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Attenuation of organic contaminants in leachate by mineral landfill liners

Integrated Catchment Science programme
Science report: SC020039/SR5

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Steve Killeen

Steve Killeen

Head of Science

Executive summary

Modern landfills are constructed with basal liner systems designed to restrict the release of contaminants to the surrounding environment. In accordance with the requirements of the Landfill Directive, these systems generally include a synthetic liner underlain by a mineral layer and a geological barrier. These liner systems act by reducing the flow of leachate from the site, with the mineral component of the liner and the geological barrier also lowering concentrations of migrating contaminants by attenuation processes such as sorption and biodegradation. However, the attenuation of organic contaminants within landfill liner systems is still poorly understood.

This project carried out a series of laboratory experiments to investigate the attenuation of List I substances typically found in UK landfill leachates (Mecoprop, naphthalene, toluene, trichlorobenzene (TCB) and trichloroethene (TCE)) by materials commonly used for the mineral component of liners and geological barriers (London Clay, Mercia Mudstone, Oxford Clay). Sorption and desorption were measured in batch and column tests. Biodegradation was assessed under anaerobic conditions since these are expected to occur at the base and beneath landfills. The majority of experiments were carried out using synthetic leachates based on municipal solid waste (MSW) and MSW incinerator residues where the dissolved organic carbon (DOC) was replicated using tannic acid. Some additional biodegradation tests used real leachate collected from an active landfill.

This report summarises the results of the experimental programme and highlights key issues for groundwater risk assessment at landfills. The main results and conclusions of the research project are summarised below.

Sorption

- Sorption coefficients (K_d) derived from batch tests for Mecoprop on Oxford Clay and London Clay were three to six times greater than the maximum literature values for soils and 20 to 40 times greater than the literature values for aquifer materials; sorption coefficients obtained for Mercia Mudstone were three times greater than values reported in the maximum literature values for aquifer materials, but within the range of values for soils.
- Mecoprop sorption coefficients (K_d) estimated from column leaching tests were about three times lower than comparative batch test values. Average K_d value determined from column tests for Mercia Mudstone was within the range of literature values for soils and 30% greater than maximum literature aquifer values; the K_d value for Oxford Clay was 30% greater than maximum literature values for soils and nine times greater than maximum literature aquifer values.
- Sorption of the volatile List I substances was found to increase with increasing hydrophobicity (TCE < toluene < naphthalene < TCB).
- Sorption of the volatile List I substances was found to increase with increasing f_{oc} of the mineral liners (Mercia Mudstone < London Clay < Oxford Clay).
- The experimental sorption coefficients normalised to the amount of organic carbon in the liners (K_{oc}) for toluene, naphthalene and TCB on London Clay fall within the range of literature values and empirical correlations based on the octanol-water distribution coefficient (K_{ow}) of the contaminants. However, experimental K_{oc} values for Oxford Clay were much higher (up to more than an order of magnitude) than literature and calculated values, whilst values for Mercia Mudstone were lower. Mechanisms to explain these variations based on the type of organic carbon in the mineral liners are suggested.

- These results confirm that relying on literature values or empirical correlations to estimate K_{oc} (and hence retardation) for predictive modelling may not give an accurate assessment of the risk of pollution. This project has shown that retardation may be over- or underestimated.
- Tests were undertaken to assess the importance of replicating the presence of DOC in leachate using tannic acid in batch sorption tests. The presence of tannic acid in leachate decreased the sorption of TCB and naphthalene by Oxford Clay. The effect on Mecoprop was less pronounced.

Desorption

- Sorption of Mecoprop, naphthalene and TCE was reversible on all mineral liner materials.
- A small fraction of the toluene and TCB sorbed by London Clay and Oxford Clay was irreversibly bound to the liner material.

Biodegradation

- No evidence of biodegradation of Mecoprop was found in any of the tests. This is in agreement with the literature which reports little or no biodegradation of this compound under anaerobic conditions.
- In initial tests using synthetic leachate and a bacterial seed cultured from leachate obtained from a UK landfill known to contain a range of List I substances, no biodegradation of hydrophobic organic compounds (HOCs) (naphthalene, toluene, TCB or TCE) was found over a period of eight months, although there was an active bacterial population producing biogas.
- However, in tests involving real leachate containing a bacterial population obtained from a landfill known to biodegrade tetrachloroethene (PCE), biodegradation of TCE, toluene and TCB was observed. Furthermore, when this same seed was added to the synthetic leachate tests, biodegradation of TCE was observed, albeit at a slower rate. Biodegradation of Mecoprop, naphthalene, toluene and TCB was not observed.
- The results suggest that biodegradation of certain List I substances is possible under anaerobic conditions such as might be found in a landfill liner environment. However, the characteristics and activity of the bacterial community in the specific leachate are critically important in determining which contaminants are degraded. Therefore, whilst no degradation of Mecoprop was observed in this study, it is possible that specific conditions could exist in anaerobic landfill liner systems that would allow Mecoprop to degrade.

LandSim modelling

A series of LandSim models was run to compare the effect of using retardation values selected from the literature with the experimentally derived K_d values for the different mineral liner materials. Significant differences in the predicted time of arrival and peak concentrations of List I contaminants at various compliance points were demonstrated, indicating the importance of using site-specific sorption data wherever possible. In particular, it is suggested that more account should be taken of the influence of the organic material in mineral liners on sorption coefficients.

Recommendations for future research

- The research demonstrated that sorption is controlled not just by the quantity of organic carbon (OC) but also by its composition (for example, a combination of organic matter (OM) source, age, and diagenetic alteration history). Further research is required into the fundamental mechanisms by which the composition of solid phase OM can affect sorption/desorption of HOCs.
- Further work is required to understand the sorption mechanism of Mecoprop to mineral liners and explain why the sorption of Mecoprop by the three mineral liner materials is greater than literature values for soils and sediments.
- Further research is required to characterise the nature of DOC in leachates and its role in sorption and transport of polar and non-polar organic contaminants.
- Further work is required to compare the results of batch and column sorption tests, to improve the method of estimating K_d values for landfill operators.
- Results from the biodegradation tests suggest that biodegradation of organic contaminants in leachate can take place as long as the appropriate microbial community is present. Further work should be carried out to characterise the microbial communities found in leachates and understand the conditions required for removal of contaminants, including Mecoprop.
- While biodegradation rates are commonly available for aerobic environments, and for soils and sediments under anaerobic conditions, there is still a lack of data for landfill environments, in particular for mineral liners and geological barriers, and further work is needed to determine biodegradation rates for a range of contaminants found in leachates.

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1 Introduction

1.1 Background

Contaminated land and groundwater are now a major concern in many industrialised countries. Britain has a long history of industrial activity including landfilling of wastes that has left a legacy of contamination within the soil and groundwater environments. In England and Wales, about one-third of drinking water is derived directly from groundwater (Environment Agency, 2006a). Given the importance of groundwater as a source of drinking water and the cost and difficulty of cleaning up polluted water, the best way to guarantee continued supplies of clean water is to prevent pollution.

Regulation of landfills is driven by the EU Landfill (1991/31/EC) and Groundwater Directives (80/68/EEC) which have been implemented in the UK through various regimes including Environmental Permitting, Landfill, Pollution Prevention and Control, Waste Management and Groundwater Regulations. The new Groundwater Daughter Directive (2006/118/EC) will replace the 1980 Groundwater Directive by 2013 (see Environment Agency, 2008 for more information). The overarching requirements of both Groundwater Directives are to prevent hazardous (equivalent to List I) substances from entering groundwater, and limit the entry of non-hazardous (broadly equivalent to List II) pollutants to avoid groundwater pollution.

Over the last thirty years, as a result of the threat of groundwater pollution, regulators have increasingly required installation of low permeability landfill liners to contain leachate. The Landfill Directive requires an artificial sealing liner, combined with a leachate drainage and extraction system, to ensure that leachate accumulation at the base of the landfill is kept to a minimum. In addition, there must be a natural and/or artificial low permeability geological barrier beneath the landfill to provide sufficient attenuation capacity to prevent a potential risk to soil and groundwater. The function of the mineral component of a landfill liner is to lower the flow rate of leachate out of the landfill, and reduce the concentration of organic and other contaminants in the leachate as a result of natural attenuation processes such as sorption and biodegradation during flow through the liner (Christensen *et al*., 2001). Since leachates from hazardous and non-hazardous waste landfills will invariably contain List I (hazardous) substances, attenuation in the liner and unsaturated zone must be relied upon to lower contaminant concentrations and avoid pollution of groundwater.

The UK applies a risk-based approach to the design, construction and operation of landfill sites which is detailed in Environment Agency (2003) and elsewhere. To protect groundwater, this approach requires a thorough understanding of the polluting potential of leachate, and the attenuating capacity of geological barriers. However, there is considerable uncertainty over the fate and persistence of pollutants below landfill sites, and particularly the effectiveness of attenuation mechanisms in low permeability mineral liners to sufficiently protect groundwater in the medium to long term by lowering contaminant concentrations.

Investigations beneath landfills containing biodegradable wastes have shown that anaerobic conditions rapidly develop due to the migration of landfill gas ahead of the leachate plume (Brun *et al.*, 2002). These investigations include the work at Stangate East landfill on behalf of the Environment Department and the Environment Agency (Robinson and Lucas, 1985). Therefore, risk assessment models should use values for attenuation processes in low permeability mineral liners and the unsaturated zone that are appropriate for anaerobic conditions; values derived from soils or other materials under aerobic conditions may not be suitable.

1.2 Overview of natural attenuation processes

The Environment Agency has adopted the following definition of natural attenuation in groundwater (Environment Agency, 2000a):

> *"The effect of naturally occurring physical, chemical and biological processes, or any combination of those processes to reduce the load, concentration, flux or toxicity of polluting substances in groundwater"*

Natural attenuation processes include destructive mechanisms such as biodegradation, abiotic oxidation and hydrolysis, and non-destructive mechanisms such as sorption, dispersion and volatilisation.

The main attenuation mechanisms investigated in this project are sorption/desorption processes and anaerobic biodegradation.

1.2.1 Sorption/desorption

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.

In this report the term sorption refers to adsorption or absorption of the solute (namely the contaminant dissolved in the leachate) to the solid (the mineral liner materials). Desorption refers to the process of contaminants detaching from the solid surface and re-entering solution. Sorption and desorption are frequently described in terms of the partition coefficient, K_d (detailed further in Section 3).

At any given 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. The time taken to reach sorption equilibrium depends on the reaction rate kinetics, and may take hours, days or years depending on the sorbent/sorbate system.

Sorption retards the transport of contaminants through the sub-surface (Chiou *et al.*, 1983; Karickhoff, 1984; Pignatello, 1998; Delle Site, 2001). Sorbed contaminants are potentially unavailable for biodegradation due to their inability to pass through the cell membrane of biodegradative micro-organisms (the molecule must first be in the aqueous phase) and/or the contaminant is effectively masked from attack by microbial exo- and ectoenzymes (Meyer-Reil, 1981 and 1987).

The extent of sorption depends on the properties of the sorbent and the contaminant, including the size, shape, molecular structure, functional groups, solubility, polarity, charge distribution and acid-base characteristics (Bailey and White, 1970; Pignatello and Xing, 1996).

Hydrophobic organic compounds (HOCs, for example aromatic and aliphatic hydrocarbons) repel water and accumulate at the soil-water interface or sorb to organic matter by partitioning. For HOCs, including many of the List I organic substances found in leachates, sorption is controlled by the fraction of organic carbon in the matrix when f_{oc} is greater than 0.001 (0.1 per cent organic carbon; Schwarzenbach and Westall, 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:

$$K_{oc} = \frac{K_d}{f_{oc}} \qquad (1.1)$$

Where:
K_{oc} = the partition coefficient for organic carbon
K_d = the partition coefficient
f_{oc} = the fraction of organic carbon in the matrix

Using K_{oc} decreases the range of reported K_d values since K_{oc} takes account of the variation of organic carbon content found in different sub-surface materials.

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.

Ionic polar compounds (which include many pesticides and herbicides) may bind to soil mineral such as clays and iron oxyhydroxides by cation exchange, metal ion bridges, and hydrogen bonding. These contaminants may also bind to natural organic material since this contains reactive functional groups (such as carboxylic acids) although this cannot be predicted in the same way (K_{oc}) as the sorption of HOCs.

The capacity for an organic contaminant to sorb to organic material also relates to the nature of that organic material. 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. The greatest fraction of organic material in soils and sediments are humic substances, subdivided into three operationally defined fractions: humic acid, fulvic acid and humin. Humin includes 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. The presence of kerogen and black carbon in soils and sediments can significantly increase their sorption potential (Grathwohl, 1990; Allen-King *et al.*, 2002; Huang *et al.,* 2003). Research has shown that the diversity in composition and structure of natural organic matter can significantly affect the sorption of HOCs (Kleneidam *et al.*, 1999). This can lead to much greater sorption than that predicted by simple empirical models based on K_{oc} (Ghosh, 2000; Accardi-Dey and Gschwend, 2002).

Desorption is the release of a sorbed compound from the solid phase to the aqueous phase. Desorption does not necessarily release 100 per cent of the sorbed contaminant which can result in hysteresis (where the partition coefficient for sorption and desorption are different at a constant aqueous phase concentration) or irreversible sorption (Huang *et al.*, 1998).

1.2.2 Biodegradation

Organic contaminants can be transformed into intermediate products or completely mineralised to carbon dioxide or methane by the action of bacteria naturally present in the geological matrix. Intermediate products may be more or less persistent, and more or less hazardous, than the parent compound.

Microbes use organic substances as a source of carbon and a source of reducing power for energy (electron donors), while using a respiratory substrate (the terminal electron acceptor). In aerobic metabolism, oxygen is the respiratory substrate. Aerobic processes occur when there is a significant concentration of dissolved oxygen in and below landfills, biodegradation of organic material rapidly consumes the available oxygen leading to anaerobic conditions and primarily the production of methane (the major component of landfill gas). Anaerobic biodegradation can involve the direct use of organic contaminants as sources of carbon and energy; this will be accompanied by reduction of nitrate, iron (ferric) oxides, sulphate and/or methanogenesis. Some organic compounds are not directly biodegraded but may be degraded as a result of other microbial action (co-metabolism). Further examples of biodegradation processes applicable to the contaminants examined in this study are given in Chapter 6.

The rate at which organic contaminants biodegrade can be calculated from laboratory or field experiments, and the values used in risk assessment modelling.

1.3 Scope and purpose of project

The attenuation of List I contaminants within geological barriers (including the mineral component of landfill liners) is still poorly understood. This project was commissioned by the Environment Agency to investigate the interaction of landfill leachate (existing and post Landfill Directive leachates) with low permeability mineral liners. The key objectives were to:

- develop a better understanding of the attenuation of specific List I organic contaminants as they migrate through geological barriers including mineral liners;
- quantify sorption parameters (K_d, K_{OC}) for these contaminants by common UK mineral liners;
- establish biodegradation rates for these contaminants in landfill leachate under anaerobic conditions.

The List I organic contaminants investigated were Mecoprop, naphthalene, toluene, trichlorobenzene (TCB) and trichloroethene (TCE). Previous work by the Environment Agency specifically recommended further research into the sorption of Mecoprop by landfill liners and its biodegradation under anaerobic conditions (Environment Agency, 2004). Three clay materials commonly used to construct landfill liners were investigated: London Clay, Mercia Mudstone and Oxford Clay.

This research has provided new data for the performance assessment of the attenuating capabilities of landfill liners. This information will help industry to carry out groundwater risk assessments for landfills using appropriate data (for example with LandSim; Section 7). Site-specific values will always be preferred, but the data reported here will be useful when such site-specific values are not available. These data will also provide the Environment Agency with confidence that risk assessment models are using appropriate data.

This report summarises the results of the experimental programme and highlights key issues for groundwater risk assessment at landfills. Full details of the experiments carried out, the literature review underpinning the project, and the full results are contained in the accompanying project record (SC020039-5/PR) which is available on the Environment Agency's publications catalogue: http://publications.environment-agency.gov.uk

2 Experimental programme

2.1 Overview

Prior to the start of the laboratory work, a comprehensive review was undertaken to identify liner materials, leachate matrices and List I contaminants to test. This is discussed in Sections 2.2 to 2.4.

A variety of laboratory tests were carried out, including batch sorption tests, batch desorption tests, column sorption tests and degradation experiments. Details of each of these tests are given in Chapters 3 to 6. An overview of which tests were undertaken on which combination of liner material, contaminant and leachate matrix is given in Section 2.5.

2.2 Selection and characterisation of liner materials

Any material used for the construction of geological barriers at landfills, including mineral liners, will need to be engineered to meet certain performance criteria, which typically includes a maximum hydraulic conductivity of 1×10^{-9} m/s. Most UK clays and many mudrocks can be engineered to meet these requirements, and consequently a wide range of geological units are currently in use as artificial geological barriers (mineral liners).

In terms of the ability of a liner to attenuate contaminants, the following characteristics will have an impact:

- percentage and type of organic material;
- percentage and type of clay minerals;
- percentage of iron oxyhydroxides.

The amount of organic material in a liner has a large effect on sorption of HOCs whilst the percentage of the clay mineral smectite provides an approximate indication of the plasticity of a material, and therefore its suitability for use in constructing landfill liners. These two parameters have been plotted in Figure 2.1a 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. A trilinear diagram showing the ratio of the three dominant clay groups (smectite, illite and kaolinite) in UK clays and mudrocks is given in Figure 2.1b.

The experimental programme only allowed three different clay materials to be tested. The information in Figure 2.1 was used to aid the choice of clays, and the following were selected to provide a wide variation in mineralogy and organic carbon content:

- Oxford Clay was selected as a high organic carbon, low smectite clay, and was obtained from the Peterborough Member at a site in Buckinghamshire.
- London Clay was chosen as a moderate organic carbon clay with similar proportions of illite and smectite and was obtained at a site in south Essex.

- Mercia Mudstone was selected as a low organic carbon material with a high proportion of illite (in relation to other clay minerals), and obtained at a site near Kidderminster. It was anticipated that its low organic content would mean that it would be the least effective in terms of attenuation, although the presence of free iron oxides could provide some absorption capability.

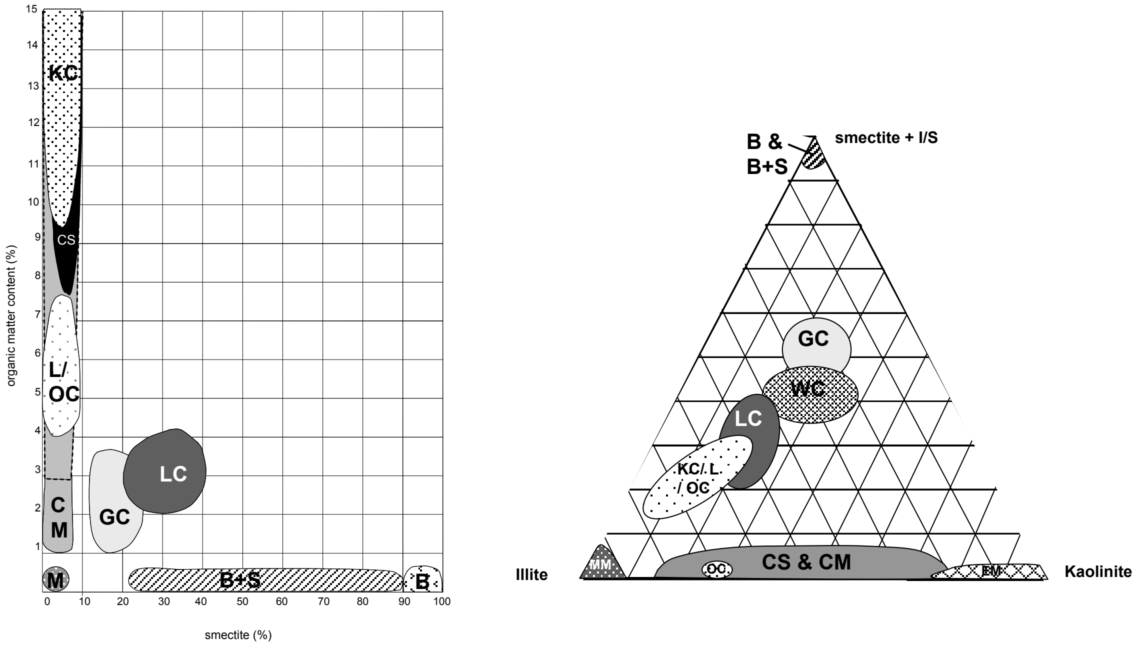


Figure 2.1 (a) Organic matter and smectite in mudrocks used in landfill liners, (b) representation of clay mineralogy of mudrocks used in landfill mineral liners. LC= London Clay, GC= Gault Clay, M= Mercia Mudstone, B= Bentonite, B+S= Bentonite and Sand, CM= Coal Measures, L= Lias, OC= Oxford Clay, CS= Colliery Spoil, KC= Kimmeridge Clay, WC= Weald Clay, EM= Etruria Marl.

Characteristics of the clays used are detailed in Table 2.1. The organic carbon (OC) content of the Oxford Clay samples was in agreement with the f_{OC} usually found for the Peterborough Member (0.03 - 0.16). The f_{OC} of the London Clay samples (0.006) was less than expected from the literature (0.02 - 0.04); Mercia Mudstone was as expected.

Because of the importance of organic matter in the sorption of hydrophobic organic compounds (HOCs), and particularly the kerogen fraction, the OC content of the Oxford Clay was characterised according to commonly used classifications in organic petrography for kerogen using the method described by Hillier and Marshall (1988). London Clay and Mercia Mudstone were not examined by petrology because of the low organic carbon content of these clays. The kerogen components present in the isolated organic matter from the Oxford Clay were found to be dominated by liptinite (92 per cent) consisting of amorphous organic matter, spores, pollen and algae. Vitrinite, semi-fusinite and inertinite were minor components of the organic material (eight per cent). These results are in accordance with previous petrographic studies of the Oxford Clay Formation. The presence of kerogen in Oxford Clay may result in much greater sorption than that predicted by simple empirical models based on $K_{oc.}$

Table 2.1 Primary characteristics of clays used in testing

Parameter		Oxford Clay	London Clay	Mercia Mudstone
Water content (%) [6-8]		33.0	28.7	6.7
f_{OC}[a] [8-13]		0.055	0.006	0.003
CEC (meq/100g)[b] [3]		31	27	22
Clay minerals (%)	Smectite[c]	32	31	18
	Illite	15	29	36
	Kaolinite	9	11	0
Major non-clay minerals (%)	Dolomite	0	0	17
	Calcite	9	9	1
Specific surface area (m^2/g) [2][d] [3][e]		56[1] 50[2]	54 [2]	32[1] 45[2]
Total Fe_2O_3 [f] (%)		4.5	8.33	6.3
Extractable Fe[g] (%) [3]		1.4	2.4	2.8

[ ] number of samples analysed

[a] Rosemount Analytical Dohrmann DC-190 Carbon Analyser - calculated from difference between total carbon and inorganic carbon; [b] cation exchange capacity (Environment Agency, 2000b); [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 method (Chihacek and Bremner, 1979); [f]Philips Magix-Pro wavelength XRF spectrometer, [g]Dithionite-citrate method (Mehra and Jackson, 1960).

2.3 Selection and preparation of synthetic leachates

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 containing domestic and similar pre-Landfill Directive wastes).
- MSWI leachate resulting from landfilling of bottom ash from incineration of MSW (representing post-Landfill Directive leachate from a landfill with primarily sulphate-reducing conditions).

The characteristics of leachates from these landfill types are well known and the synthetic leachates were created to mimic the major ion content, organic carbon content, ammoniacal nitrogen and pH values of these leachates (Table 2.2). Both leachates were used in the biodegradation tests, but only the MSW leachate was used in the batch sorption and desorption tests.

The organic carbon content of the leachates is particularly important as it is known that hydrophobic organic pollutants sorb to dissolved organic carbon (DOC) and it was deemed necessary to use a stable source of DOC in the synthetic leachates. Tannic acid was considered to be a reasonable surrogate for the type of fulvic (rather than humic) acids found in methanogenic MSW leachates; it has 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). Tannic acid has not previously been used to represent DOC in synthetic bottom ash leachates, but since such leachates have not been well characterised, it was considered a valid DOC surrogate. During the early stages of 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.

There are known differences between commercially available humic and fulvic acids and naturally occurring DOC (Malcolm and McCarthy, 1986). Thus, it is possible that the tannic acid used 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 and the sorption of tannic acid to the clays was also measured (Section 3.3.4).

Table 2.2 Composition of synthetic leachates used in the study

	MSW leachate (mg/l)	MSWI leachate (mg/l)
Reagents added:		
Tannic acid ($C_{76}H_{52}O_{46}$)	1,000	500
Ammonium chloride, NH_4Cl	2,000	150
Sodium chloride, NaCl	2,000	4,000
Sodium bicarbonate, $NaHCO_3$	4,000	2,000
Calcium sulphate, $CaSO_4$		-
Sodium hydroxide, NaOH		297
Calcium chloride, $CaCl_2$		816
Sulphuric acid, H_2SO_4		721
Resulting calculated concentrations:		
TOC	540	270
Cl^-	2,541	3,049
Na+	1,882	2,322
NH_4-N	523	39
Ca^{2+}	2,381	294
SO_4^{2-}		706
pH	7.6	6.80

2.4 Selection of List I organic compounds for study

The compounds chosen for laboratory investigation in this project were selected as key representatives of major contaminant groups likely to be found in UK landfill leachates. Five substances were listed as a priority for this study. Toluene, naphthalene and Mecoprop are the three most widely detected List I substances in UK leachates and were obvious choices for inclusion (Environment Agency, 2001). Trichloroethene, although not found in the UK Pollution Inventory study (Environment Agency, 2001) has been widely reported in Europe and the USA, and is an example of an aliphatic halogenated volatile organic compound (VOC) that has been extensively investigated in the natural environment. Inclusion of 1,2,4-trichlorobenzene is mainly to provide continuity with research already in progress on this compound. It is occasionally found in UK leachates. Concentrations of the substances used in the experimental work are shown in Table 2.3. They were derived using three criteria:

- The concentration should not be less than the median found in UK leachates, so that the findings are relevant 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 that the experimental results will not produce behaviour that would not occur at lower concentrations.

These criteria may conflict with one other. In practice, the experimental concentrations used for toluene, naphthalene and Mecoprop (Table 2.3) are reasonably consistent. For the remaining two, trichloroethene (TCE) and 1,2,4-trichlorobenzene (TCB), values are dictated by the analytical detection limits although they may be unrealistically high for most UK landfill leachates.

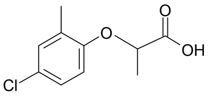
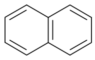
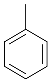
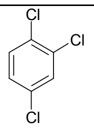
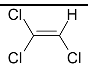
Table 2.3 Leachate concentrations of List I organic substances used in this study

Substance	**Contaminant group**	**Median concentration in UK leachates µg/l**	**Typical detection limit in leachate µg/l**	**Concentration used in biodegradation tests µg/l**	**Concentration used in sorption tests µg/l**
Mecoprop (MCPP)	Phenoxyalkanoic herbicide	11	0.1	15	1-100
Naphthalene	Poly aromatic hydrocarbon	0.46	0.1	5	0.5-50
Toluene	Aromatic hydrocarbons, BTEX compounds(1)	21	10	100	10-1,000
Trichlorobenzene	Chlorinated aromatic hydrocarbons	1(2)	0.3	3	0.3-30
Trichloroethene	Chlorinated aliphatic hydrocarbons	5.6(3)	1	10	1-100

[1] BTEX compounds include benzene, toluene, ethyl benzene and xylene.
[2] Approximate median in those UK leachates, where found.
[3] Mean values reported in study of US landfills, where compound was present in 70 per cent of samples

Two important characteristics of the List I substances under study are their hydrophobicity, which can be described in terms of the octanol-water partition coefficient (K_{ow}), and water solubility (S). Reference data are shown in Table 2.4.

Table 2.4 Structure, octanol-water partition coefficient values (K_{ow}) and solubility (S) of landfill leachate contaminants

List I substance	Structure	log K_{ow} (-)	S (mg/l)[a]
Mecoprop[d]		2.94[b] 0.1[c]	193.7
Naphthalene		3.17	142.1
Toluene (BTEX)		2.54	573.1
1,2,4-trichlorobenzene		3.93	20.0
Trichloroethene (TCE)		2.47	778.7

[a] SRC (1988)
[b] Mecoprop in neutral (non-ionised) form at pH2
[c] Mecoprop in anionic dissociated form (Tomlin, 1997)
[d] In landfill leachate (typically circumneutral) it is likely that mecoprop will be in the dissociated form (anionic) and so the log K_{ow} value will be 0.1.

The hydrophobic organic contaminants were analysed by headspace gas chromatography-mass spectroscopy (GC-MS).

Mecoprop analysis was carried out both at the Environment Agency laboratories in Leeds (primarily for the biodegradation tests) and at the University of Southampton (batch sorption and column tests). In summary the Environment Agency method involved a solid phase extraction (ENV+ Cartridges, 3 ml bed-volume, Argonaut Ltd) to concentrate the sample from the liquid phase. A volume of the sample was passed through the cartridge and the sample components were then eluted with dichloromethane (DCM 2ml). The eluted DCM was treated with diazomethane (1-2 ml) such that methyl esters of the components were formed. The DCM and diazomethane were then blown off and the sample taken up in ethyl acetate prior to GC-MS analysis.

The method used by the University of Southampton concentrated samples acidified to pH 2 by solid phase extraction (SPE) using Chromabond Easy cartridges (Machery-Nagel) according to the method for removal of phenoxycarboxylic acids from water Application No:302860 (Machery-Nagel). It was found that recovery of Mecoprop (and the internal standard Dichlorprop) was enhanced by using a) Chromabond Easy cartridges rather than the ENV+ cartridges and b) by the presence of tannic acid in the synthetic leachate. Therefore, to improve the sensitivity of the technique, tannic acid was added (1 g/L) to tannic acid-free samples and standards prior to SPE.

2.5 Summary of work programme

Table 2.5 summarises the range of tests undertaken within this research programme. In the batch sorption and desorption tests, losses of each of the contaminants from the aqueous solution other than by sorption to the clay (such as sorption to glass or Teflon®-coated septa, or biodegradation) was observed to be less than five per cent from control experiments. Control tests were also carried out in the biodegradation experiments; the results from these are discussed in Section 6.

Table 2.5 Overview of work programme

		Oxford Clay		**London Clay**		**Mercia Mudstone**		**Sand**
		HOC	MCPP[a]	HOC	MCPP	HOC	MCPP	HOC
Batch sorption	With tannic	x	x	x	x	x	x	
	Without tannic	x	x[b]			x	x[b]	
Batch desorption	With tannic	x	x	x	x	x	x	
	Without tannic							
Column sorption/ desorption	Synthetic leachate or tap water		x				x	
Biodegradation	A - Synthetic leachate	x	x	x	x	x	x	
	B – Real leachate	x	x			x	x	x
	C – Leachate matrix A seeded with leachate B	x	x	x		x	x	x

[a] MCPP = Mecoprop

[b] Mecoprop in non-tannic synthetic leachate and in tap water for Oxford Clay, tap water only for Mercia Mudstone

3 Batch sorption tests

3.1 Overview

Batch tests are a quick and relatively inexpensive method of estimating sorption parameters. Batch testing involves placing uncontaminated soil materials into a number of reaction vessels. A solution containing the contaminants at the required concentration is added, then the vessels are sealed and shaken until chemical equilibrium is reached between the solute and the sorbent. The 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 (Figure 3.1). 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, ml/g).

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. If the sorbed concentration is directly proportional to the aqueous concentration, then the slope of the isotherm is constant and linear, and K_d is independent of concentration. The Freundlich and Langmuir models describe different types of non-linear sorption behaviour. The different shape of these sorption isotherms is shown in Figure 3.1.

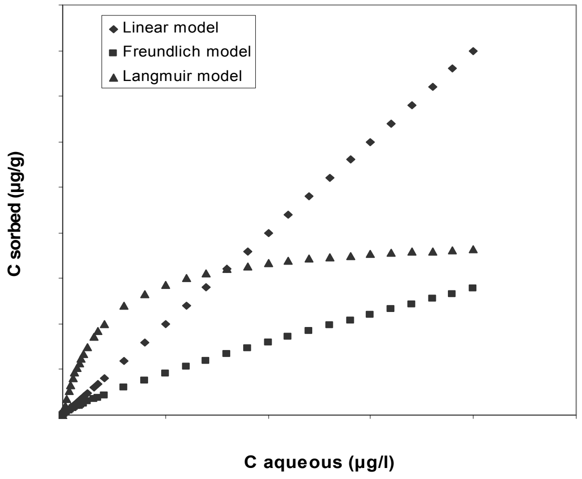


Figure 3.1 Freundlich, Langmuir and Linear models for sorption isotherms (Stumm, 1992)

3.1.1 Linear model

The linear sorption model is the simplest representation of sorption and takes the form

$$C_S = K_d C \qquad (3.1)$$

where: C_S = sorbed contaminant concentration (mass of contaminant/mass of solid, µg/g)
K_d = equilibrium coefficient for the sorption reaction (ml/g)
C = dissolved contaminant concentration (µg/ml)

Theoretically there is no upper limit to the amount of solute that can be sorbed. The linear sorption model is widely used in risk assessment modelling for groundwater contamination (for example LandSim) by assuming that K_d is constant for the concentration range of interest.

3.1.2 The Freundlich sorption model

The Freundlich sorption model (Stumm, 1992) 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. The Freundlich isotherm is described by the equation:

$$C_S = K_F C^n \qquad (3.2)$$

where: K_F = Freundlich equilibrium coefficient for the sorption reaction ($\mu g^{1-n}\ ml^n/g$)

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

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 frequently been used for trace metal adsorption to soils and sediments and the sorption of organics, including pesticides, to soils. Typically n is in the range 0.5-0.8. 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 partition coefficient K_d for the Freundlich isotherm is given by:

$$K_d = K_F C^{n-1} \qquad (3.3)$$

3.1.3 Combined sorption models

The linear and Freundlich models are most frequently used in practice, but there is a wide body of evidence that these models inadequately describe sorption, particularly when highly sorbent condensed or thermally altered organic carbon is present in a sample, even at very low concentrations (reviewed in Allen-King *et al.*, 1997; Luthy *et al.*, 1997; Huang *et al.*, 2003). Research suggests that dual or multi-mode sorption occurs in most soils and sediments with **ab**sorption to amorphous carbon and **ad**sorption to one or more types of condensed carbon (such as kerogen, black carbon, coal). More complex models have been developed which take account of the presence of different sorption domains in the solid matrix, so that sorption can be represented by:

$$C_S = C_S^{Abs} + C_S^{Ads} \qquad (3.4)$$

Where C_S^{Abs} can be described by the linear model (or Freundlich with n = 1), and sorption is considered reversible. C_S^{Ads} may be described by non-linear approaches such as the Freundlich or Langmuir models. The Langmuir model (Equation 3.5) 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).

$$C_s = \frac{K_L C\ M}{(1 + K_L C\ )} \qquad (3.5)$$

where: 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, μg/g).

Sorption to condensed carbon may be irreversible, that is, less than 100 per cent of the sorbed contaminant can be removed from the solid matrix. Dual or multi-domain models have been developed by a number of researchers (Weber *et al.*, 1992; Kan *et al.* 1994, 1997; Cornelissen *et al.*, 2005) to estimate the mass of contaminant in the irreversible fraction. An example from Kan *et al.* (1998) is given in Equation 3.6:

$$C_S = K_{OC} f_{OC} C + \frac{K_{OC}^{irr} f_{OC} C_{S\max}^{irr} F C}{C_{S\max}^{irr} F + K_{OC}^{irr} f_{OC} C} \qquad (3.6)$$

Where K_{OC}, f_{oc}, C_s and C are as in Equations 1.1 and 3.1, K_{OC}^{irr} is the sorption coefficient of the irreversible compartment (ml/g), $C_{S\max}^{irr}$ is the maximum sorbed concentration in the irreversible compartment (μg/g), and F($0 \le F \le 1$) is the fraction of $C_{S\max}^{irr}$ that is filled at the time of exposure.

3.1.4 Models of sorption to organic material

As noted in Section 1.2.1, for hydrophobic organic contaminants sorption is controlled by the fraction of organic carbon in the matrix when f_{oc} is greater than 0.001. The partition coefficient, K_{oc}, can be estimated from the octanol-water partition coefficient K_{ow}:

$$\log K_{OC} = a \log K_{OW} + b \qquad (3.7)$$

where: K_{oc} = the organic carbon partition coefficient (ml/g)

K_{ow} = the octanol-water partition coefficient (defined as the ratio between a compound’s concentration in octanol to its concentration in water at equilibrium).

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. Databases of K_{oc} values are available via the internet (e.g. Environmental Fate Database, Syracuse Research Corporation) or in the literature (Verschueren, 2001; Delle Site, 2001).

Table 3.1 Empirical models for sorption of hydrophobic organic contaminants

	Soil or sediment	Contaminants	Reference
$\log K_{oc} = \log K_{ow} - 0.21$	River and pond sediments	PAHs and chlorinated hydrocarbons	Karickhoff *et al.*, 1979
$\log K_p = 0.72 \log K_{OW} + \log f_{oc} + 0.49$	River, lake and aquifer sediments, f_{OC} 0.0004-0.058	Aromatic hydrocarbons, chlorinated aromatic hydrocarbons and alkenes	Schwarzenbach and Westall, 1981
$\log K_{OM} = 0.904 \log K_{OW} - 0.543$	Silt loam soil, organic matter content 1.9%	Aromatic hydrocarbons, chlorinated aromatics hydrocarbons and PCBs	Chiou *et al.*, 1983
$\log K_d = 1.07 \log K_{ow} + \log f_{oc} - 0.51$	Silt loam soil, f_{OC} 0.0149	Benzene, chlorinated aromatic hydrocarbons, PAHs	Xia and Ball, 1999

For low f_{OC} soils, mineral surfaces such as clays and iron oxyhydroxides also play a role in sorption, and the simple K_{OC} approach may not be valid (Environment Agency, 2003). McCarty *et al.* (1981) developed a relationship based on the specific surface area of the soil and the K_{ow} to estimate the f_{OC} below which mineral surfaces become more important than organic carbon for sorption:

$$f_{OC} = \frac{SSA}{(2x10^5)K_{OW}^{0.84}} \qquad (3.8)$$

where: *SSA* = specific surface area (m^2/kg)

This relationship is particularly relevant to ionic polar organic contaminants such as Mecoprop. Using Equation 3.8, the critical lower f_{OC} for Mecoprop (at ~pH7) in the liner materials used in this study (SSA = 32,000 – 56,000 m^2/kg) is f_{OC} = 0.13 to 0.23. Comparison with Table 2.1 suggests the K_{OC} approach is not relevant for Mecoprop sorption onto these liner materials.

3.2 Experimental methods

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 clay liner material was weighed into the bottles which were then filled in an anaerobic glovebox with synthetic MSW leachate containing sodium azide (100 mg/l) and mercuric chloride (0.05 mg/l) to inhibit biological activity. Known quantities of the contaminants under investigation were added, the bottles topped up with further leachate to leave no headspace and the bottles sealed immediately with aluminium caps and Teflon®-coated septa to avoid any volatilisation of the compound (Figure 3.2). The bottles containing clay and leachate were mixed on a tilting rotary roller (Stuart Scientific).

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.

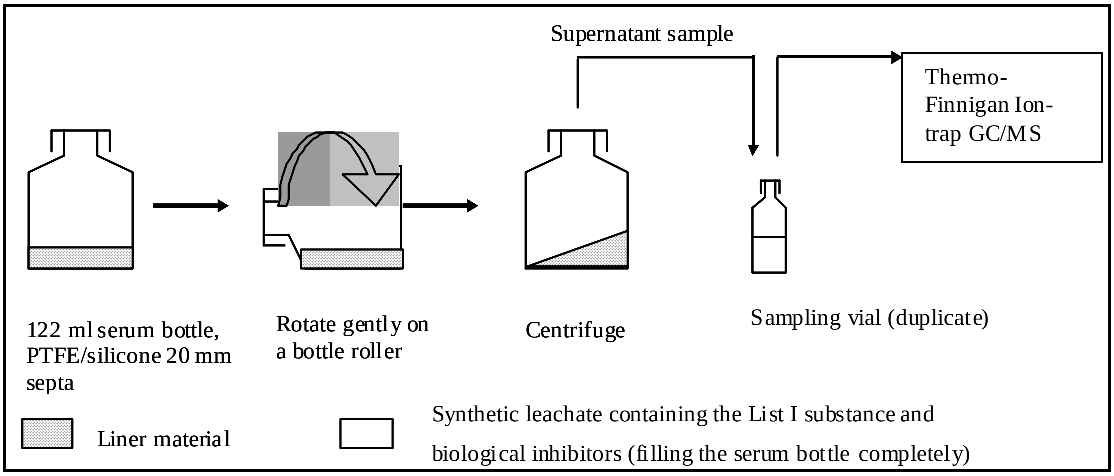


Figure 3.2 Experimental set-up of the sorption batch tests

Separate control tests indicated that losses of contaminant from the aqueous solution other than by sorption to the clay (e.g. sorption to glass or septa, or biodegradation) were negligible for the contaminants and experimental conditions used in this study.

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). The solid/liquid ratios used for the different clay/contaminant combinations are shown in Table 3.2.

Table 3.2 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)[a]	% 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

[a] m/v solid dry mass (g)/ aqueous volume of contaminant at maximum concentration listed in Table 2.
n/c = test not undertaken

In the case of Oxford Clay, only small quantities of clay were needed to achieve 50-60 per cent sorption of the hydrophobic contaminants. With Mercia Mudstone, high solid/liquid ratios were needed with some contaminants (such as TCE and Naphthalene) to achieve sufficient sorption. At these ratios, the mass of clay needed resulted in problems with mixing the clay and leachate and removing all air from the bottles (for example, 120 g clay in a 122 ml serum 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.

3.2.1 Sorption kinetics

Although sorption is often regarded as instantaneous for modelling purposes, it may take weeks, months or years to reach equilibrium. In most cases, uptake or release of hydrophobic organic contaminants is biphasic, occurring in an initial fast stage, then a slow stage (Leenheer and Ahlrichs, 1971; Karickhoff, 1980; Ball and Roberts, 1991).

Before starting the sorption isotherm tests, sorption kinetic tests were carried out over 30 days to determine the contact time to reach semi-equilibrium for each of the clay/contaminant combinations. The results of the kinetic 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 which accounted for 75-90 per cent of the total observed sorption, followed by slower uptake *towards* equilibrium. Therefore the subsequent sorption isotherm tests were carried out using four to seven days contact time.

3.3 Key results and findings

3.3.1 Sorption isotherms

Batch tests were carried out to obtain sorption isotherms over a contaminant concentration range covering two orders of magnitude, as given in Table 2.. In these tests DOC (as tannic acid) was included in the leachate matrix.

The equilibrium sorption data was fitted by two sorption models, the linear model and the Freundlich model (for example, see Figure 3.3 for data for the sorption of HOCs to Oxford Clay and London Clay). Least squares regression analysis was carried out to obtain the sorption parameters of the linear isotherm and the linearised logarithmic Freundlich isotherm. Freundlich and linear model parameter fits for all contaminants studied on each of the three clay liners are summarised in Table 3.3.

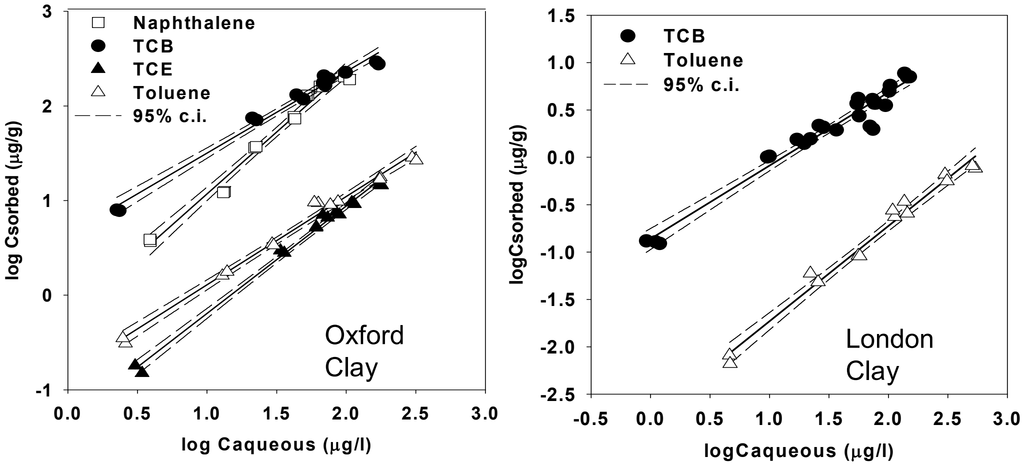


Figure 3.3 Freundlich sorption isotherms for toluene, naphthalene, TCB and TCE for Oxford Clay and London Clay

Table 3.3 Sorption coefficients for toluene, TCB, TCE, naphthalene and Mecoprop on London Clay, Mercia Mudstone and Oxford Clay

Clay liner	Contaminant	Linear model		Freundlich model			Log Koc (ml/g)
		K_d (ml/g)	R^2	K_F ($\mu g^{1-n} ml^n/g$)	n	R^2	
London Clay	Mecoprop	17.8	0.96	18.3	1.01	0.95	n/a
	Toluene	1.7	0.93	1.8	1.01	0.98	2.5
	TCB	49.8	0.88	137	0.77	0.96	3.9
Mercia Mudstone	Mecoprop	1.2	0.67	2.8	0.87	0.85	n/a
	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
Oxford Clay (Peterborough Member)	Mecoprop	8.4	0.98	8.4	0.98	0.97	n/a
	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

Leachate matrix containing tannic acid. n/a = Not applicable. As noted in section 3.1, the K_{oc} approach is not applicable to Mecoprop sorption by these clay materials.

Sorption of HOCs was found to increase with increasing contaminant hydrophobicity (TCE < toluene < naphthalene < TCB) and with increasing f_{oc} of the clay liners. The observed increase in sorption of the organic pollutants with increasing OC content suggests that this component dominates sorption of these contaminants, a trend observed in many other studies.

K_{oc} values for toluene, TCB, TCE and naphthalene determined in this study were compared with both literature K_{oc} values and with empirical K_{oc}-K_{ow} correlations found in the literature (see section 3.1.4 and Table 3.4). Results are summarised further in Simoes *et al.* (2009). 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.

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. 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.

Table 3.4 Comparison of K_{oc} values determined from this study for selected List I compounds with values in the literature and predicted by empirical correlations

List I compound	Literature values Log K_{oc} (ml/g)	Predicted values* Log K_{oc} (ml/g)	This study Log K_{oc} (ml/g)		
			London Clay	Mercia Mudstone	Oxford Clay
Naphthalene	2.7-3.9	2.3-3.0	-	1.8	4.6
Toluene	1.6-2.4	1.8-2.3	2.5	1.5	3.2
TCB	2.5-4.0	3.0-3.7	3.9	2.3	4.6
TCE	2.1-3.4	1.7-2.3	-	1.6	3.2

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

3.3.2 Sorption isotherms – Mecoprop

Sorption of Mecoprop by the liner materials decreased in order London Clay > Oxford Clay >> Mercia Mudstone. Sorption was linear for London Clay and Oxford Clay (the fitted values for n in the Freundlich model being approximately one) but non-linear for Mercia Mudstone synthetic leachate (n=0.87) as shown in Figure 3.4.

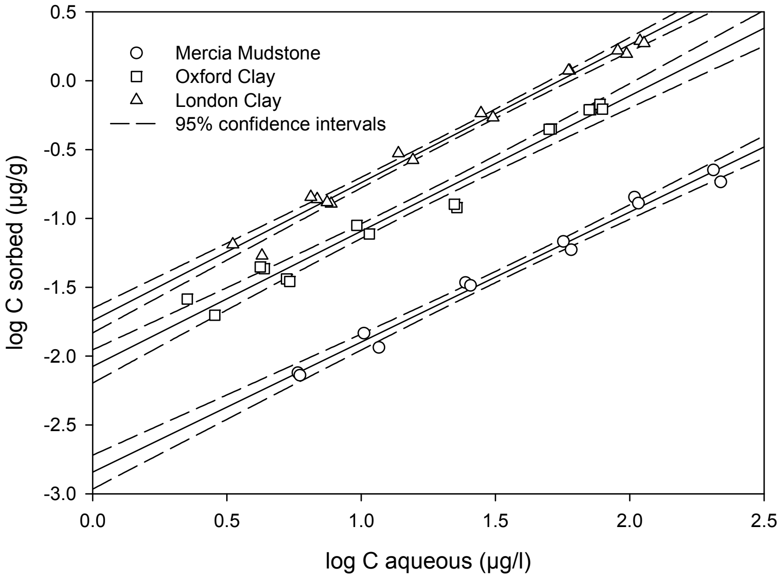


Figure 3.4 Freundlich sorption isotherms for Mecoprop on Mercia Mudstone, Oxford Clay and London Clay

The linear sorption coefficient for Mecoprop 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 Mecoprop by London Clay and Oxford Clay was much greater than literature values (Hauberhauer *et al.* (2000); Madsen *et al.* (2000); Harris *et al.* (2000)) for both aquifer sediments and soils (Figure 3.5).

The factors which might affect sorption of Mecoprop include interactions of the carboxylic group with negatively charged clay surfaces and organic matter via metal ion bridges (Celis *et al.*, 1999; Clausen *et al.*, 2001a and 2001b) or partitioning via lipophilic interactions with soil organic matter (Chiou *et al.*, 1979; Karickhoff, 1984). No individual physicochemical characteristic (cation exchange capacity (CEC), specific surface area, organic carbon content or iron oxyhydroxide content) fully explained the sorption mechanism of Mecoprop to the three clays in the study. Oxford Clay has the highest OC content and CEC, Oxford and London Clays have a higher specific surface area than Mercia Mudstone. London Clay had the highest percentage of iron oxyhydroxides followed by Mercia Mudstone and Oxford Clay. It appears that a combination of factors influence sorption of Mecoprop; further work is required to elucidate the sorption mechanism.

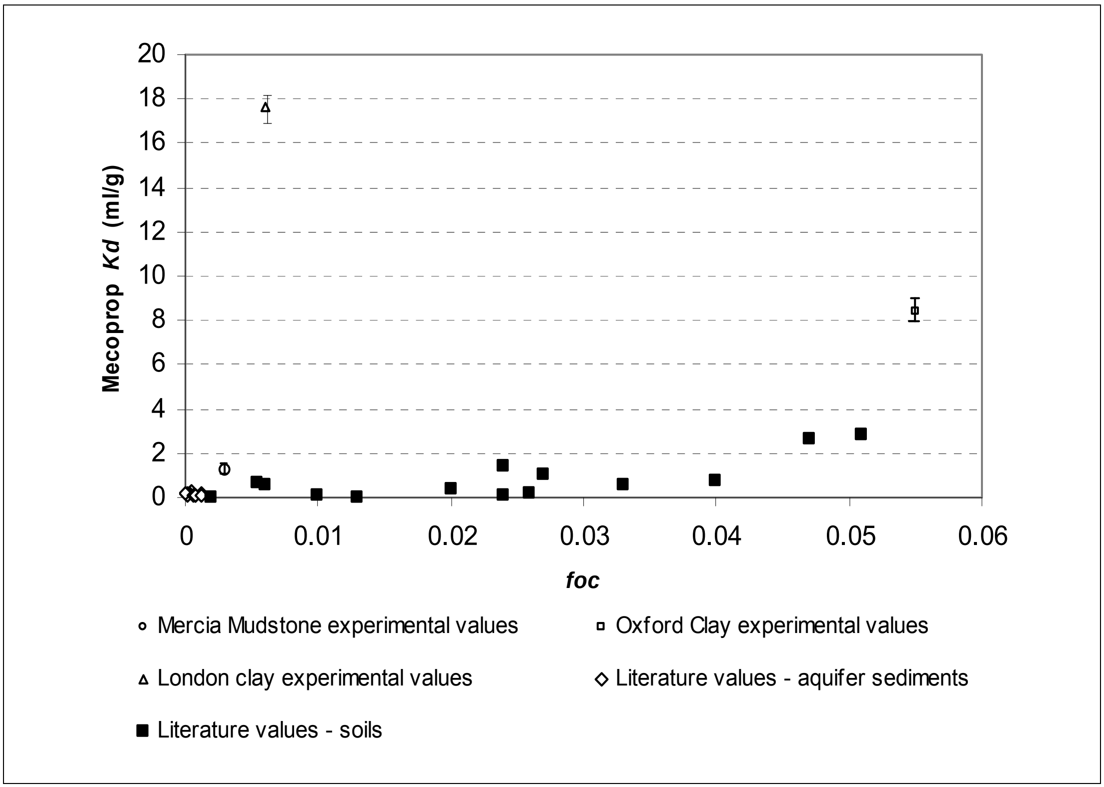


Figure 3.5 Measured and literature K_d values for Mecoprop

3.3.3 Competitive sorption of List I substances

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 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 61 µg/l and 326 µg/l. The results demonstrated that, at these concentrations, there was no decrease in toluene sorption when TCB was present. At higher contaminant concentrations, competition may have an effect on sorption of HOCs.

3.3.4 Effect of dissolved organic carbon (DOC) on sorption of List I substances

Tannic acid was used to mimic the natural DOC of the MSW and MSWI leachates. Most batch sorption tests in the literature have not taken into account the presence of DOC in the aqueous phase, and consequently a set of batch sorption tests using synthetic leachate without any tannic acid were carried out.

These tests showed that sorption of TCB by Oxford Clay (and to some extent by Mercia Mudstone) and that of naphthalene by Oxford Clay decreased in the presence of tannic acid in the MSW leachate (Table 3.5). This may have been caused by sorption of the tannic acid (1,000 µg/l) to the clay in preference to TCB and naphthalene which were present in much smaller concentrations (below 300 µg/l). In addition, the difference in molecular size between tannic acid ($C_{76}H_{52}O_{46}$) and TCB ($Cl_3C_6H_3$) or naphthalene ($C_{10}H_8$) suggests that tannic acid molecules sorbed to the clay may block access of TCB and naphthalene molecules to sorption sites.

Alternatively, the tannic acid may bind with the HOC in solution and thus inhibit HOC sorption by the clays.

Table 3.5 Sorption data for HOCs and Mecoprop on Oxford Clay and Mercia Mudstone in synthetic leachate with and without tannic acid, or in tap water.

Contaminant/ Clay liner	**MSW leachate**	**Linear model**		**Freundlich model**		
		K_d (ml/g)	**R^2**	**K_F ($\mu g^{1-n} ml^n/g$)**	**n**	**R^2**
Mecoprop/ Mercia Mudstone	Tannic	1.2	0.67	2.8	0.87	0.85
	Tap water	1.9	0.98	2.7	0.92	0.99
Mecoprop/ Oxford Clay	Tannic	8.4	0.98	8.4	0.98	0.97
	Tap water	12.3	0.99	12.3	0.99	0.99
Naphthalene/ Oxford Clay	Tannic	1,702	0.97	1,188	1.08	0.99
	No tannic	2,325	0.95	2,523	1.01	0.98
TCB/ Mercia Mudstone	Tannic	0.5	0.94	2.4	0.66	0.92
	No tannic	0.7	0.96	3.8	0.65	0.99
TCB/ Oxford Clay	Tannic	2,060	0.82	4,364	0.86	0.99
	No tannic	3,623	0.95	9,398	0.78	0.99

Batch sorption tests were also carried out in tap water for Mecoprop on Mercia Mudstone and Oxford Clay to produce sorption coefficients which could be compared directly with those derived from the column tests (Section 5). Sorption of Mecoprop was greater in tap water than it was in synthetic leachate with tannic acid (Table 3.5). Electrolytes in the high ionic strength synthetic leachate may be in competition with Mecoprop for positive surface sites, possibly contributed by iron oxyhydroxides (Clausen *et al.*, 2001) present in the clays. The high ionic strength leachate may also have reacted with minerals in the clays, leading to changes in the structure of the clays (Batchelder *et al.*, 1998).

To develop a better understanding of the influence of DOC in leachate on the sorption of hydrophobic List I substances, a brief study into the sorption of tannic acid in synthetic leachate and sorption of DOC in real leachate by Oxford Clay and Mercia Mudstone was undertaken. Batch sorption tests were carried out as previously described but without List I contaminants. DOC was measured by high temperature catalytic combustion. The DOC in both the synthetic and real leachate was shown to sorb to the clay materials. From the synthetic leachate, Mercia Mudstone sorbed 0.5 mg DOC/g clay, while Oxford Clay sorbed 6 mg DOC/g clay. DOC in the real leachate was sorbed more strongly than tannic acid: 2.4 mg DOC/g Mercia Mudstone and 10 mg DOC/g Oxford Clay perhaps indicating different sorption characteristics between the two types of DOC.

Limited kinetic tests were carried out over 60 days to assess sorption of DOC by Mercia Mudstone and Oxford Clay. These tests showed that sorption increased between 15 and 30 days after which no further sorption was observed. 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 observation.

The results from the sorption batch tests confirm that both HOCs and tannic acid/leachate DOC sorb to clays. Since the presence of tannic acid decreases sorption of the List I substances, it is possible that the DOC competes for sorption sites in the clays or that DOC inhibits sorption of HOCs by binding with them in solution.

4 Desorption tests

4.1 Introduction

The distribution coefficient for the desorption isotherm of a given contaminant-sorbent system is often greater than that of the sorption isotherm for the same system (Huang *et al.*, 2003). Such sorption-desorption hysteresis may indicate entrapment or irreversible binding of contaminants to binding sites, or slow desorption rates (Weber *et al.*, 1998), and is more usually associated with older condensed forms of organic carbon. If irreversible sorption occurs, contaminants may remain sorbed for many years without significant release back into solution, even if the contaminant concentration in the dissolved phase (groundwater or leachate) decreases (Kan *et al.*, 1998).

4.2 Overview of methodology

The experimental set up for the batch desorption tests was based on the batch sorption tests (Section 3.2 and Figure 3.2) using the decant and refill method (Bowman, 1979). After the batch sorption test, the supernatant solution was removed and replaced with a contaminant free solution, allowing the contaminant sorbed to the solid phase to desorb into the aqueous phase until a new equilibrium condition was reached.

The contaminant-free leachate used in the desorption tests was produced by mixing clay and fresh synthetic leachate (including tannic acid) in the same ratio as in the sorption tests and for the same contact time. This was done so that the contaminant-free solution in the desorption phase 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 (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 were identical because of the variation in both the content and nature of the organic carbon present in the clays which may leach into solution during the tests.

The results of kinetic 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. Subsequent desorption tests were carried out after 10 to 15 days contact time. Single step desorption isotherm tests were carried out over an aqueous contaminant concentration range spanning two orders of magnitude. The desorption data were plotted as a standard isotherm, allowing a comparison to be made with the equivalent sorption isotherm (Section 3.3.1).

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 still sorbed may be approximated to the irreversible fraction. Repeat desorption tests were therefore carried out on a limited number of clay/contaminant combinations. Starting with a standard batch sorption at a high aqueous concentration, the supernatant liquid was replaced (as above) 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.

4.3 Key results and findings

4.3.1 Single step desorption tests

Desorption tests were carried out for four of the contaminants (toluene, TCB, naphthalene and Mecoprop) on the three clay liners. Desorption was generally close to linear although the Freundlich model provided a slightly better fit to the data. Freundlich model fits to the sorption and desorption equilibrium data of toluene on London and Oxford Clays are shown in Figure 4.1 and for Mecoprop in Figure 4.2. Sorption and desorption parameters for the linear and Freundlich models are given in Table 4.1.

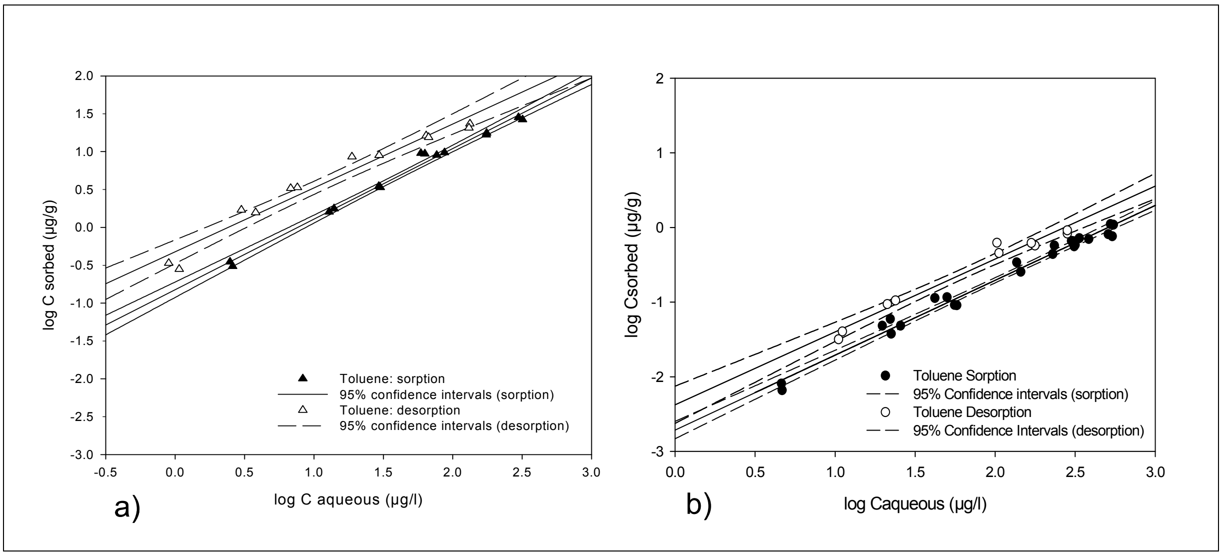


Figure 4.1 Freundlich sorption and desorption isotherms for toluene on (a) Oxford Clay and (b) London Clay

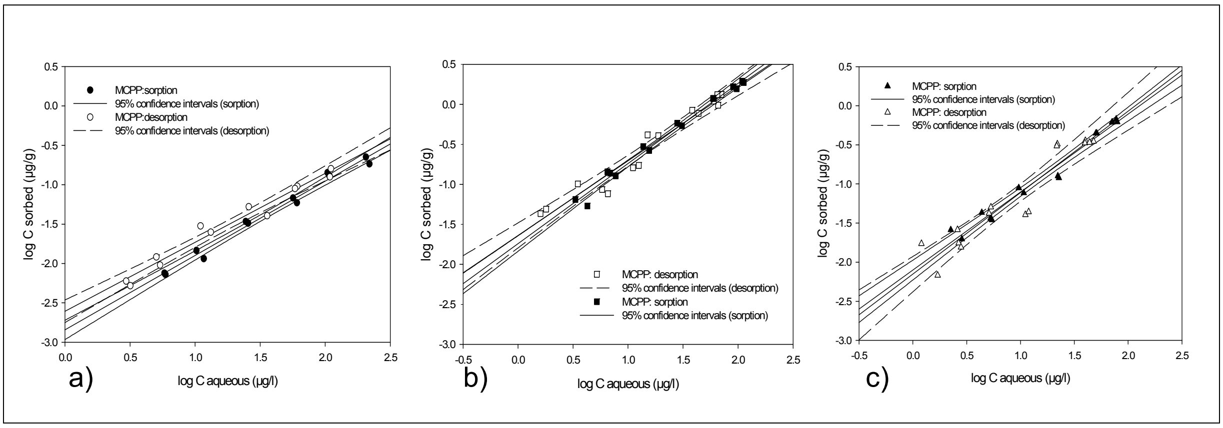


Figure 4.2 Freundlich sorption and desorption of Mecoprop on (a) Mercia Mudstone, (b) London Clay, and (c) Oxford Clay

Table 4.1 Parameters of the linear and Freundlich models fit to sorption and desorption data

Clay	Contaminant	Sorption or desorption	Linear model		Freundlich model		
			K_d (ml/g)	R^2	K_F ($\mu g^{1-n} ml^n/g$)	n	R^2
London Clay	Mecoprop	Sorption	17.6	0.99	18.1	1.0	0.99
		Desorption	18.4	0.96	23.7	0.93	0.95
	Toluene	Sorption	1.7	0.96	1.97	0.99	0.99
		Desorption	3.4	0.89	4.21	0.98	0.97
	TCB	Sorption	49.8	0.88	137	0.77	0.96
		Desorption	65.6	0.9	165	0.74	0.93
Mercia Mudstone	Mecoprop	Sorption	1.2	0.67	2.8	0.87	0.85
		Desorption	1.4	0.95	2.47	0.88	0.97
	Naphthalene	Sorption	0.2	0.84	0.52	0.80	0.94
		Desorption	0.4	0.93	0.68	0.83	0.96
	Toluene	Sorption	0.1	0.96	0.02	1.26	0.94
		Desorption	0.09	0.84	0.13	0.91	0.96
	TCB	Sorption	0.6	0.98	2.02	0.74	0.96
		Desorption	1.0	0.97	1.4	0.89	0.95
Oxford Clay	Mecoprop	Sorption	8.4	0.99	8.4	0.98	0.97
		Desorption	8.6	0.88	7.6	1.01	0.89
	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	0.96	150	0.93	0.99
		Desorption	186.8	0.88	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

R^2 - correlation coefficient

If sorption was reversible, the sorption and desorption coefficients would not be significantly different. Whilst the linear and Freundlich desorption coefficients are greater than (in many cases, double) the sorption coefficients for the same contaminant/clay combinations after one desorption step (Table 4.1), for most contaminant/clay combinations the sorption and desorption coefficients are not significantly different at 95 per cent confidence intervals (see Figure 4.1(b) for toluene on London Clay). The exception is the first desorption step for toluene on Oxford Clay which shows significant difference between the sorption and desorption isotherms (Figure 4.1(a)) indicating sorption-desorption hysteresis. Given the presence of highly sorbent organic carbon in Oxford Clay, it is likely that diffusion and entrapment of toluene into organic matter matrices or slow rates of desorption may be responsible for the hysteresis observed.

Least squares regression analysis was carried out to obtain desorption parameters of the linear isotherms and linearised logarithmic Freundlich isotherms for Mecoprop on the three clays in synthetic leachate (Figure 4.2); the model parameters are given in Table 4.1. Model fits for Mecoprop desorption from Oxford Clay and London Clay are approximately linear, however desorption on Mercia Mudstone appears to be non-linear (n=0.88). There is little difference between sorption and desorption coefficients which suggests that sorption of Mecoprop is reversible in synthetic leachate.

4.3.2 Multi-step desorption tests

Multi-step desorption tests were carried out 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 (Figure 4.3). Oxford Clay had the largest capacity with approximately 35 µg/g TCB and 2.5µg/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. The 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 clay liners may have a much greater capacity to retain certain contaminants than might be predicted from conventional models.

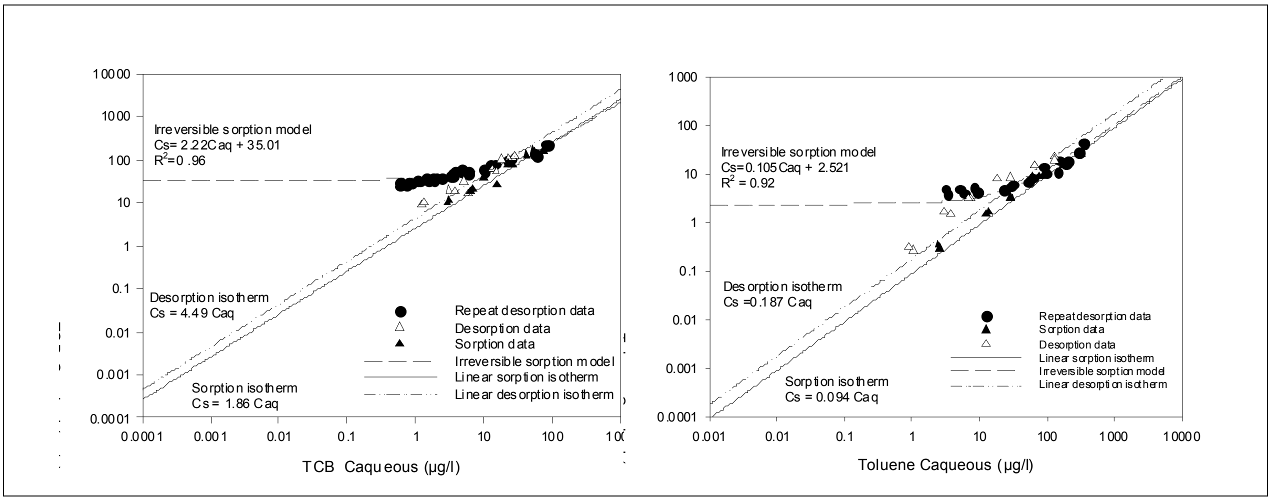


Figure 4.3 Batch sorption, desorption and multistep desorption for a) TCB and b) toluene on Oxford Clay

Table 4.2 Multistep desorption tests

Clay	Contaminant	Number of desorption steps	Irreversible sorption (µg/g)
Oxford Clay	TCB	12	35.1
	Toluene	9	2.52
London Clay	TCB	10	0.56
	Toluene	12	0.16

5 Column tests

5.1 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 Mecoprop through clay liner materials with reference to bromide, a ‘conservative’ tracer. The aim was to establish whether Mecoprop was subject to any irreversible sorption and to quantify the extent and nature of retardation due to sorption.

5.2 Overview of methodology

The retardation of Mecoprop by Mercia Mudstone and Oxford Clay was tested. Clay samples were prepared by drying, grinding, sieving (to under 63 µm). The ground clay was 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, sufficient to produce a sample of good stiffness for the triaxial cell. The sample was then unloaded in stages to the effective stress to be used in the test (90 kPa). The sample was recovered from the oedometer tube, trimmed (to 50 mm) and transferred to the triaxial cell.

The standard triaxial cell apparatus (Figure 5.1) was modified to minimise any potential for sorption of Mecoprop. Polytetrafluoroethylene (PTFE) was used in contact with the sample to prevent sorption of Mecoprop by the latex membrane. The interaction between Mecoprop and PTFE was evaluated in batch tests and no sorption was found; however, sorption of Mecoprop (20%) by the latex membrane was observed. The sample was 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 at a depth of nine metres. The sample was permeated with tap water until steady flow was obtained. Mecoprop and potassium bromide were introduced to the column and samples of the eluant were taken for analysis. Pressure, temperature and flow rate were monitored constantly.

Samples were collected at the outlet and, after measuring the bromide, the samples were acidified to pH 2 and refrigerated to preserve the Mecoprop, prior to analysis by the method described in Section 2.4. Bromide concentrations in the tap water samples were measured by ion selective electrode (Thermo Orion).

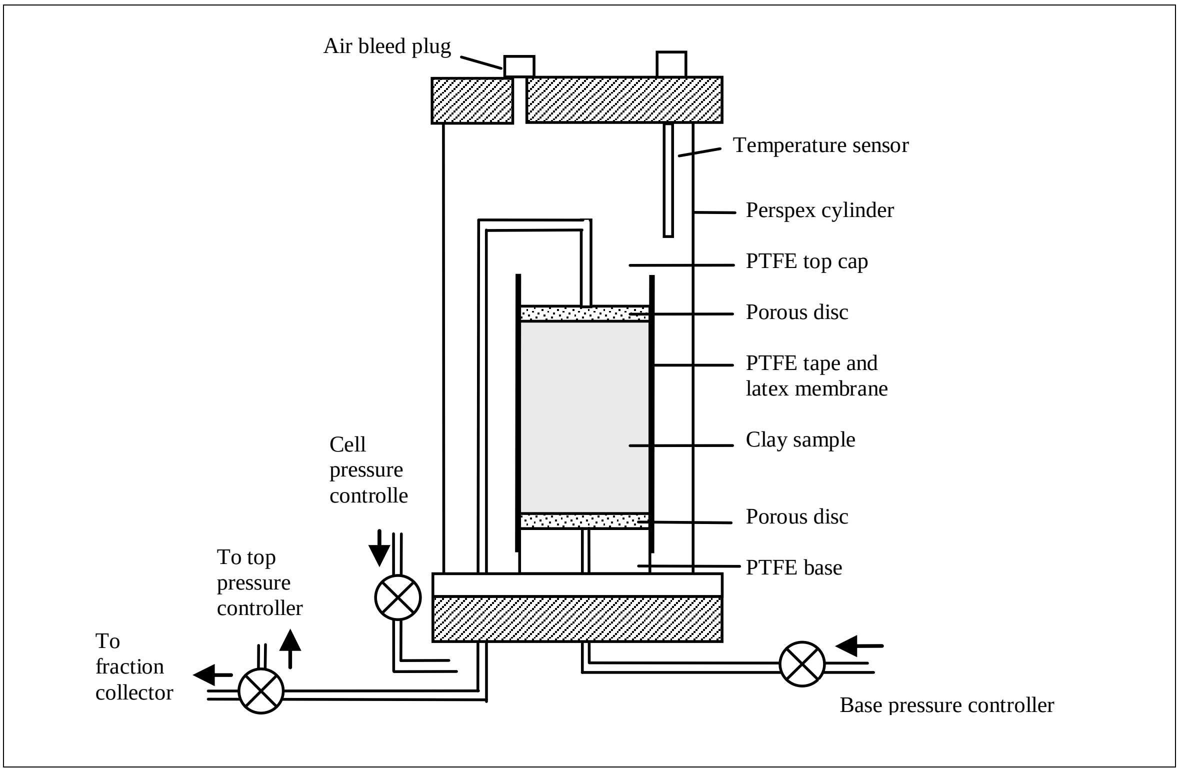


Figure 5.1 Triaxial cell used in the column tests

Retardation of Mecoprop was calculated by fitting the contaminant breakthrough curve to a simple transport model given by a basic 1D advection dispersion equation (Bear, 1972), Equation 5.1:

$$R\frac{\partial C_r}{\partial t} = D\frac{\partial^2 C_r}{\partial x^2} - v\frac{\partial C_r}{\partial x} \qquad (5.1)$$

where R is the retardation coefficient [-], C_r is the (volume-averaged) concentration [g/ml], x is the distance along the column [cm], D is the hydrodynamic dispersion coefficient [$\text{cm}^2/\text{s}^{-1}$] and v is the linear velocity [cm/s].

The derived values of R can be converted to equivalent values of the partition coefficient K_d by:

$$R = 1 + \frac{\rho_b K_d}{\theta} \qquad (5.2)$$

where ρ_b is the soil dry density (g/ml); θ the effective porosity; and K_d the partition coefficient (ml/g).

Analysis of the transport model fits by Woodman *et al.* (2009) showed that the simple advection-dispersion model described above is adequate for the transport of bromide and Mecoprop at the laboratory scale.

5.3 Key results and findings

In total, ten triaxial cell tests were performed: eight on Mercia Mudstone and two on Oxford Clay. The average hydraulic conductivity of the Mercia Mudstone samples was 1.7×10^{-9} m/s, whereas for Oxford Clay, it was 3.6×10^{-10} m/s.

In three of the Mercia Mudstone tests, Mecoprop was added alongside the bromide tracer. The retardation of Mecoprop, *R,* in Mercia Mudstone was calculated by fitting the transport model; *R* was also estimated on the basis of sorption isotherms in tap water (Table 5.1). Only one test provided a reasonable fit for the Mecoprop data on Oxford Clay (Table 5.1). Greater retardation of Mecoprop was observed for Oxford Clay than Mercia Mudstone.

Table 5.1 Mecoprop sorption (column and batch tests)

Clay	Hydraulic conductivity (m/s)	Column tests		Batch tests	
		R	K_d (ml/g)	R	K_d (ml/g)
Mercia Mudstone	1.7×10^{-9}	2.4 – 4.3	0.3 – 0.7	9.95	1.9
Oxford Clay	3.6×10^{-10}	19.7	3.6	65.6	12.3

K_d values derived from the batch sorption tests appear to overestimate column test retardation and therefore, the results from batch tests must be treated cautiously. While batch sorption tests can be used to rapidly obtain empirical relationships between solute and sorbed concentrations for different materials and solutes, the ratio of the solid mass to the volume of liquid in the pore space in column tests is significantly different to that of batch tests (Table 5.2). Overestimation of *R* by the batch tests is consistent with the ‘normal’ trend for sorption (per unit mass) to increase as the ratio of solid mass to pore volume decreases (Limousin *et al.*, 2007).

Table 5.2 Solid/solution ratio (column and batch tests)

Clay	Solid/solution ratio	
	Column tests	Batch tests
Mercia Mudstone	4.7	0.5
Oxford Clay	5.2	0.11

6 Biodegradation tests

6.1 Introduction

Biodegradation is generally regarded as the principle 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 normally microbially mediated. The propensity for a chemical to undergo biodegradation depends on an array of interacting biological and physicochemical parameters including the structure of the chemical 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 upon the environmental niche under evaluation. It is beyond the scope of this report to present a complete evaluation of these processes but for a detailed overview, a text by Alvarez and Illman (2006) on bioremediation and natural attenuation is recommended.

In this study, the biodegradation of a range of chemical types was studied under conditions mimicking those in landfill sites, that is, anaerobic, where the principal biodegradatory mechanisms are via sulphate-reducing bacteria, iron-reducing bacteria, methanogenic bacteria or by a microbial consortia of all groups growing synergistically. The chemical types include polycyclic aromatic hydrocarbons (PAH, naphthalene), BTEX aromatic hydrocarbons (toluene), chlorinated aliphatic (TCE) and aromatic (1,2,4-trichlorobenzene) compounds and a phenoxyalkanoic acid herbicide (Mecoprop). The hydrophobic and solubility properties of these compounds have already been presented in Table 2.4. Numerous publications and reviews on biodegradative pathways and mechanisms for all of these chemical types, under many different environmental conditions, are available, including more recently PAH anaerobic biodegradation (Meckenstock *et al*., 2004), anaerobic biodegradation of aromatic hydrocarbons (Foght, 2008), biodegradability of chlorinated aliphatic compounds (Leisinger, 1996; Field and Sierra-Alvarez, 2004), microbial degradation of chlorinated benzenes (Field and Sierra-Alvarez, 2008) and Mecoprop degradation (Buss *et al*., 2006). Because of the general availability of this data, only a brief description of the biodegradability of chemicals used in this study is given.

6.1.1 Mecoprop

There have been few reports of anaerobic degradation of Mecoprop and the degradative pathway is unknown. Very little or no biodegradation of Mecoprop has been demonstrated in anaerobic aquifers (Harrison *et al.*, 1998). However, initial transformation by reductive dechlorination and dealkylation has been observed for the phenoxyacetic acid herbicides 2,4-D and 2,4,5-T in aquifer sediments (Gibson and Suflita, 1990; Mikesell and Boyd, 1985). Other monoaromatic compounds are dearomatized by reduction under sulphate-reducing and methanogenic conditions (Heider and Fuchs, 1997), and reduction could be a potential pathway in the mineralization of Mecoprop. Indeed, Williams *et al*. (2003) observed preferential use of (R)-Mecoprop under nitrate-reducing conditions, recording its first order removal rate at 0.65 mg/l/day in laboratory microcosm experiments ((S)-Mecoprop was not degraded).

6.1.2 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. Christensen *et al*. (2004) and Chang *et al*. (2003) have reported bacterial growth using naphthalene under nitrate-, sulphate- and methanogenic-reducing conditions, but whether it is acting as a true substrate or its removal is a result of co-metabolic oxidation remains unresolved

6.1.3 Toluene

Toluene in sharp contrast to the other BTEX compounds shows little recalcitrance under all terminal electron acceptor conditions. It has been observed to biodegrade readily under anaerobic conditions in aquifers with methanogenic, denitrifying, sulphate-reducing and iron-reducing environments (Aronson and Howard, 1997). Bacterial metabolic pathways of BTEX and other aromatic compounds can be divided into two main categories: peripheral pathways and trunk pathways. Peripheral pathways transform a unique compound into a compound common to many metabolic pathways. For example, toluene is anaerobically metabolized to benzoyl-CoA by a system of peripheral pathway enzymes. In turn, benzoyl-CoA is metabolized by trunk pathway enzymes and used as a growth substrate. Many anaerobic aromatic peripheral pathways end in the production of benzoyl-CoA. These pathways are said to "funnel" into the benzoyl-CoA trunk pathway. This compound is the most common central intermediate of anaerobic aromatic metabolism (Heider *et al*., 1997). The aromatic ring of benzoyl-CoA is reduced and eventually transformed to acetyl-CoA and subsequent oxidation to carbon dioxide.

6.1.4 1,2,4-Trichlorobenzene

Biodegradation of chlorinated benzenes under anaerobic conditions seems 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. Reductive dechlorination of 1,2,4-trichlorobenzene has been observed under methanogenic conditions. 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 the bacteria to the chlorinated benzene. Low *in situ* temperatures might be a major obstruction of 1,2,4-trichlorobenzene dechlorination under natural conditions as in the laboratory, dechlorination was observed to cease at temperatures below 10°C (Middeldorp *et al*. 1997).

6.1.5 Trichloroethene

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 cometabolism. In addition, abiotic hydrolysis reactions are known to be involved in some of the degradative pathways. The chemical transformation can be abiotic dechlorination/hydrolysis with half-lives in the order of 0.5, 0.7 and 0.9 years at 20°C for 1,1,1-TCA, PCE and TCE respectively (Vogel *et al*. 1987) or metal-catalysed degradation with half-lives in the order of 5, 18, and 14 hours for the same compounds (Gillham *et al*. 1993). Biodegradation is often faster than chemical transformation, but heavily depends on the redox conditions. Most of the compounds are not degraded unless primary substrates are available (Oldenhuis *et al*., 1989; Freedman and Gossett, 1989; Tandol *et al*., 1994).

(1) 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.

(2) Chlorinated solvents can also act as electron acceptors in a process known as reductive dechlorination in which hydrogen replaces chlorine atoms (US EPA, 1996). 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 the landfill leachate. In general, reductive dechlorination occurs by sequential dechlorination from tetrachloroethene (PCE) to trichloroethene (TCE) to dichloroethene (DCE) to vinyl chloride (VC) to ethane. 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; Skubal *et al*., 2001). 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 VC; 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 ethene (Freedman and Gossett, 1989). Less chlorinated compounds and the daughter products of reductive dechlorination can be biodegraded in less reducing environments (Vogel, 1994).

(3) Most chlorinated solvents degrade by co-metabolism in which the chlorinated compound is converted to another substance during microbial metabolism of another compound, which is the primary growth substrate. Degradation is catalysed by an enzyme or cofactor that is produced by the microorganisms for other purposes.

No data was found in the literature for the degradation of PCE, TCE in landfill leachates and clay liners. However, there are reports on attenuation of chlorinated aliphatics in leachate and in groundwater studies. In leachate microcosm studies, Leahy and Shreve (2000) showed that PCE biodegraded at a rate of 23.8 µg per day. When the microcosms were supplemented with organic carbon, biodegradation was quicker (61 µg per 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.

6.2 Brief overview of methodology

The purpose of the biodegradation tests was to determine the potential for biodegradation of List I substances under conditions which simulated landfill liner environments, that is, anaerobic conditions. A variety of tests were carried out using:

- (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.
- (B) Real landfill leachate in which dechlorination of tetrachloroethene had been observed in previous work (Environment Agency, 2009).
- (C) Synthetic MSW and MSWI leachates seeded with real leachate (B).

Synthetic leachate was used for the majority of experiments (A) to allow consistent conditions to be maintained in experiments taking place over many months. All of the above tests were undertaken in the presence of different mineral liners and with controls (including tests with biological inhibitors). A number of control tests were carried out over two months to investigate the sorption of List I substances to the bottle components (glass, PTFE tube and cap) and the effect of this on biodegradation/ sorption of the List I substances.

Biodegradation tests were carried out using three groups of List I substances to investigate possible competitive biodegradation effects at the contaminant concentrations shown in Table 6.1 and 6.2. Group I contained all five substances under investigation (toluene, naphthalene, Mecoprop, trichloroethene and 1,2,4-trichlorobenzene). Group II contained toluene, naphthalene and Mecoprop. All these substances are widely found in UK leachates, such that a mixture containing them all was a realistic scenario to investigate. Group III contained only naphthalene.

Table 6.1 Target concentration of the List I substances at the start of the biodegradation tests (A)

Substance	Concentration (µg/l)
Mecoprop	15
Naphthalene	5
Toluene	100
Trichlorobenzene	3
Trichloroethene	10

Table 6.2 Aqueous concentration of the List I substances measured at the start of the biodegradation tests (B) using real leachate

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

0.5-1.5 mg of toluene, TCB and TCE and 0.5 mg of naphthalene and Mecoprop were added to the leachate at the start of the biodegradation tests

The tests were carried out using 1,000 ml Duran type bottles with appropriate air tight OMNI fittings (Kinesis Ltd) for sampling. Each bottle contained the synthetic or real leachate, bacterial seed, clay liner and biological inhibitors (20 mM sodium molybdate and 50 mM 2-bromoethanesulphonic acid) as appropriate, and the List I substance or mixture of substances (Figure 6.1).

Bacterial seeds (methanogenic and sulphate-reducing bacteria) for the biodegradation tests (A) using synthetic leachates were enriched from sludges obtained from a sewage works and a leachate treatment plant located at a landfill site in South East England known to contain List I substances. The seeds were slowly acclimatised to the contaminants and bacterial activity was observed at the target concentrations of the List I substances (such as production of biogas comprising CH_4 and CO_2). No additional bacterial seed was used in tests (B) with the real landfill leachate and leachate from the same landfill as used in tests (B) was used as the seed in tests (C).

A gas headspace of 80/15/5 (% nitrogen/carbon dioxide/hydrogen) was applied above the liquid level of the bottles. All test bottles were sealed and stored in an anaerobic cabinet containing the same gas mixture at 20°C. The List I contaminants were analysed using GCMS as described in Section 2.4.

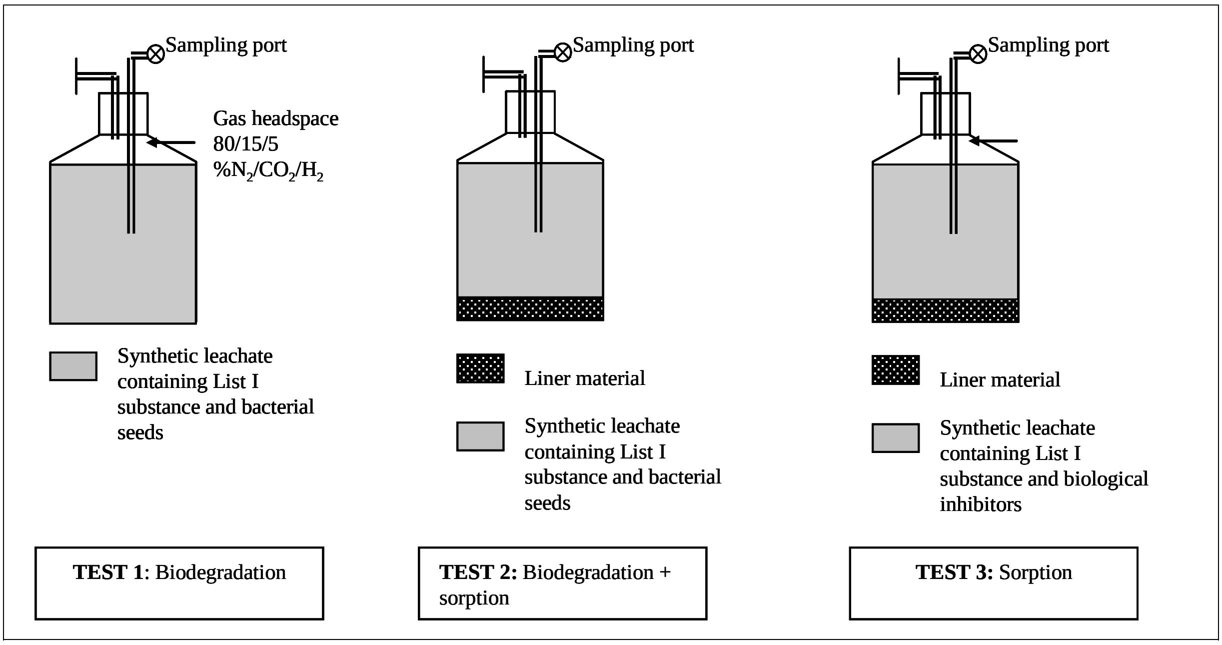


Figure 6.1 Experimental set-up of the biodegradation tests using synthetic leachates

The main biodegradation tests (A) were undertaken over a period of eight months, during which time up to 10 leachate samples were taken from each of the 68 bottles. The volume of leachate removed for analysis from each bottle at each sampling event was 24 ml, such that no more than 25 per cent of the original leachate volume was removed. Samples were analysed for List I components and their degradation products, major ions, DOC and pH. Account was taken of the effect of partitioning of the volatile List I substances (TCE, TCB, toluene and naphthalene) into the gas headspace present in the biodegradation bottles.

Biodegradation tests (B) were carried out using 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 as part of the Environment Agency's vinyl chloride study). Tests were undertaken using the Group I combination of contaminants and Mecoprop (as a single contaminant), with Oxford Clay, Mercia Mudstone and sand (to replicate tests undertaken at Newcastle University).

Finally, biodegradation tests (C) were run in which landfill leachate was added as a bacterial seed to MSW and MSWI synthetic leachates from tests (A) after eight months incubation. The landfill leachate was collected from the same UK landfill site as that used in tests B. Existing bottles from the biodegradation tests containing MSW and

MSWI synthetic leachates and the five List I substances (Group I) were spiked with 50 ml of the UK landfill leachate (less than 10 per cent of the total volume in the bottle) using the liquid sampling port. Bottles were kept sealed and stored in the anaerobic cabinet at an incubation temperature of 20°C. Samples were collected (initially every 10-15 days of incubation, then over several months) and analysed for the List I substances being investigated.

6.3 Key results and findings

Control tests indicated some long-term sorption of List I substances to bottle components over the eight month period of the biodegradation tests, particularly to the PTFE cap and sampling valves which affected interpretation of the results. (Note that sorption to PTFE septum used in the batch sorption and desorption tests was found to be negligible over the short duration (four to seven days) of the batch tests).

6.3.1 Synthetic leachate (tests A)

Biological activity was evident in all bottles without inhibitors. Biogas, comprising mainly methane and carbon dioxide, was produced in the bottles with MSW synthetic leachate, seed and clay. Sulphate concentrations in the bottles containing MSWI synthetic leachate decreased in all bottles where no biological inhibitors were added, and more significantly in the bottles containing clay liners. These results indicate that active methanogenic and sulphate-reducing bacterial populations were supported by the synthetic leachates and that the clays provide an attachment medium for these bacteria.

Results of the biodegradation tests (A) using the MSW and MSWI synthetic leachates indicated that the four hydrophobic organic compounds (HOCs) appeared to be recalcitrant to biodegradation over an incubation period of eight months. Common biodegradation products of TCB 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 1 µg/l).

There were some problems with the analysis of Mecoprop, and all bottles showed a decrease in concentration during the tests. However, there was no clear difference in the change in Mecoprop concentration between bottles with and without biological inhibitors (Figure 6.2). Since biogas production indicated an active microbial population in all bottles without inhibitors, it was concluded that there was no evidence for biodegradation taking place (although the presence of Mecoprop degradation products was not tested) and the decrease in Mecoprop concentration was attributed to sorption.

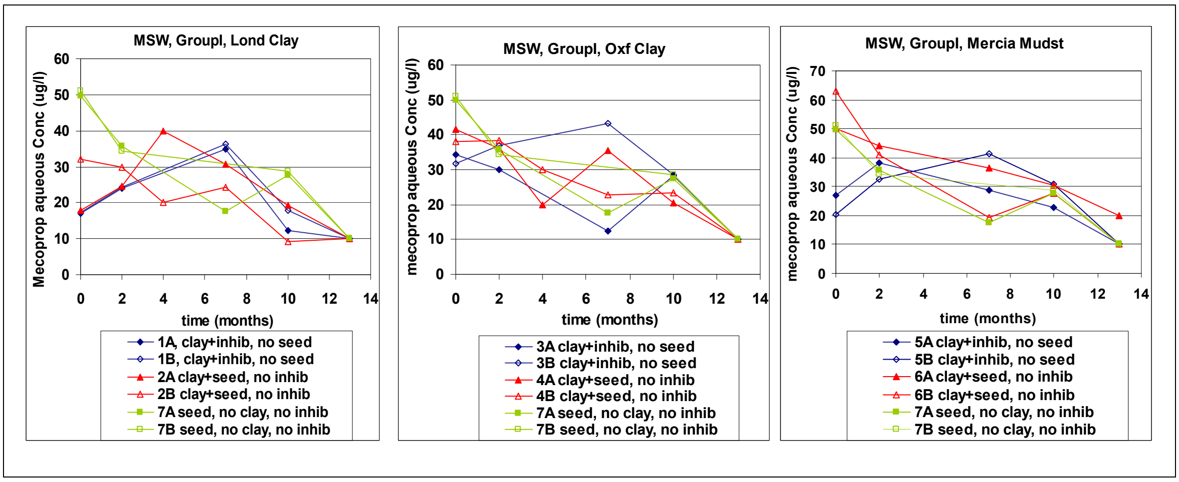


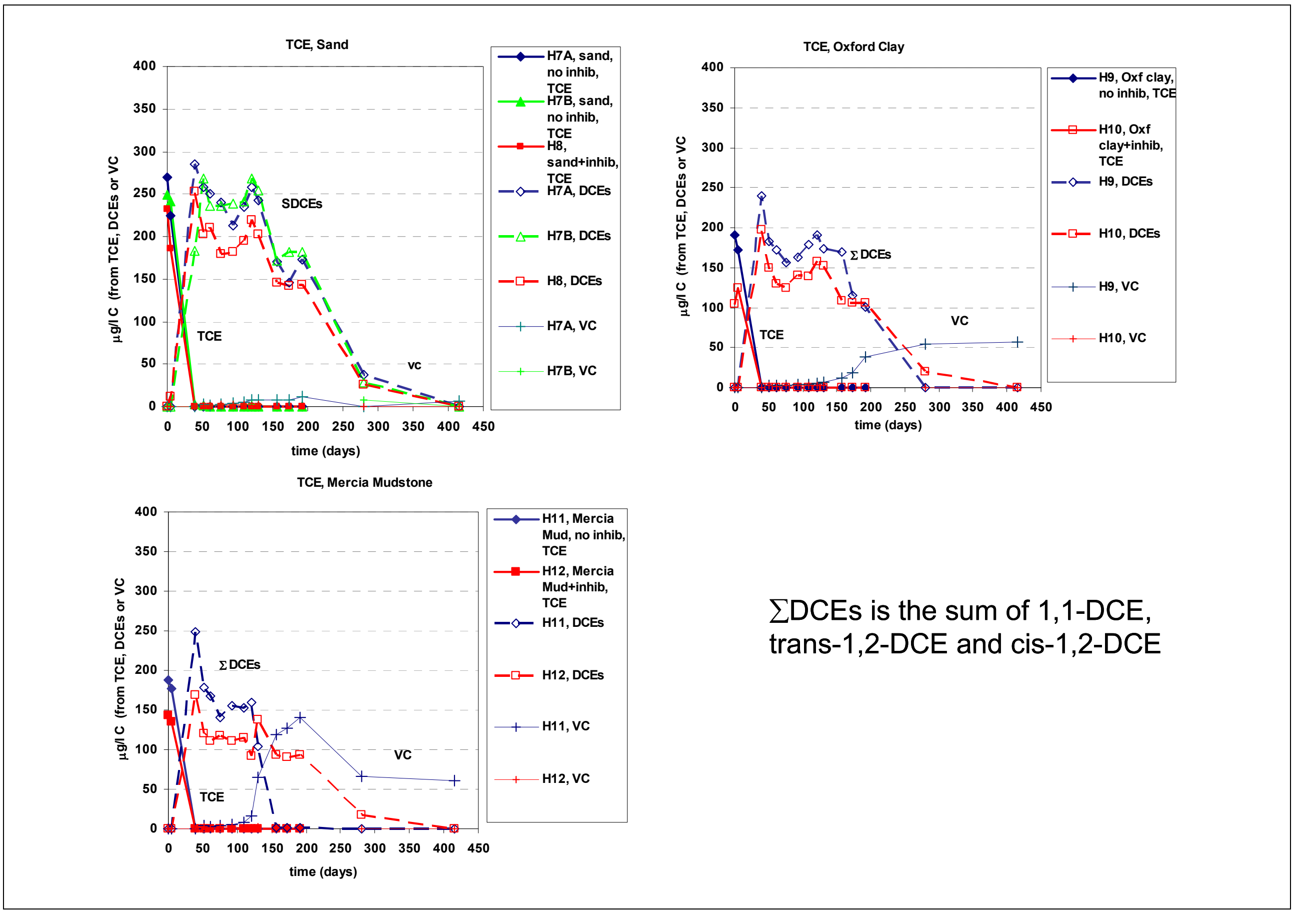
Figure 6.2 Variation with time of Mecoprop aqueous concentration in synthetic MSW leachate (London Clay, Oxford Clay and Mercia Mudstone)

6.3.2 Real leachate (tests B)

Further biodegradation tests (B) were used to evaluate biodegradation using leachate from a landfill known to support biodegradation of tetrachloroethene. The tests provided strong evidence of complete TCE biodegradation, evidence for some degradation of toluene and TCB, and little evidence of any degradation of naphthalene. As with the (A) tests, there were problems with analysis of Mecoprop, however there was no evidence of Mecoprop degradation (based on comparison of bottles with and without biological inhibitors) and the observed decrease in concentration was attributed to sorption.

TCE aqueous concentrations were found to decrease to less than one per cent of initial concentrations after only 40 days of incubation in all of the test bottles with an estimated half-life ($t_{1/2}$) of four to six days (Figure 6.3) where $t_{1/2} = 0.693/\lambda$ (the first order decay constant). Common reductive dechlorination products of TCE (1,1-DCE, trans-1,2-DCE, cis-1,2-DCE and vinyl chloride (VC)) which were not present in the leachate at the start of the tests were detected after 40 days of incubation suggesting, that TCE was converted to DCEs. An active methanogenic bacterial population was identified in the reactors which may be involved in the dechlorination process. Conversion of DCEs to VC was observed after 110 days of incubation which suggests that it was produced at a slower rate or that a suitable bacterial population took longer to establish. Conversion of TCE to VC took place in the absence of clay liners and was in general slower in the presence of Oxford Clay than in Mercia Mudstone; little VC was produced in the presence of sand. VC concentration decreased after 200 days in the presence of Mercia Mudstone; the metabolic reasons for this change are not understood.

TCE degradation was observed with and without biological inhibitors, although separate tests (in which the leachate was autoclaved and additional biological inhibitors were added) indicated that abiotic processes were not a significant contributor to TCE degradation. This is consistent with observations by Freedman and Gossett (1989) who reported that the complete inhibition of PCE biodegradation under methanogenic conditions required successive additions of 2-bromoethanesulphonic acid.



∑DCEs is the sum of 1,1-DCE, trans-1,2-DCE and cis-1,2-DCE

Figure 6.3 Variation with time of aqueous TCE concentration in bottles containing real landfill leachate and clay liners.

Biodegradation of toluene was identified in the tests containing Oxford Clay, but not in the presence of sand or Mercia Mudstone (possibly due to different geochemical characteristics of Oxford Clay). Following a lag phase of around 72 days, toluene in the presence of Oxford Clay was degraded with a calculated half-life ($t_{1/2}$)of 12 days: the toluene concentration decreased from 600 µg/l to less than 20 µg/l between 80 and 120 days of incubation, with a concomitant increase in benzylsuccinate, a common anaerobic biodegradation product of toluene (Figure 6.4).

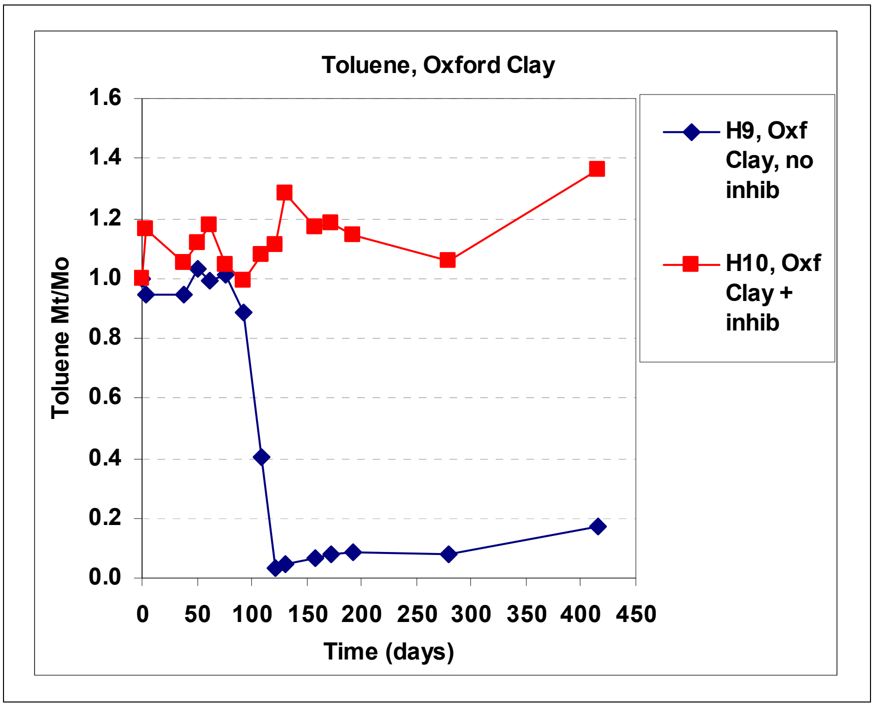


Figure 6.4 Variation with time of aqueous toluene concentration in bottles containing real landfill leachate and Oxford Clay

There was some evidence for limited biodegradation of TCB in all bottles. Although it was not possible to attribute any reductions in total TCB concentrations to degradation (rather than sorption), common biodegradation products of TCB from reductive dechlorination processes (dichlorobenzenes and chlorobenzene) were detected in all bottles (with and without biological inhibitors) at very low concentrations (under 7 µg/l) and found to slowly increase with time.

6.3.3 Synthetic leachate with real leachate seed (tests C)

The results from tests (C) indicate that addition of bacterial seed from the real leachate 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. 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. Common reductive dechlorination products of TCE 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 with and without biological inhibitors is consistent with the results from tests in real leachate which indicated that autoclaving of the leachate, in addition to biological inhibitors, was required for complete biological inhibition. 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 dilution of active bacterial seed from the real leachate in synthetic leachate (less than 10 per cent of the total volume in the bottle). TCE dechlorination was generally faster in the bottles without biological inhibitors, suggesting that the bacterial population responsible for the dechlorination process may include methanogenic bacteria as these should be affected by the inhibitors. Dechlorination was faster in the presence of the clay liners, particularly Mercia Mudstone (half-life 48 to 61 days).

The concentration of contaminants used in biodegradation tests B was greater than used in tests A (table 6.1 and 6.2). The low concentration used in tests A did not appear to be responsible for the lack of biodegradation in these tests, since the addition of seed from tests B resulted in biodegradation of TCE.

6.3.4 Summary

The observed biodegradation of TCE in the real leachate highlights the differences in biodegradation between leachates from different sites. TCE was degraded in the synthetic leachate after addition of the leachate seed from tests B, but the seed did not promote degradation of other List I substances. Biogas production in the synthetic leachate confirmed that an active methanogenic and sulphate-reducing microbial population was present. The seed for the synthetic leachate tests (A) came from a real landfill containing List I substances but this bacterial leachate seed was unable to degrade these contaminants.

In research into factors affecting the degradation of PCE to vinyl chloride, carried out as part of Environment Agency Project P1-517/1 (Environment Agency, 2009), it was found that the potential for biodegradation varied between and within landfill sites. PCE was degraded fully in samples collected from the TCE-degrading landfill used in this study (tests B), whereas at another site PCE was only degraded to TCE. In another landfill site, degradation of PCE was found in samples from some wells but not in other wells on the same site. This confirms that the potential for List I degradation in a particular landfill is difficult to predict, and is not necessarily consistent across all phases of a landfill. Further investigation of biodegradation of List I substances by real MSW leachates collected from different landfill sites is recommended.

7 LandSim modelling

7.1 Background

This report reviewed retardation parameters for various List I organic contaminants, and their interactions with mineral liners. New parameter values for the partition coefficient, K_d, were calculated based on the experimental programme. To illustrate the importance of using appropriate K_d values, a series of simple risk assessment simulations was carried out using the Environment Agency's preferred model, LandSim. Detailed information on groundwater risk assessment of landfill sites and LandSim can be found in Environment Agency (2003a and 2003b).

7.2 LandSim conceptual model and parameters

The basic conceptual model for LandSim is shown in Figure 7.1. A simple landfill conceptual model was used for the LandSim simulations based on the generic landfill used in discussions for the Landfill Directive (Environment Agency, 2006b; Slack *et al.*, 2007). The basic landfill scenario was kept simple since the purpose was to illustrate the effect of changing sorption parameters. Default LandSim values were used where available, and 1,001 iterations were run.

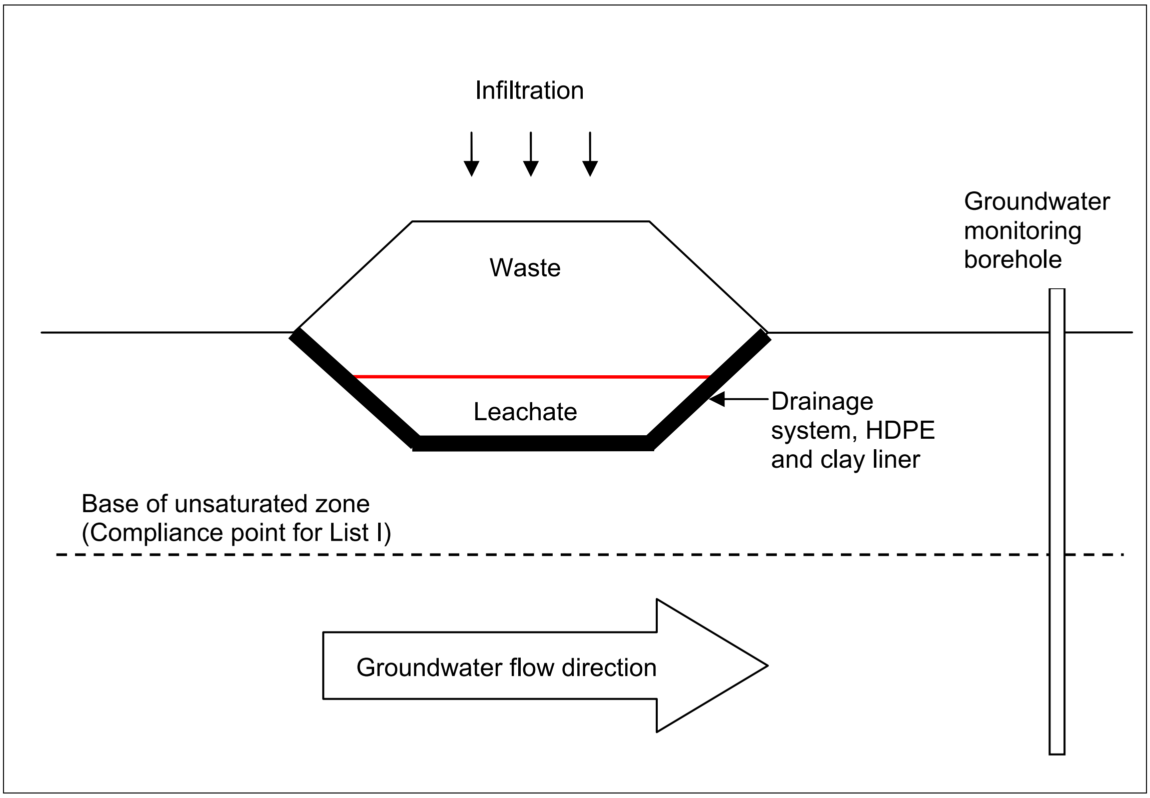


Figure 7.1 Conceptual model for LandSim simulations

A composite barrier was modelled using default LandSim values for the HDPE whilst the engineered clay barrier was assigned a hydraulic conductivity of 1 x 10^{-9} m/s. The two-metre thick unsaturated zone was assumed to be the same material as the clay liner with the same retardation values but a higher hydraulic conductivity (1 x 10^{-8} m/s). The underlying aquifer had a Darcy flux of 1 x 10^{-5} m/s and mixing depth of five metres.

The compliance point for List I substances was the base of the unsaturated zone although an additional compliance point in groundwater at the site boundary was also considered. Only dilution within the groundwater was allowed for List I substances and not sorption or biodegradation.

All landfill scenarios included gas extraction during the period of management control and the default half-life of 10 years was applied to volatile organic contaminants (VOC – naphthalene, toluene, TCE, TCB). The kappa value for Mecoprop was set to be the same as chloride in the absence of other data, using the approach taken in Environment Agency (2003b). Two periods of management control were investigated: 60 and 20,000 years. This primarily affects the leachate head within the landfill which is fixed at one metre until the management control period ceases, and is then allowed to vary according to the LandSim water balance model.

Retardation parameters were varied for each of the different clays used in the barrier (London Clay, Mercia Mudstone, Oxford Clay). Table 7.1 shows the initial contaminant concentrations in the leachate; the declining source term option was chosen. Table 7.2 summarises the sorption parameters; these were applied to the liner and unsaturated zone. Ammonium and chloride were included in the model runs to ensure the results for leachate transport were reasonable. Literature values were used for the initial LandSim simulations (Table 3.4) with K_d calculated from the f_{OC} reported in Table 2.1 for the different clays. For Mecoprop, the range of values reported for soils and aquifer sediments was used (Environment Agency, 2004). A second set of simulations was run using the K_d estimated during the experimental programme (Table 3.3). Biodegradation was not included since the experimental programme found no evidence of biodegradation in the synthetic leachate.

Table 7.1 Leachate concentrations

Contaminant	Concentration range (mg/l)
Mecoprop	0.001 – 0.011 – 0.14
Naphthalene	0.0001 – 0.00046 – 0.042
Toluene	0.01 – 0.021 – 1.287
Trichlorobenzene	0.001
Trichloroethene	0.0056
Ammonium	32.1 – 267 – 1,100
Chloride	227 – 997 – 2,650

[1] Log triangular distributions were used except for TCB and TCE where single values were considered more appropriate.

Table 7.2 Leachate concentrations and retardation parameters

Contaminant	K_d (literature)[1]			K_d (experimental)		
	London Clay	Mercia Mudstone	Oxford Clay	London Clay	Mercia Mudstone	Oxford Clay
Mecoprop	0 – 0.17 – 2.80	0 – 0.17 – 2.80	0 – 0.17 – 2.80	17.8	1.2	8.4
Naphthalene	3 – 50	1.5 – 25	28 – 456	N/A[2]	0.18	2,137
Toluene	0.2 – 1.6	0.1 – 0.8	2 – 15	1.7	0.1	94
TCB	1.9 – 60	0.9 – 30	17 – 549	49.8	0.6	2,152
TCE	0.4 – 8	0.7 – 16	7 – 148	N/A[2]	0.11	82

[1] Triangular distribution used for Mecoprop, uniform for other contaminants.
[2] N/A: data not available.

7.3 LandSim modelling results

LandSim allows parameters to be entered as a range of values, so the outputs are in the form of probabilistic plots. This enables the results to be assessed at difference confidence intervals, with the 95th percentile typically used for groundwater risk assessments. Concentrations of List I contaminants were compared with the minimum reporting values given in Environment Agency (2003a); these are shown in Table 7.3 along with environmental assessment levels (EAL) used for ammonium and chloride.

Table 7.3 Environmental assessment levels (EAL)

Contaminant	EAL (µg/l)
Mecoprop[1]	0.04
Naphthalene[1]	0.001
Toluene[1]	4
TCB[1]	0.01
TCE[1]	0.1
Ammonium[2]	0.5 mg/l
Chloride[2]	250 mg/l

[1] List I: compliance assessed at base of unsaturated zone
[2] Compliance assessed in groundwater at site boundary

Different scenarios were modelled to illustrate the effects of varying:

- sorption values for different clays and contaminants;
- length of the management control period (60 or 20,000 years).

The decline in the source term is shown in Figure 7.2 which illustrates the different behaviours of selected volatile and non-volatile contaminants.

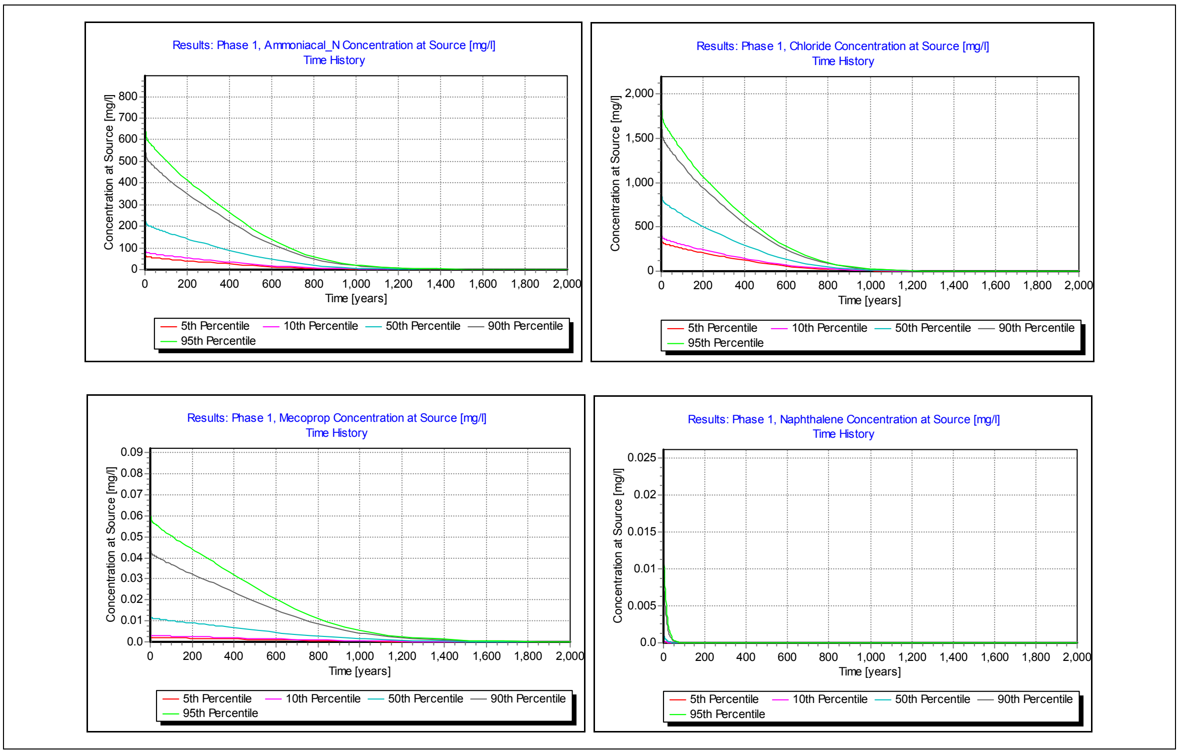


Figure 7.2 Source term decline – London Clay (20,000 year management control)

For all landfill scenarios with a 20,000 year management control period, LandSim predicted no groundwater pollution at the site perimeter by ammonium or chloride.

In all scenarios using literature values for retardation of contaminants by London Clay (Figure 7.3a, c) and Mercia Mudstone liners, the predicted concentration of all List I substances at the base of the unsaturated zone exceeded the target EAL values. For the Oxford Clay simulations using literature values, LandSim predicted groundwater pollution by Mecoprop, naphthalene and toluene. If dilution in groundwater was allowed, only Mecoprop was discernible above the target EAL value at the site boundary. Therefore none of these landfill scenarios using literature retardation values would be acceptable.

Table 7.4 LandSim predictions for Mecoprop (20,000-year management control)

Liner material	Maximum at base of UZ (µg/l)	Years till pollution (base of UZ)[1]	Maximum at compliance point (µg/l)	Time of maximum conc. (years)
London Clay[2]	40	340	0.044	370
London Clay[3]	11	2,000	***0.022***[4]	2,500
Mercia Mudstone[2]	42	370	0.044	425
Mercia Mudstone[3]	45	380	0.046	430
Oxford Clay[2]	50	350	0.051	500
Oxford Clay[3]	23	1,200	***0.037***[4]	1,500

[1] Predicted time at which EAL exceeded.
[2] Sorption values from literature (Table 2.1).
[3] Sorption values from this project (Table 3.3).
[4] Predicted concentration below minimum reporting value (not discernible).

The LandSim simulations were repeated using the values for retardation from the experimental programme (Table 3.3). The London Clay liner still failed to prevent discernible concentrations of Mecoprop and toluene from discharging to groundwater although TCB concentrations were below the EALs (Figure 7.3d). However, the time until Mecoprop reached the water table was much longer with the experimental values: around 2,000 years compared with 370 years (Figure 7.3b).

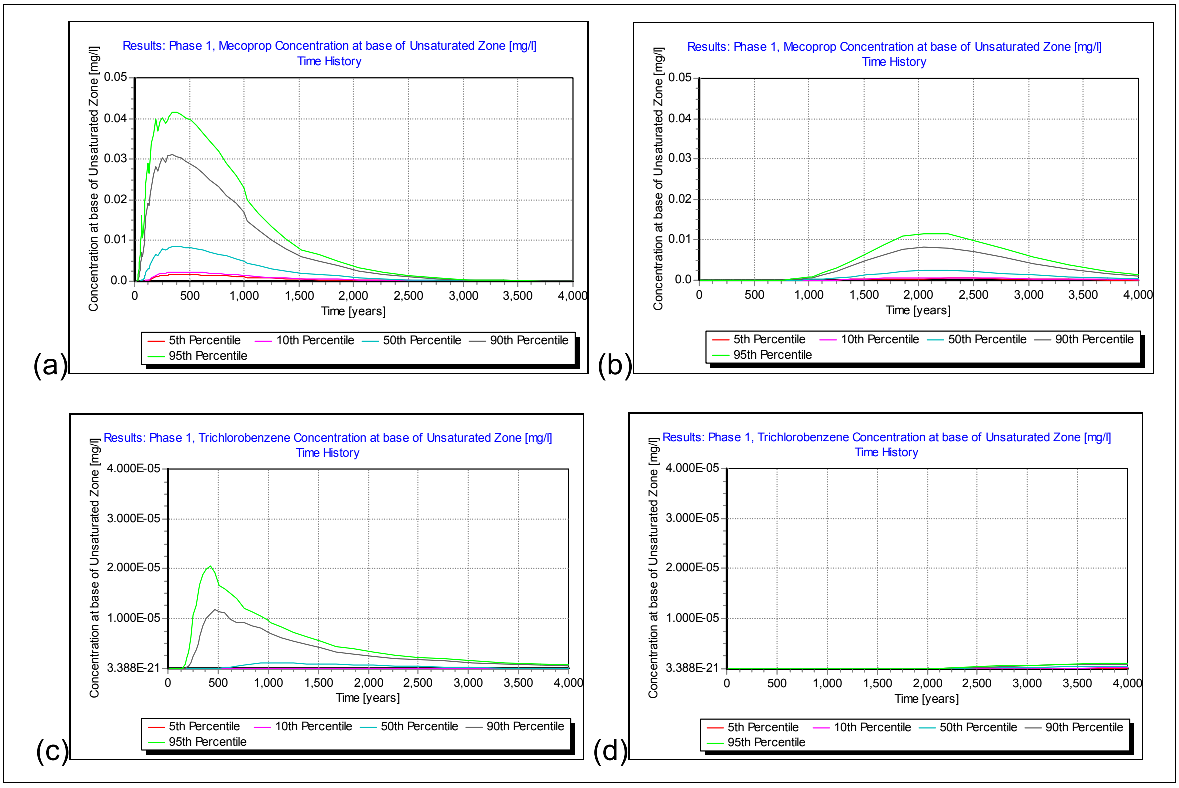


Figure 7.3 LandSim modelling – London Clay: literature (a, c), experimental (b, d)

All List I substances exceeded their EAL values at the base of the unsaturated zone with the Mercia Mudstone liner; Mecoprop behaved in a similar way to the predictions based on the literature, but the VOCs were discharged more quickly and at higher concentrations. Even after dilution in groundwater, the Mercia Mudstone landfill still failed for Mecoprop (0.046 µg/l at 430 years) and naphthalene (0.002 µg/l at 50 years) so using this liner material in this landfill scenario is clearly unacceptable.

Simulations of the Oxford Clay liner using the experimental retardation values predicted discernible concentrations of Mecoprop at the base of the unsaturated zone, but the other List I contaminants would not cause pollution (Figure 7.4d); the time for Mecoprop to reach the groundwater was 1,200 years (compared with 350 years when literature K_d were used) (Figure 7.4b). After dilution in groundwater, Mecoprop was predicted to be below the minimum reporting value. Using the batch test K_d values therefore has a significant effect on the groundwater risk assessment.

Simulations were also carried out using a short management control period of 60 years. As expected, LandSim predicted the List I substances would be discharged to groundwater more rapidly and at higher concentrations than when leachate levels were controlled at one metre depth for an infinite time.

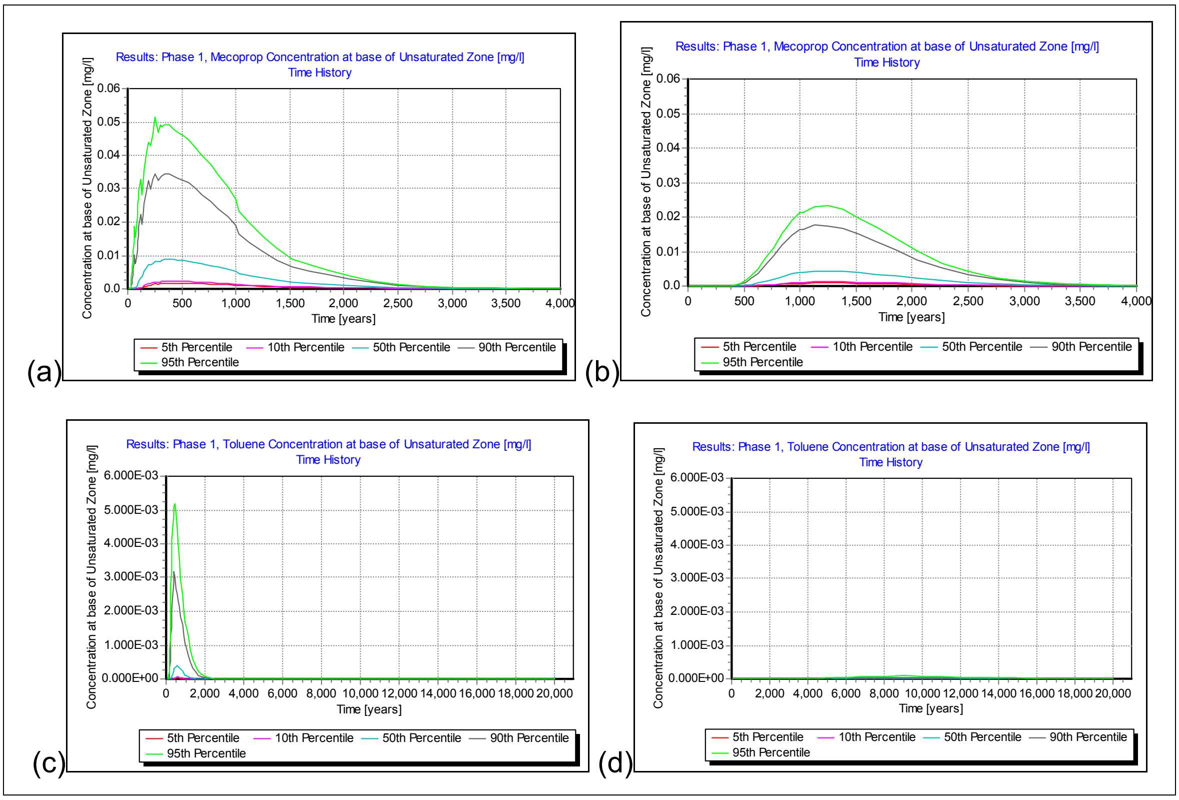


Figure 7.4 LandSim modelling – Oxford Clay: literature (a, c), experimental (b, d)

7.4 Mecoprop K_d values (batch and column tests)

A series of simulations was carried out using K_d values estimated from experiments carried out in tapwater (batch and column tests – Section 5) and synthetic MSW leachate without tannic acid (Table 7.5). Results were assessed at the 95th percentile.

Table 7.5 Mecoprop K_d values from batch and column tests

Liner	**K_d (column)[1]**	**K_d (Batch)[1]**	**K_d (Batch – no tannic acid)[2]**
Mercia Mudstone	0.3 – 0.7	1.9	-
Oxford Clay	3.6	12.3	9.2

[1] Tapwater
[2] Synthetic MSW leachate without tannic acid

Mecoprop is predicted to significantly exceed the EAL value at the base of the unsaturated zone in all scenarios with both clays (Table 7.6). However, for Mercia Mudstone (Figure 7.5) the time until Mecoprop reaches groundwater varies from 190 years (column K_d) to 510 years (batch K_d).

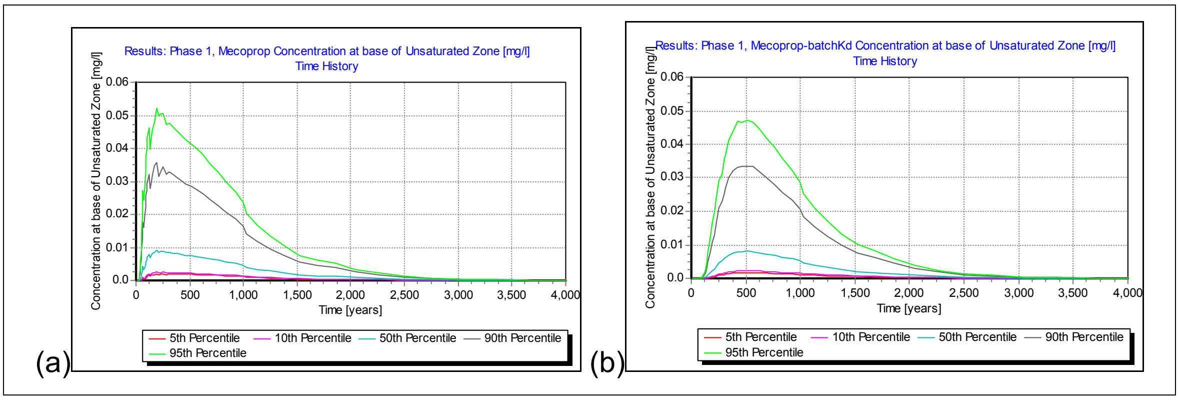


Figure 7.5 Mecoprop transport in Mercia Mudstone: (a) column K_d, (b) batch K_d

For Oxford Clay, Figure 7.6 shows that the effect on the degree and timing of pollution from choosing the column K_d rather than the batch test (in tap water) is dramatic (column: 700 years; batch: 1,750 years). If dilution in groundwater beneath the site is allowed, LandSim predicts that Mecoprop is discernible at the site boundary in all scenarios except when the Oxford Clay batch K_d is applied; in this case, the predicted concentration of Mecoprop is below the minimum reporting value.

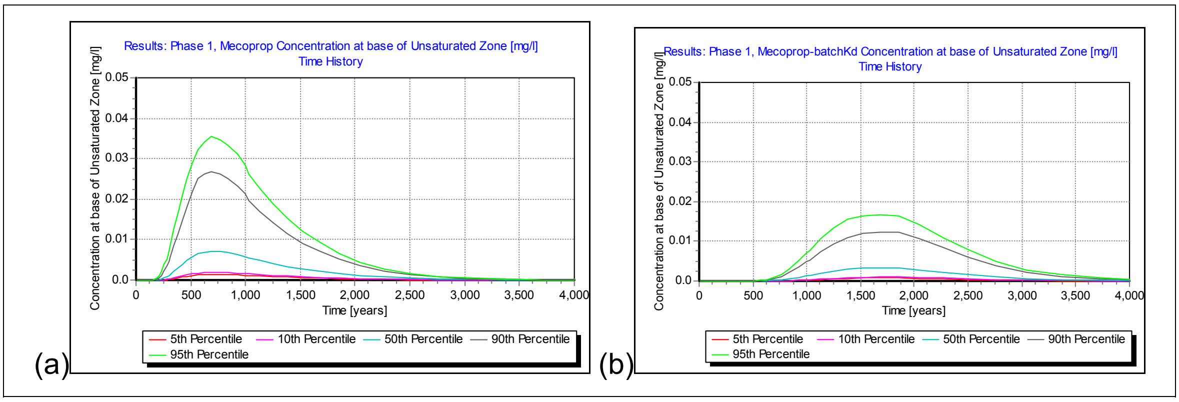


Figure 7.6 Mecoprop transport in Oxford Clay: (a) column K_d, (b) batch K_d

Since the column tests mimic the high solid/solution ratio found in a mineral landfill liner, the column K_d values are likely to be more reflective of reality; this highlights the need for caution when choosing appropriate retardation parameters.

Table 7.6 Mecoprop – batch versus column K_d

Clay	K_d	Base of UZ (µg/l)	Time (yrs)	Groundwater (µg/l)	Time (yrs)
Mercia Mudstone	Column	52	190	0.053	350
	Batch	47	510	0.048	600
Oxford Clay	Column	36	700	0.044	780
	Batch	16	1,750	0.031	1,900

7.5 LandSim modelling - conclusions

These LandSim simulations highlight the critical importance of sorption parameters being based on site-specific testing for groundwater risk assessments. The significant differences in contaminant sorption capacity shown by different clays should be taken into account to a greater extent, as this has a strong influence on the outcome of groundwater risk assessments. Many clay soils can be engineered to achieve a low hydraulic conductivity but not all are able to prevent leachate causing groundwater pollution. Caution must be used in applying K_d values derived from batch tests. The much higher solid/solution ratio found in the field (and reflected in column test K_d values) will lead to less retardation and hence shorter travel times. The difference between batch and column test K_d values is likely to be more important for liner materials with a high sorption capacity such as the London and Oxford Clays than for less reactive materials like the Mercia Mudstone. Careful selection of reactive clays to construct mineral liners should provide greater confidence that engineering measures will protect the environment in the short, medium and long term.

8 Conclusions and recommendations

This project has carried out a series of laboratory experiments to investigate the attenuation of List I substances typically found in UK landfill leachates (Mecoprop, naphthalene, toluene, trichlorobenzene and trichloroethene) by common mineral liner materials (London Clay, Mercia Mudstone, Oxford Clay). Sorption and desorption were measured in batch and column tests. Biodegradation was assessed under anaerobic conditions since these are expected beneath landfills. The majority of experiments were carried out using synthetic leachates based on municipal solid waste (MSW) and MSW incinerator residues, whilst additional biodegradation tests used leachate collected from a landfill that received hazardous and non-hazardous waste.

8.1 Summary of key findings

8.1.1 Sorption

- Sorption of the volatile List I substances was found to increase with increasing hydrophobicity (TCE < toluene < naphthalene < TCB and with increasing f_{oc} of the clay liners (Mercia Mudstone< London Clay<Oxford Clay).
- For London Clay, the experimental K_{oc} values for toluene, naphthalene and TCB fall within the range of literature values, and the values calculated using empirical correlations based on the contaminant K_{ow} (Table 8.1).
- For Mercia Mudstone, the experimental K_{oc} values were lower than expected from literature and empirical estimates for all contaminants (Table 8.1).
- Experimental K_{oc} values for Oxford Clay were much higher (up to more than an order of magnitude) than literature and calculated values for naphthalene, toluene and TCB (Table 8.1). This is attributed to older kerogen components of the natural organic matter which is known to be highly sorptive. Further investigation of the nature of organic carbon in liner materials to elucidate the contaminant sorption mechanism and predict sorption values is recommended.
- These results confirm that relying on literature values or empirical correlations to estimate K_{oc} (and hence retardation) for predictive modelling may not give an accurate assessment of the risk of pollution. This project has shown that retardation may be over- or underestimated.

Table 8.1 Summary of K_{oc} values (experimental and literature)

Contaminant	**Log K_{oc} (ml/g) (literature)**	**Log K_{oc} (ml/g) (empirical)[1]**	**Log K_{oc} (ml/g) (this study)**		
			LC[2]	**MM[2]**	**OC[2]**
Naphthalene	2.7 – 3.9	2.3 – 3.0	-	1.8	4.6
Toluene	1.6 – 2.4	1.8 – 2.3	2.5	1.5	3.2
Trichlorobenzene	2.5 – 4.0	3.0 – 3.7	3.9	2.3	4.6
Trichloroethene	2.1 – 3.4	1.7 – 2.3	-	1.6	3.2

[1] Calculated from K_{ow}

[2] LC: London Clay; MM: Mercia Mudstone; OC: Oxford Clay

- The estimated K_d for Mecoprop on Mercia Mudstone determined from batch sorption tests was greater than reported in the literature for aquifer materials, but within the range of values for soils (Table 8.2).
- Sorption coefficients derived from batch tests for Mecoprop on London Clay and Oxford Clay were significantly greater than literature values for aquifers and soils (Table 8.2). The sorption mechanism of Mecoprop to the three clays could not be fully explained – a combination of factors including surface area, iron oxyhydroxide content and organic carbon content are believed to be important.
- Mecoprop sorption coefficients (K_d) estimated from column leaching tests were about three times lower than batch test values (Table 8.2). This is because the contaminants come into contact with less of the liner material, and so there is less opportunity for sorption by the reactive surface. K_d values derived from batch tests should thus be used with caution for risk assessment modelling.

Table 8.2 Summary of sorption data, K_d (ml/g)

Contaminant	Liner material	Literature[1]	Batch (MSW)[2]	Batch (water)[3]	Batch (MSW no tannic)[4]	Column (water)[5]
Mecoprop	London Clay	0 – 2.8[6] 0 – 0.4[7]	17.8	-	-	-
	Mercia Mudstone	0 – 2.8[6] 0 – 0.4[7]	1.2	1.9	-	0.3 – 0.7
	Oxford Clay	0 – 2.8[6] 0 – 0.4[7]	8.4	12.3	9.2	3.6
Naphthalene	London Clay	3 – 50	-[8]	-	-	-
	Mercia Mudstone	1.5 – 25	0.18	-	-	-
	Oxford Clay	28 – 456	1,900	-	2,300	-
Toluene	London Clay	0.2 – 1.6	1.7	-	-	-
	Mercia Mudstone	0.1 – 0.8	0.1	-	-	-
	Oxford Clay	2 – 15	94	-	-	-
Trichlorobenzene	London Clay	1.9 – 60	49.8	-	-	-
	Mercia Mudstone	0.9 – 30	0.6	-	0.7	-
	Oxford Clay	17 – 549	2,100	-	3,600	-
Trichloroethene	London Clay	0.4 – 8	-	-	-	-
	Mercia Mudstone	0.7 – 16	0.11	-	-	-
	Oxford Clay	7 – 148	82	-	-	-

[1] $K_d = K_{oc} \times f_{oc}$ (K_{oc} values from Table 8.1; f_{oc} from Table 2.1); [2] Synthetic MSW leachate (section 3.3.1); [3] Tap water (section 3.3.4); [4] Synthetic MSW leachate without tannic acid (section 3.3.4); [5] Column leaching tests with tap water (section 5.3); [6] Mecoprop sorption by soils; [7] Mecoprop sorption by aquifer materials (Environment Agency, 2004); [8] - : data not available.

- Tannic acid in the synthetic leachate and organic matter in real leachate sorbs to clays, and may form soluble complexes with contaminants. The presence of tannic acid in leachate decreased the sorption of TCB and naphthalene by Oxford Clay. This may be due to the preferential sorption of tannic acid by the clay, blockage of sorption sites and/or the effect of high ionic strength solutions on the reactivity of clay minerals.

- Mecoprop sorption was greater in tap water than synthetic MSW leachate or MSW leachate without tannic acid (Table 8.2).

8.1.2 Desorption

- Sorption of Mecoprop, naphthalene and TCE was reversible on all clays.
- A small fraction of the toluene and TCB sorbed by London Clay and Oxford Clay was irreversibly bound to the liner material.

8.1.3 Biodegradation

- No evidence of biodegradation of Mecoprop was found in any of the tests. This is in agreement with the literature which reports little or no biodegradation of this compound under anaerobic conditions
- In synthetic leachate tests (A), no biodegradation of HOCs (naphthalene, toluene, TCB or TCE) was found over a period of eight months, although there was an active bacterial population producing biogas.
- In real leachate tests (B) containing a bacterial population known to biodegrade tetracholoroethene, biodegradation of TCE, toluene and TCB was observed in tests lasting 14 months. TCE decreased to less than one per cent of initial concentrations after a lag period of 40 days, with an estimated half-life of four to six days. Toluene was degraded with an estimated half-life of 12 days in the presence of Oxford Clay after a lag period of 72 days. Common biodegradation products of TCB were identified in these tests at low concentrations but degradation rates could not be determined.
- When seed from the real leachate tests (B) was added to the synthetic leachate tests (A), biodegradation of TCE was observed. TCE dechlorination occurred at a slower rate than in test B, with a half-life of 50 days following a lag period of 46 days. Biodegradation of Mecoprop, naphthalene, toluene and TCB was not observed.
- The results suggest that biodegradation of certain List I substances is possible under anaerobic conditions such as might be found in a landfill liner environment. However, the characteristics and activity of the bacterial community in the specific leachate are critically important in determining which contaminants are degraded. Further investigation of biodegradation of List I substances by real MSW leachates collected from different landfill sites is recommended. This would help predict the likelihood of biodegradation of List I contaminants at a particular landfill phase, and hence support the inclusion of biodegradation processes in groundwater risk assessments.

8.1.4 LandSim modelling

A series of LandSim models was run to compare the effect of retardation values selected from the literature with K_d values derived for the different clay liner materials during the experimental programme.

- In scenarios using literature K_d values, LandSim predicted groundwater pollution by all List I substances for liners constructed with London Clay and Mercia Mudstone.

- For the Oxford Clay liner, LandSim predicted an unacceptable discharge of Mecoprop, naphthalene and toluene but TCE and TCB did not cause pollution.
- For London Clay the use of experimental K_d values predicted that TCB would be prevented from reaching groundwater but Mecoprop and toluene remained discernible. However, the time for Mecoprop to reach the water table was 2,000 years compared to 370 years with literature K_d.
- All List I substances exceeded minimum reporting values for the Mercia Mudstone liner using experimental K_d values. VOCs were discharged more quickly and reached the water table at higher concentrations than with the literature values.
- LandSim predicted that only Mecoprop was discernible for the Oxford Clay liner using experimental K_d values, and the travel time increased from 350 years to 1,200 years.
- Simulations carried out using a short management control period (60 years) predicted greater and more rapid groundwater pollution.
- Simulation of Mecoprop transport using K_d values derived from batch and column tests demonstrated that batch tests overestimate the retardation likely to be observed in liners and the subsurface by at least a factor of three. This should be taken into account when using batch tests
- Significant differences in contaminant sorption capacity shown by different clays should be taken into account to a greater extent, as this has a strong influence on the outcome of groundwater risk assessments. Many clay soils can be engineered to achieve low hydraulic conductivity but not all are able to prevent leachate causing groundwater pollution. Careful selection of reactive clays to construct mineral liners should provide greater confidence that engineering measures will protect the environment in the short, medium and long term.

8.2 Recommendations for further research

- This research demonstrated that sorption is controlled not just by the quantity of organic carbon (OC) but also by its composition (such as a combination of organic matter (OM) source, age, and diagenetic alteration history). For clays, such as Oxford Clay, which contain kerogen or other diagenetically altered organic carbon, the sorption capacity may be significantly under-predicted by published sorption correlations. A recently awarded Engineering and Physical Sciences Research Council (EPSRC) grant *Dissolved and solid phase organic carbon influences on the sorption/desorption of hydrophobic organic contaminants in clay barriers* (EP/G016305/1, Southampton University) will determine the fundamental mechanisms by which the composition of solid phase OM can affect sorption/desorption of HOCs, with the ultimate goal of guiding further refinement of contaminant transport and fate predictive models for clays and clay liners.
- The study on sorption of Mecoprop by the three clays found that sorption coefficients were greater than literature values for soils and sediments, especially for London Clay and Oxford Clay, but the sorption mechanism could not be explained. Further work is required to understand the sorption mechanism of Mecoprop to clay liner materials.

- The study carried out to assess the effect of DOC on sorption of HOCs and Mecoprop demonstrated that tannic acid in the synthetic leachate and organic matter in real leachate sorbs to clays. In addition, the presence of tannic acid in synthetic leachate decreased the sorption of TCB and naphthalene by Oxford Clay. Further work is required to characterise the types of DOC in real leachates in terms of aromaticity, surface charge, functional groups and molecular size, particularly with reference to post Landfill Directive leachates. This will be the subject of a grant application to EPSRC (*Contaminant transport in clay barriers – influences of mobile sorbent nanoparticles*). The capacity and mechanism for sorption of DOC by clays needs to be determined to boost our understanding of the effect of DOC on sorption and transport of polar and non-polar organic contaminants.
- Simulation of Mecoprop transport using K_d values derived from batch and column tests showed that batch tests overestimate the retardation likely to be observed in liners and the subsurface by at least a factor of three. Further work is required to estimate K_d values from column tests for a range of polar and non-polar organic contaminants found in leachate. The relationship between batch and column tests should be further investigated to improve the method for estimating K_d values for landfill operators. The use of the quasi-steady centrifuge (QSC) as a rapid method for elucidating HOC sorption processes in low hydraulic conductivity saturated clay materials is being investigated by Southampton University (EP/G016305/1).
- Results from the biodegradation tests suggest that biodegradation of organic contaminants in leachate can take place as long as the appropriate microbial community is present. Further work should be carried out to characterise the microbial communities found in leachates and understand the conditions required for removal of contaminants. This is particularly important with regard to Mecoprop since evidence suggests that sorption does not prevent (only retards) its transport through clay liners. Anaerobic biodegradation of other phenoxyalkanoic acid herbicides (2,4-D and 2,4,5 T) has been observed (Gibson and Suflita, 1990; Mikesell and Boyd, 1985) and some degree of mineralisation of Mecoprop has been reported in laboratory microcosms under methanogenic conditions (Larsen and Armand, 2001; Larsen *et al.*, 2001). This has not been observed in landfills but may occur and should be further investigated.
- While biodegradation rates are commonly available for aerobic environments, and for soils and sediments under anaerobic conditions, there remains a lack of data for landfill environments, in particular for clay liners, and further work is needed to determine biodegradation rates for a range of contaminants found in leachates.

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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
GCMS	Gas chromatography-mass spectroscopy
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
PTFE	Polytetrafluoroethylene
PCE	tetrachloroethene
SPE	solid phase extraction
TCE	Trichloroethene
TCB	1,2,4 Trichlorobenzene
TOC	Total organic carbon
VOC	Volatile organic contaminant
VC	Vinyl chloride
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 (the 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 (µg^{1-n} ml^{n}/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, µg/g)
R	Retardation coefficient
SSA	Specific surface area (m^2/kg)

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incident hotline **0800 80 70 60** (24hrs)
floodline **0845 988 1188**

* Approximate call costs: 8p plus 6p per minute (standard landline).
Please note charges will vary across telephone providers

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