate containing Group I of List I substances

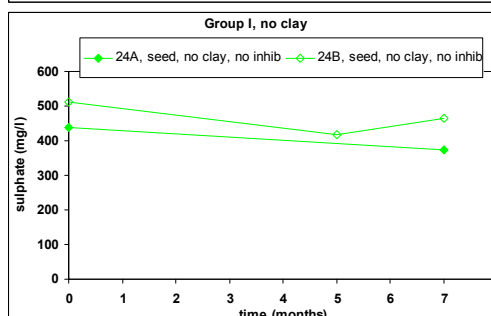
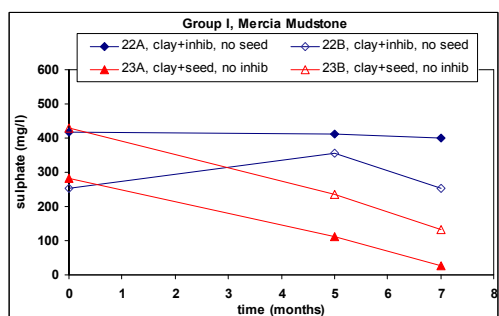
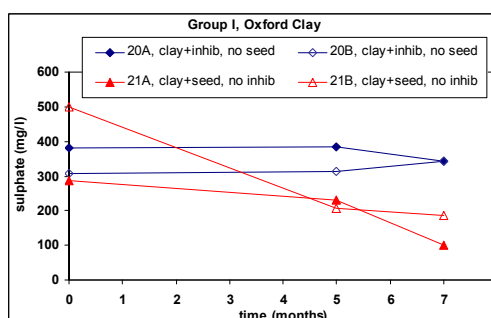
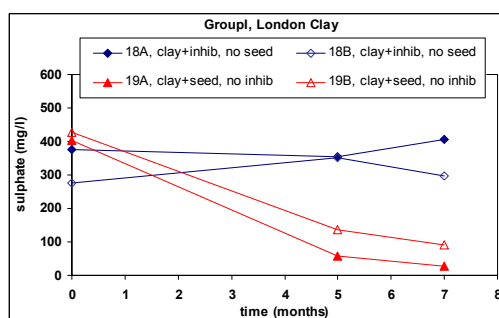
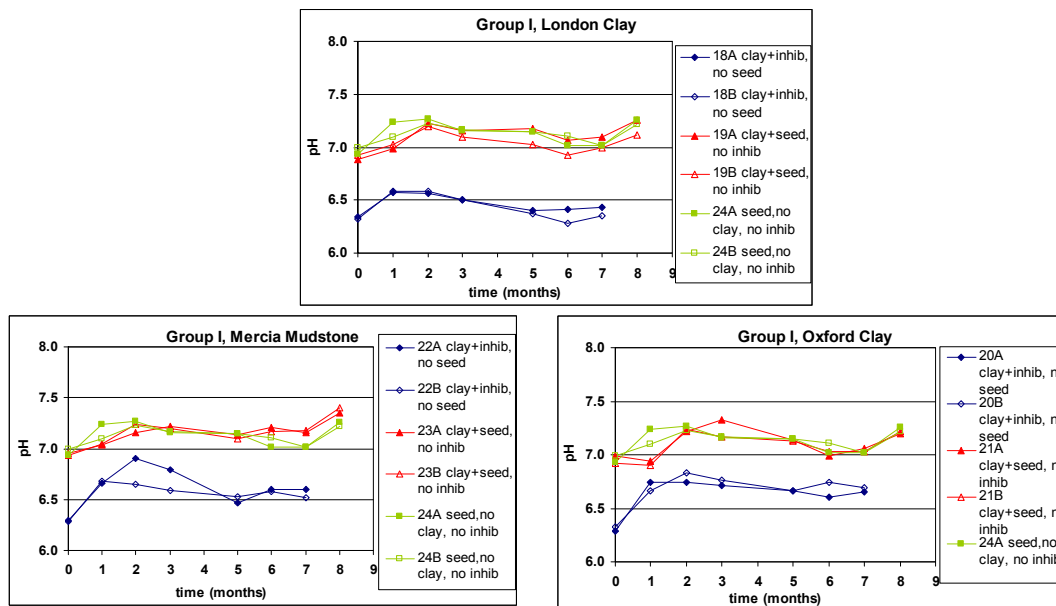


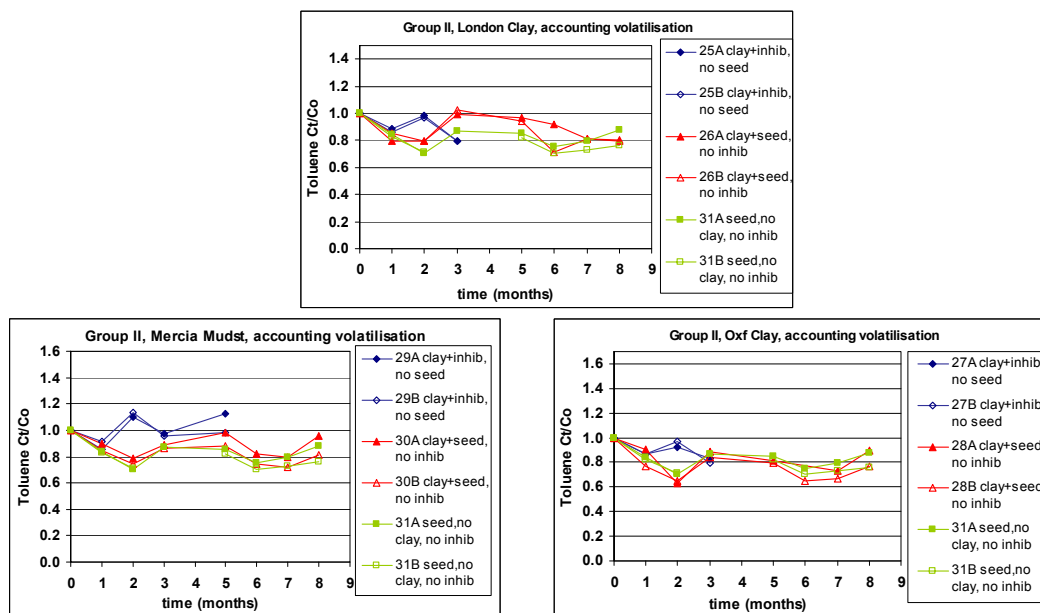
Figure A5.6 Variation with time of sulphate concentration in MSWI leachate containing Group I of List I substances



The pH of the MSWI leachate is lower in the bottles containing biological inhibitors due to the presence of bromoethane sulphonic acid (50 mM).

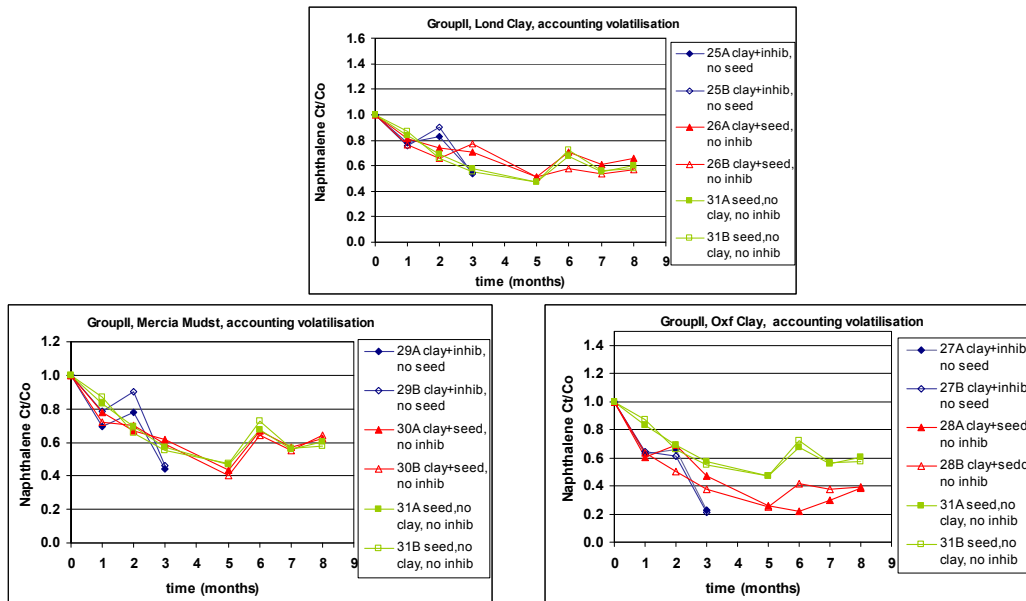
Figure A5.7 pH of MSWI leachate containing Group I of List I substances

Group II List I substances



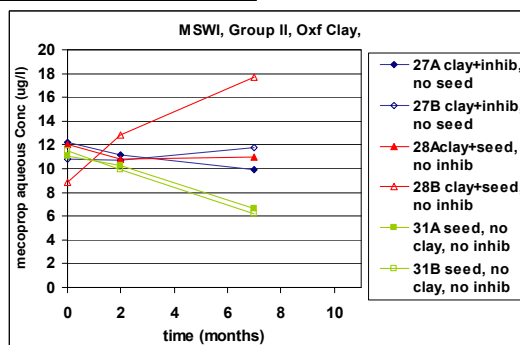
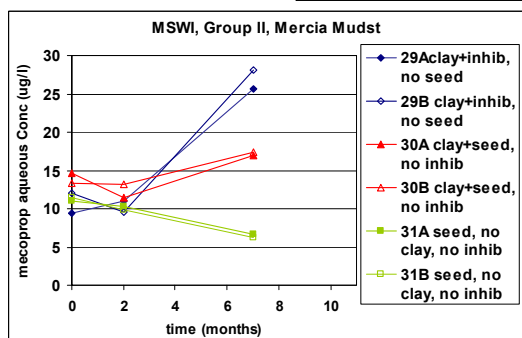
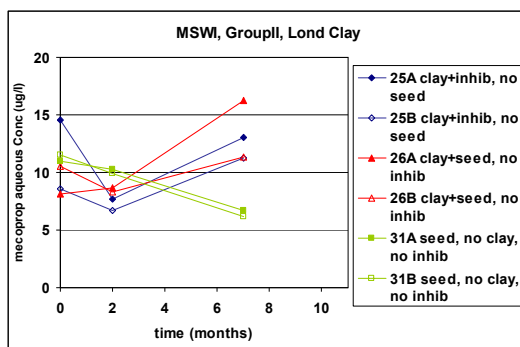
Toluene aqueous concentration decreased to about 20 per cent of its initial concentration in leachate with and without biological inhibitors. This may be due to abiotic processes (sorption to the liner materials and bacterial seed), losses to the bottle and/or deviation from theoretical calculations of losses by volatilisation.

Figure A5.8 Variation with time of toluene in MSWI leachate containing Group II List I substances



Apart from bottles containing Oxford Clay, naphthalene total concentration was found to decrease to about 60 per cent of its initial concentration. Given that this decrease was also found in bottles containing biological inhibitors (25 and 29) and in bottles without liner material (31), it may be due to abiotic processes, such as long-term sorption to bacterial seed and/or losses to bottle components. In bottles containing Oxford Clay (27 and 28), naphthalene concentration was found to decrease to about 30 per cent of its initial concentration. Sorption to Oxford Clay should account for 86 per cent reduction in naphthalene aqueous concentration.

Figure A5.9 Variation with time of naphthalene in MSWI leachate containing Group II List I substances



Measured mecoprop aqueous concentrations at start of tests were within expected range (each bottle was initially spiked with $15 \pm 5 \mu\text{g/l}$). Mecoprop aqueous concentration in bottles containing mineral liner materials was similar with or without biological inhibitors suggesting that biodegradation did not occur. Mecoprop aqueous concentration in bottles without liner materials and biological inhibitors decreased to about 50 per cent of its initial concentration, suggesting that biodegradation processes and/or losses to bottle components may have occurred.

Figure A5.10 Variation with time of Mecoprop aqueous concentration in MSWI leachate containing Group II of List I substances

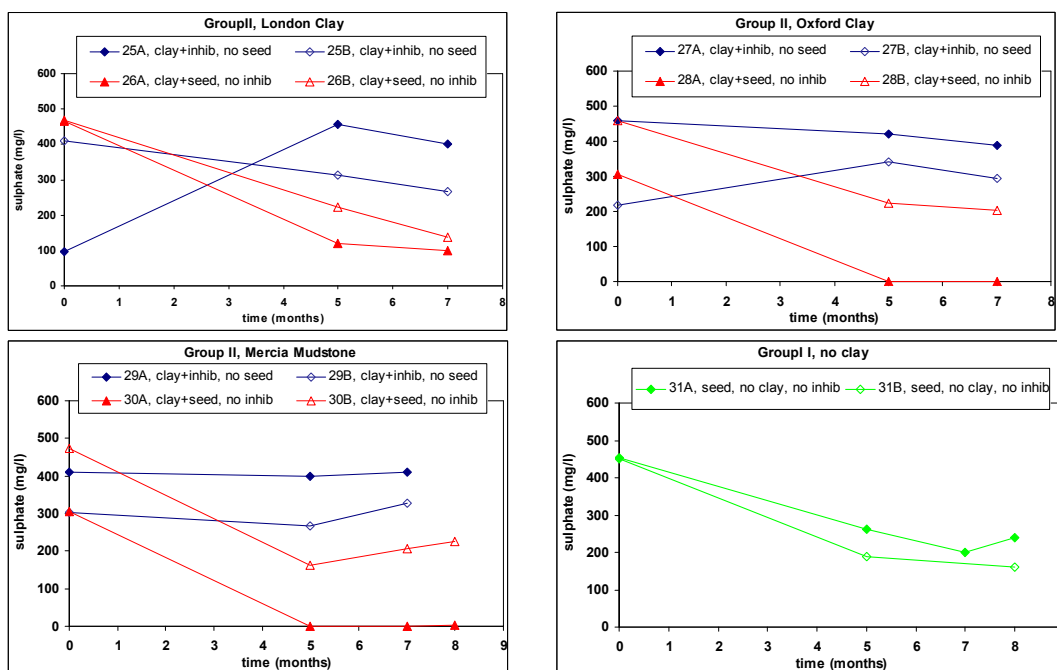
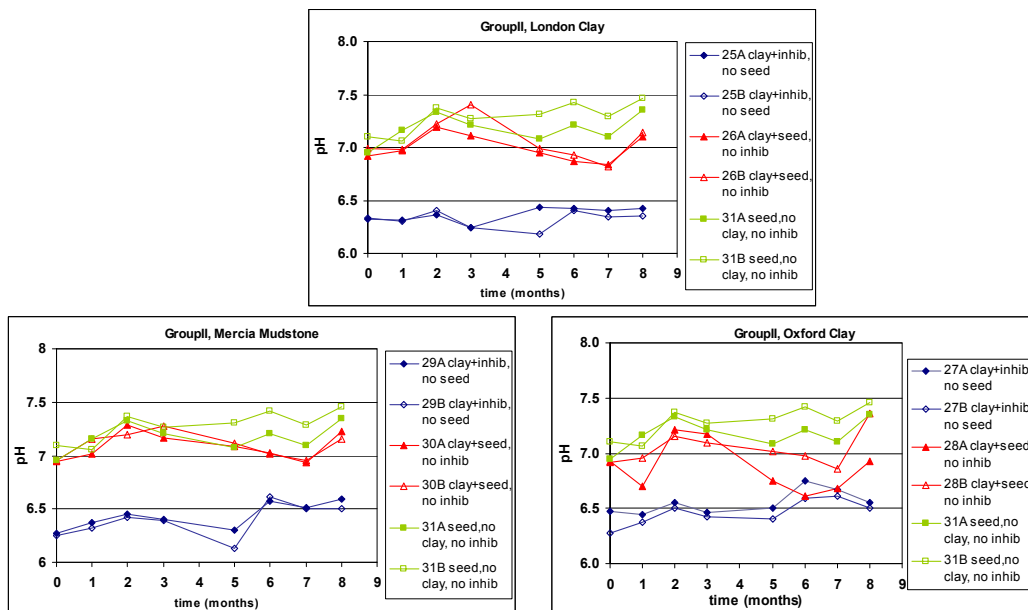


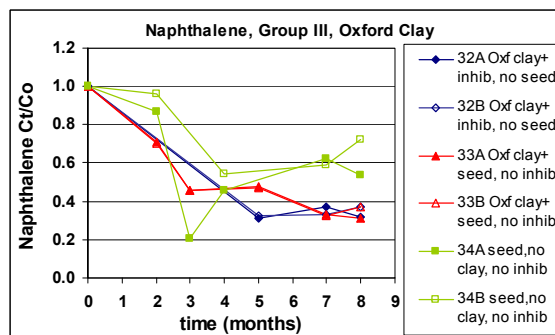
Figure A5.11 Variation with time of sulphate concentration in MSWI leachate containing Group II of List I substances



The pH of the MSWI leachate is lower in the bottles containing biological inhibitors due to the presence of bromoethane sulphonic acid (50mM).

Figure A5.12 Variation with time of pH of MSWI leachate containing Group II of List I substances

A5.3. Group III List I substance



The naphthalene concentration was observed to slowly decrease with time (from its initial average aqueous concentration of 20.2 µg/l) in all bottles but more significantly in the ones containing Oxford Clay (both with and without biological inhibitors). This could be due to biodegradation and/or abiotic processes such as sorption to the liner material, bottle and bacterial seed. The pH of the MSWI leachate was lower in the bottles containing biological inhibitors due to the presence of bromoethane sulphonic acid (50 mM).

Figure A5.13 Naphthalene concentration in Group III biodegradations tests in MSWI leachate

Appendix 6 – Biodegradation: real leachate (additional results)

A6.1. Introduction

Section 10.6 contains the main results from tests undertaken to evaluate biodegradation with real landfill leachate instead of synthetic leachate. Additional results are given here.

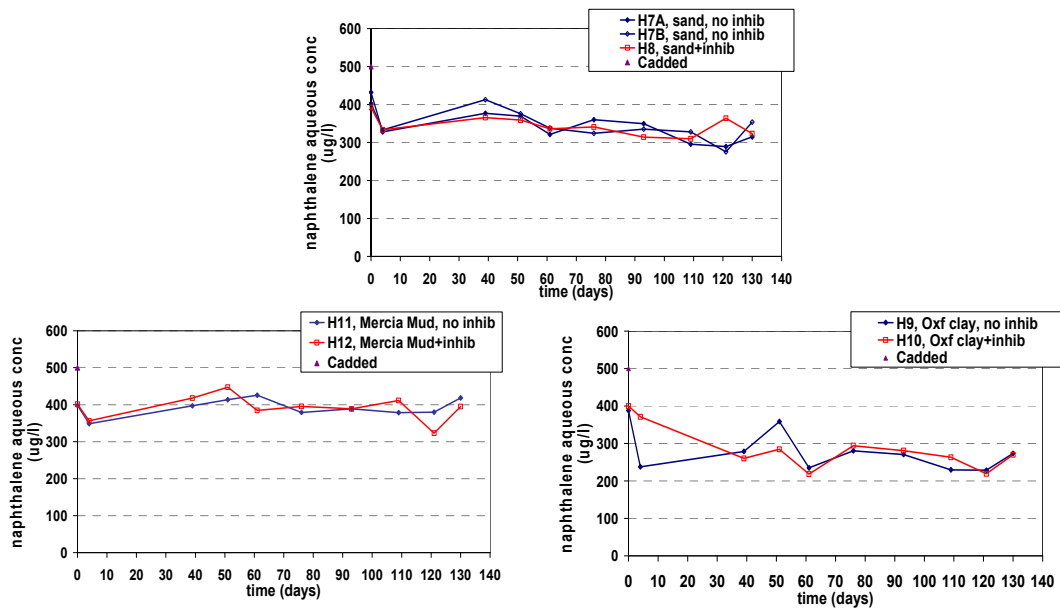
Table A6.1 Experimental conditions of biodegradation tests using real landfill leachate

List I substances	Solid phase	Leachate (l)	Biological inhibitors ^b
Mecoprop ^c	Sand (500ml=790g)	0.5	no
Mecoprop	Sand (500ml=790g)	0.5	yes
Mecoprop	Oxford Clay (2g)	1	no
Mecoprop	Oxford Clay (2g)	1	yes
Mecoprop	Mercia Mudstone (2g)	1	no
Mecoprop	Mercia Mudstone (2g)	1	yes
Group I ^{a,c}	Sand (500ml=790mg)	0.5	no
Group I ^a	Sand (500ml=790mg)	0.5	yes
Group I ^a	Oxford Clay (2g)	1	no
Group I ^a	Oxford Clay (2g)	1	yes
Group I ^a	Mercia Mudstone (2g)	1	no
Group I ^a	Mercia Mudstone (2g)	1	yes

^a Mecoprop, toluene, naphthalene, TCE, TCB.

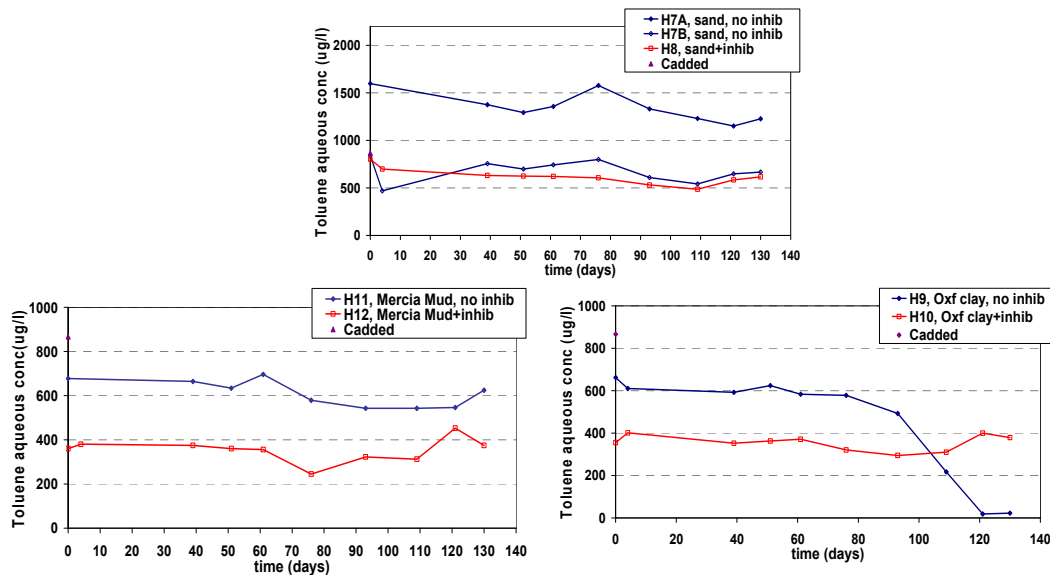
^b 20 mM Ammonium molybdate; 50 mM 2-bromoethanesulphonic acid (Oremland and Capone, 1998); and HgCl₂ 5 mg/l (used at Newcastle University) .

^c Tests carried out in duplicate.



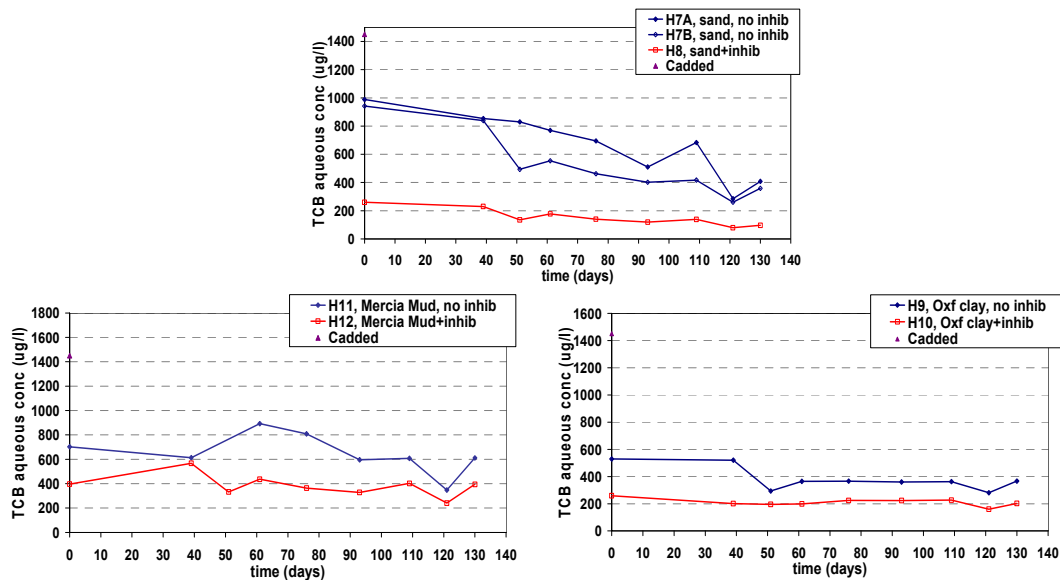
Naphthalene aqueous concentrations did not change significantly over a period of 130 days of incubation both in the presence and absence of biological inhibitors. The decrease in naphthalene aqueous concentration in the bottles containing Oxford Clay was probably due to sorption to the clay.

Figure A6.1 Variation with time of naphthalene aqueous concentration in bottles containing leachate and mineral liner materials or sand



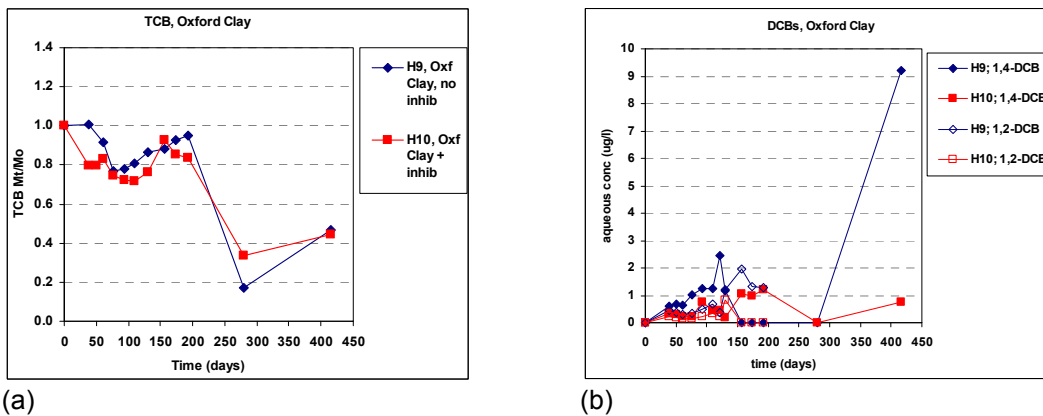
Toluene aqueous concentrations did not change significantly over a period of 130 days of incubation both in the presence and absence of biological inhibitors. The only exception is bottle H9 (containing Oxford Clay and without biological inhibitors) in which toluene concentration decreased from 600 ug/l to 20 ug/l between 80 and 109 days of incubation. Given that this variation was not observed in the presence of biological inhibitors, it suggests that biodegradation processes may be responsible for toluene depletion from aqueous solution. Common anaerobic biodegradation products of toluene include benzylosuccinate (Beller and Edwards, 2000).

Figure A6.2 Variation with time of toluene aqueous concentration in bottles containing leachate and mineral liner materials or sand

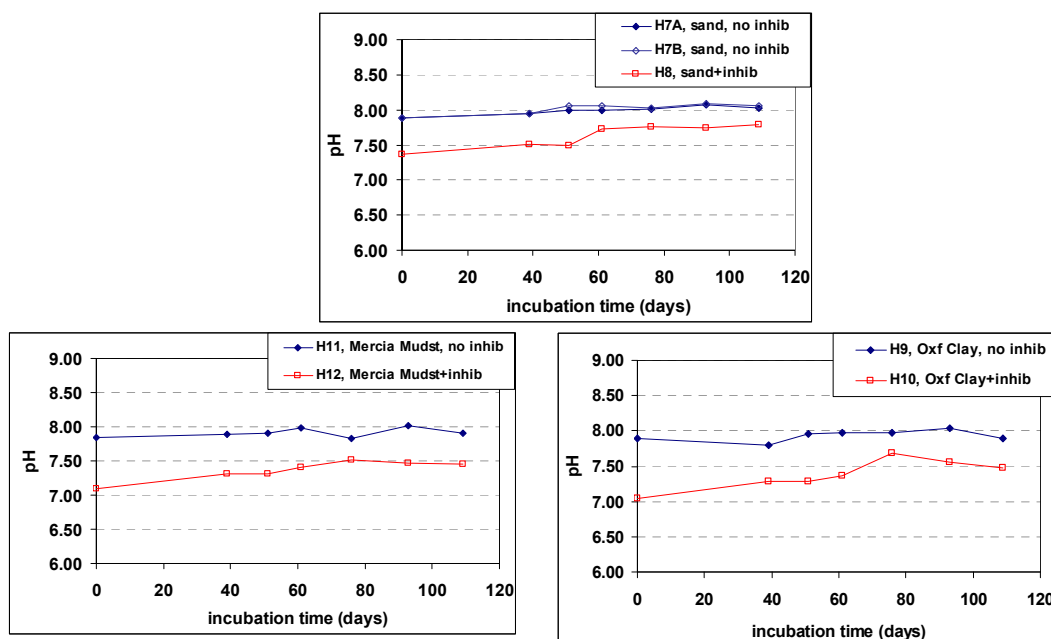


TCB aqueous concentrations did not change significantly over a period of 130 days of incubation both in the presence and absence of biological inhibitors. The only exception are bottles H7A, H7B and H8 (containing sand) in which TCB concentration was found to slowly decrease with time. This decrease was more significant for bottles without biological inhibitors (H7A and H7B; 900 to 400 ug/l) than with biological inhibitors (H8; 300 to 100 ug/l). This suggests that both biotic and abiotic processes may be contributing to TCB depletion from aqueous concentration. After 200 days, the concentration of TCB in bottles H9 and H10 containing Oxford Clay decreased significantly and biodegradation products of TCB from reductive dechlorination processes (dichlorobenzenes and chlorobenzene) were found (Figure A6.4).

Figure A6.3 Variation with time of TCB aqueous concentration in bottles containing leachate and mineral liner materials or sand



(a) (b)
Figure A6.4 Biodegradation of TCB in real landfill leachate, variation with time of (a) TCB and (b) DCB concentrations



The pH of the leachate was lower in the bottles containing biological inhibitors due to the presence of bromoethane sulphonic acid (50mM).

Figure A6.5 pH variation with time in biodegradation tests using real leachate

A6.2. Control tests in real leachate

Additional biologically inhibited tests were set up to establish whether abiotic processes were contributing to the degradation of list I substances in real leachate (Table A6.2). A new batch of leachate was collected from the same landfill site and kept under anaerobic conditions until use. The tests were prepared following the same experimental procedure used for biodegradation of the five List I substances (described in Appendix 3). Inhibition of biological processes was achieved by autoclaving the leachate three times (120°C for 15 minutes: Kroman *et al.* (1998)) and adding a range of biological inhibitors (20 mM ammonium molybdate, 50 mM 2-bromoethane sulphonic acid, HgCl₂ 5 mg/l, NaN₃ 100 mg/l). Results are presented in Section 10.6, with additional results given here.

The variation in TCE, TCB, toluene and naphthalene aqueous concentration over 40 days of incubation was not significant (Figure A6.6) suggesting that abiotic processes were not contributing to the degradation of List I substances in real leachate. This also indicates that autoclaving is required for complete inhibition of biological activity.

Table A6.2 Experimental conditions of the biologically inhibited biodegradation tests using real leachate

Bottle	List I substances	Solid phase	Leachate (l)	Biological inhibitors
CTR1	5 List I substances ^a	Sand (500ml=790g)	0.5	yes
CTR2	5 List I substances ^a	Oxford Clay (2g)	1	yes
CTR3	5 List I substances ^a	Mercia Mudstone (2g)	1	yes
CTR4	5 List I substances ^a	No clay	1	yes

a- Mecoprop, toluene, naphthalene, trichloroethylene, 1,2,4-trichlorobenzene

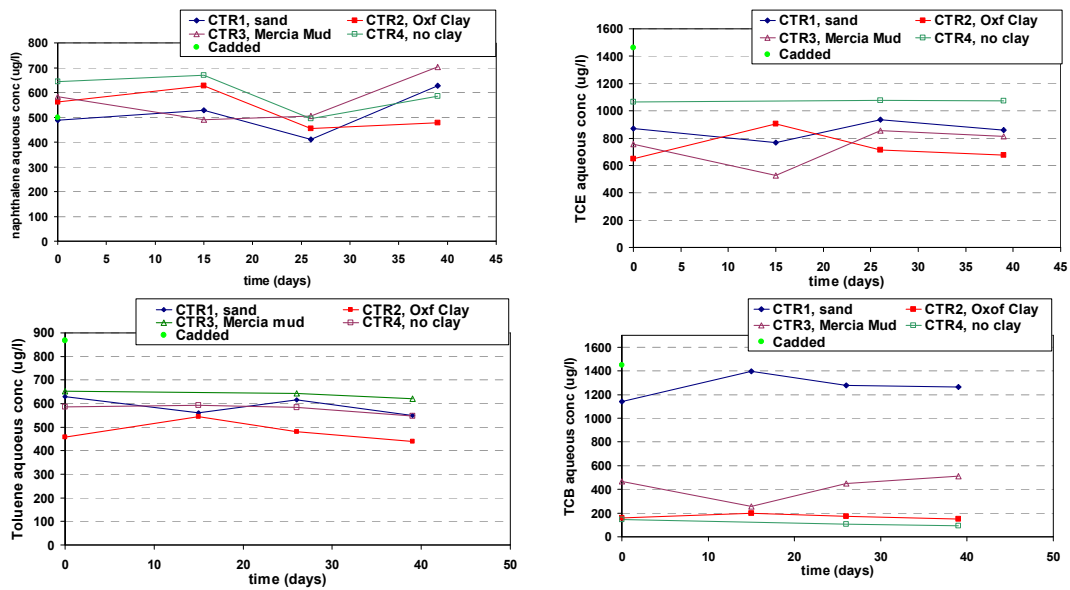


Figure A6.6 Variation with time of naphthalene, toluene, TCE and TCB aqueous concentration in biologically inhibited tests

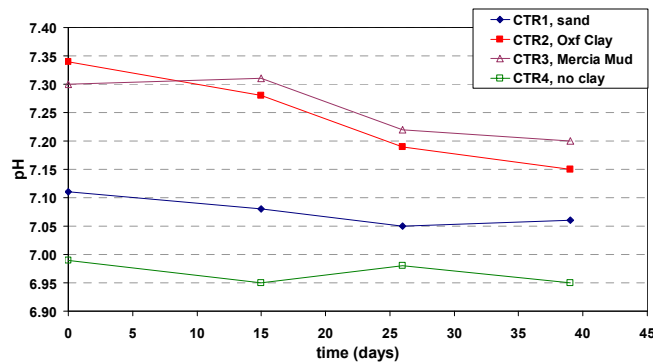


Figure A6.7 pH variation with time of biologically inhibited tests using real leachate

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