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Contaminant fluxes from hydraulic containment landfills - a review

Science Report SC0310/SR

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Professor Mike Depledge Head of Science

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EXECUTIVE SUMMARY

Hydraulic containment is the practice of operating a landfill with a lower leachate level than the external groundwater head. The hydraulic gradient into the landfill therefore causes groundwater to enter the landfill, and prevents advective movement of leachate, and therefore contaminants, from the waste into groundwater. However, there remains potential for contaminants to diffuse out of the landfill, especially since the advective velocities permitted through low permeability liners are low. In 2001 it was estimated that there were between 40 and 50 such landfills in the UK.

This report has been written to contribute to the understanding of the significance of contaminant diffusion across landfill liners, particularly liners in sites operated using hydraulic containment. It is not a design manual for hydraulic containment landfills and does not advocate the construction of such sites. The report, and accompanying spreadsheet tool, may be used to aid decision-making for landfill risk assessments within the framework set out in the Environment Agency's guidance on *Hydrogeological Risk Assessments for Landfills*.

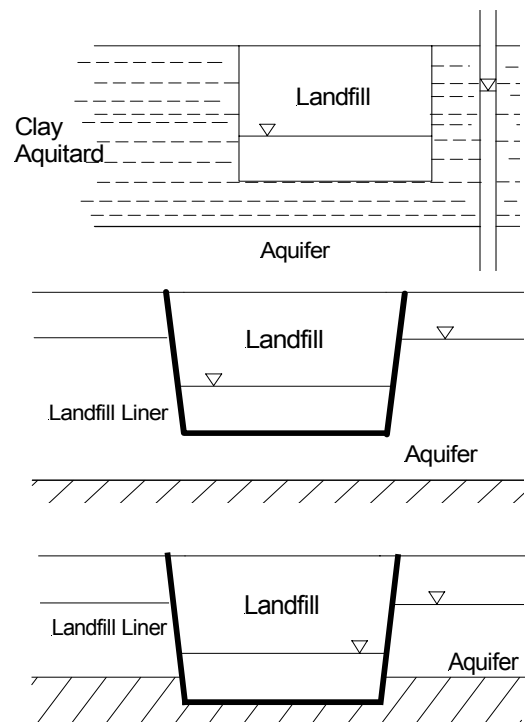
The report contains a literature review relating to diffusion across mineral liners and other low permeability materials used in landfill basal and sidewall liners and artificially established geological barriers. A collation of indicative values of key parameters for the hydrogeological risk assessment of hydraulic containment landfills is provided. These values are intended to be illustrative of the ranges that such parameters might take rather than a comprehensive list, and are not intended as a database of acceptable values for any specific risk assessment since values obtained from detailed site-specific or laboratory investigation will always be preferred for UK hydrogeological risk assessments.

A spreadsheet tool has been developed to help assess the impact on groundwater of landfills operated under hydraulic containment. It computes diffusive fluxes from hydraulic containment landfills for the following three scenarios. Landfills corresponding to these scenarios may not be compliant with the Landfill Regulations, but it should be noted that these scenarios have been created to allow the spreadsheet tool to support the assessment of existing, as well as new landfill cells.

Scenario 1: A landfill without an artificial sealing liner, but which has been excavated in a low permeability clay stratum above a confined aquifer. This can also be used as a conservative approximation to simulate a new landfill site with an artificially constructed clay liner and *in situ* geological barrier by consideration of each component alone.

Scenario 2: A landfill with an artificially formed geological barrier and artificial sealing liner (e.g. geomembrane composite, compacted clay or geosynthetic clay liner) constructed wholly within a permeable formation.

Scenario 3: A landfill with an artificially formed geological barrier and artificial sealing liner (e.g. geomembrane composite, compacted clay, geosynthetic clay liner) constructed in a permeable formation but with a low permeability base.



The literature review firstly discusses the various types of landfill lining system that have been used in UK hydraulic containment landfills, particularly issues regarding delamination of composite liners under such conditions. Diffusion and other solute transport processes that occur in porous media are described with particular reference to their role in solute transport within low permeability mineral (e.g. clay) barriers. Solute transport through composite liners is also discussed, including transport through defects and intact geomembrane.

The spreadsheet model is a scoping tool that computes diffusive contaminant fluxes from hydraulic containment landfills, and their concentrations in groundwater (or pore water at the outer edge of the liner for List I substances). It is pre-configured to use landfill geometries that comply with the three scenarios described above. Diffusion, dispersion, retardation and decay processes can be modelled where appropriate.

A user manual has been compiled that explains how to use the spreadsheet model, and how to interpret the results. Two key aspects of the performance of hydraulically contained landfills are predicted by the spreadsheet for typical parameters. These are summarised below:

- In landfills with mineral liners a balance is struck between the water flux into the landfill and contaminant concentrations outside the landfills. As the hydraulic conductivity of the liner is decreased, the water flux decreases, but so does the inward velocity. Hence, for a given effective diffusivity, solutes can more readily diffuse through clay liners with the lowest hydraulic conductivities since the advective flux of water into the site is decreased. Conversely, as the hydraulic conductivity of the liner increases, increased advective flux will lead to greater volumes of leachate being generated.
- Organic contaminants relatively readily diffuse through polymer geomembrane liners. Advective flow within a zone of influence beneath defects can limit the concentration at the base of the mineral liner. However, beneath intact geomembrane away from the defects, pore water is immobile and the contaminant diffuses through the mineral liner. Therefore, given appropriate transport properties, organic compounds can diffuse through a composite liner with a defect-free geomembrane more readily than through one with many defects.

The results of the literature review and spreadsheet calculations confirm that diffusion can cause significant flux of contaminants out of landfill sites, even against an inward advective flow of groundwater. Hydraulic containment landfills therefore have the potential to cause pollution if they are not designed, constructed and operated in an appropriate manner.

1 INTRODUCTION

1.1 Background

Recent legislation (Groundwater Regulations 1998, Pollution Prevention and Control Regulations 2000 (PPC), Landfill Regulations 2002 and the Water Framework Directive) requires that groundwater is protected from polluting substances. As such, applications for permits to operate landfills are required to be accompanied by an assessment of the risks to groundwater from the installation – it is assumed that the reader is familiar with the guidance on *Hydrogeological Risk Assessments for Landfills* (Environment Agency, 2003d). Whilst advective transport through landfill liners is now routinely assessed during the preparation of hydrogeological risk assessments for landfill PPC permits, quantitative assessment of contaminant flux due to diffusion is rarely undertaken. This may be of particular importance in sub-water table landfills which are operated on the principle of hydraulic containment.

The basic conceptual model of a hydraulically contained landfill is illustrated in Figure 1.

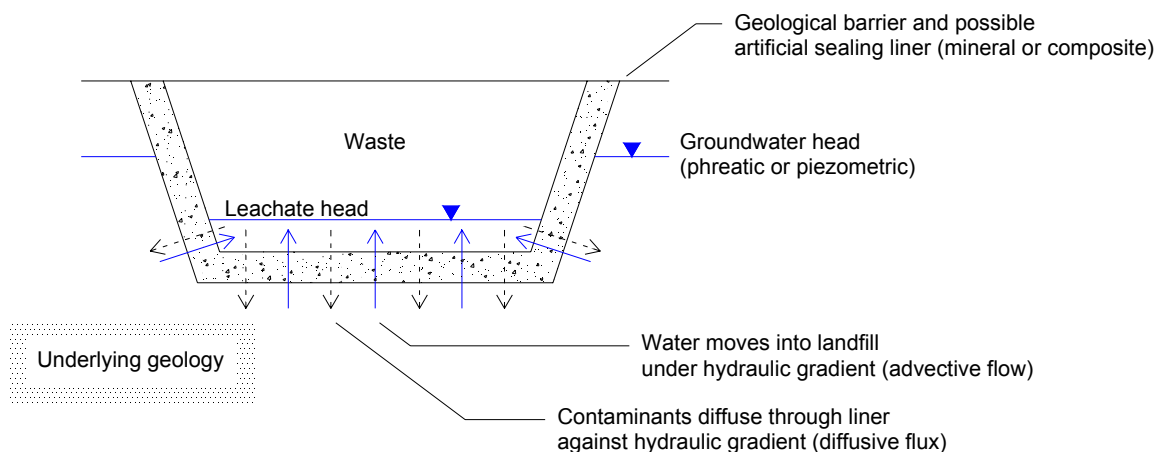


Figure 1. Basic conceptual model of a hydraulically contained landfill

Hydraulic containment is the practice of operating a landfill with a lower leachate level than the external groundwater head¹. There is therefore a hydraulic gradient into the landfill that causes groundwater to enter the landfill and prevents outward advective movement of leachate and contaminants from the waste into the groundwater. However, there remains potential for contaminants to diffuse out of the landfill, especially since the advective velocities permitted through low permeability liners are low. In a sub-water table landfill the groundwater is in contact with the landfill and therefore to comply with the Groundwater Directive there must be no discernible release of List I substances (e.g. chlorinated organics, certain heavy metals) beyond the geological barrier. In the absence of an unsaturated zone that may allow attenuation of contaminants, the landfill liner design (including any artificially established geological barrier) is critical for protection of the environment. The Groundwater Directive also states that any discharge of List II substances should be controlled to prevent pollution of groundwater. A List II substance of particular concern in many UK risk assessments is ammonium because of its high concentration in leachate relative to its drinking water standard and its relatively high mobility in many groundwater environments (Environment Agency, 2003b).

The Environment Agency has therefore identified a need to understand the significance of contaminant diffusion across landfill liners better, particularly liners in sites operated using

¹ Hydraulic containment includes situations where either the groundwater level or the piezometric head (e.g. where the landfill is constructed in low permeability strata overlying a confined aquifer) is above the leachate head.

hydraulic containment. This report has been written to contribute to that understanding and contains a literature review relating to diffusion across mineral liners and other low permeability materials used in landfill basal liners (Section 2). Because of a lack of information on diffusion under conditions of hydraulic containment, the literature review is not specific to that topic. A collation of indicative values of key parameters for the hydrogeological risk assessment of hydraulic containment landfills is provided. These values are intended to be illustrative of the ranges that such parameters might take rather than a comprehensive list, and are not intended as a database of acceptable values for any specific risk assessment since values obtained from detailed site-specific or laboratory investigation will always be preferred for UK hydrogeological risk assessments.(Section 3). A spreadsheet tool has been developed that computes diffusive fluxes from hydraulic containment landfills for the following three scenarios (Section 4). It should be noted that these scenarios have been created to allow assessment of existing, as well as new landfill cells.

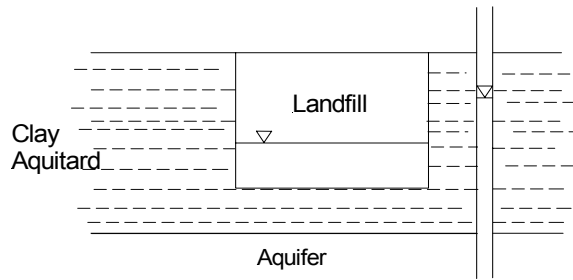
- A landfill without an artificial sealing liner, but which has been excavated in a low permeability clay stratum above a confined aquifer, (Scenario 1). This can also be used as a conservative approximation to simulate a new landfill site with an artificially constructed clay liner and *in situ* geological barrier by consideration of each component alone.
- A landfill with an artificially formed geological barrier and artificial sealing liner (e.g. geomembrane composite, compacted clay or geosynthetic clay liner) constructed wholly within a permeable formation, (Scenario 2).
- A landfill with an artificially formed geological barrier and artificial sealing liner (e.g. geomembrane composite, compacted clay, geosynthetic clay liner) constructed in a permeable formation but with a low permeability base, (Scenario 3).

Reference should be made to the Agency's current guidance (e.g. RGN6: Environment Agency, 2003a; Hydrogeological Risk Assessments for Landfills: Environment Agency, 2003d) to ensure designs are compliant with the Landfill Regulations (see Section 1.3). It is unlikely that a compacted clay or GCL liner would be appropriate for scenarios 2 and 3 as the sole component of the artificial sealing liner.

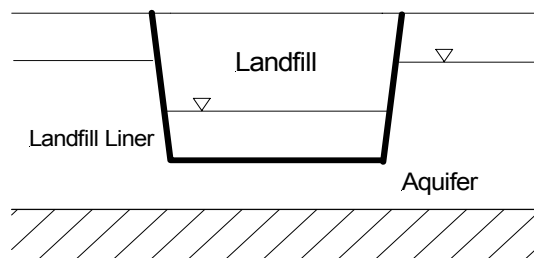
This report is not a design manual for hydraulic containment landfills and makes no recommendations for policy in relation to current or future sites. It considers generic hydrogeological settings and designs that are relevant to many of the UK's existing sub-water table landfill sites and assumes that the landfills are constructed with adequate means to manage leachate heads (e.g. drainage media, pumps, etc.). Experience shows that control of groundwater levels during construction of sub-water table landfills is critical with most failures being due to loss of such control.

The spreadsheet has not been designed to calculate Trigger and Control Levels in PPC Permit Applications. The spreadsheet will predict the compliance of the site with respect to the Groundwater Regulations, however the location of monitoring boreholes and the value of Trigger and Control Levels should be decided based on the specific design and setting of such boreholes.

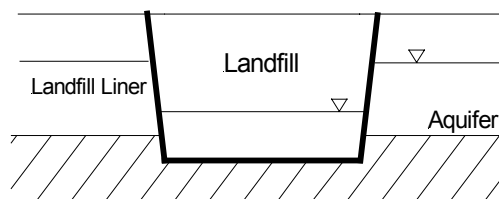
The report, and accompanying spreadsheet, may be used to aid decision-making for landfill risk assessments within the framework set out in the Environment Agency's guidance on *Hydrogeological Risk Assessments for Landfills* (Environment Agency, 2003d). As with other modelling tools, the development of a robust conceptual model is essential before any predictive calculations can be undertaken. This report considers those aspects of the hydrogeological risk assessment that are specific to hydraulic containment landfills, and other regulatory requirements relating to landfill construction, design and operation must also be addressed.



Scenario 1: A landfill without an artificial sealing liner, but which has been excavated in a low permeability clay stratum above a confined aquifer. This can also be used as a conservative approximation to simulate a new landfill site with an artificially constructed clay liner and *in situ* geological barrier by consideration of each component alone. This can be done by simulating the geological barrier alone (ignoring the mineral liner), and then comparing these results with a separate simulation of the mineral liner (assume the low permeability stratum does not exist). Alternatively, if the artificial clay liner is constructed from the same source as the *in situ* geological barrier, it may be appropriate to consider both layers together by assigning a composite value for the hydraulic conductivity.



Scenario 2: A landfill with an artificially formed geological barrier and artificial sealing liner (e.g. geomembrane composite, compacted clay or geosynthetic clay liner) constructed wholly within a permeable formation.



Scenario 3: A landfill with an artificially formed geological barrier and artificial sealing liner (e.g. geomembrane composite, compacted clay, geosynthetic clay liner) constructed in a permeable formation but with a low permeability base. This scenario only considers the case where leachate levels are above the base of the aquifer. The pathways through the base of the landfill and then laterally back to the aquifer are neglected as less significant. If the leachate levels are maintained below the base of the aquifer in this setting, the system will afford better protection of the aquifer. If judged to be necessary, these reduced risks might be modelled using Scenario 1 to represent a pathway through the low permeability basal material back to the aquifer by an appropriate choice of effective thickness and area of the low permeability basal material comprising the pathway.

Figure 2. Typical hydrogeological settings for hydraulically contained landfills

1.2 Hydraulic containment in the UK

Crozier *et al.* (2001) performed a survey of existing hydraulically contained landfills in the UK. It was estimated, at that time, that there were between 40 and 50 such landfills in the UK, mostly in southern and eastern England, some of which had been operating since the late 1970s. Most were constructed in low permeability formations, but there were some sites within sand and gravel aquifers and at least one in the Sherwood Sandstone. Engineered containment systems varied from non-existent, to engineered clay, to composite liners of geomembrane underlain by clay or bentonite enriched sand. Leachate levels were typically no more than 10 m below the local groundwater head (or potentiometric level) but at five sites the difference in levels was greater than 10 m. It was found that the average amount of groundwater ingress was between 20 and 50 m³/day.

1.3 Regulatory position

With regard to the construction of future landfills, the current Environment Agency position is laid out in the *Policy and Practice for the Protection of Groundwater* (Environment Agency, 1998) and Landfill Directive Regulatory Guidance Note 3 [RGN3] (Environment Agency, 2002b); RGN3 states:

“The Agency will object to any proposed landfill site in groundwater Source Protection Zone I.

For all other proposed landfill site locations, a risk assessment must be conducted based on the nature and quantity of the wastes, and the natural setting and properties of the location. Where this risk assessment demonstrates that active long-term site management is essential to prevent long-term groundwater pollution, the Agency will object to sites:

- *below the water table in any strata where the groundwater provides an important contribution to river flow or other sensitive surface waters;*
- *on or in a Major Aquifer;*
- *within Source Protection Zones II or III.”*

RGN3 details how this position should be applied, and should be referred to for further information.

If a sub-water table landfill is being considered that needs active long-term management to prevent long-term groundwater pollution, RGN 3 (Environment Agency, 2002b) requires that it should not be constructed in any strata where the groundwater provides an important contribution to river flow or other sensitive surface waters. This is a consideration including the maintenance of the quantity of baseflow to surface water receptors as well as the water quality. The term ‘water table’ is used, but RGN 3 (Environment Agency, 2002b) states that this is a general term that is taken to include the piezometric head of an underlying aquifer where there is sufficient connectivity to allow free-flowing water to enter the landfill void. Consideration should therefore also be given to whether or not these underlying aquifers provide baseflow to sensitive surface waters.

Landfill Regulatory Guidance Note 6 (Environment Agency, 2003a) details the engineering requirements to comply with the Landfill Regulations, and states:

“There is a fundamental requirement for a geological barrier in all instances, and also a bottom liner (artificial sealing liner) wherever leachate needs to be collected. This cannot be altered by the outcome of a risk assessment. Both of these elements are always required wherever there is a need to collect leachate. It should always be borne in mind that containment engineering for the purposes of groundwater protection cannot be undertaken in isolation from gas management. As well as the interaction between the necessary containment barriers, leachate management can directly impact upon gas management. What may be acceptable for groundwater protection may not be acceptable for landfill gas management.”

With respect to geological barriers and artificial sealing liners, RGN6 continues:

“The geological barrier must provide sufficient attenuation to prevent a potential risk to soil and groundwater...In hazardous and non-hazardous landfills an artificial sealing liner is required in addition to the geological barrier. The purpose of the artificial sealing liner is to control leachate leakage from the site and enable its collection, ensuring leachate accumulation at the base of the landfill is kept to a minimum. The main property required of this element is therefore low permeability. This requirement for an artificial sealing liner would therefore be met by a liner system such as a geomembrane or dense asphaltic concrete (DAC). There may, however, be site specific circumstances (for instance in some non-aquifers) that would allow other sealing systems that, in combination with the leachate collection system, could ensure the necessary leachate removal. These systems could use liner components such as some geosynthetic clay liners; bentonite enriched soil or artificially established compacted clay.”

RGN6 (Environment Agency, 2003a) specifically addresses sub-water table landfilling in Section 11:

“The requirement in Schedule 2, paragraph 2 [of the Landfill Regulations] to prevent groundwater from entering into the landfilled waste will be interpreted by the Agency in a risk-based manner. Groundwater must be prevented from entering the landfill as far as is necessary to ensure that there is no unacceptable risk to the stability or effectiveness of engineering controls (e.g. the lining and leachate collection systems), other environmental protection measures and the environment. What constitutes acceptable risk must be determined on a site-specific basis through risk assessments that satisfy the requirements of the Groundwater Regulations and explicitly address:

- *the geotechnical stability of the lining system, wastes and underlying geological strata;*
- *the efficacy of the leachate collection system (e.g. drainage layer, pipework, pumps and abstraction chambers);*
- *the effectiveness of any groundwater control systems (e.g. drainage layers, pumps, abstraction points);*
- *the ability to maintain operational and management control of the leachate and groundwater regimes in the long term (i.e. until the licence or permit may be surrendered);*
- *the ability to effectively collect landfill gas and control the migration of landfill gas.”*

The Landfill Regulations (Schedule 2, paragraph 6) require:

“that leachate accumulation at the base of the landfill is kept to a minimum”.

This is an important consideration for the design and operation of hydraulically contained landfill sites. The Landfill Regulations and associated Agency guidance (e.g. Environment Agency, 2003d) therefore allow some flexibility in the design of the liners and the geological barrier providing it can be demonstrated by risk assessment that there is no risk of unacceptable discharges over the entire lifecycle of the landfill (RGN6: Environment Agency, 2003a).

Clearly there are many UK landfill sites already constructed below the water table for which this report (and accompanying spreadsheet) will be useful in hydrogeological risk assessments, and it may be used to assess potential future landfills in certain low sensitivity locations such as clay pits and other poorly permeable strata. It has been argued that landfills operated by hydraulic containment provide excellent protection to the environment (Leeds-Harrison & Youngs, 2001). However, these arguments appear to be based on relatively little scientific evidence regarding contaminant transport, tend to focus on the hydraulics of the situation, and do not consider the sustainability of long-term active management.

1.4 Literature Search Strategy

There has been a considerable amount of literature published on water and contaminant movement through landfill liners; however, much has been repetition of previous work under site-specific conditions. The literature review therefore concentrated on identifying all publications that referred to these processes under hydraulic containment conditions (of which there are few)

and identifying key publications that deal with the processes under normal (above water table) conditions. Specific emphasis was also given to UK landfills, but again, there was found to be little relevant literature.

A large proportion of the references cited were already in the collections of the authors and the Environment Agency project managers. Further literature searching was conducted by use of online commercial abstracting services and internet resources.

1.5 This Report

Following this introduction, the second section of this report presents a review of the literature related to water and contaminant movement across landfill mineral liners and other low permeability porous materials. This is followed by discussion of the diffusion processes involved in contaminant transport through clay barriers, geomembranes and composite liners.

The third section of this report provides a collation of indicative values of key parameters for the hydrogeological risk assessment of hydraulic containment landfills that are referred to in the report. These values are intended to be illustrative of the ranges that such parameters might take rather than a comprehensive list, and are not intended as a database of acceptable values for any specific risk assessment since values obtained from detailed site-specific or laboratory investigation will always be preferred for UK hydrogeological risk assessments.

The fourth section presents the equations and assumptions that are used in the spreadsheet that accompanies this report. The software is intended as a scoping tool.

The series of papers by Giroud and others on calculation of water flux through defects in geomembranes is reviewed in Appendix A.

Appendix B presents the development and verification of numerical solutions that compute concentration profiles and contaminant fluxes through liner systems.

Appendix C lists the organisations who were consulted during the development of this report, and the accompanying spreadsheet.

The spreadsheet tool and accompanying User Manual (*Contaminant fluxes from hydraulic containment landfills spreadsheet v1.0: User Manual*) are published separately but have the same reference as the main report (*SC0310/SR*).

All units in the equations presented in this report are strictly SI units for consistency. In the discussion, units that are typically presented in non-SI units in hydrogeological reports are presented as such, for example aqueous concentrations in mg.l^{-1} and molarity in mol.l^{-1} . For consistency all hydraulic conductivities are presented as m.s^{-1} including those of high permeability formations that might normally be reported as m.day^{-1} .

2 PROCESSES IN LANDFILL BARRIERS

2.1 Introduction

Landfills that operate on the principle of hydraulic containment have been constructed, by definition, beneath the water table (Figures 1 and 2 show a number of scenarios). Leachate is extracted from the landfill body so that the leachate head is lower than the local groundwater level (or piezometric head) and the hydraulic gradient is therefore inwards. Hydraulic containment also requires the base of the landfill and the level of leachate to be at an elevation such that seasonal fluctuations in the water table outside do not affect the inward hydraulic gradient (Crozier *et al.*, 2001). It is conventional wisdom that, under these circumstances, the outward diffusive flux of solutes can be reduced to negligible levels if the inward advective flow exceeds a certain value.

Many studies at both field and laboratory scale have shown that diffusion is the dominant transport property in low permeability materials (King *et al.*, 1993; Johnson *et al.*, 1989). For example, Sawatsky *et al.* (1997) report that diffusion is the dominant form of dispersion (i.e. it is more important than hydraulic dispersion) at velocities of about 10^{-9} m.s⁻¹ and becomes the dominant form of mass transport at velocities of 10^{-11} m.s⁻¹ (i.e. it is more important than advection and hydraulic dispersion). These are typical velocities for well-engineered clay barriers.

To illustrate the importance of landfill liner design, Rowe (1994) explored the importance of diffusion against the advective velocity in the clay liner of a hypothetical hydraulically contained landfill. For chloride (independent of concentration) to have negligible flux through a 1 m thick liner, it was calculated that the inward Darcy velocity² should exceed 1.6×10^{-9} m.s⁻¹. If, therefore, such a liner has a hydraulic conductivity of 10^{-9} m.s⁻¹, the leachate head should be maintained at more than 1.6 m beneath the local groundwater head to prevent egress of solute. However, a less permeable clay barrier would require a greater excess head outside the landfill to prevent egress of solute – perhaps exceeding the common range of head differences in current UK landfills (for example, using Rowe's calculations, a hydraulic conductivity of 10^{-10} m.s⁻¹ requires a 16 m head difference).

Similar issues are considered by Devlin and Parker (1996) in the context of designing cut-off walls for hydraulic containment. They similarly concluded that for a 1 m thick cut-off wall the hydraulic conductivity should be in the range 10^{-10} to 10^{-8} m.s⁻¹ for optimal performance. Higher hydraulic conductivities may lead to very significant volumes of water being pumped to maintain hydraulic containment, whilst lower hydraulic conductivities lead to large drawdowns being required to prevent diffusive outward fluxes of contaminants which may lead to potential stability problems. As in Rowe (1994) these are reasonably low permeabilities but certainly not the lowest attainable.

There is relatively little literature concerning solute migration out of hydraulically contained landfills and in general it is not reported at the same level of sophistication as that for conventional landfills. Al-Naimi and Rushton (1977) showed that the advection-dispersion equation is equally solvable for advective velocities into the landfill as it is for velocities out of the landfill. However, modern landfill liners rarely consist of just a single low permeability porous barrier and the equations describing solute movement under hydraulic containment therefore need updating.

² The Darcy 'velocity' (or 'specific discharge') is defined as the flux (quantity) of groundwater flow per unit cross-sectional area in the plane perpendicular to the direction of flow.

This report concentrates on the processes that occur in low permeability landfill liners irrespective of the direction of advective flow. Applicability of the processes and equations to the particular situation of hydraulically-contained landfills is discussed in Section 2.7.

In the following sections the processes relevant to contaminant transport in landfill barriers are discussed and the equations used to represent these processes are presented. They also present key solutions to these equations for simple choices of boundary conditions to help illustrate the processes. For real hydraulically contained landfill systems, the applicable boundary conditions are more complex. The spreadsheet model presented in Section 4 uses solutions developed with specific boundary conditions chosen to give conservative results for List I and List II substances migrating out of a number of particular landfill scenarios. These particular solutions are presented in Appendix B and the boundary conditions are discussed in Section 4.3.3.

2.2 Landfill Barrier Systems

Whilst the Landfill Regulations prescribe certain minimum engineering requirements, the process of hydraulic containment does not in itself strictly require the presence of a low permeability liner to operate, only a sufficient inward advective velocity. However, in addition to the regulatory requirement for an artificial sealing liner when leachate needs to be collected, and a geological barrier, a low permeability liner would generally be installed for three main reasons (Crozier *et al.*, 2001):

- When constructing a landfill beneath the water table, dewatering is often required to gain access. The landfill therefore starts life above an artificially depressed water table and physical containment is required to protect against initial escape of leachate. Ineffective groundwater control during this stage is the most common cause of liner failures (e.g. instability, delamination).
- Low permeability liners reduce groundwater inflow to the landfill and therefore the amount of leachate that requires abstraction, treatment and disposal. Large inflows could also impact on the local water resources.
- Hydraulic containment requires active abstraction of leachate to maintain the inward flows and if this were to fail, physical containment would be required until hydraulic containment could be restored.

However, engineering of liners to a very low permeability could result in a greater contaminant flux out of the landfill by diffusion than would occur through a less impermeable liner. This is because there will be practical limits to the differences that can be achieved between the leachate head and groundwater head, and therefore the inward advective flux will be lower. Furthermore large head differences may cause instability in the liner system, particularly since the leachate head must be minimised to comply with the Landfill Regulations. The design and operation of hydraulic containment landfills to ensure environmental protection is consequently different from that typical at above-water table sites.

The following sections discuss the different broad types of lining systems available for modern landfill engineering that comply with the requirements of the Landfill Regulations. Although dense asphaltic concrete (DAC) can be considered as a lining system for a hydraulically-contained landfill, the material has not been considered in this report because there is greater uncertainty regarding solute movement through it at this time.

2.2.1 Compacted Clay Liners (CCLs)

The environmental protection for many of the older landfills in the UK comprises a single layer of compacted clay. In situations where an existing landfill has been constructed in moderately low

permeability formations, often only the base of the landfill is lined and the walls are unlined. Their composition ranges from reworked local clay materials to bentonite enriched soil (BES) typically equivalent to a thickness of one metre with a hydraulic conductivity not exceeding $1 \times 10^{-9} \text{ m.s}^{-1}$. If they have appropriate qualities, locally-derived clay materials may be used for CCLs and, depending on the quality of the source, may require significant reworking before the hydraulic conductivity standard is met (Clark and Davies, 1996).

Degradation of compacted clay liners may occur by desiccation before and/or after emplacement of waste. Before emplacement the primary desiccation mechanism is direct evaporation of the pore water to the atmosphere. Covering the CCL with a polymer geomembrane can promote solar heating of the liner: temperatures of 60-70°C are not unusual in the summer (Rowe, 1998). After emplacement, desiccation can occur if the CCL is above the water table but can also be caused by reaction with leachates (Spooner and Guisti, 1999), or by heating due to the exothermic reactions that occur as putrescible waste degrades (Allen, 2001). Furthermore, inadequately installed clay liners can deform, which can increase the hydraulic conductivity of intact clay or compromise containment completely if fissuring occurs (Arch *et al.*, 1996). Conversely, the hydraulic performance of CCLs can improve as a result of consolidation and densification under the weight of waste.

Use of hydraulic containment at a landfill that is lined with a CCL lends the advantage that the clay is permanently saturated. It is therefore less likely to suffer from post-emplacement desiccation, which can be a problem in conventional landfill (Crozier *et al.*, 2001), as discussed above. Care must, however, be taken during construction and early operation when groundwater levels are suppressed. Outward diffusion of contaminants coupled with inward advection of groundwater is likely to lead to lower ionic strength solution permeating the liner than in an above-water table landfill, and so the hydraulic conductivities are likely to be less affected. Inward flux of groundwater will also likely reduce temperatures (as groundwater will typically be, at 10-11°C, cooler than leachate) although it is noted that these effects may be marginal for very low permeability lining systems.

2.2.2 Geosynthetic Clay Liners

Geosynthetic clay liners (GCL) comprise a thin layer of sodium or calcium bentonite bonded to a layer or layers of geotextile and have often been used as a component in landfill lining systems. Currently they have seldom been used in the UK without either a geomembrane or a CCL (although the CCL may be thinner than if it were the sole liner). Some GCLs are supplied with a bonded polymer geomembrane.

The hydraulic performance of geosynthetic clay liners is dependent on the following factors associated with their manufacture, and the *in-situ* conditions (Petrov *et al.*, 1997; Rowe, 1998; Bouazza, 2002).

- Hydraulic conductivity and thickness of the bentonite used in manufacture.
- The technique(s) used to bond the bentonite to the geotextile.
- Presence of a geotextile filter to prevent loss of bentonite.
- Presence and quality of any bonded geomembrane.
- Installation quality:
 - distribution of bentonite;
 - quality of seams;
 - absence of wrinkles or punctures;
 - initial hydration conditions;
- Applied confining stress.
- Leachate or groundwater chemistry.

The hydraulic conductivity of typical GCLs with typical applied stresses, to distilled water or potable groundwater, varies between 2×10^{-12} and $2 \times 10^{-10} \text{ m.s}^{-1}$ (Bouazza, 2002). However, hydraulic conductivity to leachate tends to be significantly increased and values of 10^{-9} to 10^{-8} m.s^{-1} are observed with high ionic strength permeant solutions (Rowe, 1998). In a hydraulically contained landfill, outward diffusion of contaminants coupled with inward advection of groundwater is likely to lead to lower ionic strength solution permeating the liner than in an above-water table landfill, and so the lower range of hydraulic conductivities are likely to be applicable.

GCLs are susceptible to accidental punctures during handling and installation, which may compromise their hydraulic performance. However, they are to some extent self-healing, as bentonite swells on hydration (by up to 700%) into the void space created and generally only a minor increase in hydraulic conductivity can be expected (Bouazza, 2002). Rowe (1998) reports that a GCL punctured with 25 mm diameter holes repaired itself with a minor increase in hydraulic conductivity. With 75 mm diameter holes the holes did not repair and hydraulic containment was compromised. Self-healing can also be impeded if there is simultaneous ion exchange (Lin and Benson, 2000; Mazzieri and Pasqualini, 2000), as is likely with typical landfill leachates. Other local defects in GCLs can be caused by flow of hydrated bentonite away from stress points, or by the presence of wrinkles in an overlying geomembrane. High hydraulic gradients across GCLs are also known to induce internal erosion of the finest clay particles and the creation of local pipes through the material (Stam, 2000); there is also the potential for separation (delamination) of the GCL from the underlying substrate and from adjacent GCL sheets (see also Section 2.2.3).

Giroud *et al.* (1997c) presented a system of comparison tests that may be used to compare the performance of GCLs with CCLs. In general, CCLs perform much better than GCLs under high imposed leachate heads but, under low heads, they are approximately equivalent (depending on the construction of each). Solute travel times through CCLs are also significantly greater. Although there are benefits in using GCLs in engineering terms, in aquifer protection terms (i.e. minimisation of solute flux and delay of breakthrough) an ordinary GCL is generally considered to be inferior to a CCL (Bouazza, 2002).

2.2.3 Composite Liners for Hydraulically Contained Landfills

Composite Liners

Geomembrane liners are used as barriers in landfills to either contain leachate (and gas) or to impede the flow of groundwater into the landfill in hydraulic containment. Geomembranes lining the base and sides of landfills are usually made from high density polyethylene (HDPE). The geomembrane should be used in conjunction with a mineral liner such as compacted clay or BES; in hydraulic containment landfills, the 'mineral liner' may act as the 'geological barrier'. The hydraulic conductivity of HDPE is very low and an intact geomembrane can be thought of as impermeable to water or leachate (Foose *et al.*, 2002). Water therefore only moves through a geomembrane via the holes, tears and other defects that geomembranes inevitably accumulate over time (Environment Agency, 2004b).

Combined geomembrane and mineral liners are referred to as composite liners and their performance as a barrier to contaminant transport can be very effective. The performance of such a composite liner can be orders of magnitude better than that of either component by itself.

Composite liners have only been in use for approximately 30 years (although in the UK they have only been in use for around 15 years) and their long-term stability as hydraulic barriers is untested (Allen, 2001). This has been considered (Environment Agency, 2004b) and a time-variant defect generation rate has been implemented in the latest release of LandSim (version 2.5 – Environment Agency, 2003c). Development of stress cracks and oxidation of the polymer

is expected to continue for hundreds or thousands of years after closure of the landfill. Organic solvents have been detected in groundwater flowing beneath composite lined landfill sites (Edil, 2003) so some, at least, clearly leak to some degree even over their short lifetimes so far.

Potential Problems with Composite Liners and Hydraulic Containment³

Whilst composite liners can provide very effective barriers between the waste and the groundwater environment they may raise some specific issues in relation to the hydraulic containment setting (Richard Thomas, *pers. comm.*, 2004). A particular concern is the potential for separation of the geomembrane from the underlying mineral liner – *delamination* – which may increase the contaminant flux out of the site.

When waste has been placed, a considerable confining pressure is provided by the vertical load from the engineering of the cell, the leachate head, landfilled waste, and the capping system, including restoration soils.

The distribution of the vertical confining pressure applied to the geomembrane will normally be very uniform because it is transmitted through the lower layers of waste, and then through any granular leachate collection/protection layer. This distributes the load very evenly to the geomembrane. In such sites therefore, intimate contact will always be maintained between the geomembrane and the mineral element of the lining system. For a well constructed and operated hydraulic containment site, the risks of delamination would be small. The following subsections identify scenarios that might give rise to delamination, but these should not arise at sites operated with good practice.

Large scale delamination

For hydraulically contained landfill sites, the internal confining stresses maintaining good contact between the membrane and the mineral layer will rely on the overburden of waste and engineering material, with internal leachate heads being exceeded by external groundwater heads. This is inherently less stable than above water table landfill designs. If the external head exceeds the internal confining stress then large scale delamination and failure of the integrity of the lining system may occur.

Such large scale failure of the composite lining system might occur if groundwater control fails prior to filling of the cell with waste or if groundwater heads are allowed to rise too early during filling. In particular, the confining stresses against steep wall sections of the lining system may be significantly less than the confining stresses over the base and careful design and construction will be needed to ensure that the confining stresses against any steep wall composite lining systems exceed external hydraulic pressures for the full range of possible groundwater heads. Consideration needs to be given to possible future variation and trends in groundwater heads when specifying the operational parameters for groundwater and leachate management.

This is particularly relevant to scenario 2 (e.g. sand and gravel pits) and underlines the Agency's caution over permitting such sites. Furthermore, the introduction of a geomembrane can create a slippage plane and therefore cause stability problems. Whilst such failures are very unlikely for well designed sites with a robust stability risk assessment, it is a particular concern for the Agency due to the potential severity of the consequence of such failure and the difficulty of remediation in such cases.

³ The authors are very grateful to Richard Thomas, Technical Director of Enviros Consultants, Shrewsbury, for helpful contributions for this review of engineering issues for hydraulic containment using composite liners.

Small scale delamination

A liner emplaced with poor construction quality assurance (CQA) or onto a difficult geometry may develop wrinkles. Clearly a wrinkle will have poor contact with the clay material and will also be under stress during burial.

One possible but unlikely scenario which would allow only very localised delamination to occur is the case of a rigid open box being landfilled, face down immediately above the granular leachate collection / liner protection layer. Neither white goods nor robust open metal box-like waste items are normally landfilled. Such items would be recycled or at least crushed and, in any event, the careful monitoring and selection of waste in the first one or two layers should prevent this occurrence. Nevertheless, this 'open box' case is discussed further.

Even for the case of the "inverted robust open box", resisting forces would apply to the hydrostatic pressure beneath the geomembrane. The forces resisting deformation are the tensile strength of the geomembrane, the tensile strength of any geotextile protection layer present, the confining and arching effect of the granular layer (around 0.5 m thick) and the confining effect of any established leachate layer in the base of the landfill. It is becoming more common to include a geotextile separation layer above the granular leachate collection /protection layer. The tensile strength of such a separation layer would also contribute to the resisting forces.

Nevertheless, if there were significant external excess head there would be delamination within the footprint of the open box. Outside of that footprint, the geomembrane would remain confined, as described above. In practical terms, it is likely that the maximum footprint of the open box would be of the order of 1 m². This risk is normally represented in modelling by one of these two scenarios.

- The first approach is to allow for local areas of delamination by representing the membrane as being in poor contact with the underlying mineral layer. This generally has a relatively small impact on the risk.
- Of greater significance would be delamination as described in the previous paragraph followed by tearing of the geomembrane due to strain or it being pushed against a sharp object. The clamping effect of the box is likely to reduce strain on any delaminated area of membrane beneath such an 'open box' making this risk less likely than the previous scenario. A conservative worst case could account for this scenario by including the possibility of a tear with dimensions consistent with the possible length scale of the any conceivable 'open box'.

2.3 Diffusion and Solute Transport in Porous Media

In most hydrogeological environments, bulk movement of water and solutes is predominantly by advection. Water moves according to Darcy's Law and, notwithstanding attenuation processes, the entrained (dissolved) solute moves with the water. Hydraulic conductivity, K (m.s⁻¹), is the constant of proportionality that relates the water flux with the hydraulic gradient (head gradient). However in fine-grained porous materials such as compacted clays used for landfill barriers the hydraulic conductivity is extremely low and when coupled with low hydraulic gradients, the flux of contaminants due to diffusion will exceed that due to advection.

2.3.1 Diffusive Flux and Material Properties

Solutes move from regions of higher concentration toward regions with less concentration by the process known as molecular diffusion. The rate of diffusion is proportional to the concentration⁴

⁴ Diffusion should strictly be calculated according to activity gradients since differences in the chemical potential are the driving force for diffusion, rather than concentration (a numerical measure of solute quantity). For a complete

gradient and is governed by Fick's first law, adapted for use in porous media. In one dimension this is:

$$J_D = -nD_e \frac{\partial C}{\partial x} \quad (1)$$

where J_D is the diffusive flux ($\text{kg}\cdot\text{m}^{-2}\cdot\text{s}^{-1}$)
 n is the porosity of the material (dimensionless)
 D_e is the effective diffusion coefficient ($\text{m}^2\cdot\text{s}^{-1}$)
 C is concentration ($\text{kg}\cdot\text{m}^{-3}$)
 x is distance (m)

The minus sign in Equation 1 indicates that migration is from areas of higher concentration to lesser concentration.

2.3.2 Diffusion Coefficient

Diffusion coefficients in free aqueous solution are well known (e.g. Li and Gregory, 1974) so it is convenient to express the effective diffusion coefficient using these values. The effective diffusion coefficient, D_e , is related to the diffusion coefficient in free aqueous solution D_w ($\text{m}^2\cdot\text{s}^{-1}$) by:

$$D_e = \frac{D_w}{\tau} \quad (2)$$

where τ is the tortuosity (dimensionless)
 D_w is the free water diffusion coefficient ($\text{m}^2\cdot\text{s}^{-1}$)

There are several different definitions of the tortuosity coefficient in the literature. All of the definitions in this document are internally consistent but the reader is encouraged to take care when collating relationships from several sources. Note also that literature values of the diffusion coefficient may be presented as a free water diffusion coefficient, effective diffusion coefficient or intrinsic diffusion coefficient (nD_e) and again, care should be taken to ensure the correct interpretation of literature values of these parameters are used.

Section 3.1 presents a list of free water diffusion coefficients for substances that may be useful in landfill risk assessments. In general, smaller molecules and those with less charge (therefore smaller hydration shells) have higher values. As can be seen, D_w is not very sensitive to the chemical species.

Because of their increased size (relative to inorganic ions such as Cl^-), organic molecules have lower free water diffusion coefficients (Kim *et al.*, 2001). Where chemical-specific data are unavailable, free water diffusion coefficients of organic molecules can be estimated using empirical relationships based on the size of the molecules. Johnson *et al.* (1989) propose from empirical data that the diffusion coefficient of an organic molecule can be estimated from the known diffusion coefficient of another using the following relationship:

$$\frac{D_{w1}}{D_{w2}} = \left(\frac{MW_2 \rho_1}{MW_1 \rho_2} \right)^{0.6} \quad (3)$$

explanation, see Appelo and Postma (1993). Many diffusion parameters have, however, been calculated using concentration gradients so there will be no loss of accuracy in using concentrations.

where D_{w1} and D_{w2} are the free diffusion coefficients of the molecules
 MW_1 and MW_2 are the molecular weights of the molecules ($\text{kg}\cdot\text{mol}^{-1}$)
 ρ_1 and ρ_2 are the densities of the compounds at their boiling points (these are generally not known and substitution of the densities at standard temperature introduces an error of approximately 10%).

The free water diffusion coefficient of dissolved species varies significantly with temperature and values measured at 25°C are approximately twice those measured at 5°C (Fetter, 1999; Langmuir, 1997). This may be significant for conventional landfills as temperatures at the base sometimes reach 30 to 50°C (Rowe, 1998); this can lead to faster diffusion through the liner. In a landfill that is hydraulically contained the cooling effect of contact with groundwater at ~11°C may ameliorate this effect.

2.3.3 Tortuosity

Tortuosity, τ , is a measure of the geometry of the flow path followed by water molecules in a porous medium (Figure 3) and is also related to the clay microstructure and the amount of external water in the clay microstructure. According to its simplest definition it is the ratio of the actual length of the path followed by a water molecule in a porous material to the direct straight line distance travelled (i.e. $\tau = x'/x$). At any scale greater than pore-scale it is always greater than one. Measured or estimated values of tortuosity are presented in Section 3. The factor n/τ is sometimes referred to as the effective porosity (e.g. Foged and Baumann, 1999).

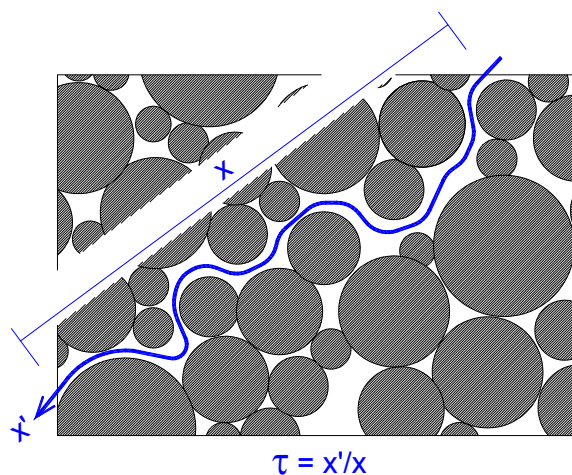


Figure 3. Illustration of tortuosity in a porous medium

Neither τ or D_e can currently be measured independently (Foged and Baumann, 1999) but a combined value can be experimentally calculated. Furthermore the porosity of clay materials measured by standard methods may not relate to the porous volume through which solute transport actually occurs (see “Porosity” below). There are also few current specified laboratory standards for the determination of D_e but the techniques of Rowe *et al.* (2000) may be used for GCLs, or Barbour *et al.* (1996) for unsaturated soils or clay materials.

Rowe (1998) presents effective diffusion coefficients of chloride in three GCLs under effective stresses between 20 and 350 KPa. The effective diffusion coefficients (and therefore tortuosity, assuming J_D uses the total porosity in Equation 1) decrease approximately linearly with effective stress (Figure 4).

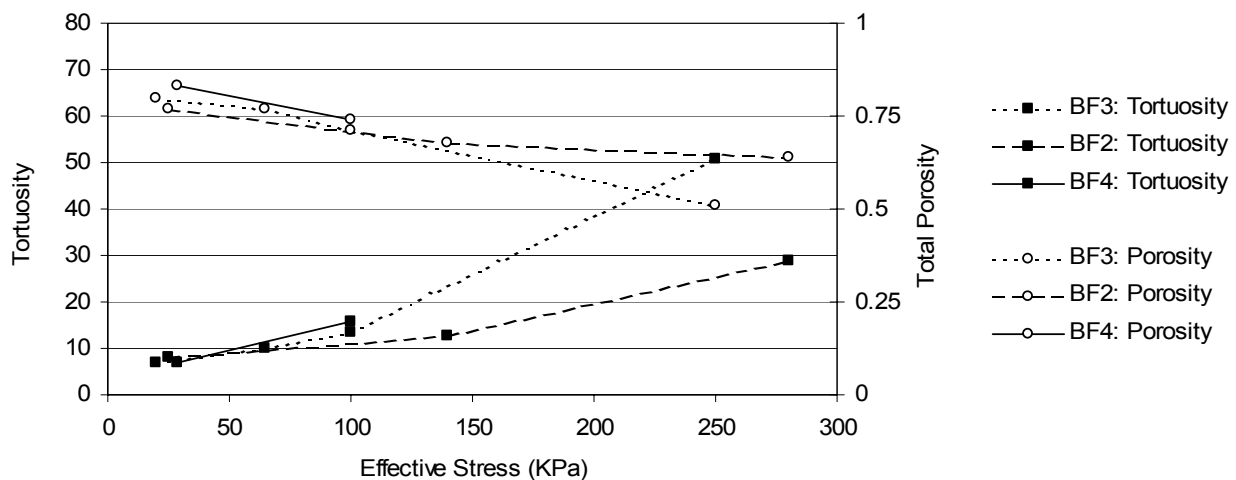


Figure 4. Tortuosity and total porosity variation with effective stress on three GCL samples (BF3, BF2 & BF4): after Rowe (1998)

This document uses the definition of tortuosity of Fetter (1999) and Domenico and Schwartz (1998) shown in Figure 3. In some texts tortuosity has a different definition, for example Bear (1972) uses $1/\tau$ for the tortuosity (but also names it τ) so it is always less than one, while in other texts, for example, Pearson (1999), $\sqrt{\tau}$ is referred to as tortuosity (again named τ).

2.3.4 Porosity

Pearson (1999) describes four types of porosity in a clay material, each referring to a subtly different space in a porous material within which a particular process occurs. In addition, two other types of porosity can be identified in a low permeability (clayey) rock as follows.

- Total porosity (n_{TOT}): the total void space within a dry porous medium.
- Water content porosity (n_{WAT}): this is the porosity measured conventionally by water saturation methods and the one most commonly used in risk assessments. Because in a clayey material its value depends on the drying conditions, $n_{WAT} \leq n_{TOT}$.
- Diffusion porosity (n_{DIFF}): the porosity within which diffusion occurs; this may be an anisotropic parameter as within a natural clayey formation diffusive fluxes can vary according to the flux direction relative to bedding. There may also be a distinction between the porosity available for diffusive transport (i.e. the area through which it occurs) and that available for diffusive mixing (i.e. the volume through which it occurs). However Pearson (1999) suggests that they are approximately equal for clayey materials. In general, for clayey materials $n_{DIFF} \leq n_{WAT} \leq n_{TOT}$.
- Advective transport porosity (n_{ADV}): the porosity through which water moves by advective flow. In clayey materials this may be significantly less than the total porosity as there will be isolated pores and static water at mineral surfaces. This is what is normally termed 'effective porosity' in hydrogeological studies and may be orders of magnitude smaller than the total porosity in a clayey material (Pearson, 1999), therefore $n_{ADV} \leq n_{DIFF} \leq n_{WAT} \leq n_{TOT}$.
- Drainage porosity (n_{DRAIN}): not listed in Pearson (1999), but this is also known as 'specific yield' or 'field capacity' in different branches of hydrogeology, is the porosity from which water can drain freely under gravity. In a clayey material this will be close to zero.

- Advective mixing porosity (n_{MIX}): also not listed in Pearson (1999), this porosity is that porosity within which mixing occurs and its size lies somewhere between advective porosity and the diffusion porosity. Its size depends on the pore water velocity, so that if the velocity is great, there is limited mixing of porewaters by diffusive exchange with the water in the diffusion porosity. When pore water velocities are slow, there is more opportunity for mixing of flowing water and pore water.

However, due to the complexity of measuring different types of porosity, and then using each individual value appropriately, only one type of porosity is normally used in a typical risk assessment. This may sometimes be taken as the total porosity, but should be an estimated effective porosity to try to better represent one of the transport porosities. The footnote for Equation 6 illustrates a typical example. In the same way as for tortuosity, total porosity varies with effective stress (Figure 4, and e.g. Rowe, 1998).

For the purposes of this report it is assumed that the porosity used is available for flow and diffusion and that it is a material property independent of the composition or temperature of the solute under consideration.

2.3.5 Transport Equations

For diffusive solute transport systems where the concentrations are changing with time, Fick's second law as applied to porous media can be used. In one dimension this is:

$$n \frac{\partial C}{\partial t} = nD_e \frac{\partial^2 C}{\partial x^2} \quad (4)$$

where t is elapsed time (s).

The solution to Equation 4 for the case where there is a constant concentration (C_0) boundary condition at $x = 0$, representing the source of solute for an infinite one-dimensional porous medium is given by (Domenico and Schwartz, 1998):

$$C(x, t) = C_0 \operatorname{erfc} \left(\frac{x}{2\sqrt{D_e t}} \right) \quad (5)$$

The function $\operatorname{erfc}()$ is the complimentary error function⁵ (Fetter, 1999). This means that the concentration breakthrough of the diffusing solute is described by a normal distribution.

Equation 4 describes only the passive spreading of solute by diffusion. In most hydrogeological environments there is an advective flux of water (and entrained solute) and diffusion is a dispersive process (Section 2.3.3 and Equation 9). The equation that describes both advection and dispersion is⁶:

$$n \frac{\partial C}{\partial t} = nD \frac{\partial^2 C}{\partial x^2} - nv \frac{\partial C}{\partial x} \quad (6)$$

⁵ The complimentary error function can be calculated using $\operatorname{erfc}(x) = 1 - \operatorname{erf}(x)$ where $\operatorname{erf}(x)$ is the error function. Note, however, that the error function in Microsoft Excel, $\operatorname{ERF}()$, is unreliable and often gives wrong values for arguments of interest. For contaminant transport calculations an independently-coded function should be used. Abramowitz and Stegun (1972) provide robust series expansions of the function.

⁶ The three values of porosity in this equation are usually assumed to be equal, however, they are strictly: mixing porosity, diffusive porosity and advective porosity in that order.

where v is the advective velocity of water through the system ($\text{m}\cdot\text{s}^{-1}$).

The parameter D in Equation 6 is no longer solely the effective diffusion coefficient, but is a combination of the effective diffusion coefficient and a mechanical dispersion coefficient (Section 2.3.6). However in clay materials it does approach the value of the effective diffusion coefficient since the advective velocity is low (Sawatsky *et al.*, 1997). An appropriate solution to the advection-dispersion equation for the infinite one-dimensional porous medium with a constant concentration at $x = 0$ is (Domenico and Schwartz, 1998):

$$C(x,t) = \frac{C_0}{2} \left(\operatorname{erfc} \left[\frac{x-vt}{2\sqrt{Dt}} \right] + \exp \left(\frac{vx}{D} \right) \operatorname{erfc} \left[\frac{x+vt}{2\sqrt{Dt}} \right] \right) \quad (7)$$

In the case of hydraulic containment, assuming that distance x is measured outward from the base of the landfill, then the velocity of water in the liner system is negative ($v < 0$). For positive x and negative v , Equation 7 calculates the concentration at a point outside of the landfill. Contaminants can only be transported to such a point through diffusive processes (Figure 1) and use of the usual representation of the dispersion coefficient will be inappropriate (see Section 2.3.6 below). Note that for real systems, the lining system does not extend to infinity and the diffusive flux will mix with natural groundwater at the edge of the lining system. Therefore use of the above solution (Equation 7) gives an overestimation of concentration at the edge of the lining system and so is an appropriate conservative approach for List I substances, but a different boundary condition should be used to consider the discharge of List II substances where the compliance point is in the groundwater at some distance from the liner. These solutions are developed in Appendix B and the choice of boundary condition used in the spreadsheet model is discussed in Section 4.3.3. Section 2 is limited to a discussion of the processes and equations used to represent the movement of contaminants and boundary conditions. Example solutions, widely reported in the literature, are given to help illustrate the consequence of these representations.

2.3.6 Hydrodynamic Dispersion

Mechanical dispersion is the process of solute spreading by mixing that occurs at the moving front of a solute plume. At the pore scale, this arises due to the following three causes (Bear, 1972; Fetter, 1999):

- fluid travels faster through the centre of pores than along the edges (due to friction effects at the edge),
- some fluid parcels travel around grains along longer flow paths than others,
- some pores are larger than others and there is less friction through them.

Mixing that occurs along the average direction of travel is termed longitudinal dispersion and in a one-dimensional representation, such as is often used for landfill liner systems, it is the only type of dispersion that is considered. For the sake of simplicity in this report, lateral dispersion, which may be important where CCLs have greater horizontal than vertical hydraulic conductivity, has been ignored. Mechanical dispersion is commonly taken to be proportional to porewater velocity (Bear, 1972) so that the coefficient of longitudinal mechanical dispersion, D_L ($\text{m}^2\cdot\text{s}^{-1}$) is given by the following:

$$D_L = \alpha_L v \quad (8)$$

where α_L is the dynamic longitudinal dispersivity, or dispersion length (m) and is characteristic of the porous medium at the scale of consideration.

However in groundwater environments, mechanical dispersion cannot be identified separately from diffusion as they have the same effects on solute concentrations. The two processes are combined to give the coefficient of hydrodynamic dispersion ('dispersion coefficient'):

$$D = \alpha_L v + \frac{D_w}{\tau} \tag{9}$$

It is this dispersion coefficient that is used in Equations 6 and 7. Figure 5 illustrates the relationship between the two contributions to the dispersion coefficient under typical groundwater velocities. At low velocities, diffusive flux will generally dominate the movement of solutes but at increasing velocities the dispersion term dominates. For example, in a number of column experiments Rowe *et al.* (1988) did not observe any mechanical dispersion at groundwater velocities around $3 \times 10^{-9} \text{ m.s}^{-1}$.

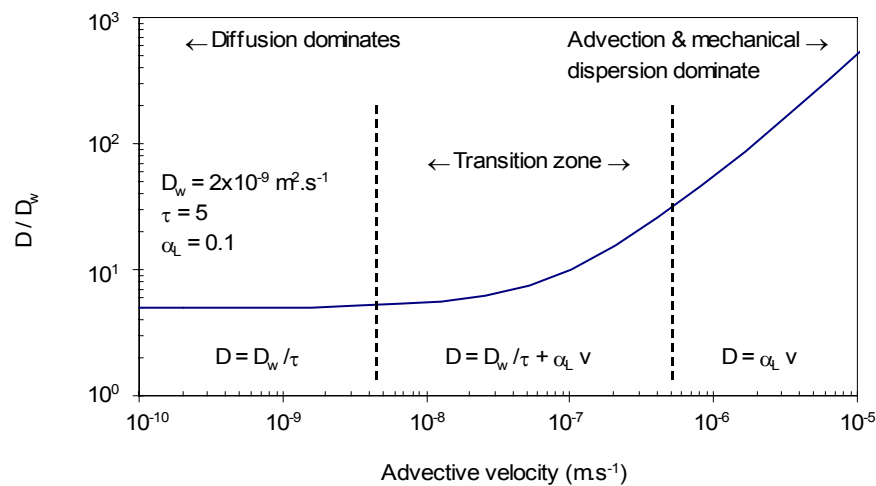


Figure 5. Dispersion coefficient as a function of groundwater velocity

The above discussion characterises the process of hydrodynamic dispersion for general problems of contaminant transport. The three bullet points identify the physical process of mixing and spreading that apply when there is advective transport through heterogeneous systems. The main contribution is often due to the different flow paths taken through the heterogeneous medium as contaminants are advected downstream.

The representation of this by a diffusive term in contaminant transport equations can lead to significant spreading of contaminants upstream, against the hydraulic gradient, at late times close to a constant source of contaminants. This is unrealistic, and an artefact of the representation of heterogeneous flow paths indirectly by the diffusion equation. Only the first of the mechanisms, operating at the pore scale, is likely to lead to spreading against the hydraulic gradient, and this is likely to be small. For this reason, only pore-scale dispersion is included in the calculations provided in the spreadsheet tool, and this mechanism is discussed in more detail in the next section.

2.3.7 Diffusion Against Advective Flow

The usual assignment of hydrodynamic dispersion is associated with spreading due to heterogeneous flow paths and often results in significant upstream spreading near a source which is artificial. One-dimensional solutions to the advection-dispersion equation (such as

Equation 7) assume that the velocity of advective solute movement would counteract the velocity of solute movement by diffusion.

At the scale of individual pores there is a variable velocity profile of advective flow across the pore (parabolic in shape if it is assumed that the pore boundaries are two parallel plates). This leads to fast transport of water in the centre of pores, but there is a slow-moving skin of water at the edges. Diffusion through this slow-moving water layer is not limited by the advective flow and therefore is faster than predicted by the one-dimensional advection-dispersion equation (Figure 6). Taylor (1953) shows that the magnitude of this diffusive flux, j_{Tay} ($\text{kg}\cdot\text{s}^{-1}$), through a single capillary tube is given by:

$$j_{Tay} = -\frac{\pi r^4 u_{max}^2}{192 \cdot D_w} \frac{\partial C}{\partial x} \quad (10)$$

where r is the radius of the tube (m)
 u_{max} is the velocity of water along the centre line of the tube ($\text{m}\cdot\text{s}^{-1}$)

Therefore the average mass flux within the open area of the pipe is:

$$\frac{j_{Tay}}{\pi r^2} = -\frac{r^2 u_{max}^2}{192 \cdot D_w} \frac{\partial C}{\partial x} \quad (11)$$

and the diffusive flux through a unit area of bundled capillary tubes with open area fraction, n (as a model of a porous medium) is given by:

$$J_{Tay} = -\frac{n r^2 u_{max}^2}{192 \cdot D_w} \frac{\partial C}{\partial x} \quad (12)$$

The solute is therefore being dispersed relative to the average water movement through such a capillary tube according to a relationship that obeys Fick's first law with diffusion coefficient, D_{Tay} :

$$D_{Tay} = \frac{n r^2 u_{max}^2}{192 \cdot D_w} \quad (13)$$

Assuming that the porous medium can be represented by a bundle of capillary tubes, this diffusive flux can therefore be summed with the other pore scale diffusion terms and substituted into a solution to the advection-diffusion equation (e.g. Equation 7) as:

$$D = \alpha_L v + \frac{1}{\tau} (D_w + D_{Tay}) \quad (14)$$

Values for r and u_{max} should be estimated as they cannot be measured or predicted directly. r in a porous medium will be approximately the average radius of a pore. Assuming that the velocity profile is parabolic, u_{max} is related to the advective velocity by the ratio, $u_{max} = 1.5v$.

Taylor dispersion is increasingly significant for larger pore radii where the variations in velocity are larger. In a hydraulic containment landfill liner, with larger pore radii, the inward advective fluxes ought also to provide additional protection. It is important therefore not to specify unrealistically large values for the pore radius that are inconsistent with very low barrier permeability values. If unfeasibly large values are chosen, then unrealistically conservative

results might follow from significant overestimation of the dispersive flux. The impact of charged clay surfaces on solute transport in clay liners should also be considered (see section 2.4).

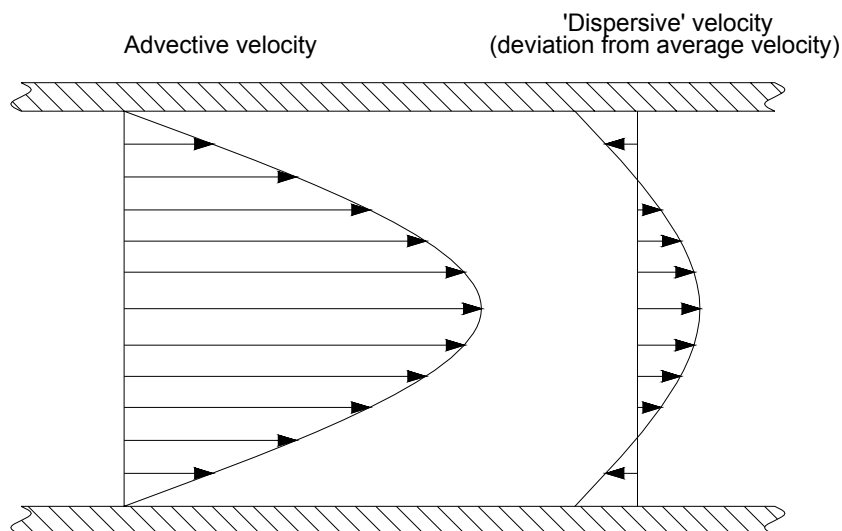


Figure 6. Schematic representation of advective (water) and diffusive (solute) velocities in a capillary tube.

2.4 Solute Transport Through Mineral Barriers

The following sub-sections describe specific physical and chemical processes that occur when leachate or groundwater moves through clayey porous materials. For the purposes of this section there are assumed to be no differences between the chemistry of compacted clay liners, bentonite enriched soil liners or geosynthetic clay liners, other than the clay mineral composition and thickness.

2.4.1 Clay Geochemistry

Clays are ubiquitous in modern landfill liners because of their very low hydraulic conductivity and relatively high capacity for sorption of leachate solutes. These result, in part, from the small sizes of clay particles; the standard geological description of clay applies to any particles smaller than 64 μm in size, but smectite grains tend to be between 0.01 μm and 1 μm in diameter (Brady and Weil, 2002).

Clay minerals comprise stacked layers of connected tetrahedra or octahedra of oxygen atoms or hydroxyls surrounding a central cation (Deer *et al.*, 1992). The central cation in the tetrahedra is usually silicon and in the octahedra aluminium, magnesium or other cations are present: the composition controls the type of clay mineral (Figure 7). The layers may be separated by relatively fixed or absorbed cations or by water molecules. The reactive (charged) nature of clay minerals originates from two sources:

- isomorphous substitution at formation of the clay mineral, e.g. Al^{3+} replacing Si^{4+} in the clay lattice – this creates permanent negative charge;
- broken bonds at the edge of particles where the clay lattice is incomplete, and hence the cation (e.g. Al^{3+}) charge is unsatisfied – this creates pH-dependent positive or negative charge.

The generic term 'clay mineral' incorporates a number of mineral groups with different stacking arrangements for the octahedral and tetrahedral layers. These include the mica group, kaolinite

group, illite group and the smectite group. Of these, the most important for landfill liners are the smectites, which include the minerals montmorillonite and beidellite (bentonite being a mixture of the two). The montmorillonite structure comprises layers of octahedra sandwiched between two tetrahedral layers. Between the bases of the tetrahedra is a void which water molecules or exchangeable cations can occupy – the interlayer space (Figure 7). Water molecules form hydration shells around the interlayer cations rather than forming discrete layers but it is convenient to think of them as forming layers. When magnesium or calcium occupy the interlayer space, two or three water layers separate the clay layers (Deer *et al.*, 1992). However, if sodium is the exchange cation, significantly more than three water layers can enter and swelling occurs (up to 700% of its original bulk volume). This is the origin of the extremely low hydraulic conductivity of sodium bentonite, especially following hydration after dry emplacement.

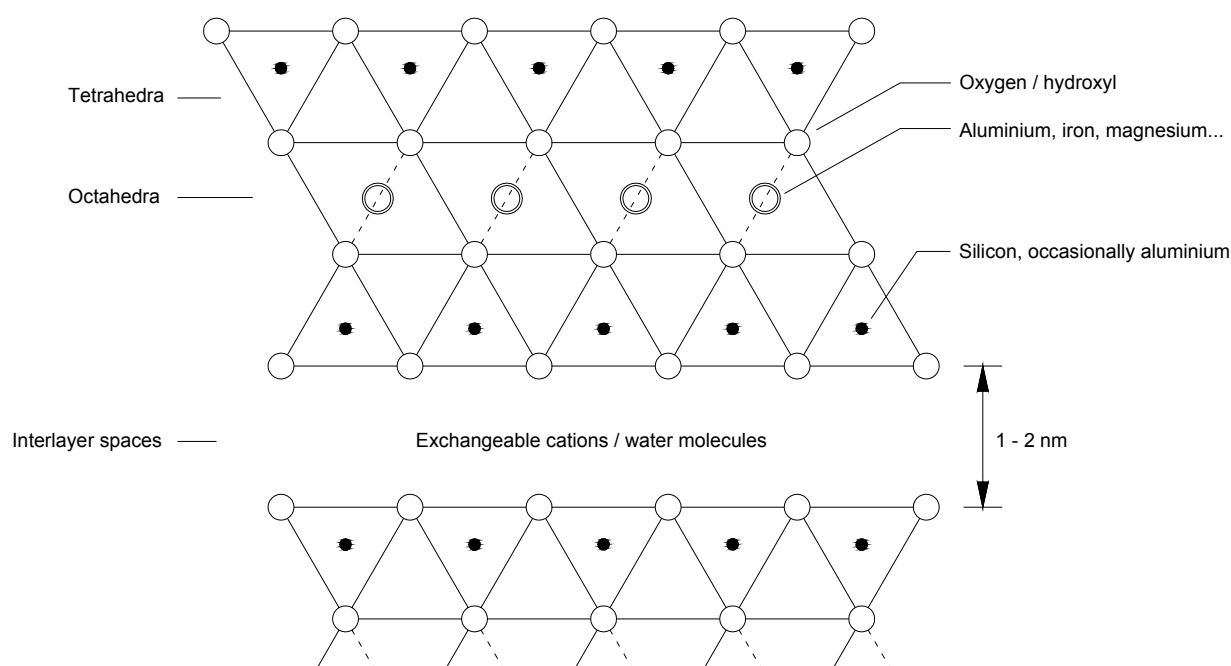


Figure 7. Diagrammatic representation of the structure of montmorillonite.

Because clay mineral grains, especially those of montmorillonite, are very small (often $<1 \mu\text{m}$), they have a high specific surface area. These therefore have a relatively large number of unsatisfied surface charge sites that are available for dissolved species in water to sorb onto. In solutions with pH greater than approximately pH 3, the surfaces of montmorillonite particles are predominantly negatively charged (Stumm, 1992). Protons and certain cations and anions can bond to the surface oxygens in a plane next to the surface (Figure 8). These specifically sorbing ions form inner-sphere complexes with the surface. Cation species that can form inner-sphere complexes include calcium, magnesium and the transition metals. At low pH some anions can also form inner-sphere complexes. Sodium retains a hydration sheath and is more loosely bonded by electrostatic attraction. It forms an outer-sphere complex and resides in a second layer outside the specifically sorbing ions. The surface charge will not be fully satisfied by the inner- and outer-sphere complexes, and so additional counter-ions are held in the diffuse double layer (e.g. Cl^- in Figure 8); within this diffuse layer, counter-ions will show decreasing attraction for the surface with increasing distance from it.

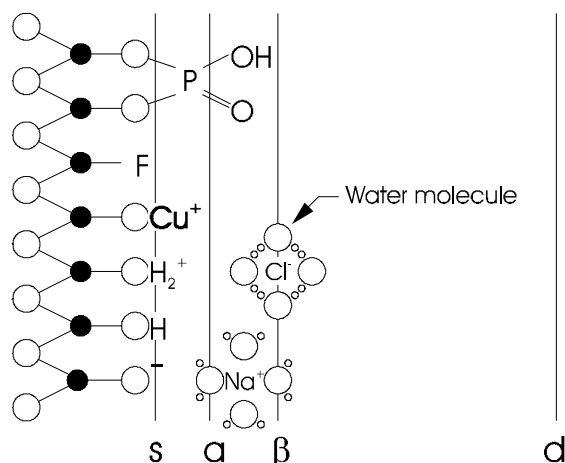


Figure 8. Schematic portrayal of a clay surface, showing planes associated with surface hydroxyl groups (s), inner-sphere complexes (α), outer-sphere complexes (β) and the diffuse counter ion cloud (d) (after Stumm 1992).

2.4.2 Reactions of Landfill Leachate with Mineral Barriers

Landfill leachate is, in general, a chemically aggressive liquid but its composition varies considerably over the lifetime of a landfill (DoE, 1995). Domestic waste normally degrades over three phases:

- Phase 1: Aerobic microbial decomposition uses up the oxygen in the waste and generates a significant amount of heat. A relatively short stage, typically less than a month.
- Phase 2: Bacterially-mediated anaerobic reactions degrade cellulose and other putrescible materials producing volatile fatty acids, alcohols and ammonium (compounds typical of 'acetogenic' leachate). This stage lasts from years to decades.
- Phase 3: More pH-sensitive and slower-growing methanogenic bacteria start to consume compounds in the acetogenic leachate, releasing a mixture of gases. A dynamic equilibrium is established between the acetogenic and methanogenic bacterial populations. The transition from Phase 2 to Phase 3 can take months or decades and the whole phase can take decades to centuries before the waste is completely degraded.

Table 1 presents summary statistics for the inorganic composition of leachates from landfills receiving primarily domestic wastes (DoE, 1995). It shows that landfill leachate is dominated by sodium and chloride ions but with considerable amounts of other components, especially the organic acids that contribute to the chemical oxygen demand (COD).

Table 1. Summary of the composition of leachates from landfills receiving primarily domestic wastes (after DoE, 1995).

Determinand	Median	Maximum	UK drinking water standard	Median as proportion of drinking water standard	Comments
pH (pH units)	7.1	8.0	-	-	Minimum pH 6.4
Conductivity ($\mu\text{S}\cdot\text{cm}^{-1}$)	7180	19 200	2500 ^a	2.87	
COD*	954	> 33 700	-	-	
BOD* (20 day)	360	> 4800	-	-	
TOC*	305	5690	-	-	
Ammoniacal N	453	1700	0.39 ^a	1160	
Calcium	155	1440	250 ^b	0.62	
Magnesium	125	470	50 ^b	2.5	
Sodium	688	3000	200 ^a	3.44	
Potassium	492	1480	12 ^b	41	
Chloride	1140	3410	250 ^a	4.56	
Sulphate	70	739	250 ^a	0.28	
Alkalinity (as CaCO_3)	3580	8840	-	-	
Phosphate	1.1	15.8	2.2 ^b	0.5	

Note: All concentrations in $\text{mg}\cdot\text{l}^{-1}$ except pH and conductivity.

* COD = Chemical oxygen demand, BOD = Biological oxygen demand, TOC = Total organic carbon

^a Water Supply (Water Quality) Regulations 2000 (SI 2000/3184) as amended

^b Water Supply (Water Quality) Regulations 1989 (SI 1989/1147) as amended

Significant interactions have often been observed between clay minerals and landfill leachate that cause increases in the hydraulic conductivity of the barrier (Spooner and Guisti, 1999). In some countries (e.g. Germany) there has been increasing demand for non-smectite clays such as illite and kaolinite because there are fewer concerns over their long-term stability, despite their hydraulic and attenuation properties being inferior to the smectites (Spooner and Guisti, 1999). Most commonly, such reactions are due to substitution of water or cations in the interlayer spaces of the clays. An excess of monovalent ions (Na^+ and K^+) causes swelling and excess divalent ions (Ca^{2+} and Mg^{2+}) causes contraction of the interlayer spacing (Langmuir, 1997). In general, increasing the ionic strength of the leachate leads to shrinkage of the interlayer spacing due to a decrease in the diffuse double layer (particularly for swelling clays) and may lead to tension cracking.

Although excess sodium would seem to encourage clay swelling, some studies have found that reactions with leachate can cause the smectite minerals to alter into illite, a poorly swelling clay mineral. This promotes agglomeration in the clay and was seen to reduce the hydraulic conductivity of the material by three orders of magnitude (Quigley *et al.*, 1988). Leachate can also be a very aggressive fluid and coupled with the high reactivity of bentonite, it can cause degradation or dissolution of the mineral. Spooner and Guisti (1999) undertook a wide-ranging review of leachate reactions within landfill mineral liners – primarily smectites. In a hydraulic containment landfill, however, the clay liner should not come into contact with much leachate, due to the ingress of groundwater, so the subject is not treated in depth in this report.

Although sodium bentonite swells as it absorbs water on installation, in calcium-rich groundwaters the sodium exchanges with calcium and the swelling reverses; this can cause a hydraulic conductivity rise of three to seven times over a few years (Egloffstein, 2001). This may be important in the long-term for hydraulic containment landfills, as it is groundwater that moves through the liner, not sodium-rich leachate.

2.4.3 Clay Barriers as Semi-Permeable Membranes

Exclusion of Charged and Uncharged Molecules From Pores

Clay materials are often sufficiently dense that the diffuse double layers of adjacent clay platelets overlap. The material is therefore able to permit the passage of water but impedes a solute. Restricted movement of inorganic charged solutes has been observed in clayey materials due to the electrostatic repulsion of anions by the negatively-charged clay mineral surfaces – named ‘Donnan exclusion’ or ‘negative adsorption’ (Keijzer, 2000). To maintain charge balance in the pore fluid cations are also blocked. In addition, cations are repelled by the predominantly positively charged, diffuse double layers of the clays.

The ionic strength of the pore water solution affects the amount of anion exclusion – the effect is stronger in solutions with low ionic strength as the electric fields associated with the charged surfaces extend further into the pores (Figure 9). In solutions with low ionic strengths (0.001 mol.l^{-1}) the effect reaches greater than 100 nm into the pores (Fetter, 1999). By comparison, pore throats of London Clay (predominantly illite) are slits with apertures of approximately 0.7 nm (Bourke *et al.*, 1988).

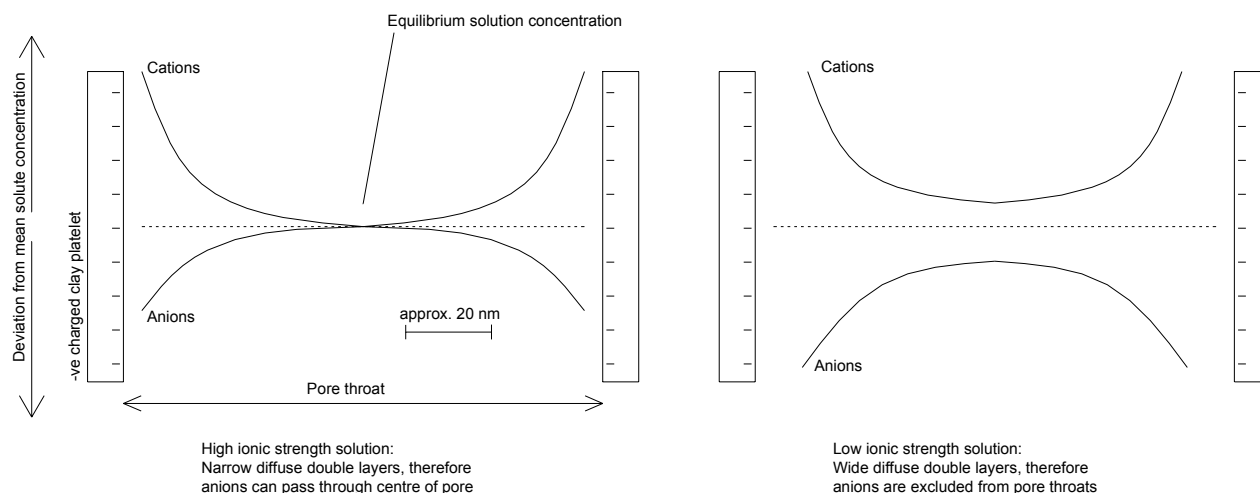


Figure 9. Origin of anion exclusion in clay materials

Uncharged species such as miscible organic compounds may be restricted from moving through clay soils due to the steric hindrance (or ‘hyperfiltration’) of molecules larger than the pore size (Malusis *et al.*, 2003). For example, Sawatsky *et al.* (1997) found that a proportion of naphthalene was excluded from the pores of a compacted weathered shale (primarily montmorillonite). Despite naphthalene having no detectable sorption on to the material, steady-state pore water concentrations were only 40% of the concentration applied to the outside of the test sample. The length of the carbon-carbon bond in benzene is 0.14 nm (Hawkins, 1981), so naphthalene should be just less than half a nanometre in size (Figure 10). This is comparable with the 0.7 nm average pore throat size of London Clay (Bourke *et al.*, 1988) and illustrates well why steric hindrance can be effective.

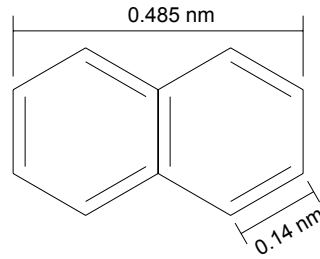


Figure 10. Approximate size of a naphthalene molecule

Both negative adsorption and hyperfiltration can be effectively modelled by adopting the effective porosity concept from hydrogeology in which only a fraction of the porosity is available for water movement, or in this case, for solute transport (Bourg *et al.*, 2003):

$$n_e \frac{\partial C}{\partial t} = n_e D_e \frac{\partial^2 C}{\partial x^2} \quad (15)$$

where n_e is an effective porosity ($n_e < n$) obtained empirically.

Advective solute fluxes can be scaled down in the same way. Alternatively, the effective diffusion coefficient can be scaled by a factor, χ , termed the 'constrictivity' which is always less than one (Pearson, 1999). However, since the amount of exclusion depends on the charge of an anion (for anion exclusion) or the size of a molecule (for steric hindrance) the effective porosity (or constrictivity) is species dependent.

Chemico-osmosis in Clay Liners

Osmotic movement of water can also play a significant part in retarding solute transport, as water will tend to move under an osmotic potential gradient from groundwater to leachate to try to balance the concentrations in each solution (Malusis *et al.*, 2003). The total liquid flux through a clay barrier (Figure 11), q , at steady-state includes a hydraulic liquid flux, q_h , in response to the difference in hydraulic head, and an osmotic liquid flux, q_π , in response to a difference in solute concentration (Malusis *et al.*, 2003), ($\text{m}^3 \cdot \text{s}^{-1}$) or:

$$q = q_h + q_\pi = -K \frac{\Delta h}{\Delta x} + \omega \frac{K}{g\rho_w} \frac{\Delta \pi}{\Delta x} \quad (16)$$

where K is the hydraulic conductivity of the clay barrier ($\text{m} \cdot \text{s}^{-1}$)
 Δh is the hydraulic head difference (m)
 Δx is the thickness of the liner (m)
 g is gravitational acceleration ($\text{m} \cdot \text{s}^{-2}$)
 ρ_w is the density of the solute ($\text{kg} \cdot \text{m}^{-3}$)
 ω is the osmotic efficiency coefficient of the liner (dimensionless)
 $\Delta \pi$ is the theoretical chemico-osmotic pressure ($\text{J} \cdot \text{m}^{-3}$)

ω varies from zero for a membrane with no solute restriction to unity, which represents a membrane that completely restricts the movement of solutes (i.e. $0 \leq \omega \leq 1$). In most cases involving membrane behaviour in a clay soil only a portion of the pores is restrictive ($0 < \omega < 1$) and the soils are to some extent 'leaky'. The theoretical chemico-osmotic pressure (as opposed to electro-osmotic or thermo-osmotic pressures) results from the difference in concentration across the barrier. For a single salt system the theoretical chemico-osmotic pressure difference according to the van't Hoff equation is given by (Malusis *et al.*, 2003):

$$\Delta\pi = \nu MW \cdot \mathfrak{R}T\Delta C \quad (17)$$

where ν is the number of ions per molecule of the salt,
 MW is the molecular weight of the molecule ($\text{kg}\cdot\text{mol}^{-1}$)
 \mathfrak{R} is the universal gas constant ($\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$),
 T is the absolute temperature (K) and,
 ΔC is the concentration difference across the barrier ($\text{kg}\cdot\text{m}^{-3}$).

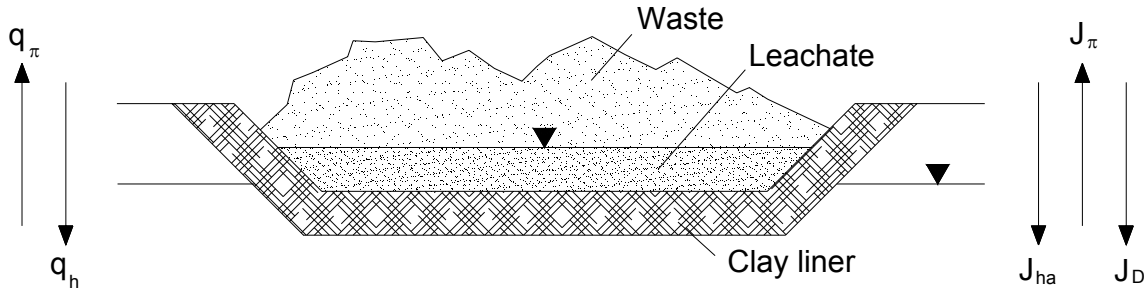


Figure 11. Containment scenario for clay liners with groundwater head lower than leachate head (after Malusis *et al.* 2003)

The one-dimensional solute flux, J [$\text{kg}\cdot\text{m}^{-2}\cdot\text{s}^{-1}$], across a barrier that exhibits semi-permeable membrane behaviour is therefore (neglecting mechanical dispersion):

$$J = J_{ha} + J_{\pi} + J_D = (1-\omega)q_h C + q_{\pi} C + nD_e \frac{\partial C}{\partial x} \quad (18)$$

where J_{ha} is the hyperfiltrated advective solute flux that comprises the advective flux reduced by a constrictivity of $(1-\omega)$ due to steric hindrance
 J_{π} is the osmotic solute flux due to the osmotic liquid flux, q_{π}
 J_D is the diffusive solute flux in the form of Fick's first law (Equation 1, Figure 11).

Malusis *et al.* (2003) explore the consequences of the semi-permeable membrane properties of a 10 mm thick sodium bentonite GCL with potassium chloride (KCl) solution on one side and fresh water on the other. At low concentrations (approximately $< 47 \text{ mg}\cdot\text{l}^{-1}$) the liner acts as a perfect membrane (i.e. $\omega = 1$, no water or solute passes) whereas at high concentrations (approximately $> 7400 \text{ mg}\cdot\text{l}^{-1}$) the liner exhibits no membrane properties (i.e. $\omega = 0$, all water and solute passes). Since the ω factor is highly dependent on the source concentration, this may have implications for landfills lined with clays that do not have full-strength leachate flowing through, such as hydraulically contained landfills. Low solute concentrations in the liner can result in high osmotic efficiency (i.e. ω approaches unity). Diffusive movement of solutes could therefore be significantly impeded by both hyperfiltration and by groundwater flowing into the landfill under the osmotic gradient.

Finally, it is of note that not all low permeability materials exhibit the behaviour of a semi-permeable membrane. Bourke *et al.* (1988), for example, tested cores of London Clay for osmotic behaviour but failed to observe any effects. This is the only example identified in this literature review where osmotic behaviour was not observed, but that could be due to other researchers not reporting negative results, rather than its scarcity.

2.4.4 Retardation of Solutes

As in advective flow regimes, charged solutes may be sorbed to clay mineral surfaces resulting in retarded movement through the material (Fetter, 1999). Indeed, in a clay landfill liner, the

capacity for sorption is huge compared to most geological materials and sorption is a key process for contaminant attenuation. However, this capacity is finite and could potentially be fully utilised during the early stages of landfill leakage when the leachate is strongest; as the leachate strength decreases over time (due to dilution and degradation), previously sorbed contaminants may be desorbed. In a purely diffusive regime (i.e. no mechanical dispersion due to advection) where a linear sorption isotherm applies, with partition coefficient K_d (ml.g^{-1}), an apparent diffusion coefficient, D , can be written as (Bourg *et al.*, 2003):

$$D = \frac{D_e n}{n + \rho_b K_d} \quad (19)$$

where ρ_b is the dry bulk density of the material (kg/m^3).

This relationship can be simplified by the use of the retardation factor, R , which is the same retardation factor used for retardation of advective solute transport:

$$D = \frac{D_e}{R}, \quad R = 1 + \frac{\rho_b K_d}{n} \quad (20)$$

Note that there are now two independent variables (τ and R) that are used to transform the free water diffusion coefficient, D_w , to the measured effective diffusion coefficient, D_e . These are difficult to separate in practice so when R is reported it may actually be the parameter $R \cdot \tau$ or another combination of factors, maybe including the constrictivity.

The diffusion equation given by Fick's second law (Equation 4) can then be rewritten:

$$\frac{\partial C}{\partial t} = \frac{D_e}{R} \frac{\partial^2 C}{\partial x^2} \quad (21)$$

therefore the solution to the one-dimensional diffusion equation (analogous to Equation 5) becomes (Domenico and Schwartz, 1998):

$$C(x, t) = C_0 \operatorname{erfc} \left(\frac{Rx}{2\sqrt{D_e t R}} \right) \quad (22)$$

In a regime where advective transport of solutes occurs, the one-dimensional advection-dispersion equation (Equation 6) becomes:

$$R \frac{\partial C}{\partial t} = D_e \frac{\partial^2 C}{\partial x^2} - v \frac{\partial C}{\partial x} \quad (23)$$

For an infinite one-dimensional region with a boundary condition of $C=C_0$ at $x=0$, the solution to this equation (analogous to Equation 7 and where again the D_e parameter is a combination of both diffusion and mechanical dispersion) (Domenico and Schwartz, 1998) is:

$$C(x, t) = \frac{C_0}{2} \left(\operatorname{erfc} \left[\frac{Rx - vt}{2\sqrt{D_e t R}} \right] + \exp \left(\frac{vx}{D_e} \right) \operatorname{erfc} \left[\frac{Rx + vt}{2\sqrt{D_e t R}} \right] \right) \quad (24)$$

The K_d approach to computing retardation is a good approximation for sorption from relatively low solute concentrations (e.g. Environment Agency, 2003b). However, one of its main criticisms is that it does not account for a limited sorption capacity at high solute concentrations. This has been dealt with in most cases by using the Langmuir isotherm (e.g. Roehl and Czurda, 1998; Bell *et al.*, 2002). These relationships between sorbed and aqueous concentrations are non-linear so R becomes a function of C and the analytical solutions given above cannot be used. Instead, numerical solution schemes have to be developed to combine transport and non-linear sorption.

The partition coefficient, K_d of a solute in a particular clay material can be obtained directly from laboratory experiments (Environment Agency, 2000; 2004d) or by using an approximation based on the cation exchange capacity of the material (Appelo and Postma, 1993; Environment Agency 2002a). The former technique is preferable as it provides a site-specific measurement (the K_d approach can be used if a reliable linear isotherm is obtained) but the second technique is acceptable for many risk assessment purposes and still incorporates a degree of site-specific data. Partition coefficients for ammonium can be found in Environment Agency (2003b).

For organic chemicals, unless site specific sorption data are available, it is most usual to compute the partition coefficient using the equation:

$$K_d = K_{OC} \cdot f_{OC} \quad (25)$$

where K_{OC} is the organic carbon-water partition coefficient
 f_{OC} is the fraction of organic carbon in the mineral liner

However, many landfill mineral liners (especially artificial bentonite mixtures) have essentially zero f_{OC} and, according to Equation 25, should not be able to attenuate organic compounds. Clay minerals do have a measurable sorption capacity for organic compounds but this is inevitably much less than the capacity for charged (ionic) species. Organic-poor sediments have been observed significantly retarding many types of organic compound (Williamson, 1993) and the large surface areas of clays offer a greater potential for sorption than other mineral surfaces (McCarty *et al.*, 1981). Bright *et al.* (2000) found that the sorption of volatile organic compounds to a mineral liner was up to four times greater than predicted using the linear f_{OC} relation (see also Thornton *et al.*, 1999). Further discussion of these issues in relation to the attenuation of mecoprop can be found in Environment Agency (2004c). It is therefore often conservative to use Equation 25 for organic compounds but if relevant sorption data are identified then an experimental K_d value may be used.

Use of the linear sorption isotherm model in the advection-dispersion equation assumes that the sorption is perfectly reversible, i.e. that once a slug of contaminant has passed, the sorbed phase will be flushed off and back into the groundwater. However, sorption of many contaminants may be irreversible ('binding') as ions may move into the clay lattice, or form strong bonds with the surface. The following examples discuss different species that have shown to exhibit a degree of irreversible sorption.

- Metal sorption is partly irreversible because at low concentrations they may form inner-sphere complexes with mineral surfaces. These cannot be formed by major cations and therefore the metals cannot be flushed (cation exchange) by clean groundwater (McLean and Bledsoe, 1992). At high concentrations, however, metals tend to occupy exchange sites. Roehl and Czurda (1998) reproduced these results with cadmium and lead. Eriksen *et al.* (1999) also found immobilisation of cobalt by the formation of outer-sphere complexes. Appelo and Postma (1993) describe in detail the specific adsorption of heavy metals.
- Atrazine molecules fit into the interlayer space of montmorillonite, with an increased affinity to sodium montmorillonite (Prima and Evangelou, 2002). Binding of benzene to

sandy aquifer materials was noted by Baek *et al.* (2003) but this may have been due to the activated carbon added to the aquifer material. Davies *et al.* (1996) also reported that an increasing affinity of organic acids for clay minerals approximately correlated with their solubility in water.

- Ammonium sorption to illite and other 2:1 layer clays may be irreversible as the ammonium ion fits snugly into the intra-layer clay lattice which is usually occupied by potassium (Environment Agency, 2003b). Likewise, potassium can be adsorbed from solution into the clay lattice, and may not sorb reversibly like other exchangeable cations.
- Phosphate adsorption to clay surfaces is partly irreversible and it cannot be flushed off by chloride (for example) under the same pH and ionic conditions as when it was sorbed (Hingston *et al.*, 1967). Phosphate also tends to precipitate when mixed with alkaline groundwaters.

Irreversible sorption can be included in the advection-dispersion equation by the use of a first order decay coefficient, in the same way as biodegradation or radioactive decay (Fetter, 1999; Baek *et al.*, 2003). The use of a rate constant is due to the assumption that binding is a rate-limited reaction:

$$R \frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} - v \frac{\partial C}{\partial x} - \lambda_s C \quad (26)$$

where λ_s is the first-order decay coefficient for irreversible sorption (s^{-1}).

A solution to Equation 26 for one-dimensional transport for an infinite region with $C=C_0$ at $x=0$ with both reversible sorption and irreversible sorption is (Domenico and Schwartz, 1998):

$$C(x,t) = \frac{C_0}{2} \left(\exp \left[\frac{vx}{2D_e} \left\{ 1 - \sqrt{1 + \frac{4\lambda_s R D_e}{v^2}} \right\} \right] \operatorname{erfc} \left[\frac{1}{2\sqrt{D_e t / R}} \left\{ x - \frac{vt}{R} \sqrt{1 + \frac{4\lambda_s R D_e}{v^2}} \right\} \right] + \exp \left[\frac{vx}{2D_e} \left\{ 1 + \sqrt{1 + \frac{4\lambda_s R D_e}{v^2}} \right\} \right] \operatorname{erfc} \left[\frac{1}{2\sqrt{D_e t / R}} \left\{ x + \frac{vt}{R} \sqrt{1 + \frac{4\lambda_s R D_e}{v^2}} \right\} \right] \right) \quad (27)$$

2.4.5 Surface and Interlayer Diffusion

Diffusion of solutes through clay materials does not only occur in the dissolved phase through pores. Many studies have found that the diffusivity of cations was higher than predicted by the pore water diffusion model (Bourg *et al.*, 2003; Kozaki *et al.*, 1999). Cations, particularly the 'hard' Lewis acids, e.g. K^+ , Cs^+ , Sr^{2+} and Ba^{2+} (Langmuir, 1997), can diffuse across the surface of the clay minerals (within the diffuse double layer) and through the interlayer spaces within the minerals themselves (Figure 12).

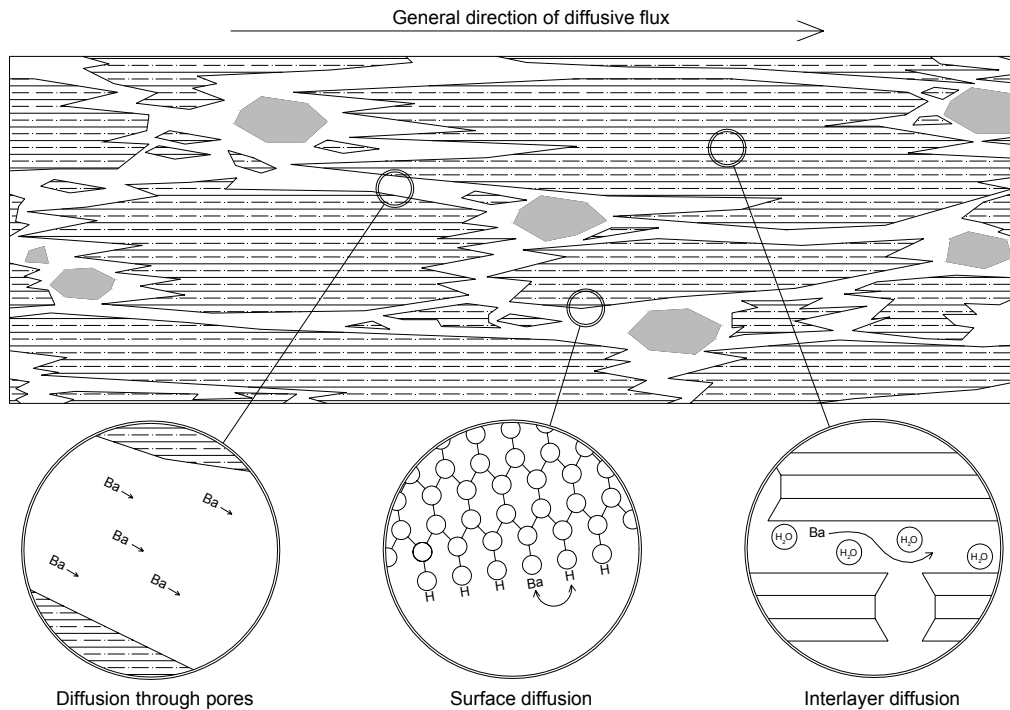


Figure 12. Diffusion mechanisms in a clayey material

In cases where surface diffusion is important the apparent diffusion coefficient, D , is given by (Eriksen *et al.*, 1999):

$$D = \frac{1}{R} \left(D_e + D_s \frac{\rho_b K_d}{n} \right) \quad (28)$$

where D_s is the coefficient of surface diffusion ($\text{m}^2 \cdot \text{s}^{-1}$).

Most texts do not separate out a tortuosity term from the surface diffusivity (except Cole *et al.*, 2000) but it is believed that in a clay material the surface tortuosity is approximately equal to the pore tortuosity (Cole *et al.*, 2000).

Eriksen *et al.* (1999) measured D_s values in bentonite for caesium and strontium of 6×10^{-13} and $1 \times 10^{-11} \text{ m}^2 \cdot \text{s}^{-1}$ respectively and found that they were 1300 and 30 times less than the measured $D_w \tau$ values respectively. Caesium was found to have a higher K_d than strontium and it is probably because of this greater affinity to the mineral that the surface diffusion coefficient is lower. This was also a conclusion quoted in Kozaki *et al.* (1999). It was suggested that the difference in measured values could be that caesium travels through the interlayer spaces of the clay whereas strontium is excluded and travels around pore spaces.

Surface diffusion coefficients of uncomplexed cations (Cs^+ and Sr^{2+}) appear to be significantly lower than free water diffusion coefficients (Eriksen *et al.*, 1999). However, Cole *et al.* (2000) found that with a solution of strontium carbonate/sulphate the fraction of solute transport by surface diffusion exceeded that via pores in terms of mass of solute moved as the strontium carbonate complexes were relatively mobile under surface diffusion.

2.4.6 Biodegradation and Decay

It is sometimes assumed that biodegradation of contaminants should not occur within clay liners as pore throats in such materials tend to be smaller than bacterial cells (Environment Agency, 2003b). However, Kim *et al.* (2001) clearly and consistently observed degradation of seven dissolved organic solvents in column experiments with compacted clay. Half-lives of the solvents

were between 2 and 116 days. Influent solution concentrations of dissolved oxygen were less than 1 mg.l⁻¹ so the degradation appeared to be anaerobic biodegradation. The half-lives recorded are generally comparable with those for anaerobic biodegradation in Howard *et al.* (1991). Bright *et al.* (2000) and Thornton *et al.* (1999) also observed degradation of volatile organics in clay liners, but the process was very complex and some compounds (e.g. benzene) did not degrade at all during the timescale of the experiments.

Abiotic decay may occur where bacteria are excluded but these processes tend to require specific chemical conditions in the leachate or groundwater to proceed.

Without site-specific data, considerable caution should be applied when choosing the range of uncertainty for degradation rates from the scientific literature. As a conservative approach it may be appropriate not to model degradation or decay within the liner. However, if site specific data is available or other justification can be made (or the solute of concern is a radioisotope when radioactive decay will certainly occur), the relevant one-dimensional equation and its solution for an infinite region with $C=C_0$ at $x=0$ are (Domenico and Schwartz, 1998):

$$R \frac{\partial C}{\partial t} = D_e \frac{\partial^2 C}{\partial x^2} - v \frac{\partial C}{\partial x} - \lambda C \quad (29)$$

$$C(x,t) = \frac{C_0}{2} \left(\exp \left[\frac{vx}{2D_e} \left\{ 1 - \sqrt{1 + \frac{4\lambda R D_e}{v^2}} \right\} \right] \operatorname{erfc} \left[\frac{1}{2\sqrt{D_e t / R}} \left\{ x - \frac{vt}{R} \sqrt{1 + \frac{4\lambda R D_e}{v^2}} \right\} \right] + \exp \left[\frac{vx}{2D_e} \left\{ 1 + \sqrt{1 + \frac{4\lambda R D_e}{v^2}} \right\} \right] \operatorname{erfc} \left[\frac{1}{2\sqrt{D_e t / R}} \left\{ x + \frac{vt}{R} \sqrt{1 + \frac{4\lambda R D_e}{v^2}} \right\} \right] \right) \quad (30)$$

where λ is the decay constant for the reaction (s⁻¹)

λ can be calculated from the half life of a reaction, $T_{1/2}$ (s), using the formula:

$$\lambda = \frac{\ln 2}{T_{1/2}} \quad (31)$$

2.5 Solute Transport Through Composite Liners

Composite liners provide at least a dual barrier of polymer geomembrane bonded to and overlying a compacted clay or GCL liner. Although geomembranes are practically impervious to diffusion of inorganic solutes, they can more readily transmit organic solvents. The following sub-sections therefore discuss the two distinct contaminant transport mechanisms through composite liners:

- diffusion of organic solvents through intact geomembrane and the underlying low permeability barrier, and
- diffusion and advection of inorganic and organic solutes through holes and defects in geomembranes then through the underlying low permeability barrier.

These occur simultaneously and the final sub-section discusses the methods available to sum the two contaminant transport mechanisms.

2.5.1 Diffusion Through Intact Composite Liners

Intact polymer geomembranes are completely impermeable to liquid water (that is, there is no Darcy flow through intact polymer geomembranes) although molecular water can diffuse through them. Charged solutes are therefore very poorly transported through intact polymer geomembranes (Rowe, 1998). However, the non-crystalline parts of the polymer structure are permeable to organic molecules, which can therefore migrate through the geomembrane material (Edil, 2003). These follow Fick's laws of diffusion, although in these cases the diffusivity of the molecule through the geomembrane material is used in place of the effective diffusivity:

$$J_{gm} = -D_{gm} \frac{\partial C_{gm}}{\partial x} \quad (32)$$

where J_{gm} is the mass flux of organic species through the geomembrane polymer ($\text{kg}\cdot\text{m}^{-2}\cdot\text{s}^{-1}$)
 D_{gm} is the diffusion coefficient of the solvent in the geomembrane polymer ($\text{m}^2\cdot\text{s}^{-1}$)
 C_{gm} is the concentration of the organic species in the geomembrane ($\text{kg}\cdot\text{m}^{-3}$)

D_{gm} is to some extent an empirical effective diffusion coefficient because it depends on the microstructure, and therefore the manufacturing technique, of the polymer. Nevertheless, some measured values are presented in Section 3 for screening purposes.

The concentration of the organic species at the very top of the geomembrane, $C_{0,gm}$ ($\text{kg}\cdot\text{m}^{-3}$) is related to the concentration in leachate by a partition coefficient, $K_{d,gm}$ (dimensionless), sometimes also referred to in literature as a solubility (e.g. Rowe, 1998):

$$C_{0,gm} = K_{d,gm} C_0 \quad (33)$$

where C_0 is the concentration in the leachate ($\text{kg}\cdot\text{m}^{-3}$). Note, that as the contaminants are present within the matrix of the material rather than sorbed to sites on the solid mineral phase of a porous material, the definition of $K_{d,gm}$ is slightly different to the usual partition coefficient for sorption. For the porous material, the sorption site density is directly related to the mineral proportion of the material, and hence the overall concentration of sorbed contaminant expressed by mass per volume of porous material is directly related to the porous medium dry density. This factor is generally explicit, with K_d representing the equilibrium relation between a sorbed concentration expressed as mass per unit mass of mineral phase, and the aqueous concentration expressed as mass per unit volume of pore water. For geomembranes, the concentration of adsorbed contaminant is generally expressed as mass per unit volume of membrane material and so the partition coefficient is dimensionless and we have used this convention with our $K_{d,m}$ analogous to Rowe's (1998) S_{gf} ,

Similarly to the conditions at the inner boundary with the geomembrane, on emergence from the base of the geomembrane into the porewater of the underlying low permeability barrier, Equation 33 is used again to compute the aqueous concentration at the top of the clay profile. Section 3 presents a list of diffusion coefficients and partition coefficients (or solubilities) for organic solvents in polymers that may be useful in UK landfill risk assessments.

Conservative estimates of the flux through the geomembrane can be obtained by assuming that the aqueous concentration at the base is zero. However, Foote *et al.* (2002) provide an expression for the steady-state diffusive flux, J_c ($\text{kg}\cdot\text{m}^{-2}\cdot\text{s}^{-1}$), across a composite liner system comprising a geomembrane over a low permeability mineral liner:

$$J_c = -D_c \frac{\partial C}{\partial x} \quad (34)$$

$$D_C = (t_{gm} + t_s) \left(\frac{t_{gm}}{D_{gm} K_{d, gm}} + \frac{t_s}{D_w n} \right)^{-1} \quad (35)$$

where D_C is the effective diffusion coefficient for the polymer and clay liner system ($\text{m}^2 \cdot \text{s}^{-1}$)
 C is the aqueous concentration of organic solute ($\text{kg} \cdot \text{m}^{-3}$)
 t_{gm} and t_s are the thicknesses of the geomembrane and mineral liners (m)

Equations 34 and 35 are only valid for the steady-state condition. Foose *et al.* (2002) used numerical methods to compute transient solute breakthrough at the base of the mineral liner because the jump in concentration between the geomembrane and mineral liner does not allow a straightforward analytical solution. Breakthrough curves for toluene through a GCL composite liner (6.5 mm geomembrane over a 1.5 cm GCL) and a compacted clay composite liner (6.5 mm geomembrane over a 61 cm compacted clay) were computed. Although the solute flux through the GCL composite stabilised within two or three years, the flux through the compacted clay composite started to stabilise around 50 years but was still increasing at 100 years.

It is of interest to note that Park *et al.* (1996a) found that the diffusion coefficients of four organic solvents in HDPE decrease with decreasing aqueous concentrations, suggesting that the diffusion may not be strictly Fickian. Exponential relationships between D_{gm} and C_0 were found, but they are probably relationships between D_{gm} and $C_{0, gm}$ however concentrations in the geomembrane material could not be measured to corroborate this. $K_{d, gm}$ did not change with aqueous concentration. Park *et al.* (1996b) found in the laboratory that as the influent concentration above an HDPE disc decreased by a factor of 10, from $100 \text{ mg} \cdot \text{l}^{-1}$ to $10 \text{ mg} \cdot \text{l}^{-1}$, the corresponding steady-state mass flux from the base decreased by a factor of 15. Such an exponential concentration dependent relationship was also observed by Joo *et al.* (2001).

Park *et al.* (1996a) compared three geomembrane materials for transport of organic solvents: high density polyethylene (HDPE), very low density polyethylene (VLDPE) and polyvinyl chloride (PVC). The results clearly showed that HDPE had the lowest diffusion coefficient and partition coefficient for all organic compounds tested (because it is more crystalline), PVC was intermediate in terms of solvent diffusion and VLDPE had the highest diffusion coefficient (least crystalline/more amorphous). D_{gm} and $K_{d, gm}$ of the HDPE membrane changed under tension; both increased significantly with tension up to 5% elongation and slightly more up to 8% elongation. In contrast, Xiao *et al.* (1999) extended the liner to 60% elongation – past its elastic threshold – and the diffusion coefficient decreased. It is thought that the irreversible change to the polymer structure enhances barrier properties, while purely reversible elastic deformation increases the diffusion coefficients.

2.5.2 Flow and Diffusion Through Defects in Geomembranes

Liquid flows through composite liners are entirely through the holes, tears or other defects that are introduced during installation of the liner, the operational phase of the landfill and subsequently. Environment Agency (2004b) presents a comprehensive review of the state-of-the-art understanding of development of such holes and suggests areal frequencies for holes and tears with time. Water flux through geomembrane is dependent not only on the size of the holes but the hydraulic conductivity of the surrounding mineral layers and the quality of contact between the liner components. It is usually assumed that the flux is limited by the hydraulic conductivity of the overlying mineral layer, the underlying mineral layer or the size of the hole itself. With these assumptions suitable empirical equations can be used to estimate the flux (Appendix A).

Models for calculating flows through holes in conventional landfills (i.e. higher leachate head than groundwater head) are often based on the capacity of a cylinder of the porous mineral layer adjacent to the hole to transmit water under the local hydraulic gradient. The radius of the hole is

determined by an empirical factor that depends upon the quality of the contact between the geomembrane and mineral layer – poor contact results in a larger radius cylinder (Giroud, 1997; Rowe, 1998). Equations for calculating flow through holes in geomembranes under a range of hydraulic conditions are presented in Appendix A.

However, these equations were inferred from empirical data for leakage above an unsaturated zone and therefore none of these were demonstrated to apply to the hydraulic containment case where water is flowing from a low permeability porous medium (the mineral liner) through a hole and into a higher permeability waste. In particular, Giroud uses corrections to gravity driven head gradients in his relations and these head gradients will only be relevant to drainage above the water table. In fact no treatment of flow through geomembrane defects in hydraulic containment landfills has been identified during this study. Relying on the fact that for a linear system the flow equations lead to exact flow path reversal when the head difference is reversed, and the assumption that flow is sufficiently slow that linear flow is a good approximation, the Giroud (1997) equations have been adapted to the hydraulic containment setting. A simple head gradient across the liner is used in place of the correction to gravity drainage used in Giroud's work, and using excess leachate head in place of leachate level.

Numerical techniques have also been used to calculate flows through holes in liners. Foose *et al.* (2002), for example, used a MODFLOW model to predict flow through a geomembrane hole and the mineral layer beneath. Solute fluxes and breakthroughs were calculated with MT3D. The flow results agreed with the analytical models of Rowe (1998) but gave significantly lower leakage rates than the Giroud (1997) equations. This was due to the use of laboratory-derived parameters for the numerical model and the Rowe (1998) equations, but field parameters in the Giroud (1997) equations. Again, the flow regime was for a conventional landfill but the numerical modelling technique may provide a method to understand flows into hydraulically contained landfills.

2.5.3 Total Solute Transport Through Composite Liners

Coupled solute transport through both geomembrane holes and through intact geomembrane has been only rarely discussed in the literature. However, Park *et al.* (1996b) briefly compared steady-state fluxes of organic solvents through intact HDPE geomembrane alone with advective fluxes only through typical numbers of holes in the same material (using the relationship of Giroud and Bonaparte, 1989). For trichloroethene, dichloromethane and toluene the flux through the intact geomembrane was greater (up to more than 1000 times) than that through only small (1 mm diameter) and large (56 mm diameter) holes (both at a density of 3 per hectare) under all leachate heads up to 3m. *m*-xylene, however, has much lower diffusion parameters than the other three and a greater flux is predicted to come through the holes. Although this was not a vigorous comparison it serves to highlight the importance of considering the intact membrane as a migration pathway for organic solvents.

Foose *et al.* (2002) compared modelled mass fluxes through three composite liners of cadmium (transport through holes only) and toluene (transport also through intact geomembrane). For similar concentrations of cadmium and toluene and for the parameters chosen to be relevant, the mass flux of toluene was as much as seven orders of magnitude greater than cadmium (biodegradation of the toluene was not simulated). In addition, the steady-state mass flux of cadmium did not vary significantly with the type (GCL/CCL) or thickness of the mineral barrier. However, the mass flux of toluene through the GCL composite liner containing a bentonite layer of hydraulic conductivity 10^{-11} to 10^{-12} m.s⁻¹ was two to three orders of magnitude greater than through the liners with compacted clay of hydraulic conductivity 10^{-9} to 10^{-10} m.s⁻¹. This is a key result as predictions based on leakage rates through geomembrane defects alone (Giroud, 1997) would suggest the opposite.

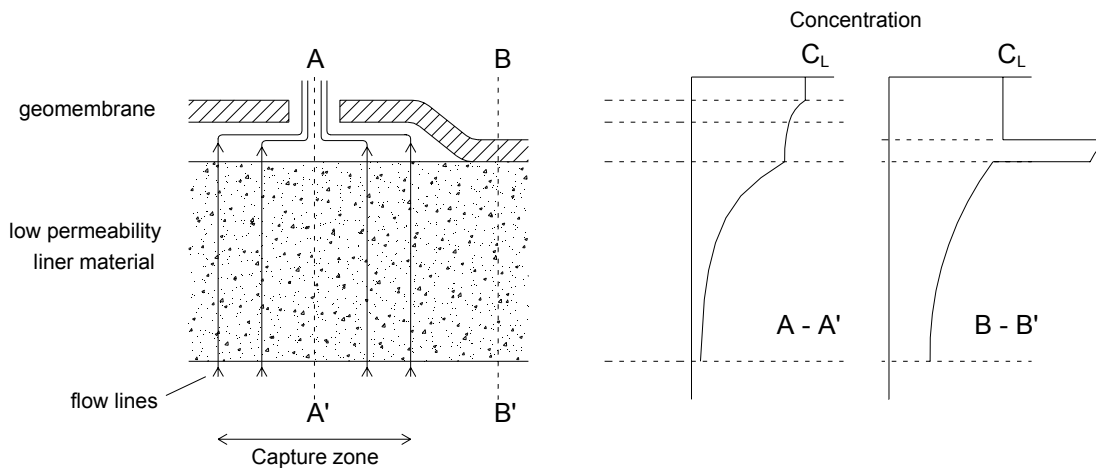


Figure 13 presents a schematic cross-section through a composite liner and steady-state concentration profiles for a typical organic compound beneath a defect (or delaminated area) and beneath intact geomembrane at the base of a hydraulically contained landfill. Profile 'A' shows an initial concentration drop through the defect, as the contaminant has to diffuse against the inward advective flux of water (N.B. the gap shown between the geomembrane and liner is for illustrative purposes only). Profile 'B' shows that the organic preferentially sorbs into the geomembrane and diffuses across that to desorb at its base. While diffusing across the low permeability mineral barrier, beneath the defect (profile 'A') there is an advective velocity in the opposite direction, but beneath intact geomembrane (profile 'B') there is not. Consequently, the advective flow limits the concentration at the base of the liner whereas beneath the intact geomembrane, the contaminant freely diffuses through the static water column. It is clear, therefore, that given appropriate transport properties, organic compounds can diffuse through a composite liner with a defect-free geomembrane more readily than through a composite liner with many defects.

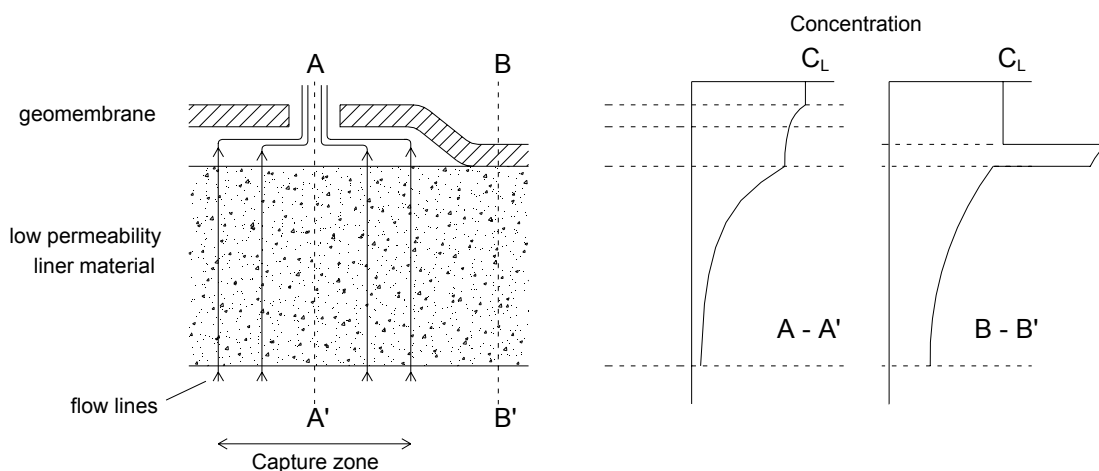


Figure 13. Schematic concentration profiles of a typical organic compound through a composite liner

3 Indicative Values of Key Properties

The following sections present indicative values of properties that may be used in the equations presented in this report and in the spreadsheet that accompanies it. These values are intended to be illustrative of the ranges that such parameters might take rather than a comprehensive list, and are not intended as a database of acceptable values for any specific risk assessment.

Values obtained from detailed site specific or laboratory investigation will always be preferred for submission of risk assessments. However it is recognised that many of the data required for use in the accompanying spreadsheet are not readily obtainable, apart from the hydraulic conductivity of liner materials. Nevertheless, if any of these values are used in risk assessment submissions the original reference must be referred to, to ensure that the values are being used appropriately.

Values presented in the tables have different numbers of significant figures or decimal places. These reflect the confidence that the authors of the original references had in those values.

3.1 Diffusion Coefficients in Water and HDPE

Diffusion coefficients for typical inorganic and organic landfill-derived contaminants are presented in Table 3.1 below. There is significant variation between some of the coefficients for several of the compounds, especially when in a polymer. Data in Table 17 of Rowe (1998) indicates that the main source of variation is in the experimental methods used. Where there is significant variation in the parameter, the original reference must be examined to determine which value is most appropriate for the risk assessment. Free water diffusion coefficients for a much greater range of species are presented in Lide (2000).

Rowe (1998) presents diffusion coefficients for both pure and dissolved phase solutes. Only diffusion coefficients from the dissolved phase are presented here; data for many other species (mostly solvents) are also presented in this paper. Otherwise, the results of different measurement techniques are not differentiated here; where there is a large range in the value, it is likely that a number of techniques have been used and reference should be made to the original documents.

Table 3.1. Diffusion coefficients

Species	D_w ($\times 10^{-9} \text{ m}^2 \cdot \text{s}^{-1}$)	Effective diffusion coefficients for membranes ($\times 10^{-12} \text{ m}^2 \cdot \text{s}^{-1}$)		
		D_{HDPE}	D_{VLDPE}	D_{PVC}
H ₂ O		0.29 - 2.6 ^j		0.44 ^j
Cl ⁻	2.03 ^a	0.002 - 0.3 ^j		
SO ₄ ²⁻	1.07 ^a			
Cr ³⁺	0.594 ^a			
Cd ²⁺	0.717 ^c			
NH ₄ ⁺	1.96 ^k			
Acetic acid		0.11 - 0.29 ^j		
Benzene	0.7 ^g	2.7 ^e 0.037 ^j		
Ethyl benzene	0.602 ^b 0.6 ^g			
<i>m</i> -xylene	0.486 ^b	0.96 ^d 0.31 - 3.7 ^j	1.53 ^d	1.61 ^d
Toluene	0.413 ^b 0.847 ^c 0.6 ^g	0.53 ^d 0.2 - 0.56 ^j	1.46 ^d	0.54 ^d
Carbon tetrachloride		48 - 57 ^j		
Dichloromethane	0.138 ^b	0.36 ^d 4.6 ^e 0.7 ^h 1.8 - 5.6 ^j	0.87 ^d	0.38 ^d
1,1,1-trichloroethane	2.37 ^b			
Trichloroethene	0.439 ^b 0.7 ^g	0.66 ^d 3.0 ^e 0.4 ^h 0.20 - 73 ^j	1.54 ^d	0.75 ^d 85 ^j
Naphthalene	0.69 ^f 0.6 ^g			
Mecoprop	0.39 ⁱ			

References:

- | | |
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| a. Fetter (1999) [at 25°C] | g. Johnson <i>et al.</i> (1989) [at 10°C] |
| b. Kim <i>et al.</i> (2001) | h. Sangam and Rowe (2001) |
| c. Yaws (1995) in Foose <i>et al.</i> (2002) | i. M. Broholm, <i>pers. comm.</i> , (2003) |
| d. Park <i>et al.</i> (1996) | j. Rowe (1998) |
| e. Xiao <i>et al.</i> (1999) | k. Lide (2000) |
| f. Sawatsky <i>et al.</i> (1997) | |

3.2 Water-Polymer Partition Coefficients

Water-polymer partition coefficients for organic species from Park *et al.* (1996a) and Rowe (1998) are presented in Table 3.2 below. The results of different measurement techniques are not differentiated here; where there is a large range in the value, it is likely that a number of techniques have been used and reference should be made to the original documents.

Table 3.2. Water-polymer partition coefficients (dimensionless)

Species	K _{d,HDPE}	K _{d,VLDPE}	K _{d,PVC}
H ₂ O	<0.0003 – 0.001 ^b		
Cl ⁻	0.00008 ^b		
Acetic acid	0.015 ^b		
Benzene	54.3 – 57.2 ^b		
<i>m</i> -xylene	192.7 – 370 ^b		
Toluene	140 ^a 63.5 – 192 ^b	245 ^a	1160 ^a
Dichloromethane	455 ^a 1.8 – 5.6 ^b	800 ^a	3300 ^a
1,1,1-trichloroethane	78.2 ^b		
Trichloroethene	113 ^a 0.11 – 189 ^b	218 ^a	770 ^a

References:

a. Park *et al.* (1996a)

b. Rowe (1998)

3.3 Tortuosity of Low Permeability Liner Materials

Tortuosity values for low permeability liner materials are presented in Table 3.3 below. There are few data on tortuosity and this uncertainty is best dealt with as part of a sensitivity analysis. In the literature an effective diffusion coefficient is often presented. Care should be taken in the use of such literature values: tortuosity factors should only be applied where it is not implicitly accounted for in the diffusion coefficient.

Table 3.3. Tortuosity values for low permeability liner materials

Formation / material	Reference	Tortuosity	Calculated ratios
Three GCLs at 20 – 350 KPa	Rowe (1998)	6.7 – 50.75	
London Clay	Bourke <i>et al.</i> (1988)		$n/\tau = 1/30$
Clays	De Marsily (1986)	10	
Average (all)	Freeze and Cherry (1979)	2 – 10	

3.4 Porosities of Low Permeability Liner Materials

The Agency expects that site-specific values for porosity will be used in risk assessments using the techniques described in this report. Where such values are obtained, only those measured at typical landfill confining stresses (up to 500 KPa) should be used. Care must be taken to use the appropriate type of porosity (e.g. total porosity vs. diffusion porosity) as this can significantly effect results [Section 2.3.4 and Pearson (1999)].

Note that if the void ratio of a material is presented in literature (e , dimensionless), this can be converted to total porosity by the relationship:

$$n = \frac{e}{1 + e} \quad (36)$$

3.5 Hydraulic Conductivities of Liner Materials

The Agency expects that site-specific values or design parameters for hydraulic conductivity will be used in risk assessments using the techniques described in this report. Where such values are obtained, only hydraulic conductivity values measured at typical landfill confining stresses (up to 500 KPa) should be used.

4 Model Construction

4.1 Introduction

A spreadsheet model has been constructed that can be used for the calculation of pollutant fluxes out of hydraulically contained landfills. One of the principal controls on the method used to calculate fluxes is the conceptual model for the scenario chosen by the user. The scenarios listed previously in Section 1.1 are described in more detail in Section 4.2 below.

Those equations used in the spreadsheet are mostly given in Section 2 where the applicable processes are defined. The order of these equations within the overall calculation scheme is presented in Section 4.3 in a more systematic way.

4.2 Landfill Scenarios

The following three landfill construction scenarios were identified as operating in the UK under hydraulic containment.

- A landfill without an artificial sealing liner, but which has been excavated in a low permeability clay stratum above a confined aquifer (Scenario 1). This can also be used as a conservative approximation to simulate a new landfill site with an artificially constructed clay liner and *in situ* geological barrier by consideration of each component alone. This can be done by simulating the geological barrier alone (ignoring the mineral liner), and then comparing these results with a separate simulation of the mineral liner (assume the low permeability stratum does not exist). Alternatively, if the artificial clay liner is constructed from the same source as the *in situ* geological barrier, it may be appropriate to consider both layers together by assigning a composite value for the hydraulic conductivity. (Figure 14).

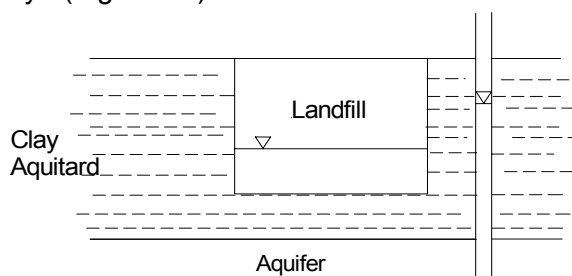


Figure 14. Scenario 1

- A landfill with an artificially formed geological barrier and artificial sealing liner [e.g. geomembrane composite, compacted clay or GCL] constructed wholly within a permeable formation, (Scenario 2, Figure 15).

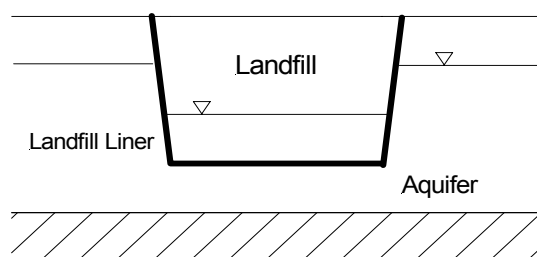


Figure 15. Scenario 2

- A landfill with an artificially formed geological barrier and artificial sealing liner (e.g. geomembrane composite, compacted clay, GCL) constructed in a permeable formation but with a low permeability base, (Scenario 3, Figure 16).

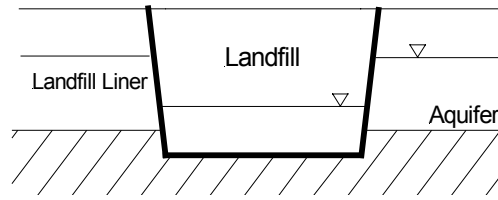


Figure 16. Scenario 3

4.3 Constitutive Relationships and Assumptions

4.3.1 Landfill Geometry and Head Gradients

When defining the geometry of the landfill and the areas in contact with leachate and groundwater, it is assumed that the local groundwater head and the leachate heads are level. It is assumed that there is essentially no difference between water and contaminant transport through the base or sides of the landfill. The area of groundwater in contact with the landfill, $A_{contact}$ (m²), and therefore the area through which contaminants can escape, is calculated using the following equations:

$$\text{Scenario 1: } A_{contact} = L_{LF}W_{LF} \quad (37a)$$

$$\text{Scenario 2: } A_{contact} = 2\Delta h_{LF}(L_{LF} + W_{LF}) + L_{LF}W_{LF} \quad (37b)$$

$$\text{Scenario 3: } A_{contact} = 2\Delta h_{LF}(L_{LF} + W_{LF}) \quad (37c)$$

where Δh_{LF} is the depth of leachate (m)
 L_{LF} and W_{LF} are the length and width of the landfill (m)

The landfill is assumed to be rectangular and while for this calculation it is irrelevant which dimensions are length and width, dilution calculations assume that the length of the landfill is that dimension parallel to groundwater flow.

In scenario 1 it is assumed that contaminants diffuse out of the base of the landfill only, i.e. $\Delta h_{LF} = 0$ (see Figure 14) since this is the most important pathway. For scenario 2 Δh_{LF} is calculated by comparison of the elevation of the base of the landfill and the elevation of the leachate, i.e. the leachate depth (Figure 17). In scenario 3 Δh_{LF} is calculated by comparison of the elevation of the top of the underlying aquitard and the elevation of the leachate (Figure 17).

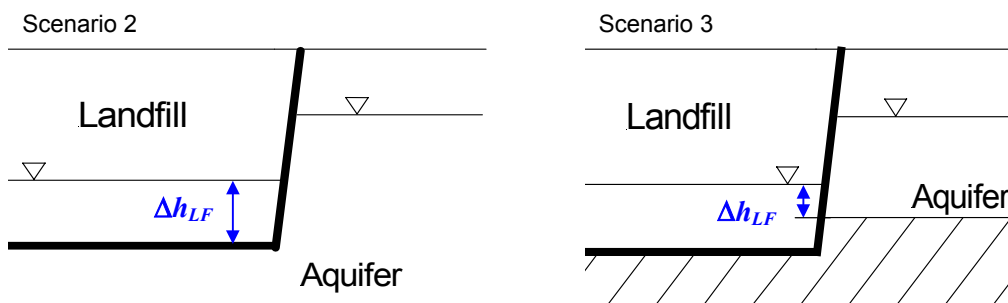


Figure 17. Depth of leachate relative to surrounding groundwater

4.3.2 Calculation of Water Flux and Velocity

Through Porous Mineral Barriers Only

Where a geomembrane is not present water flux and advective velocity through porous mineral barriers are computed using Darcy's Law. This barrier will be the *in-situ* aquitard formation in the case of scenario 1 or the mineral liner in scenarios 2 or 3.

Through Composite Liners

Where a geomembrane is present, the water flux through intact membrane is neglected and all water is assumed to flow through holes and tears. These are calculated using the equations presented in Appendix A. Equations A7, A9, A10 and A11 are used when the Giroud equations for flow through a low permeability mineral layer are valid. Equations A13a and A13b are used for circular holes where the mineral layer is considered to be semi-permeable (Section A.3)⁷. The conditions under which either formula is valid depends on the size of the holes in the geomembrane relative to the pore size of the mineral layer, the head difference across the liner system, and the quality of contact between the geomembrane and mineral layer.. As in LandSim, three types of defect are considered: pin holes (0.1 – 5 mm²), holes (5 – 100 mm²) and tears (1 mm width x 100 – 10 000 mm length).

The Giroud equations in Appendix A.2 strictly apply only to above water table landfills with unsaturated mineral liners that drain freely under gravity. It is noted that they cannot be exactly correct under saturated conditions with flow into the landfill. The issue is not the reversibility of the flow, which should be correct, but that the empirical relations were inferred for systems above the water table. Given that the flow lines should be reversible, and the difference between the two situations occurs at the outer radius of the mineral layer region through which water flows (where flows will be small), the results will be more correct than those calculated using equations for flow through an orifice alone, which would entirely neglect the resistive properties of the mineral layer. The head difference between the leachate and groundwater is therefore substituted for the leachate head term without modification.

The advective velocity through a mineral liner beneath a geomembrane is computed by assuming that the water flux travels through cylinders beneath, and centred on, the defects. Their dimensions are assumed to be given by the Giroud equation for wetted radius (Equation A8b); account is taken of the porosity of the mineral liner. Other techniques are available to compute velocity which may give different results. An optimistic (but unrealistic) approach may move the water quickly through a cylinder with the same diameter as the defect, whilst a pessimistic (but equally unrealistic) approach may move the water very slowly through the whole area of the mineral liner. The cylinder with the radius from the Giroud equation is used as a compromise.

For composite lined sites, the user can specify an area over which delamination might occur as an input to the spreadsheet. This might be appropriate if the risks discussed in Section 2.2.3 are considered significant. In such cases, the geomembrane component of the lining system is assumed to have no effect as a barrier and it is assumed that leachate can readily migrate behind the membrane. In this case, Darcy's law is used to calculate the inward groundwater flux across the area under consideration and diffusion and the outward flux of contaminant calculated by the single layer diffusion equation.

⁷ Tears in the geomembrane are always modelled assuming that the underlying mineral layer is 'low permeability'. No relationship has been developed by Giroud to interpolate between the equations for flow through a composite liner and flow through an orifice (a slit in this case). Because the distinction between the two appears to be most important at very small hole sizes, it is assumed that the Giroud equation (Equation A10) always applies for tears.

4.3.3 Contaminant Movement Against the Hydraulic Gradient

Water entering the landfills does so in essentially two phases – through the mineral liner and through the defects. Because the area of the hole is significantly less than the open area of the porous liner within the wetted radius, the water velocity through the hole will be greatest. This is an initial barrier to contaminant movement because if the contaminant cannot diffuse past this, it will not reach the mineral layer. Even when contaminants can pass through the defect, this resistance can act to reduce the concentration of leachate reaching the top of the mineral liner if the contaminant can diffuse only through the outer annular area (slowest flowing) of the defect but not through the centre.

Flow through a defect and mineral layer of a composite lining system is non-linear using Giroud's relations and the velocity within the defect of the geomembrane will be significantly higher than the average velocity in the mineral component. This short interval within the geomembrane might make a significant contribution to the hydraulic containment of the contaminants. In order to obtain a tractable analytical (or semi-analytical) solution, the transport through the two components of the composite liner are treated separately. In order that this is conservative, the time taken for transport through the geomembrane is neglected and the steady-state contaminant concentration profile that is developed along the axis of the defects against the inward flow is evaluated using Equation 7 for a sufficiently large time. The longitudinal dispersion coefficient used includes a diffusive contribution. The concentration at the inlet of the defect (upstream edge) is taken as the constant concentration boundary condition from $t = 0$ for transport through the mineral component of the liner.

Under the conditions in a conventional landfill liner (outward water flux), the Ogata-Banks solution (Equation 30) to the transport equation would be used for contaminant transport. This computes a concentration profile along a line. Dilution in an underlying geological unit can be accounted for with a simple mass balance (Environment Agency, 1999). However, this mass balance only applies if leachate is moving into the groundwater. Beneath a hydraulic containment landfill, calculation of the diluted concentrations in groundwater requires knowledge of the mass flux of contaminant.

There are two relevant boundary conditions for representing the liner system (Figure 18) as follows.

- A fixed concentration of zero at the outside edge of the liner. This is used to calculate a conservative bound to (i.e. overestimate of) the diffusive contaminant flux through the liner. This flux can then be diluted with groundwater to give a concentration in groundwater. This would normally be used only for List II substances.
- A concentration of zero at infinity. This computes a conservative approximation to (i.e. overestimate of) the concentration profile within the liner. This would normally be used for List I substances to calculate concentrations at the very base of the liner.

The real system does not have a flow or mass transport boundary at the edge of the liner: the liner is part of a larger system through which transport occurs with natural hydrogeological boundaries far from the site. The edge of the liner merely corresponds to a location where properties change and where we are interested in results.

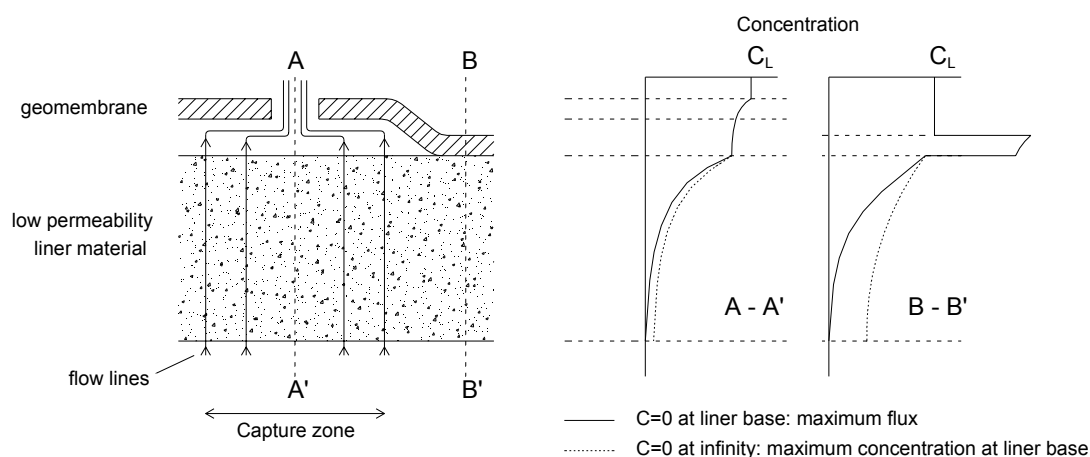


Figure 18. Effect of boundary conditions on concentration profiles of organic species through composite liners

The spreadsheet models the transport of contaminants through the landfill barrier system, and specifies boundary conditions for this system. It does not include a detailed representation of the hydrogeological system beyond the outer edge of containment, which would often need to be site specific. The outer edge of the barrier system is not however a natural boundary for which exact boundary conditions can be specified for hydraulically contained landfills, and therefore approximations have to be used. In setting approximate boundary conditions, two alternative simplifications have been used in order to provide conservative calculations for List I and List II species respectively. These are as follows.

- When a List I species is selected, the boundary condition at the outer edge of the mineral component of the lining system is set by requiring the solution to correspond to one where the concentration would tend to zero at large distances in an infinitely thick liner. The lining system is finite and in this case, the choice represents there being no explicit constraint on the solution at the physical edge of containment: the contaminant diffuses across the boundary unaffected by conditions in the aquifer. In practice this means that the concentration just inside the barrier is not reduced by proximity to the clean water immediately outside the lining system. It thus provides an over-estimate of concentration at the outer edge of containment. The true concentration at the outer edge of containment will be lower than this because clean water flushes past the edge of the boundary and leads to steeper concentration gradients across this physical boundary than are predicted by the model. The corollary of the choice of boundary condition to be conservative for predicting concentration at the outer edge of containment is therefore that the flux across this boundary is under-estimated. Indeed, an artificial aspect of the boundary condition is that the flux will rise to a peak and then decline as the diffusive front of contaminant breakthrough apparently passes the edge of containment and migrates further without the physical controls that will affect the profile as it extends into the aquifer. The true flux will be greater than the transient peak shown in the solution and can be calculated by selecting the List II button on the spreadsheet instead of List I (note that the concentration will now be incorrect).
- For List II substances, the concern is that there should be no pollution of groundwater and thus the measure of discharge of List II substances is the concentration in groundwater outside the barrier system, after allowing for dilution in the receiving groundwater. A conservative prediction of this uses a measure of the volume of groundwater which mixes with the diffusive contaminant flux out of the landfill containment barriers and requires a conservative measure of contaminant flux at the outer edge of containment. For this prediction we need to specify a conservative over-estimate of the contaminant

concentration gradient which can be evaluated by setting a zero concentration boundary condition at the outer edge of containment. This overestimates the outward diffusive flux and underestimates the inward advective flux, thus giving a net conservative estimate of the outward contaminant flux. Clearly the concentration at the boundary is zero for this solution and the concentration plot presents instead the concentration in groundwater that will be developed by mixing the outward contaminant flux calculated in the model with a volume of groundwater determined by the aquifer properties and the mixing depth in the aquifer.

In the case where an organic compound diffuses through the geomembrane and the mineral liner, single layer analytical solutions cannot be used because of the different transport velocities in each of the pathway segments. A numerical inversion of the Laplace transform solution to the dual layer transport problem has therefore been developed specifically for this spreadsheet. For the purposes of verification of this numerical solution, an analytical solution of the transport equation based on solute flux has been developed as a variant of a similar solution of Shackelford (1990). Full details of the development and verification of the Laplace transform solution are presented in Appendix B.

The following three potential attenuation processes have been accounted for in both the analytical solutions and the Laplace transform solutions (except that decay is not modelled within the geomembrane).

- Dispersion. Dispersion is modelled as a combination of diffusion and mechanical dispersion. Enhanced diffusion through the boundary layer of pores is included as a process so Equation 14 is used to determine the dispersion coefficient.
- Retardation. Retardation is modelled with the linear isotherm model (Equation 20).
- First order decay. First order decay can be applied to transport through the mineral layer. As discussed in Section 2.4.6 it is recommended that, unless the contaminant is radioactive or there are data to the contrary, considerable caution be applied to the choice of decay coefficients.

If the contaminant is able to diffuse through the geomembrane defect it is assumed to spread out over the wetted radius and to diffuse against the hydraulic gradient through the cylinder beneath the defect through which the water flows in.

Note that, on Figure 18, a lower solute concentration is predicted at the base of the liner beneath the defect. Here, advective flow is limiting the concentration whereas beneath the intact geomembrane, the contaminant freely diffuses through the static water column. It is clear, therefore, that given appropriate transport properties, organic compounds can diffuse through a composite liner with a defect-free geomembrane more readily than through a composite liner with many defects (see discussion in Section 2.5.3 above).

4.3.4 Summary of Model Logic

Scenarios 1, 2 and 3, describe the physical setting of the conceptual model whilst the options within each scenario control which of the numerical solutions are selected. In order for it to be transparent as to which solutions are being used within a particular model, the solution types have been categorised into solutions 'a', 'b' and 'c' (this is shown in cell 'solution_type' in the spreadsheet). The physical settings described by each solution type are presented in Table 4.1 along with the relevant numerical solutions and the available additional options. Occasionally, the results predicted by the spreadsheet may appear counterintuitive: this is a consequence of the different methods employed to generate the data for List I and List II contaminants. A

summary of the algorithms used to produce the concentration and flux data for List I and List II substances is also given in Table 4.1 to help identify the dominant contribution to the solution.

Table 4.1 Summary of Model Logic

	Solution 'a'	Solution 'b'			Solution 'c'	
Description	Scenario 1 and Scenario 2 and 3 without a geomembrane.	Scenario 2 and 3 for organic contaminants with geomembrane.			Scenario 2 and 3 for inorganic contaminants with geomembrane.	
Options	Inorganic/Organic, List I/List II	Delamination, List I/ List II			Delamination, List I/List II	
Flux and concentration solutions used	Single layer solution (Darcy)	For each defect type: Single layer solution (Giroud)	Delaminated area: Single layer solution (Darcy)	Intact geomembrane and clay: Two layer solution.	For each defect type:: Single layer solution (Giroud);	Delaminated area: Single layer solution (Darcy)
Outward flux areas	Contact area	Total area of capture zones (limited by geomembrane contact area)	Delaminated area (user specified)	Intact geomembrane contact area minus area of capture zones (non-zero inward velocity in capture zones).	Total area of capture zones (limited by geomembrane contact area)	Delaminated area (user specified)
Concentration	List I	Single layer concentration solution using zero concentration boundary condition at infinity.	Maximum of the concentrations obtained using the solutions described above with boundary condition at infinity.		Maximum of the concentrations obtained using the solutions described above with the zero concentration boundary condition at infinity.	
	List II	Single layer flux solution using zero concentration boundary condition at the edge of the liner, converted to concentration using dilution in the aquifer.	Sum of the fluxes obtained from the solutions described above using the zero concentration boundary condition at the edge of the liner, converted to concentration using the dilution in the aquifer.		Sum of the fluxes obtained from the solutions described above using the zero concentration boundary condition at the edge of the liner, converted to concentration using dilution in the aquifer.	
Flux	List I	Single layer flux solution using zero concentration boundary condition at infinity.	Sum of the fluxes obtained using the solutions described above using the zero concentration boundary condition at infinity.		Sum of the fluxes obtained using the solutions described above using the zero concentration boundary condition at infinity.	
	List II	Single layer flux solution using the zero concentration boundary condition at the edge of the liner	Sum of the fluxes obtained from the solutions described above using the zero concentration boundary condition at the edge of the liner.		Sum of the fluxes obtained from the solutions described above using the zero concentration boundary condition at the edge of the liner.	

4.3.5 Conceptual Limitations of the Model

It should be noted that there are a number of limitations to the model that will generally make it a scoping tool rather than a detailed final risk assessment model. It uses a generic mathematical model rather than representing the site specific conceptual model explicitly. If the appraisal of a risk assessment does not allow a clear decision to be made, more sophisticated modelling and/or well-constrained site specific data will be required.

Additionally, a number of simplifying approximations have been made in the calculations that must be confirmed as relevant for the site specific conceptual model. It is not possible to predict definitely whether or not these are conservative assumptions but generally the consequence of these limitations will be either conservative or small. If it is not clear how important these limitations are for the site under consideration, expert advice should be sought.

- As is conventional in UK landfill risk assessment tools, the mathematical model solves for contaminant transport along one-dimensional pathways. In particular for composite lined landfills, a one-dimensional pathway is used to represent the leakage flow path and outward migration against this flow. See Rowe (1998) for further discussion.
- The water balance for the landfill is assumed to be steady state. It takes no account of deterioration of the liner through time either by desiccation of the clays or by damage and oxidation of the geomembrane (Environment Agency, 2004b).
- Since the model is designed primarily to compute contaminant transport, it does not account for any groundwater that might seep into the unsaturated waste above the level of the leachate head. The water flux into the landfill from groundwater may therefore be higher than predicted due to this component of inflow. Infiltration through the landfill cap is also not considered.
- Neither the water balance nor the contaminant transport calculations account for a period of above water table operation during construction and initial filling of the landfill. If leachate leakage occurs during this initial phase its breakthrough at a compliance point will not be predicted by this model.
- No estimate is made for the time to exhaust the cation exchange capacity in the mineral liner, as described in Environment Agency (2002a); the model assumes that it is never exhausted. If separate calculations show that this would occur at times of concern (after taking into consideration possible decline of the leachate source) then the linear isotherm partition coefficient (K_d) will not be appropriate and unretarded transport should be considered.
- The leachate concentration is assumed to remain constant over time. In reality this will decrease in time as leachate evolves and as groundwater flowing in through the cap and the liner dilutes it. This assumption will therefore be conservative, and must be carefully considered when evaluating the long-term impact of the landfill.
- No account is taken of diffusion coefficients increasing with temperature. If elevated temperatures are anticipated for the lifetime of the landfill, an Arrhenius relationship may be used to scale the diffusion coefficient of a solute (Langmuir, 1997).
- No account is taken for the membrane effects of clayey materials (e.g. osmosis, anion exclusion or steric hindrance).
- No account is taken of the degradation of liner materials with time.

- Contaminant transport in underlying geological formations is not modelled.
- The predicted concentration of List II contaminants is calculated for discharge of the List II substances mixed with groundwater flowing beneath the site. The List II contaminants are assumed to mix with all groundwater to an estimated mixing depth. This does not take into account any localised areas of greater discharge or the design of monitoring wells, and therefore whilst predicting the compliance of the site with Groundwater Regulations in the context of pollution due to discharge of List II substances, observations at specific monitoring wells may be influenced by their specific setting and completion. This should be explicitly considered in siting such monitoring boreholes and setting control and trigger levels.
- No explicit consideration is made of background concentrations of modelled contaminants and the predicted discharges will be reduced if there is significant background contamination. This can be considered by setting the leachate concentration to the excess contaminant concentration above the background (and interpreting the resulting calculated concentrations as additional excess contaminant concentration above background levels). This approach neglects the time for concentrations in the lining material to rise to the level of the surrounding natural background. Thus, the model calculations can be interpreted as assuming that the system is initially saturated with water at the background concentration and having calculated the additional impact of the excess concentration in the leachate.
- It is assumed that the leachate drainage and collection layer is effective and does not degrade with time, and therefore there is assumed to be no risk due to perched layers of leachate in contact with the lining system above the external groundwater level leading to outward advective transport pathways. It is further assumed that the leachate collection system does not allow significant leachate mounds to develop away from the leachate collection points and that the specified leachate head is an appropriate value across the entire cell or phase being modelled. For example this may be a concern if the site has only perimeter leachate collection drains and the leachate head might then exceed groundwater heads in the middle of the site leading to a loss of hydraulic containment.

5. Summary and recommendations for future work

This report has presented a review of the current state of the art in the understanding and representation of contaminant transport through landfill lining systems in the context of the hydrogeological settings of hydraulically contained landfills. It has thus emphasised diffusive processes through low permeability lining systems considering both mineral and composite lining systems. Whilst the emphasis is on hydraulically contained systems, much of the literature reviewed and many of the processes described are also relevant to conventional landfill settings, particularly where there is no benefit that can be relied upon from an unsaturated zone.

On the basis of the review a very flexible spreadsheet-based scoping tool has been developed to estimate contaminant discharges from List I and List II substances for three typical scenarios relevant to current and possible future UK hydraulically contained landfill sites. The report, and accompanying spreadsheet tool, may be used to aid decision-making for landfill risk assessments within the framework set out in the Environment Agency's guidance on *Hydrogeological Risk Assessments for Landfills* (Environment Agency, 2003d). The report considers generic hydrogeological settings and designs that are relevant to many of the UK's existing sub-water table landfill sites and assumes that the landfills are constructed with adequate means to manage leachate heads (e.g. drainage media, pumps, etc.). Experience shows that control of groundwater levels during construction of sub-water table landfills is critical with most failures being due to loss of such control.

The results of the literature review and spreadsheet calculations confirm that diffusion can cause significant flux of contaminants out of landfill sites, even against an inward advective flow of groundwater. Hydraulic containment landfills therefore have the potential to cause pollution if they are not designed, constructed and operated in an appropriate manner.

It should be noted that this report is not a design manual for hydraulic containment landfills and makes no recommendations for policy in relation to current or future sites. Reference should be made to the Agency's current guidance (e.g. RGN6: Environment Agency, 2003a; Hydrogeological Risk Assessments for Landfills: Environment Agency, 2003d) to ensure designs are compliant with the Landfill Regulations. It is unlikely that a compacted clay or GCL liner would be appropriate for scenarios 2 and 3 as the sole component of the artificial sealing liner.

Appendix B presents the derivation of the equations used and the simplified boundary conditions applied to make a conservative calculation to help determine the site's compliance with the Groundwater Regulations. A final section in this appendix presents a verification of the numerical algorithms used to invert the Laplace transforms used for one of the solutions and to confirm the accuracy of the algebraic manipulations required to match the selected boundary conditions. Whilst this gives us confidence that the analytical solutions have been accurately evaluated, it does not constitute a comprehensive verification of the tool, which would ideally involve cross comparison with alternative models offering a similar functionality.

The model has not been validated against any real case studies, and this would be a valuable additional measure to help develop confidence in the application of the model to real landfill sites and enhance the defensibility of decisions made on the basis of using this tool.

It would also be extremely valuable to undertake field investigations to confirm the validity of Giroud's relations for settings where there is no unsaturated zone beneath a composite lining

system. These relations are widely used in landfill hydrogeological risk assessment, often beyond the limits of applicability for which the empirical results were derived. Such extrapolation to reverse flow conditions are used in this spreadsheet tool for assessing transport out of hydraulically contained, composite lined landfill sites.

Finally we note that this tool does not address issues in relation to DAC (Dense Asphaltic Concrete) lining systems, which have begun to be considered for UK sites, nor does it explicitly address the evolution of lining materials over time. Whilst deterioration of the hydraulic properties would in principle improve the hydraulic containment, there would be issues regarding leachate management. There is no information on the evolution of transport properties of these landfill lining systems as the physical properties degrade. This might in principle lead to enhanced partitioning and diffusion coefficients for membrane components for example. The issues surrounding liner degradation are being actively investigated (e.g. Environment Agency, 2004b) and consideration of transport properties and the parameters of relevance to hydraulic containment would merit inclusion in these studies.

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LIST OF SYMBOLS

a	Hole area (m^2)
C	Solute concentration ($kg.m^{-3}$)
C_0	Leachate concentration ($kg.m^{-3}$)
C_{gm}	Concentration of solvent in the geomembrane ($kg.m^{-3}$)
$C_{q\infty}$	Empirical constant in Giroud equations
C_{q0}	Empirical constant in Giroud equations
d	Hole diameter (m).
D_C	Effective diffusion coefficient for composite liner system ($m^2.s^{-1}$)
D_e	Effective diffusion coefficient ($m^2.s^{-1}$)
D_{gm}	Diffusion coefficient of solvent in geomembrane polymer ($m^2.s^{-1}$)
D_s	Coefficient of surface diffusion ($m^2.s^{-1}$)
D_{Tay}	Effective longitudinal dispersion coefficient for flow in a capillary tube ($m.s^{-2}$)
D_w	Free water diffusion coefficient ($m^2.s^{-1}$)
g	Gravitational acceleration ($m.s^{-2}$)
h_w	Depth of leachate above geomembrane (m)
$i_{avg\infty}$	Hydraulic gradient beneath the centre of a circular defect (dimensionless)
i_{avg0}	Hydraulic gradient beneath the centre of an infinitely long defect (dimensionless)
J_D	Diffusive flux ($kg.m^{-2}.s^{-1}$)
J_{gm}	Mass flux of solvent through the polymer ($kg.m^{-2}.s^{-1}$)
J_{ha}	Hyperfiltrated advective solute flux
J_π	Osmotic solute flux
J_{Tay}	Longitudinal dispersive flux for flow in a capillary tube ($m^3.s^{-1}$)
k_o	Hydraulic conductivity of overlying material ($m.s^{-1}$)
k_B	Lower limit of hydraulic conductivity for validity of the Bernoulli equation ($m.s^{-1}$)
K_G	Upper limit of hydraulic conductivity for validity of the Giroud equation ($m.s^{-1}$)
k_s	Hydraulic conductivity of underlying material ($m.s^{-1}$)
K	Hydraulic conductivity of clay barrier ($m.s^{-1}$)
MW_i	Molecular weight ($kg.mol^{-1}$)
n	Porosity of the material (dimensionless)
n_{ADV}	Porosity through which water moves by advective flow (dimensionless)
n_{DIFF}	Porosity within which diffusion occurs (dimensionless)
n_{DRAIN}	Porosity from which water may drain freely under gravity (dimensionless)
n_{TOT}	Total void space within a dry porous medium (dimensionless)
n_{WAT}	Porosity measured by conventional water saturation methods (dimensionless)
q_i	Infiltration rate into the overlying material ($m.s^{-1}$)
q_π	Osmotic liquid flux
Q_B	Flux through a hole calculated by Bernoulli equation ($m^3.s$)
Q_G	Flux through a hole calculated by Bernoulli equation ($m^3.s$)
Q_h	Leakage rate through the geomembrane ($m^3.s^{-1}$)
r	Radius of tube (m)
r	radius of the defect (if circular) or half the side length (if square) (m).
r_s	Radius of the wetted area beneath the defect (m),
R	Retardation factor of the solute in the mineral liner (dimensionless)
t	Elapsed time (s)
t_{gm}	Thickness of the geomembrane (m)
t_s	Thickness of the mineral liner (m)
T	Absolute temperature (K)
u_{max}	Velocity of water along the centre of the tube ($m.s^{-1}$)
v	Advective velocity ($m.s^{-1}$)
x	Distance (m)
α_L	Dynamic longitudinal dispersivity (m)

ΔC	Concentration difference across the barrier ($\text{kg}\cdot\text{m}^{-3}$)
Δh	Hydraulic head difference (m)
Δh_w	Leachate head difference across the membrane (m)
$\Delta \pi$	Theoretical chemico-osmotic pressure ($\text{J}\cdot\text{m}^{-3}$)
Δx	Thickness of the liner (m)
κ_B	Dimensionless coefficient
λ	Decay constant for the reaction (s^{-1})
λ_s	First-order decay coefficient for irreversible sorption (s^{-1})
ν	Number of ions per molecule of the salt (dimensionless)
μ	Dynamic viscosity of the leachate ($\text{kg}\cdot\text{m}^{-1}\cdot\text{s}^{-1}$)
ρ_b	Dry bulk density of the material (kg/m^3)
ρ_w	Density of the solute ($\text{kg}\cdot\text{m}^{-3}$)
τ	Tortuosity (dimensionless)
ω	Osmotic efficiency coefficient of the liner (dimensionless)

APPENDIX A: FLOW THROUGH DEFECTS IN GEOMEMBRANES

Defects in geomembranes comprising holes and tears are caused by defects in geomembrane seams, punctures from sharp objects above or beneath the sheet, tension due to loading and material failure due to creep or cyclic loading. The quantity of defects is reduced if good quality assurance is in place on installation of the liner, but some defects are inevitable. The sizes of holes and other defects in existing landfills range from pin-holes less than a millimetre in size to tears several metres long. Statistics of defect frequencies and size ranges are discussed in Environment Agency (2004b). This appendix presents an overview of the approaches available to estimate the flow through individual defects.

The following sections present formulae for calculating the flow through geomembrane defects either alone or as part of composite liners. None were developed specifically for the purposes of computing flows under hydraulic containment conditions. In particular, many of the equations developed by Giroud (see below) were developed specifically for above water table landfills where the mineral liner is unsaturated at the base. The relations used to estimate the hydraulic gradient rely on this assumed setting and are thus not suitable for below water table landfill settings. Giroud's formulae are presented in this appendix for completeness but they are not used in this study. The applicability of Giroud's formulae for flow through defects, adapted by using a modified estimate of the hydraulic gradient for use in hydraulic containment systems, is discussed further in the main text.

The key equations are identified in the main text, however, a number of varieties have been published and have been used in landfill risk assessments. It is important, for sites where composite liners are used, both to recognise that a legitimate version of Giroud's empirical relations has been used, and also to be aware of the underlying assumptions. This requires awareness of a significant amount of background material, which, because it applies to a limited number of settings, has been presented in this appendix so as to avoid distorting the balance of the main text.

A.1. Flow Through Holes in Geomembranes

The relationships in this section are applicable for geomembranes supported above and below by high permeability granular media such as drainage layers. The first two of these neglect the hydraulic conductivity of the surrounding media and assume that the pore openings are larger than the hole in the geomembrane. They can either be used in situations where there is a single geomembrane liner, or for the upper geomembrane in a double liner system. They are based upon fundamental fluid dynamics for slow flows and can be used with equal validity whichever direction the water is flowing. In particular, it provides an upper bound to the flow through a defect as it neglects any resistance to flow from material either side of the defect.

Firstly, the leakage rate through a hole whose diameter is less than the thickness of the geomembrane, the leakage rate (Q_h) depends on viscosity and the rate can be expressed using Poiseuille's equation for flow through a capillary tube (see, for example, Giroud and Bonaparte, 1989a):

$$Q_h = \frac{\rho_w \Delta h_w a^2}{8\pi\mu t_g} \quad (\text{A1})$$

where ρ_w is the density of leachate (kg.m^{-3})
 Δh_w is the leachate head difference across the membrane (m)
 μ is the dynamic viscosity of the leachate ($\text{kg.m}^{-1}.\text{s}^{-1}$)
 t_g is the thickness of the geomembrane (m)
 a is the area of the hole (m^2)

From a practical point of view the density and viscosity of water can be used in Equation A2 (999.7 kg.m^{-3} and $0.001307 \text{ kg.m}^{-1}.\text{s}^{-1}$ at 10°C). Under conditions of free drainage (i.e. saturated above the geomembrane but unsaturated below), Δh_w becomes h_w , the depth of leachate above the geomembrane and the relation is often presented with this definition. It is valid also for h_w to be replaced by Δh_w where both sides of the membrane are saturated.

Secondly, if the diameter of the hole is greater than the thickness of geomembrane, Bernoulli's equation for free flow through a circular orifice can be used (again this is presented in the review given in Giroud and Bonaparte, 1989a):

$$Q_h = \kappa_B a \sqrt{2g\Delta h_w} \quad (\text{A2})$$

where κ_B is a dimensionless coefficient reflecting the flow geometry in the medium on either side of the defect.

Benson *et al.* (1995) found that $\kappa_B = 0.6$ is appropriate for most geomembrane holes. This is also the value assumed in Giroud and Bonaparte (1989a) and subsequent papers authored by Giroud. Again, under conditions of free drainage (i.e. saturated above the geomembrane but unsaturated below, Δh_w becomes h_w , the depth of leachate above the geomembrane.

In some cases, a geomembrane may be underlain by a free draining porous material but overlain by a porous material that is unable to sustain the potential leakage rate through the hole that would be predicted by Bernoulli's Law (Figure A.1). In this case, a significant cone of depression develops in the leachate level above the defect corresponding to radial flow towards the defect. Where the hydraulic conductivity of the overlying material controls the flow through the hole, Giroud (1997f) present an empirical relationship for the leakage rate:

$$Q_h = 1.64(aq_i)^{0.075} h_w^{1.85} k_o^{0.925} \quad (\text{A3})$$

where q_i is the infiltration rate into the overlying material (m.s^{-1})
 h_w is the head over the membrane distant from the hole (m)
 k_o is the hydraulic conductivity of the overlying material (m.s^{-1})

This relationship may often be used in place of Equations A1 or A2 but it is specific to systems where flow is downwards and it must not be applied to sub-water table settings.

Where the geomembrane is not horizontal, the head over the membrane distant from the hole can be obtained by balancing h_w with the down-slope flow through the material under gravity. However, where the geomembrane is horizontal, the head is given by:

$$h_w = \sqrt{\frac{aq_i}{2\pi k_o} + \frac{Q_h}{2\pi k_o} \left(\ln \left[\frac{Q_h}{aq_i} \right] - 1 \right) + \frac{1}{4g^2} \left(\frac{Q_h}{0.6a} \right)^4} \quad (\text{A4})$$

Since the value of h_w and Q_h are co-dependent the two equations are solved simultaneously. Giroud (1997f) presents an equation to give the limiting value of k_o above which the Bernoulli

equation gives accurate results. However, more practically, the values of Q_h from Equations A2 and A3 can be compared and the minimum value used.

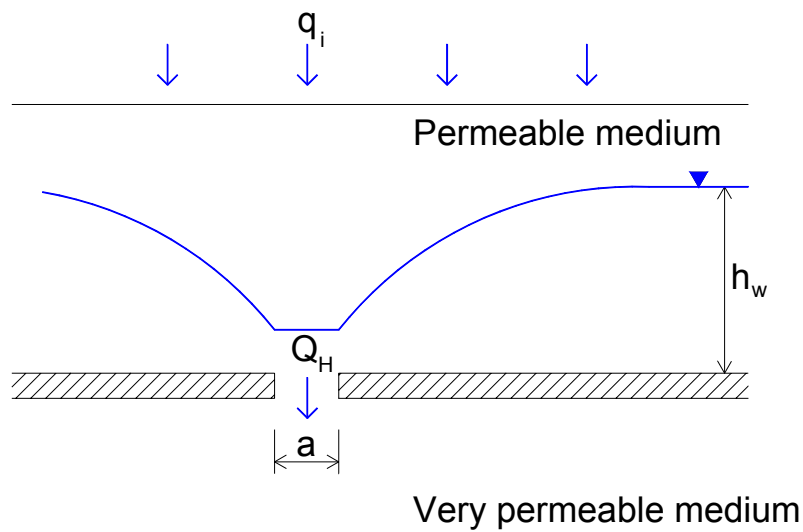


Figure A.1. Flow through a defect in a geomembrane overlain by a permeable medium and underlain by a very permeable medium (from Giroud, 1997f)

A.2. Geomembranes Underlain by Low Permeability Materials

Where geomembranes are underlain by low permeability materials, the hydraulic conductivity of the underlying material needs to be considered as it controls the flow that can drain through the defect in the geomembrane. Giroud and Bonaparte (1989b) explored this at length for systems underlain by low permeability material above the water table. It was shown that the flow through a defect is controlled by the diameter and hydraulic conductivity of a column of the low permeability material beneath the defect, and that the size of this column is determined by the quality of the contact between geomembrane and the material (Figure A.2). The separation between the geomembrane and low permeability layer may be due to local undulations or by a geotextile and will be influenced by the care with which the lining system is constructed.

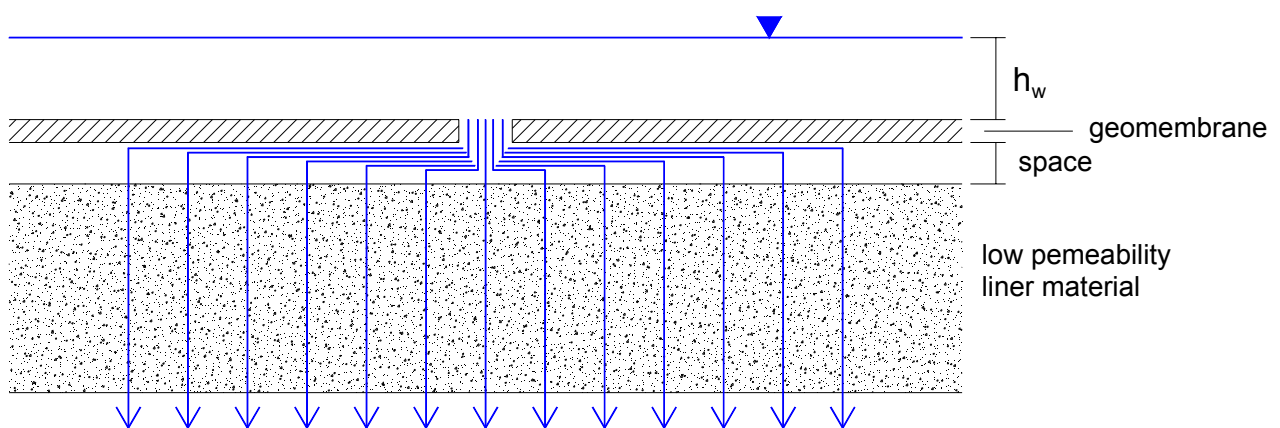


Figure A.2. Flow through a defect in a geomembrane underlain by a low permeability medium (from Giroud and Bonaparte, 1989b)

Giroud *et al.* (1997b) place a lower limit on the hydraulic conductivity of the medium underlying a geomembrane liner, k_B ($\text{m}\cdot\text{s}^{-1}$), below which account has to be taken of its hydraulic conductivity in leakage calculations (N.B. This is an empirical relationship and not a balanced equation):

$$k_B = 10^5 d^2 \quad (\text{A5})$$

where d is the diameter of the defect (m)

Where a geomembrane is in perfect contact with the underlying porous medium, it may be assumed that there is no enhanced lateral flow at the interface and the leachate flows into a semi-infinite medium beneath the hole. The flow rate is given by Forchheimer's equation (Rowe, 1998):

$$Q_{hole} = 2dk_s \Delta h_w \quad (\text{A6})$$

where Δh_L is the head drop across the composite liner (m)

This relationship does not depend on the material below the geomembrane and can be applied to predict flow for hydraulic containment landfill sites, where perfect contact is a reasonable assumption.

Giroud *et al.* (1990) extended the work of Giroud and Bonaparte (1989b) and developed relationships for the calculation of leakage rates through circular and square holes and linear defects for varying degrees of contact between the geomembrane and mineral liner. For a circular or square hole with diameter (or side length) greater than the thickness of the geomembrane, flow through the hole, Q_{hole} ($\text{m}^3 \cdot \text{s}^{-1}$) is given by:

$$Q_{hole} = C_{q0} i_{avg0} a^{0.1} h_w^{0.9} k_s^{0.74} \quad (\text{A7})$$

where C_{q0} is an empirical constant

i_{avg0} is the hydraulic gradient through the low permeability layer (dimensionless)

k_s is the hydraulic conductivity of the underlying material ($\text{m} \cdot \text{s}^{-1}$)

The constant C_{q0} scales the leakage rate according to the quality of contact between the geomembrane and the underlying porous medium. It takes the value 0.21 for 'good' contact conditions and 1.15 for 'poor' contact conditions. 'Good' and 'poor' are defined in Giroud (1997) and are based on empirical estimation of the transmissivity of the space between the geomembrane and low permeability layer (or of the intermediate geotextile). With modern quality assurance programmes being followed, new liners installed with intimate contact between the geomembrane and underlying mineral layer can be assumed to have 'good' contact.

The hydraulic gradient across the low permeability layer, i_{avg0} , for sites above the water table can be assumed to be unity when the leachate head is less than the thickness of the low permeability liner, but for greater leachate heads it is calculated. Two formulae for calculating i_{avg0} are in use in the UK. The oldest, from Giroud *et al.* (1990), was used in LandSim 1:

$$i_{avg0} = 1 + \frac{h_w}{2t_s \ln(r_s/r)} \quad (\text{A8a})$$

$$r_s = \sqrt{\frac{C_{q0}}{\pi} a^{0.05} h_w^{0.45} k_s^{-0.13}} \quad (\text{A8b})$$

where t_s is the thickness of the underlying low permeability layer (m)

r_s is the radius of the wetted area beneath the defect (m)

r is the radius of the defect (if circular) or half the side length (if square) (m)

However, Giroud (1997) superseded Equation A8a with a simpler empirical relationship that eliminates the need for Equation A8b. Equation A9 was derived and is the relationship now used in LandSim 2 and LandSim 2.5 and is the preferred relationship for calculating hydraulic gradients across low permeability barriers in this context:

$$i_{avg0} = 1 + 0.1 \left(\frac{h_w}{t_s} \right)^{0.95} \quad (A9)$$

These estimates of the hydraulic gradient are only relevant for leakage through lining systems installed above the water table and represent corrections to simple unit (gravity) drainage. For sites where the lining system is below the water table we replace this by a simple head gradient. This neglects head losses associated with convergent flows to the defect. The errors associated with this assumption are likely to be small relative to other uncertainties as the leakage rate depends linearly on the gradient. The magnitude of the error associated with this substitution has not been investigated by experimental methods such as used by Giroud to derive his empirical relationships that apply to above water table sites. Further experimental work to investigate leakage rates for below water table settings would be useful.

Flow through rectangular defects can also be calculated using equations from Giroud (1990):

$$Q_{tear} = C_{q0} i_{avg0} b^{0.2} h_w^{0.9} k_s^{0.74} + C_{q\infty} i_{avg\infty} (B-b) b^{0.1} h_w^{0.45} k_s^{0.87} \quad (A10)$$

where b and B are the width and length of the rectangular defect respectively (m),

$C_{q\infty}$ is an empirical constant,

$i_{avg\infty}$ is the hydraulic gradient across the low permeability liner beneath the centre of the tear.

Again, the constant $C_{q\infty}$ scales the leakage rate according to the quality of the contact between the geomembrane and the low permeability liner, and takes the values 0.52 and 1.22 respectively for 'good' and 'poor' contact.

The hydraulic gradient across the low permeability layer, $i_{avg\infty}$, can again be assumed to be unity when the leachate head is less than the thickness of the low permeability liner. In Giroud (1990) and LandSim 1 the value of $i_{avg\infty}$ is assumed to be the same as i_{avg0} , given in Equation A8a above. However, Giroud (1997) also superseded this with the following formula (also used in LandSim 2 and LandSim 2.5):

$$i_{avg\infty} = 1 + 0.2 \left(\frac{h_w}{t_s} \right)^{0.95} \quad (A11)$$

As for equation A9, this relation for the head gradient is only appropriate for above water table settings and in this study we have assumed that it can be replaced by a simple head gradient. This neglects head losses associated with convergent flows to the defect. The errors associated with this assumption are likely to be small relative to other uncertainties as the leakage rate depends linearly on the gradient.

The limits of the validity of the equations presented are as follows (Giroud, 1997 and Giroud *et al.*, 1997b):

- advection or diffusion of water through the intact geomembrane is not considered,

- solutes in the leachate do not affect the hydraulic properties of the low permeability materials,
- the diameter of circular defects should be no less than 0.5mm and no greater than 25mm. If the defect is not circular these limits should be used for the defect width,
- the hydraulic head on top of the geomembrane should not exceed 3m,
- the hydraulic conductivity of the low-permeability soil underlying the geomembrane should not exceed a certain value k_G (Section A.3). Giroud (1997b) proposed the following value of k_G for a circular defect:

$$k_G = \left\{ \frac{0.3891d^{1.8}}{C_{qo}i_{avg0}h_w^{0.4}} \right\}^{1/0.74} \quad (A12)$$

Clearly in a hydraulically contained landfill setting the validity of these empirical relations is questionable, however, they are based on flow fields which will be similar to those developed under saturated conditions. The difference will be that in the case for defect flow through a liner above the water table, only a region close to the defect will be wetted. Away from the defect the hydraulic gradient will be determined by gravity drainage. To take some account of the benefits afforded by the mineral layer for saturated systems (i.e. sub-water table sites) the following approach has been used.

It has been assumed to be reasonable to use the relationships A7 and A10 for flow through the defect where flow is into a larger volume of material (saturated conditions) so long as h_w and $i_{avg0/\infty}$ are replaced by the excess head across the liner and the simple average head gradient across the liner as a whole. These substitutions can equally be made for outward or inward (hydraulically contained) flow as the flow field will be reversible. While not ideal, this is the best available way to estimate flow through defects in composite liners for hydraulic containment settings (neglecting the benefit of the resistance of the mineral component by applying Equations A1 or A2 would be unduly pessimistic in the sense of over-estimating groundwater or leachate fluxes through the liner) and this approach has been applied to the spreadsheet tool.

A.3. Geomembranes Underlain by Semi-Permeable Materials

Equation A12 presents a maximum hydraulic conductivity of the underlying porous material below which the Giroud equations are valid. Likewise Equation A6 presents a lower limit of hydraulic conductivity above which the Bernoulli equation is valid. These are not the same value and to ensure a smooth transition between the two flow regimes, Giroud *et al* (1997b) proposed a relationship to analytically interpolate between the two sets of equations for circular or quasi-circular holes:

$$\log\left(\frac{Q_B}{Q}\right) = \log\left(\frac{Q_B}{Q_G}\right) \left(\frac{\log(k_B/k_s)}{\log(k_B/k_G)} \right)^m \quad (A13a)$$

$$m = 0.74 \frac{\log(k_B/k_G)}{\log(Q_B/Q_G)} \quad (A13b)$$

where Q_B and Q_G are the theoretical flows calculated with Equations A2 and A7 respectively,
 k_B and k_G are the limiting hydraulic conductivities from Equations A5 and A12 respectively,

Q is the interpolated flow for a system underlain by material of hydraulic conductivity k_s .

The range of hydraulic conductivities over which this equation is valid is:

$$k_G \leq k_s \leq k_B \quad (A14)$$

The limits of validity of these relationships are the same as for the case where a geomembrane overlies a low permeability liner and are given at the end of Section A.2.

These relationships are often not used and a valid approximation is to extrapolate the Giroud and Bernouilli relationships into the intermediate region and regard them as upper bounds, choosing the smaller of the resulting flows.

A.4. Taking Things Further

The limitations of the Giroud (1997) solution (for geomembranes underlain by low permeability materials) are discussed in depth in Rowe (1998), and analytical, but complex, relationships for computing flow through holes in geomembranes are derived. They take account of the transmissivity of the gap between the geomembrane and low permeability layer, the hydraulic conductivity of the subsoil beneath the mineral liner and can be applied to any combination of layer properties, hole size, leachate head or groundwater head. The transmissivity of the gap (unless it is that of a geotextile) remains empirically-derived, however.

A comparison of the results of the Giroud (1997) solution, the Rowe (1998) solution and a 3D numerical model is presented in Foose *et al.* (2001). Flow rates were computed through a 100 mm² circular defect in a composite liner comprising geomembrane and 5 mm clay with hydraulic conductivity 10⁻¹⁰ m.s⁻¹. A range of interface transmissivities that had been measured in the laboratory was tested with the Rowe (1998) solution and the numerical model. The results are as follows:

	Leakage rate (m ³ .a ⁻¹)
Giroud (1997), poor contact	1.564
Giroud (1997), good contact	0.286
Rowe (1998)	3x10 ⁻⁵ – 4x10 ⁻³
3D MODFLOW model	7x10 ⁻⁵ – 4x10 ⁻³

At relatively high interface transmissivities, the Rowe (1998) solution and the numerical model were in good agreement. However, for lower values of interface transmissivity the Rowe (1998) solution significantly under-predicted leakage rates. In these cases the modelled flow lines are shorter than those assumed by the analytical solutions (Figure A.2).

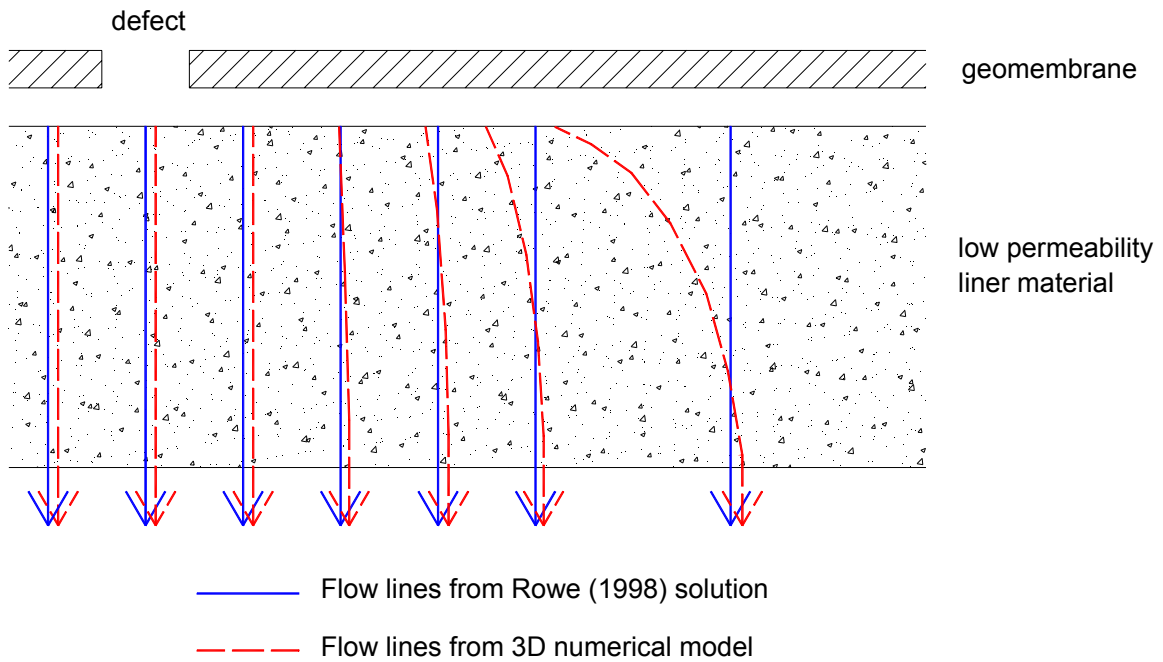


Figure A.2. Flow lines for flow through a circular defect in a composite liner with imperfect contact. After Foese *et al.* (2001)

Flows calculated using the Giroud (1997) solution were considerably higher than the more detailed models. Whilst the possibility that Giroud relations overestimate the outward fluxes can be regarded as reassuring for conventional containment settings it should be noted that for hydraulic containment settings, overestimation of inward velocities would lead to underestimation of the outward diffusive fluxes. However, the empirical constants for the Giroud (1997) equations were obtained from field data whereas those for the Rowe (1998) solution and the numerical model were obtained in the laboratory. It is considered therefore that the Giroud (1997) equations are likely to be more representative of field conditions and more appropriate for use in the models developed in this study.

APPENDIX B: CONTAMINANT TRANSPORT EQUATIONS

B.1 Analytical Solutions

Advection, dispersion, retardation and decay are the key transport processes controlling the migration of a contaminant through a porous medium. The contaminant concentration within the medium is described by

$$R \frac{\partial C}{\partial t} + v \frac{\partial C}{\partial x} - D_e \frac{\partial^2 C}{\partial x^2} + \lambda RC = 0 \quad (\text{B1})$$

where,

- x is distance away from the contaminant source (m);
- t is elapsed time (s);
- C is concentration (kg.m^{-3});
- R is the retardation factor;
- v is the advective velocity of water through the system (m.s^{-1});
- D_e is the coefficient of hydrodynamic dispersion ($\text{m}^2.\text{s}^{-1}$) and
- λ is the first-order decay constant for irreversible sorption or degradation (s^{-1}).

Note that the contaminant source is positioned at $x=0$ and the contaminant release begins at $t=0$.

The differential equation given in Equation B1 has been solved using the boundary condition that $C(\infty,t)=0$ (Domenico and Schwartz, 1998) and the solution is given below:

$$C(x,t) = \frac{C_0}{2} \left(\exp \left[\frac{vx}{2D_e} \left\{ 1 - \sqrt{1 + \frac{4\lambda RD_e}{v^2}} \right\} \right] \operatorname{erfc} \left[\frac{1}{2\sqrt{D_e t/R}} \left\{ x - \frac{vt}{R} \sqrt{1 + \frac{4\lambda RD_e}{v^2}} \right\} \right] + \exp \left[\frac{vx}{2D_e} \left\{ 1 + \sqrt{1 + \frac{4\lambda RD_e}{v^2}} \right\} \right] \operatorname{erfc} \left[\frac{1}{2\sqrt{D_e t/R}} \left\{ x + \frac{vt}{R} \sqrt{1 + \frac{4\lambda RD_e}{v^2}} \right\} \right] \right) \quad (\text{B2})$$

Here, the function $\operatorname{erfc}()$ is the complimentary error function^{B1} (Fetter, 1999).

The contaminant flux per unit area is given by:

$$J(x,t) = -nD_e \frac{\partial C}{\partial x} + nvC \quad (\text{B3})$$

where n is the porosity of the medium (-).

^{B1} The complimentary error function can be calculated using $\operatorname{erfc}(x) = 1 - \operatorname{erf}(x)$ where $\operatorname{erf}(x)$ is the error function. Note, however, that the error function in Microsoft Excel, $\operatorname{ERF}()$, is unreliable and often gives wrong values for arguments of interest. For contaminant transport calculations an independently-coded function should be used. Abramowitz and Stegun (1972) provide robust series expansions of the function.

Combining Equations B2 and B3 gives:

$$J(x, t) = \frac{nvC_0}{2} \left(\begin{aligned} & \frac{1}{2} \left\{ 1 + \sqrt{1 + \frac{4\lambda RD_e}{v^2}} \right\} \exp \left[\frac{vx}{2D_e} \left\{ 1 - \sqrt{1 + \frac{4\lambda RD_e}{v^2}} \right\} \right] \operatorname{erfc} \left[\frac{1}{2\sqrt{D_e t / R}} \left\{ x - \frac{vt}{R} \sqrt{1 + \frac{4\lambda RD_e}{v^2}} \right\} \right] + \\ & \frac{1}{2} \left\{ 1 - \sqrt{1 + \frac{4\lambda RD_e}{v^2}} \right\} \exp \left[\frac{vx}{2D_e} \left\{ 1 + \sqrt{1 + \frac{4\lambda RD_e}{v^2}} \right\} \right] \operatorname{erfc} \left[\frac{1}{2\sqrt{D_e t / R}} \left\{ x + \frac{vt}{R} \sqrt{1 + \frac{4\lambda RD_e}{v^2}} \right\} \right] + \\ & \frac{1}{v} \sqrt{\frac{RD_e}{\pi t}} \exp \left[\frac{vx}{2D_e} \left\{ 1 - \sqrt{1 + \frac{4\lambda RD_e}{v^2}} \right\} \right] \exp \left[- \left(\sqrt{\frac{R}{4D_e t}} \left\{ x - \frac{vt}{R} \sqrt{1 + \frac{4\lambda RD_e}{v^2}} \right\} \right)^2 \right] \end{aligned} \right) \quad (\text{B4})$$

B.2 Numerical Solutions

The solutions for concentration and fluxes presented in Section B.1 apply specifically to transport through a single layer of a porous medium, where the concentration tends to zero as x tends to infinity. Whilst this can be applied to many situations, the process of diffusion through landfill barrier systems requires Equation B1 to be solved for transport through two different layers of porous material that are in hydraulic contact and for a boundary condition at a finite distance (the thickness of the boundary system). In this section specific solutions to Equation B1 are described for the following settings:

- 1 a single layer system with concentration set to zero at infinity (identical to the analytical solution presented in Section B.1);
- 2 a single layer system with concentration set to zero at a finite distance;
- 3 a two layer system with concentration set to zero at infinity;
- 4 a two layer system with concentration set to zero at a finite distance.

The solutions are derived in Laplace transform space. The complexity of the solutions means that the expressions could not be analytically inverted, thus numerical techniques have been employed to obtain the solutions for the contaminant concentrations and fluxes. Stehfest's inversion technique (Hafner, 1992) has been used and this is described at the end of Section B.3. Note that the first of these solutions (1 above) has been included to allow the accuracy of the numerical methods to be verified against the analytical solution.

B.2.1 Single Layer Solutions

Equation B1 describes contaminant transport through a porous media subject to advection, dispersion, retardation and decay. Equation B1 can be Laplace transformed with respect to time to give:

$$R(s + \lambda)C^* + v \frac{\partial C^*}{\partial x} - D_e \frac{\partial^2 C^*}{\partial x^2} = 0 \quad (\text{B5})$$

where

s is the Laplace transform variable and
 C^* is the Laplace transformed concentration.

The Laplace transform of Equation B3 (the contaminant flux per unit area) is:

$$J^*(x, s) = -nD_e \frac{\partial C}{\partial x} + nvC \quad (\text{B6})$$

where

J^* is the Laplace transformed flux.

A general solution of Equation B5 is of the form

$$C^* = a \exp(\alpha x) \quad (\text{B7})$$

where a and α are constants.

Substituting Equation B7 into Equation B5 gives the auxiliary equation

$$R(s + \lambda) + \alpha v - D_e \alpha^2 = 0 \quad (\text{B8})$$

The roots of Equation B8 are non-identical and are given by

$$\alpha_1 = \frac{v - \sqrt{v^2 + 4D_e R(s + \lambda)}}{2D_e} \quad (\text{B9})$$

and

$$\alpha_2 = \frac{v + \sqrt{v^2 + 4D_e R(s + \lambda)}}{2D_e} \quad (\text{B10})$$

Inspection of Equations B9 and B10 indicates that $\alpha_1 < 0$ and $\alpha_2 > 0$. The corresponding general solution is given by

$$C^* = a_1 \exp(\alpha_1 x) + a_2 \exp(\alpha_2 x) \quad (\text{B11})$$

where a_1 and a_2 are constants.

For the single layer solutions, described by Solution 1 and 2, the boundary condition for the contaminant concentration at $x=0$ is described by

$$C(0, t) = C_0 \quad (\text{B12})$$

where C_0 is the concentration within the landfill and is constant. In Laplace space, this boundary condition becomes

$$C^*(0, s) = \frac{C_0}{s} \quad (\text{B13})$$

This boundary condition can be combined with the outer boundary condition to determine the values of the constants a_1 and a_2 . The two different outer boundary conditions are applied to determine Solution 1 and Solution 2 in the following subsections.

B.2.1 (a) Solution 1: Single layer solution with boundary condition at infinity

The second boundary condition for this system is given by

$$C(\infty, t) = 0 \quad (\text{B14})$$

which can be Laplace transformed to give

$$C^*(\infty, s) = 0 \quad (\text{B15})$$

Consideration of the boundary condition presented in Equation B15 and recognition that α_2 described by Equation B10 has a positive real component for the contour used in the inversion indicates that a_2 must be zero. Thus, Equation B11 becomes:

$$C^* = a_1 \exp(\alpha_1 x) \quad (\text{B16})$$

Substitution of the boundary conditions presented in Equations B13 and B15 into Equation B16 enables the expression for a_1 to be determined. The final solution for the Laplace transform of the contaminant concentration in single layer of porous medium with the boundary condition at infinity is

$$C^*(x, s) = \frac{C_0}{s} \exp(\alpha_1 x) \quad (\text{B17})$$

Substituting the expression for the concentration in a single layer of porous medium, derived using the $C=0$ boundary condition at $x=\infty$. Equation B17 into Equation B6 gives the expression for the mass flux per unit area

$$J^*(x, s) = \frac{C_0 n}{s} [v - D_e \alpha_1] \exp(\alpha_1 x) \quad (\text{B18})$$

B.2.1 (b) Solution 2: Single layer solution with boundary condition at edge of the layer

The second boundary condition for this system is given by

$$C(L, t) = 0 \quad (\text{B19})$$

where L is the layer thickness. The Laplace transform of Equation B19 is given by

$$C^*(L, s) = 0 \quad (\text{B20})$$

Consideration of Equations B11 and B20 indicate that both a_1 and a_2 are non-zero. Substitution of the boundary conditions presented in Equations B13 and B20 into Equation B11 enables expressions for a_1 and a_2 to be found. The final solution for the Laplace transform of the contaminant concentration in single layer of porous medium with the boundary condition at the edge of the layer is

$$C^*(x, s) = \frac{C_0}{s} \frac{\exp(\alpha_2 x + \alpha_1 L) - \exp(\alpha_1 x + \alpha_2 L)}{\exp(\alpha_1 L) - \exp(\alpha_2 L)} \quad (\text{B21})$$

Substituting the expression for the concentration in a single layer or porous material, derived using the $C=0$ boundary condition at $x=L$, Equation B21 into Equation B6, gives the expression for the mass flux per unit area

$$J^*(x, s) = \frac{C_0 [v - D_e \alpha_2] \exp(\alpha_2 x + \alpha_1 L) - [v - D_e \alpha_1] \exp(\alpha_1 x + \alpha_2 L)}{s \exp(\alpha_1 L) - \exp(\alpha_2 L)} \quad (\text{B22})$$

B.2.2 Two Layer Solutions for Concentration

The physical two layer system under consideration comprises a geomembrane (layer 1) and a mineral barrier (layer 2). For both two layer cases the thickness of the geomembrane is denoted by l and the thickness of the mineral barrier is denoted by L . Due to the low permeability of the geomembrane it is assumed that there is zero flow into the landfill, that is $v=0$, which is a conservative approach since advection decreases contaminant diffusion out of the landfill. Note that the two layer system is only applicable to organic contaminants, since the geomembrane is effectively impermeable to aqueous inorganic contaminants (Rowe, 1998). Thus, Equation B1 becomes

$$R \frac{\partial C}{\partial t} - D_e \frac{\partial^2 C}{\partial x^2} + \lambda RC = 0 \quad (\text{B23})$$

The contaminant flux per unit area for a system with zero advective velocity is given by

$$J(x, t) = -nD_e \frac{\partial C}{\partial x} \quad (\text{B24})$$

Note that in equation B24 the flux is scaled by a porosity and care should be taken that the effective diffusion coefficient does not already account for this. In particular, diffusion through geomembrane material is not diffusion within the water-filled porosity of the membrane. The water and contaminant molecules can better be considered as dissolved into the geomembrane material. The diffusive transport within geomembrane material is therefore represented by a directly measured diffusion coefficient and when applying these solutions to a geomembrane-mineral two layer system, the porosity for the geomembrane (layer 1), n_1 , should not be used (i.e. it should be set to unity). This is done in the spreadsheet, but the porosity of layer 1 is retained as a parameter in the derivation of the equations for generality.

Equation B23 can be Laplace transformed with respect to time to give

$$R(s + \lambda)C^* - D_e \frac{\partial^2 C^*}{\partial x^2} = 0 \quad (\text{B25})$$

The Laplace transform of Equation B24 (the contaminant flux per unit area for a system with zero advective velocity) is

$$J^*(x, s) = -nD_e \frac{\partial C}{\partial x} \quad (\text{B26})$$

Inspection of Equation B25 indicates that the solution for each layer will be of the form

$$C^* = a \exp(\alpha x) \quad (\text{B27})$$

Substituting Equation B27 in Equation B25 gives the auxiliary equation

$$R(s + \lambda) - D_e \alpha^2 = 0 \quad (\text{B28})$$

The roots of Equation B28 are given by

$$\alpha = \pm \sqrt{\frac{R}{D_e}}(s + \lambda) \quad (\text{B29})$$

The general solutions for layers 1 and 2 respectively then become

$$C_1^* = a \exp(-\alpha_1 x) + b \exp(\alpha_1 x) \quad (\text{B30})$$

and

$$C_2^* = c \exp(-\alpha_2 x) + d \exp(\alpha_2 x) \quad (\text{B31})$$

where now the subscripts 1 and 2 refer to coefficients for layers 1 and 2; a , b , c and d are constants; and coefficients α_1 and α_2 are given by

$$\alpha_1 = \sqrt{\frac{R_1}{D_{1e}}}(s + \lambda_1) \quad (\text{B32})$$

and

$$\alpha_2 = \sqrt{\frac{R_2}{D_{2e}}}(s + \lambda_2) \quad (\text{B33})$$

respectively.

For the two layer solutions, Solution 3 and Solution 4, the boundary condition at $x=0$ in is given by

$$C_1(0, t) = C_0 K_{D_gm} \quad (\text{B34})$$

where K_{D_gm} is the partition coefficient in the geomembrane. The factor of K_D describes the equilibrium change in contaminant concentration across the interface between the aqueous leachate within the landfill and matrix of the geomembrane.

The Laplace transform of Equation B34 is

$$C_1^*(0, s) = \frac{C_0 K_{D_gm}}{s} \quad (\text{B35})$$

The second boundary condition requires that the contaminant flux at the boundary between the two layers (at $x=l$) be continuous. Thus, from Equation B24 we obtain the condition

$$n_1 D_{1e} \left. \frac{\partial C_1(x, t)}{\partial x} \right|_{x=l} = n_2 D_{2e} \left. \frac{\partial C_2(x, t)}{\partial x} \right|_{x=l} \quad (\text{B36})$$

This can be Laplace transformed to give

$$n_1 D_{1e} \left. \frac{\partial C_1^*(x, s)}{\partial x} \right|_{x=l} = n_2 D_{2e} \left. \frac{\partial C_2^*(x, s)}{\partial x} \right|_{x=l} \quad (\text{B37})$$

Secondly, when the contaminant migrates across the interface between the geomembrane and the mineral barrier (located at $x=l$) it will return to the aqueous phase. Thus,

$$C_2(l, t) = \frac{C_1(l, t)}{K_{D_gm}} \quad (\text{B38})$$

The Laplace transform of Equation B38 is simply

$$C_2^*(l, s) = \frac{C_1^*(l, s)}{K_{D_gm}} \quad (\text{B39})$$

These boundary conditions can be combined with the two alternative outer boundary conditions to determine the unknown constants a , b , c and d , as was done for the single layer solutions. The two different outer boundary conditions are applied to determine Solution 3 and Solution 4 in the following subsections.

B.2.2 (b) Solution 3: Two layer solution with boundary condition at infinity

The final boundary condition for this system is given by

$$C_2(\infty, t) = 0 \quad (\text{B40})$$

The Laplace transform of Equation B40 is:

$$C_2^*(\infty, s) = 0 \quad (\text{B41})$$

Combining the boundary conditions given in Equations B35, B37, B36 and B41 with the general solutions for layer 1 and 2 (Equations B30 and B31 respectively) allows expressions for a , b , c and d to be obtained. Substituting the expressions into Equations B30 and B31 gives the Laplace transform of the concentrations in layer 1 and layer 2 as

$$C_1^*(x, s) = \frac{C_0 K_{D_gm} (\alpha_1 n_1 D_{1e} K_{D_gm} + \alpha_2 n_2 D_{2e}) \exp(-\alpha_1(x-l)) + (\alpha_1 n_1 D_{1e} K_{D_gm} - \alpha_2 n_2 D_{2e}) \exp(-\alpha_1(l-x))}{s (\alpha_2 n_2 D_{2e} (\exp(\alpha_1 l) - \exp(-\alpha_1 l)) + \alpha_1 n_1 D_{1e} K_{D_gm} (\exp(\alpha_1 l) + \exp(-\alpha_1 l)))} \quad (\text{B42})$$

and

$$C_2^*(x, s) = \frac{2C_0 \alpha_1 n_1 D_{1e} K_{D_gm} \exp(-\alpha_2(x-l))}{s (\alpha_2 n_2 D_{2e} (\exp(\alpha_1 l) - \exp(-\alpha_1 l)) + \alpha_1 n_1 D_{1e} K_{D_gm} (\exp(\alpha_1 l) + \exp(-\alpha_1 l)))} \quad (\text{B43})$$

respectively.

Substituting the expressions for the concentration in each layer of a two layer liner system, derived using the $C=0$ boundary condition at $x=\infty$ (Equations B42 and B43) into Equation B26, gives the expressions for the Laplace transforms of the mass flux per unit area as:

$$J_1^*(x, s) = \frac{n_1 D_1 \alpha_1 C_0 K_{D_gm}}{s} \left\{ \begin{array}{l} \frac{(\alpha_1 n_1 D_{1e} K_{D_gm} + \alpha_2 n_2 D_{2e}) \exp(-\alpha_1(x-l))}{\alpha_2 n_2 D_{2e} (\exp(\alpha_1 l) - \exp(-\alpha_1 l)) + \alpha_1 n_1 D_{1e} K_{D_gm} (\exp(\alpha_1 l) + \exp(-\alpha_1 l))} \\ - \frac{(\alpha_1 n_1 D_{1e} K_{D_gm} - \alpha_2 n_2 D_{2e}) \exp(-\alpha_1(l-x))}{\alpha_2 n_2 D_{2e} (\exp(\alpha_1 l) - \exp(-\alpha_1 l)) + \alpha_1 n_1 D_{1e} K_{D_gm} (\exp(\alpha_1 l) + \exp(-\alpha_1 l))} \end{array} \right\} \quad (\text{B44})$$

and

$$J_2^*(x, s) = \frac{2C_0}{s} \frac{\alpha_2 n_2 D_{2e} \alpha_1 n_1 D_{1e} K_{D_gm} \exp(-\alpha_2(x-l))}{\alpha_2 n_2 D_{2e} (\exp(\alpha_1 l) - \exp(-\alpha_1 l)) + \alpha_1 n_1 D_{1e} K_{D_gm} (\exp(\alpha_1 l) + \exp(-\alpha_1 l))} \quad (\text{B45})$$

for layer 1 and layer 2 respectively.

B.2.2 (c) Solution 4: Two layer solution with boundary condition at the edge of the second layer

The outer boundary condition Solution 4 is given by

$$C_2(L+l, t) = 0 \quad (\text{B46})$$

The Laplace transform of Equation B46 is

$$C_2^*(L+l, s) = 0 \quad (\text{B47})$$

Combining the boundary conditions given in Equations B35, B37, B39 and B47 with the general solutions for layer 1 and 2 (Equations B30 and B31 respectively) allows expressions for a , b , c and d to be obtained. Substituting the expressions into Equations B30 and B31 gives the Laplace transform of the concentrations in layer 1 and layer 2 as

$$C_1^*(x, s) = \frac{C_0 K_0}{s} \left\{ \begin{array}{l} \frac{\alpha_1 n_1 D_{1e} K_{D_gm} (1 - \exp(2\alpha_2 L)) (\exp(-\alpha_1 x) + \exp(-2\alpha_1 l + \alpha_1 x))}{\alpha_1 n_1 D_{1e} K_{D_gm} (1 - \exp(2\alpha_2 L)) (1 + \exp(-2\alpha_1 l)) - n_2 \alpha_2 D_{2e} (1 + \exp(2\alpha_2 L)) (1 - \exp(-2\alpha_1 l))} \\ - \frac{n_2 \alpha_2 D_{2e} (1 + \exp(2\alpha_2 L)) (\exp(-2\alpha_1 l + \alpha_1 x) - \exp(-\alpha_1 x))}{\alpha_1 n_1 D_{1e} K_{D_gm} (1 - \exp(2\alpha_2 L)) (1 + \exp(-2\alpha_1 l)) - n_2 \alpha_2 D_{2e} (1 + \exp(2\alpha_2 L)) (1 - \exp(-2\alpha_1 l))} \end{array} \right\} \quad (\text{B48})$$

and

$$C_2^*(x, s) = \frac{2C_0 K_{D_gm}}{s} \left\{ \frac{\alpha_1 n_1 D_{1e} \exp(-\alpha_1 l) (\exp(-\alpha_2(l-x)) - \exp(\alpha_2(2L+l-x)))}{\alpha_1 n_1 D_{1e} K_{D_gm} (1 - \exp(2\alpha_2 L)) (1 + \exp(-2\alpha_1 l)) - n_2 \alpha_2 D_{2e} (1 + \exp(2\alpha_2 L)) (1 - \exp(-2\alpha_1 l))} \right\} \quad (\text{B49})$$

respectively.

Substituting the expressions for the concentration in each layer of a two layer liner system, derived using the $C=0$ boundary condition at $x=L+l$ (Equations B48 and B49) into Equation B26, gives the expressions for the Laplace transforms of the mass flux per unit area as:

$$J_1^*(x,s) = \frac{-C_0 K_{D_gm}}{s} \left\{ \begin{array}{l} \frac{\alpha_1^2 n_1^2 D_{1e}^2 K_{D_gm} (1 - \exp(2\alpha_2 L)) (\exp(-2\alpha_1 l + \alpha_1 x) - \exp(-\alpha_1 x))}{\alpha_1 n_1 D_{1e} K_{D_gm} (1 - \exp(2\alpha_2 L)) (1 + \exp(-2\alpha_1 l)) - n_2 \alpha_2 D_{2e} (1 + \exp(2\alpha_2 L)) (1 - \exp(-2\alpha_1 l))} \\ - \frac{n_1 \alpha_1 D_{1e} n_2 \alpha_2 D_{2e} (1 + \exp(2\alpha_2 L)) (\exp(-2\alpha_1 l + \alpha_1 x) + \exp(-\alpha_1 x))}{\alpha_1 n_1 D_{1e} K_{D_gm} (1 - \exp(2\alpha_2 L)) (1 + \exp(-2\alpha_1 l)) - n_2 \alpha_2 D_{2e} (1 + \exp(2\alpha_2 L)) (1 - \exp(-2\alpha_1 l))} \end{array} \right\} \quad (B50)$$

and

$$J_2^*(x,s) = -\frac{2C_0 K_{D_gm}}{s} \left\{ \frac{\alpha_2 n_2 D_{2e} \alpha_1 n_1 D_{1e} \exp(-\alpha_1 l) (\exp(-\alpha_2 (l-x)) + \exp(\alpha_2 (2L+l-x)))}{\alpha_1 n_1 D_{1e} K_{D_gm} (1 - \exp(2\alpha_2 L)) (1 + \exp(-2\alpha_1 l)) - n_2 \alpha_2 D_{2e} (1 + \exp(2\alpha_2 L)) (1 - \exp(-2\alpha_1 l))} \right\} \quad (B51)$$

for layer 1 and layer 2 respectively.

B.3 Numerical Inversion

The solutions presented in Section B.2 provide the Laplace transforms of the concentrations and the fluxes for each scenario. It is difficult to analytically invert these solutions, thus Stehfest's numerical inversion technique has been employed in the spreadsheet.

The solution for a function $f(t)$ can be obtained from the Laplace transform of the function $f^*(s)$ using:

$$f(t) = \frac{\ln 2}{t} \sum_{n=1}^N V_n f^*\left(\frac{\ln 2}{t} n\right) \quad (B52)$$

where the constants V_n are given by

$$V_n = (-1)^{\frac{N}{2}+n} \sum_{k=(n+1)/2}^{\text{Min}(n,N/2)} \frac{k^{N/2} (2k)!}{(N/2 - k)! (k-1)! (n-k)! (2k-n)!} \quad (B53)$$

A value of $N=12$ has been used in the numerical inversion routine in the spreadsheet which is claimed to give high accuracy in Hafner (1992).

B.4 Verification of the Numerical Solutions

The numerical solutions have been verified using two methods.

First, the boundary conditions used to derive the models have been checked. This confirmed that the complex algebra used in the derivation of the constants of integration was correct.

Secondly, the numerical solutions were compared with the analytical solution in order to confirm that the Laplace transformed solutions were correctly derived and accurately inverted by Stehfests' algorithm. The latter is documented below. The following subsections describe the following test cases:

- a comparison between the numerical single layer Solution 1 and the analytical solution with a boundary condition at infinity for typical parameters;

- a comparison between the two layer numerical Solution 3 with the boundary condition at infinity and the analytical solution (with negligible inwards velocity) for typical parameters;
- a cross-comparison between the single layer numerical Solution 2 and the two-layer numerical Solution 4 with boundary condition at the outer edge of layer two where properties of the two layers have been set to be identical in Solution 4 and where the inward velocity has been set to a negligible value in Solution 2 for consistency between the two settings.

Note that the verification of the solutions is restricted to the above specific objectives, largely due to the limited availability of independently calculated results to cross-compare. In particular it is noted that no systematic evaluation of the model results for the full range of parameter values has been reported (although the model was tested for a wide range of extreme parameter values as part of the model development and it is considered that the model is robust for all reasonable parameter choices).

Secondly, it should be noted that there has been no validation study undertaken to compare model predictions with field data and confirm the validity of applying the model to predict the behaviour of real sites. Verification such as undertaken here tests that the mathematical model has been correctly and accurately solved. Validation further tests whether the mathematical model is applicable to the real landfill settings of interest.

B.4.1 Numerical single layer solution compared to analytical single layer solution with boundary condition at infinity

The numerical solution for the single layer model with the boundary at infinity can be directly compared to the analytical solution for the single layer model. The parameters used to verify Solution 1 are presented below.

2	Enter site name here	1 January 2004	trichloroethene
CONCEPTUAL MODEL AND LANDFILL CONSTRUCTION			
4	Conceptual model of landfill construction	CM	2
5	Is a geomembrane present?	GM_opt	No
8	Basal width perpendicular to groundwater flow	Width_LF	200 m
9	Basal length parallel to groundwater flow	Length_LF	610 m
10	Basal area	Base_Area	122000 m ²
11	Elevation of base of landfill	LFbase_elev	1 maOD
12	Elevation of base of aquifer	Aqbound_elev	0 maOD
14	Leachate head inside landfill	Head_inLF	5 maOD
15	Groundwater head outside landfill	Head_outLF	8 maOD
16	Area of liner below the water table	Area_contact	128480 m ²
CONTAMINANT AND WATER FLUXES			
	Water flux into landfill		1.09208E-05 m ³ /s
	Maximum contaminant concentration at compliance point at tmax	C _{comp}	6.618256331 mg/l
CHART PARAMETERS			
	Minimum axis display	tmin	0.01 years
	Maximum axis display	tmax	1.00E+03 years
CONTAMINANT PARAMETERS			
19	Contaminant name	Cont_Nlme	trichloroethene
20	Contaminant type	Cont_Tyep	Organic
21	Contaminant classification	Cont_Class	List I
22	Concentration in landfill leachate	Conc_LF	1000 mg/l
23	Free water diffusion coefficient	Dw_cl	2.00E-09 m ² /s
25	Partition coefficient in clay	Kd_cl	1 l/kg
26	Retardation factor in clay	R _{cl}	11.80246314
27	Half life in clay (0 for no decay)	thalf_cl	5000 days
28	Decay in sorbed phase?	Decay_sorb	Yes
29	Decay constant in clay	Decay_cl	1.80451E-09 1/s
MINERAL BARRIER / LINER			
35	Thickness of mineral liner	thick_olbr	1 m
36	Hydraulic conductivity	k _{cl}	8.50E-11 m/s
37	Average pore radius	pore_radius	1.00E-05 m
38	Effective porosity	n	0.162
39	Dry bulk density	rho	1750 kg/m ³
40	Tortuosity	tau_cl	2.33478

The model results for contaminant concentration and contaminant flux at the edge of the barrier are presented below.

Contaminant concentration in mg/l at the edge of the clay barrier ($x=l$ for the single layer solution and $x=l+L$ for the two layer solution, where the thicknesses of the barrier systems for each solution are equivalent)

Time (years)	Numerical Single Layer Solution (Equation B17)	Analytical Single Layer Solution (Equation B2)
0.01	-3.05E-75	0.00E+00
0.1	-1.26E-23	0.00E+00
1	-1.19E-07	1.38E-46
10	3.66E-03	1.36E-03
100	6.47E+00	6.45E+00
1000	6.62E+00	6.62E+00

Contaminant flux per unit area in $\text{kg}\cdot\text{s}^{-1}\cdot\text{m}^{-2}$ at the edge of the clay barrier ($x=l$ for the single layer solution and $x=l+L$ for the two layer solution, where the thicknesses of the barrier systems for each solution are equivalent)

Time (years)	Numerical Single Layer Solution (Equation B18)	Analytical Single Layer Solution (Equation B4)
0.01	-7.36E-86	0.00E+00
0.1	-9.64E-35	0.00E+00
1	-2.41E-19	4.20E-57
10	2.77E-15	4.26E-15
100	4.04E-12	4.03E-12
1000	4.05E-12	4.05E-12

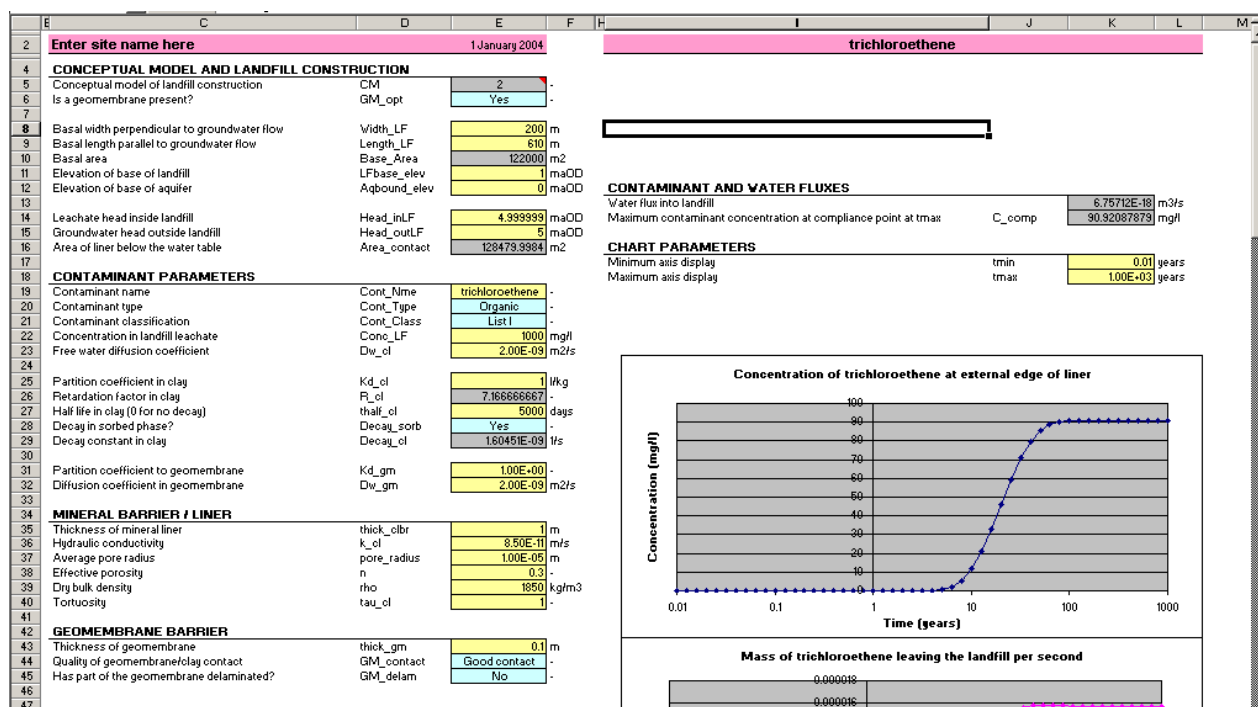
These data show excellent agreement between each of the solutions. This data shows that the numerical solution is accurate to the fourth decimal place for the maximum concentrations.

B.4.2 Numerical two layer solution compared to analytical single layer with boundary condition at infinity with boundary condition at infinity

In order to verify the single layer numerical solution with the outer boundary at the edge of the barrier and both the two layer numerical solutions against the analytical solution custom changes were made to function calls in the spreadsheet (no changes were made to the functions used to evaluate the solutions):

1. a very low inward velocity for the mineral barrier was specified ($vel_{cl} = 1e-100$). This is required since the two layer solution assumes zero water flux into the landfill, and setting an extremely low hydraulic velocity for the clay means that this condition will be replicated in both the single layer numerical solution and the single layer analytical solution;
2. the two layer solution uses two layers with properties identical to the properties of the layer used in the single layer numerical solution and the single layer analytical solution. In addition, the total thickness of the two layers is identical to the thickness of the layers represented in the single layer solutions.

The model parameters used are presented in the diagram below.



The predicted concentrations and contaminant fluxes at the edge of the barrier for the two layer solution derived using the boundary condition $C=0$ at $x=\infty$; the single layer solution derived using the boundary condition $C=0$ at $x=\infty$ and the analytical solution are presented below, calculated under the conditions described in Solution 1 and Solution 3. For this example $x > 500m$ was representative of $x=\infty$.

Contaminant concentration in mg/l at the edge of the clay barrier ($x=l$ for the single layer solution and $x=l+L$ for the two layer solution, where the thicknesses of the barrier systems for each solution are equivalent)

Time (years)	Numerical Two Layer Solution (Equation B43)	Numerical Single Layer Solution (Equation B17)	Analytical Single Layer Solution (Equation B2)
0.01	0.00	0.00	0.00
0.1	0.00	0.00	0.00
1	-0.00012	-0.00012	0.00
10	11.55	11.55	11.50
100	90.70	90.70	90.68
1000	90.92	90.92	90.92

Contaminant flux per unit area in $\text{kg}\cdot\text{s}^{-1}\cdot\text{m}^{-2}$ at the edge of the clay barrier ($x=l$ for the single layer solution and $x=l+L$ for the two layer solution, where the thicknesses of the barrier systems for each solution are equivalent)

Time (years)	Numerical Two Layer Solution (Equation B49)	Numerical Single Layer Solution (Equation B18)	Analytical Single Layer Solution (Equation B4)
0.01	-2.47 E-48	-2.47 E-48	0
0.1	-1.64 E-22	-1.64 E-22	4.86E-132
1	-2.80 E-15	-2.80 E-15	1.58 E-21
10	4.57 E-11	4.57 E-11	4.56 E-11
100	1.31 E-10	1.31 E-10	1.31 E-10
1000	1.31 E-10	1.31 E-10	1.31 E-10

These data show excellent agreement between each of the solutions. This data shows that the numerical solution is accurate to the third decimal place for the maximum concentrations.

B.4.3 Numerical two layer solution compared to numerical single layer solution with boundary condition at edge of the barrier system

The results presented in this section were calculated using the identical parameters to those presented Section B.4.2. This comparison also required the same custom changes as described in Section B.4.2 in order for the numerical solutions to be representing identical physical systems.

The predicted contaminant fluxes at the edge of the barrier system for the two layer solution derived using the boundary condition $C=0$ at $x=l+L$; the single layer solution derived using the boundary condition $C=0$ at $x=l$. These represent Solution 2 and Solution 4.

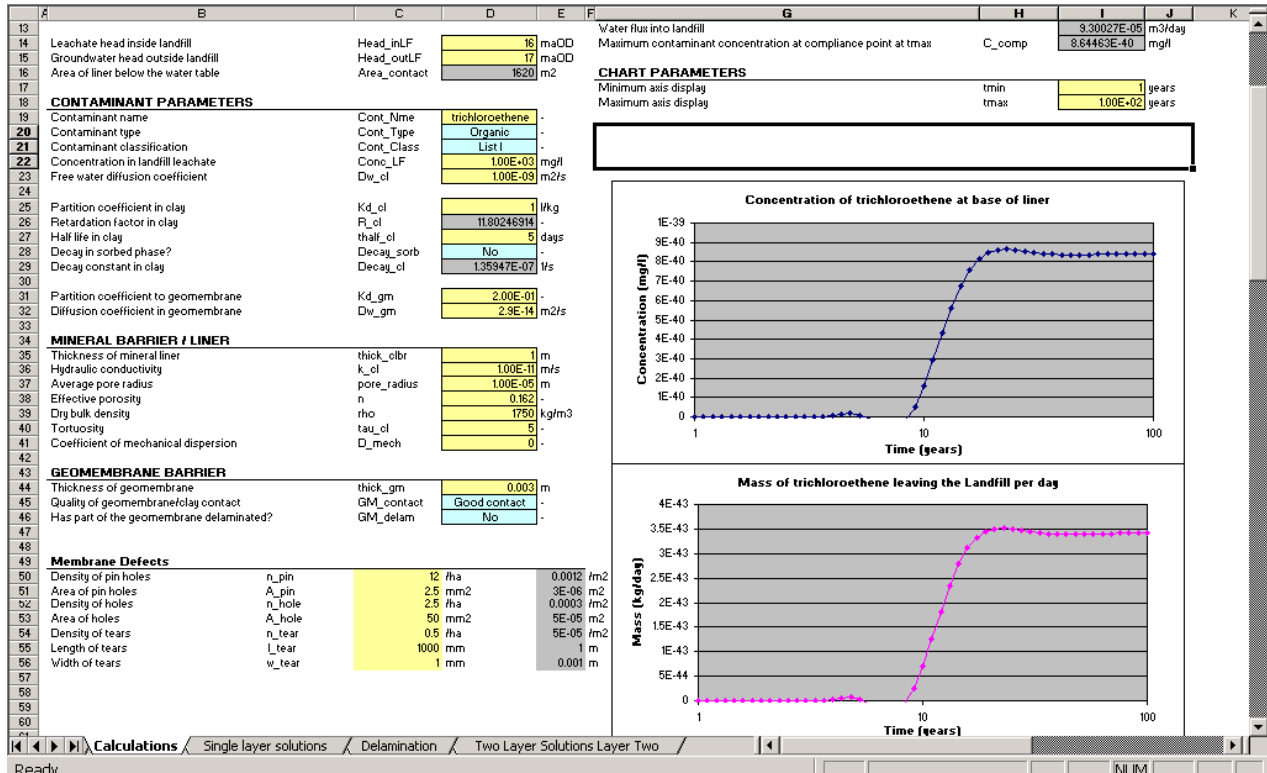
Contaminant flux per unit are in $\text{kg}\cdot\text{s}^{-1}\cdot\text{m}^{-2}$ at the edge of the barrier system.

Time (years)	Numerical Two Layer Solution (Equation B51)	Numerical Single Layer Solution (Equation B22)
0.01	-4.93 E-48	-4.93 E-48
0.1	-3.28 E-22	-3.28 E-22
1	-5.59 E-15	-5.59 E-15
10	9.14 E-11	9.14 E-11
100	2.64 E-10	2.64 E-10
1000	2.64 E-10	2.64 E-10

These data show excellent agreement between each solution: there is not an analytical solution available to verify the numerical solution against.

B.5 Numerical Accuracy

For some situations the numerical inversion will lose accuracy. This will tend to become obvious when a small half-life has been specified, as the contaminant concentration will become very small in comparison with the concentration within the landfill. This happens when the breakthrough is sharp and leads to small oscillations on the breakthrough curve. This is small for most parameter choices of relevance but if they are sufficiently large to affect decision making more accurate solutions should be used, such as Talbot's method, which are available in more sophisticated groundwater risk assessment tools.



APPENDIX C: LIST OF CONSULTEES

The report and spreadsheet were peer-reviewed by Golder Associates in June 2004.

A limited consultation was undertaken over a 1 month period in May-June 2004. The list of consultees is shown below. Comments received were incorporated into the final version of the report and spreadsheet.

External consultation list
Biffa Waste Services Ltd
Cleanaway Ltd.
EB Nationwide
EDGE Consultants UK Ltd.
Entec
Environmental Services Association
Enviros
Hafren Water
Imperial College London
Knox Associates
MJ Carter Associates
RMC Environmental Services Ltd
Shanks
SITA (UK) Ltd.
SLR Consulting Limited
University College, London
University of Cardiff
University of Sheffield
University of Southampton
Viridor Waste Management
Wyvern Waste Services

Environment Agency consultation list	
Process	Waste, Groundwater Quality
Policy	Waste, Groundwater
Strategic Permitting Groups	All
Area	Groundwater & Contaminated Land Team Leaders
LandSim Technical Discussion Group	All

We welcome views from our users, stakeholders and the public, including comments about the content and presentation of this report. If you are happy with our service, please tell us about it. It helps us to identify good practice and rewards our staff. If you are unhappy with our service, please let us know how we can improve it.