

# Experimental and modelling approaches for the assessment of chemical impacts of leachate migration from landfills: A case study of a site on the Triassic sandstone aquifer in the UK East Midlands

STEVEN F. THORNTON<sup>1,\*</sup>, JOHN H. TELLAM<sup>2</sup> and DAVID N. LERNER<sup>1</sup>

<sup>1</sup>Groundwater Protection and Restoration Group, Department of Civil and Structural Engineering, University of Sheffield, Mappin Street, Sheffield S1 3JD, United Kingdom

<sup>2</sup>Hydrogeology Research Group, School of Geography, Earth and Environmental Science, University of Birmingham, Edgbaston, Birmingham B15 2TT, United Kingdom

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**Abstract.** Current risk-based methods for assessing the effects of landfill leachate migration on groundwater resources are conservative and generalised. Cost-effective and practical strategies are required which can robustly determine the potential for contaminant attenuation on a site-specific basis. In this paper laboratory column experiments and reactive transport modelling are evaluated as a combined approach for assessing the chemical impact of leachate migration in the Triassic Sandstone aquifer. The results are compared with field data for a landfill in the East Midlands. Columns of aquifer sandstone were flushed sequentially with groundwater, followed by acetogenic or methanogenic leachate to simulate chemical interactions occurring during leachate loading episodes. The key contaminants in leachate (NH<sub>4</sub>, heavy metals, organic fractions) were attenuated by ion exchange, redox reactions, sorption and degradation. These processes produce a consistent hydrochemical signature which may help identify the extent of leachate migration in the aquifer. The laboratory results largely replicate those found in the field system, and the behaviour of inorganic contaminants during leachate flushing of the aquifer columns can be described by the reactive transport model. The experimental and modelling approach presented represents a powerful tool for risk assessment and prediction of leachate contaminant fate at unlined and lined landfills.

**Key words.** ammonium; aquifer; contamination; groundwater; landfill; leachate; natural attenuation; Triassic sandstone.

## 1. Introduction

The majority of all landfill proposals in the UK now incorporate engineered containment measures in their design, especially in situations where the local geology does not offer a high level of protection to groundwater from leachate migration. However, there remains a significant number of old landfills, located on important aquifers, which were granted waste disposal licences before these requirements became commonplace and which have few or only rudimentary environmental control

\* Corresponding author: e-mail: s.f.thornton@sheffield.ac.uk

measures in place. In these cases leachate is allowed to leak into the underlying strata where the attenuation of contaminants within the aquifer is used as a means of minimising the risk to groundwater resources. An assessment of the potential for leachate attenuation is also commonly made as part of the site evaluation and engineering design of most new, lined landfills which are developed on existing aquifers.

Measuring the leachate attenuation capacity of an aquifer and predicting the fate of specific contaminants in groundwater is often very difficult due to the complexity of each system. The main contaminants of concern from a water quality viewpoint are  $\text{NH}_4$ , heavy metals and organic fractions, including natural dissolved organic matter (DOM), such as volatile fatty acids (VFAs), and xenobiotic organic micro-pollutants (XOMs). Current risk-based approaches for landfills are often highly conservative and generalised, due to the use of simple models which cannot fully account for the processes controlling the migration of contaminants in leachate and uncertainty in the value of appropriate parameters describing these processes. Therefore, there is a need to identify practical and cost-effective methods which can robustly determine the potential for contaminant attenuation on a site-specific basis. This is necessary for unlined, leaking, landfills in order to predict their potential impact on groundwater resources and for the design of remediation strategies, and at new sites as part of the site selection protocol and for evaluating the risk from liner failure.

## 2. Approach to Study

This paper presents a proposed approach for assessing the chemical impact of leachate migration from landfills. The scheme incorporates laboratory column experiments and reactive transport modelling of the experimental data. The significance of the results and utility of the approach is evaluated by comparison with field data on leachate migration in the Triassic Sherwood Sandstone aquifer at the Burntstump landfill in the English Midlands. At the time the study formed part of a wider, ongoing research programme, sponsored by the UK Department of the Environment, to help develop waste disposal practice guidelines.

The migration of leachate from landfills located on the aquifer has been investigated in detail (Lewin et al., 1994, 1996; Young et al., 1994). This fieldwork has established the general chemical variations and distribution of leachate pollutants within the subsurface at these sites. The present study was undertaken in support of this previous work, with the following objectives:

- (i) to determine whether the chemical variations observed in the field can be replicated in the laboratory and predicted using a reactive transport model;
- (ii) to identify the key geochemical properties and processes regulating contaminant mobility;
- (iii) to provide comprehensive data on the leachate attenuation capacity of this aquifer under controlled conditions.

Representative Sherwood Sandstone Group sandstone and groundwater from the aquifer, and acetogenic (A-phase) and methanogenic (M-phase) leachate from typical domestic waste landfills have been used in the laboratory column experiments. The columns of aquifer material were saturated with groundwater and flushed with either A-phase or M-phase leachate to simulate the effects of leachate loading and identify differences in the style of contaminant attenuation as a function of leachate composition. There is a broad continuum of leachate composition between 'typical' A-phase and M-phase compositions, which can occur naturally in landfills. At many sites leachate composition may have an intermediate quality between A-phase and M-phase, reflecting passage through young and old waste in close proximity, or through blending within the leachate collection system, if present. In short, it is possible that leachate of any composition could impact an aquifer. The emphasis in this study is validation of the experimental methodology as a cost-effective tool to assess leachate impacts in the aquifer, rather than the attenuation of a specific leachate composition. For this reason, the A-phase and M-phase leachates have been selected as representative compositions which may occur, to test the proposed methodology. These leachates are valid in as much as A-phase leachate may quickly impact aquifers at unlined landfills and M-phase leachate could impact aquifers at lined sites in the future following failure of the barrier system.

The experimental data have been interpreted using PHREEQM, a 1-D numerical reactive transport model developed by Appelo and Postma (1993), which incorporates the PHREEQE chemical equilibrium and speciation code (Parkhurst et al., 1980). PHREEQM is capable of simulating ion-exchange reactions, redox processes and chemical equilibrium dissolution and precipitation using a mixing cell approach which couples chemical reactions with transport using dispersion and diffusion. Input terms for the model include transport parameters (dispersivity), aqueous chemistry, chemical reactions and mineral phase equilibria determined from the column experiments.

### **3. Experimental Design**

#### **3.1. EXPERIMENTAL MATERIALS**

Samples of Triassic Sherwood Sandstone Group aquifer material were taken from a quarry adjacent to the Burntstump landfill, north of Nottingham, Nottinghamshire. Freshly excavated material was collected and air dried prior to use with no further processing. The sandstone is very friable and readily crumbled into loose sand, so the resultant disruption of the sandstone's structure and attendant effects on the physicochemical properties are likely to be minor. The friable nature of the sandstone prevented the collection of undisturbed samples for the experiments.

Groundwater (200 l) was also collected from a regularly used private borehole near to the Burntstump landfill. The borehole was purged prior to sample collection and the groundwater was pumped into 50 l polyethylene drums which were filled completely. The groundwater sample is typical of the aquifer in the vicinity of the

Table 1. Input groundwater and leachate compositions for the column experiments

Species	Groundwater	A-phase leachate	M-phase leachate
pH	6.1	5.95	7.65
EC ( $\mu\text{S}/\text{cm}$ )	660	25 000	21 500
Eh (mV)	431	168	-76
Alkalinity ( $\text{CaCO}_3$ )	73	9 260	7 600
$\text{NH}_4$	bdl	1 398	1 977
Ca	46	3646	62
Mg	24	555	92
K	2.9	1 072	1 118
Na	10.3	2 039	1 918
Fe	bdl	448	2.2
Mn	bdl	93	0.1
Si	3.69	bdl	21.4
Cl	30.8	2 705	2 398
$\text{NO}_3$	58	bdl	bdl
$\text{SO}_4$	58	1 173	90
Total VFAs	ND	29 244	6 101
TOC	bdl	18 846	1 410
COD	bdl	247 700	14 000
Toluene ( $\mu\text{g}/\text{l}$ )	ND	123	bdl
Trichloroethene (TCE) ( $\mu\text{g}/\text{l}$ )	ND	238	bdl
Tetrachloroethene (PCE) ( $\mu\text{g}/\text{l}$ )	ND	304	bdl

bdl – Below detection limits; ND – not determined; VFAs – volatile fatty acids; TOC – total organic carbon; COD – chemical oxygen demand; All parameters in mg/l unless stated otherwise.

landfill, with a measured Eh of 431 mV and dissolved TOC below detection limits (0.5 mg/l). Leachate was collected at two different domestic waste landfills to provide samples of A-phase and M-phase compositions from representative UK domestic waste disposal sites (Table 1). The A-phase leachate was collected from a domestic waste landfill in Cheshire, whereas the M-phase leachate was collected from a similar site in Buckinghamshire. The leachate was recovered from sumps in the leachate collection system and pumped directly into gas preflushed (50%  $\text{CO}_2$ /50%  $\text{N}_2$ ) 60 l HDPE drums which were filled completely. Analysis of the leachates showed these to be similar in composition to those from other UK landfills (e.g. Robinson and Gronow, 1993). The leachates sampled contain high concentrations of  $\text{NH}_4$ , but the natural organic matter load (as TOC and organic acid fractions) of the A-phase leachate is substantially higher than that of the M-phase leachate, as expected. The A-phase leachate also contains three XOMs (toluene, TCE and PCE) in concentrations above detection limits, but no heavy metals other than Fe and Mn were detected in either leachate (Table 1).

### 3.2. EXPERIMENTAL PROCEDURES

A schematic of the laboratory set-up is presented in Figure 1. The apparatus supplied groundwater (tank GW) and leachate (tanks A, M and P) to the columns under conditions isolated from the atmosphere. The leachates were stored anaerobically

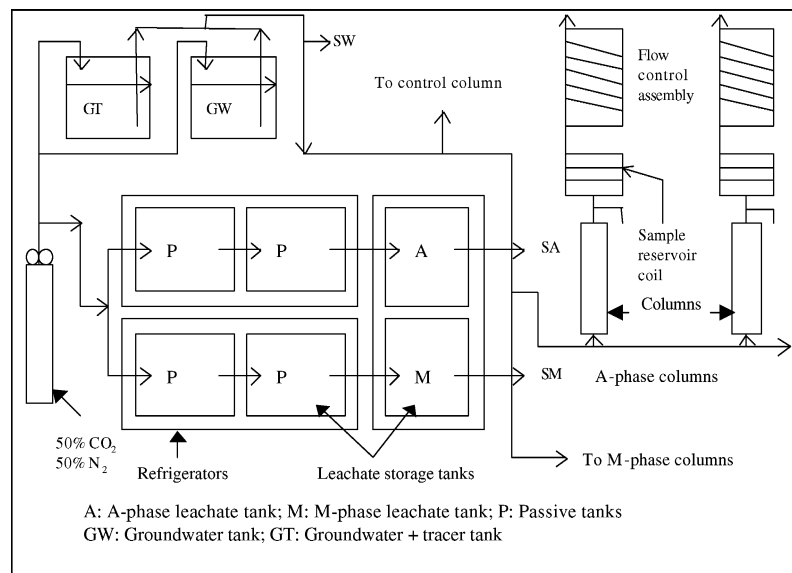


Figure 1. Laboratory set-up for the column experiments.

under a 50:50 CO<sub>2</sub>:N<sub>2</sub> atmosphere in sealed tanks at 4 °C to minimise compositional changes (Thornton et al., 2000).

A gas pressure of 30 kPa was used to supply groundwater and leachate to the experimental columns and the apparatus is designed to transfer leachate out of the active tanks (A and M) only. The passive tanks (P) provide a gas phase composition in continual equilibrium with the initial concentration of volatile organic fractions (XOMs), which is transferred to the active tanks. This gas phase compensates for headspace volatilisation losses from the leachates which would otherwise occur as the active tanks empty during the experiment. All metal components in contact with leachate were 316 grade stainless steel to minimise contamination. The groundwater and leachate compositions were monitored during the experiments at sampling ports (SA, SM and SG) in the main circuit (Figure 1).

All columns were constructed from 1 m lengths of UPVC (9.9 cm ID), fitted with endcaps, and were operated in upflow mode. Samples were collected in a 3 m stainless steel coil (8 mm ID) attached to the flow control assembly (FCA). Samples were removed through a valve at the base of the coil after filling using a syringe (Figure 1). The height of the FCA was adjusted for each column to provide a flow rate of 140 ml over a 24 h period and an average residence time of 21–23 days. The experiments were conducted at room temperature (18–21 °C).

Each column was manually packed and reweighed to determine individual packing densities and approximate void volume. The packing was carefully done using a consistent tamping method to ensure that the packed columns were of uniform density and contained no internal structure. The CI breakthrough curves in the experiments suggest that uniform flow conditions were achieved in the aquifer

columns (see below). All columns were flushed with 1 pore volume of groundwater prior to leachate percolation, to saturate the columns and establish a baseline porewater chemistry, for comparison with the leachate flushes. Operation in upflow mode ensured that no air bubbles were present in the columns and that these were fully saturated prior to flushing with leachate. The experiments were run in duplicate over a period of 10 months and a column flushed only with groundwater containing an organic (amino-G-acid) tracer (tank GT) was used as a control experiment.

### 3.3. ANALYTICAL PROCEDURES

Groundwater and leachate samples were analysed by standard methods (APHA, 1985). Samples for gas analysis were collected in glass ampoules and analysed by gas chromatography. Concentrations of the organic tracer in the groundwater were determined by fluorescence spectrophotometry. Duplicate samples of the aquifer sandstone were also analysed for pH, solid phase organic carbon content (OC), cation exchange capacity (CEC) and CaCO<sub>3</sub> content (Table 2) using standard methods of soil analysis (van Reeuwijk, 1987).

Table 2. Solid phase composition of aquifer material used in the column experiments

pH	wt% Organic Carbon <sup>a</sup>	wt% CaCO <sub>3</sub> <sup>a</sup>	CEC (meq/100g) <sup>a,b</sup>
7.07	0.147	1.22	1.63

<sup>a</sup> Values based on averages of duplicate analyses.

<sup>b</sup> CEC is determined by summation of exchangeable cations after corrections for water soluble species and dissolution of native carbonate.

### 3.4. MODELLING

The solute transport relationships in each column experiment were evaluated using an analytical solution of the advection–dispersion equation (Ogata and Banks, 1961), modified to include a first-order decay term (Domenico and Schwartz, 1998)

$$C = \left(\frac{C_0}{2}\right) \exp\left\{\left(\frac{x}{2\alpha_x}\right) \left[1 - \left(1 + \left(\frac{4\lambda\alpha_x}{v}\right)^{1/2}\right)\right]\right\} \operatorname{erfc}\left[\frac{R_f^c x - vt(1 + (4\lambda\alpha_x/v))^{1/2}}{2(\alpha_x vt R_f^c)^{1/2}}\right] \quad (1)$$

where  $C$  and  $C_0$  are the concentration and input concentration of the solute,  $x$  is column length,  $\alpha_x$  is longitudinal dispersivity,  $\lambda$  is the solute decay constant,  $v$  is the fluid average linear velocity,  $R_f^c$  is the experimentally determined solute retardation factor and  $t$  is time.

This model was used to estimate the hydraulic parameters (porewater velocity, dispersivity and kinematic porosity) of each column by least-squares fitting to the Cl tracer (input leachate Cl concentration in each experiment). The hydraulic parameters were then fixed for the reactive transport simulations and for the evaluation of solute half lives and experimental distribution coefficients ( $K_d^c$ ). The latter was estimated using the following relationship (Domenico and Schwartz, 1998):

$$R_f^c = 1 + (\rho_b K_d^c / \theta) \quad (2)$$

where  $\rho_b$  is the dry density ( $\text{g/cm}^3$ ) and  $\theta$  is the dimensionless kinematic porosity of the media. Values of  $\rho_b$  were determined for each column, based on packing densities. Values of  $\theta$  and  $R_f^c$ , were respectively determined by curve fitting of the Cl tracer profile and from the transport simulations of solutes in each experiment.

The data from the leachate flushing phases of A-phase leachate and M-phase leachate flush experiments were analysed using the reactive transport code, PHREEQM (Appelo and Postma, 1993). Solute mass balance procedures were also used to provide supplementary data on processes regulating contaminant attenuation.

## 4. Results and Discussion

### 4.1. LEACHATE FLUSHING

The experimental columns were flushed with leachate until the concentrations of inorganic solutes in the effluent had stabilised. Examples of breakthrough curves (BTC) for inorganic and organic solutes for the A-phase and M-phase leachate flush experiments are presented in Figures 2–5, respectively. The BTC are presented in terms of normalised solute concentration ( $C/C_0$ ) against pore volumes of leachate flushed (dimensionless time). Example BTC for selected inorganic solutes from duplicate A-phase and M-phase leachate flush experiments are presented in Figure 6. These results indicate excellent agreement between the repeat column experiments. The excellent reproducibility in the column experiments is further confirmed by the good agreement in modelled parameters and mass balances for the columns (Tables 3 and 4). The following discussion focuses on the attenuation issues rather than a detailed analysis of the geochemical processes.

#### 4.1.1. Attenuation of $\text{NH}_4$

The major cations (Ca, Mg, Na, K and  $\text{NH}_4$ ) achieved breakthrough in the column experiments as a series of fronts, which resulted in the elution of Ca and Mg above input concentrations ( $C/C_0$  of 1.0), but differential retardation of Na, K and  $\text{NH}_4$  by the aquifer sediment. Calcium and Mg stabilise at input leachate levels only when  $\text{NH}_4$  and K have achieved final breakthrough in each column experiment. The elution history exhibited by these cations is characteristic of multicomponent heterovalent ion-exchange reactions, which results in the chromatographic displacement of native cations from the sediment exchange complex by adsorption of leachate cations, according to the differential affinity exhibited by the aquifer material for each cation (Kjeldsen and Christensen, 1984; Ross, 1985; Christensen et al., 1994, 2001). In these experiments native exchangeable Ca and Mg were desorbed from the sediment during sorption of leachate Na,  $\text{NH}_4$  and K (Figures 2 and 4). Both  $\text{NH}_4$  and K were most strongly sorbed by the sandstone, as observed in other studies (Kjeldsen and Christensen, 1984; Ceazan et al., 1989) and mass balances indicate

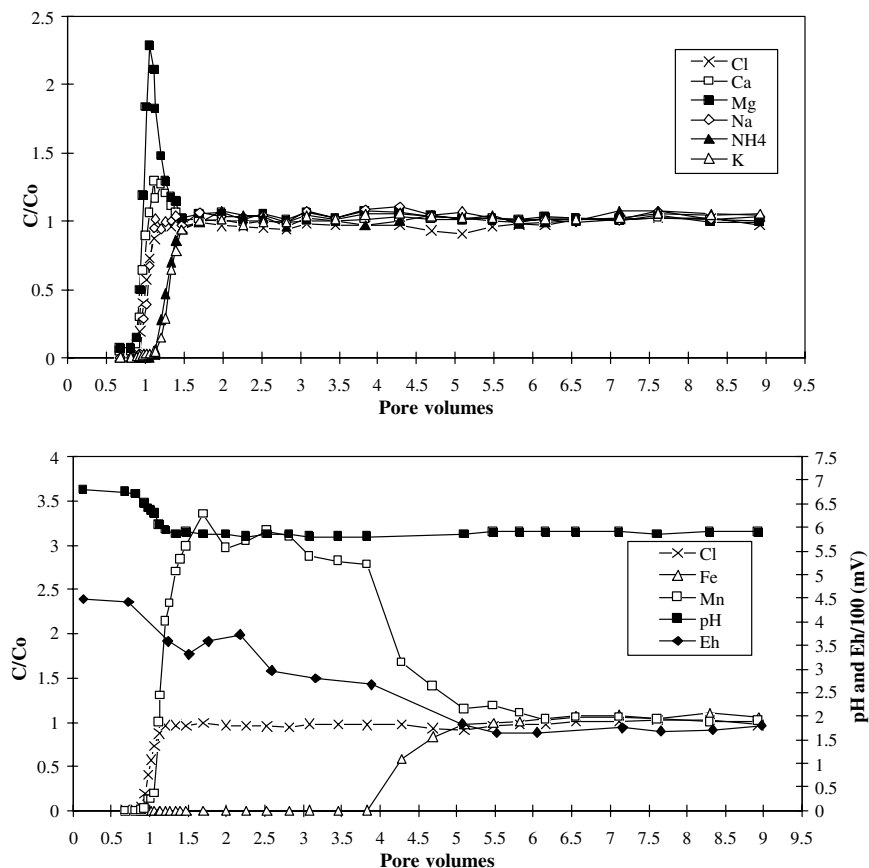


Figure 2. Breakthrough curves for inorganic solutes in A-phase leachate.

that there is almost complete substitution of the native exchangeable cation population on the sediment during flushing with the M-phase leachate (Table 3). The Ca and Mg mobilised during the A-phase leachate flush exceeded the amounts of  $NH_4$ , K and Na sorbed, but was less than the total CEC of the column (Table 3).

Table 3. Mass balance for major cations during leachate flushing of the aquifer columns

Experiment	Cations sorbed <sup>a</sup>				Cations desorbed <sup>a</sup>				Column CEC <sup>a</sup>
	Na	K	$NH_4$	Total	Na	Ca	Mg	Total	
A-phase	6	24	63	93	NA	76	50	126	180
A-phase repeat	9	25	62	96	NA	80	48	128	186
M-phase	12	35	135	182	NA	137	45	182	182
M-phase repeat	13	35	134	182	NA	132	46	178	180

<sup>a</sup> Values in meq.

ND – not determined (see text for discussion); NA – not applicable.

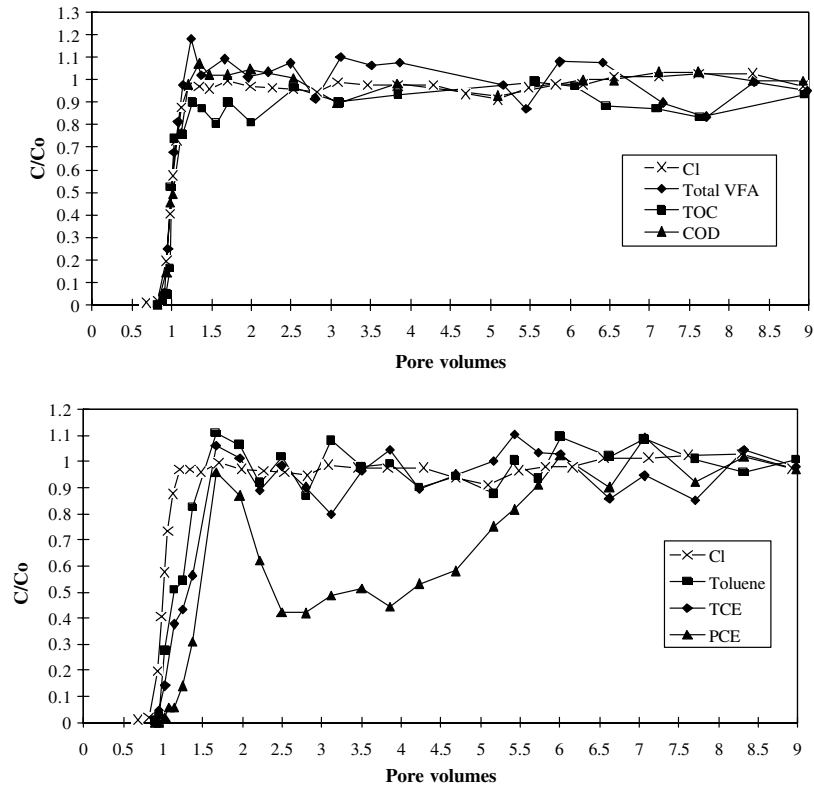


Figure 3. Breakthrough curves for organic solutes in A-phase leachate.

Assuming that ion exchange reactions are responsible for the retention of the major cations, the excess Ca (32 m eq) mobilised during these reactions is attributed to dissolution of native calcite in the aquifer material by the leachate (Thornton et al., 2000). This process has been as observed in similar studies (Ross, 1985; McMahon et al., 1995), and corresponds to ca. 1% of the  $\text{CaCO}_3$  mass in the aquifer column.

Ammonium is no longer attenuated once the sorbed cation composition of the aquifer sediment has reached equilibrium with the leachate cation composition. This occurs after two pore volumes in the columns illustrated and results in  $\text{NH}_4$  being eluted from the columns at concentrations found in the leachate (Figures 2 and 4). If extrapolated to field scale, the ion exchange reactions in the laboratory columns should result in increased Ca and Mg concentrations at the leachate Cl front but retardation of Na, K and  $\text{NH}_4$  fronts. Major ion profiles of the unsaturated zone porewaters beneath Burntstump landfill indicate that these general trends are indeed present (Figure 7). A peak in Ca and Mg at the leachate front with corresponding delayed arrival of K and  $\text{NH}_4$  fronts is clearly evident from the concentration profiles of these species. This occurs at a depth of 20 m below the landfill.

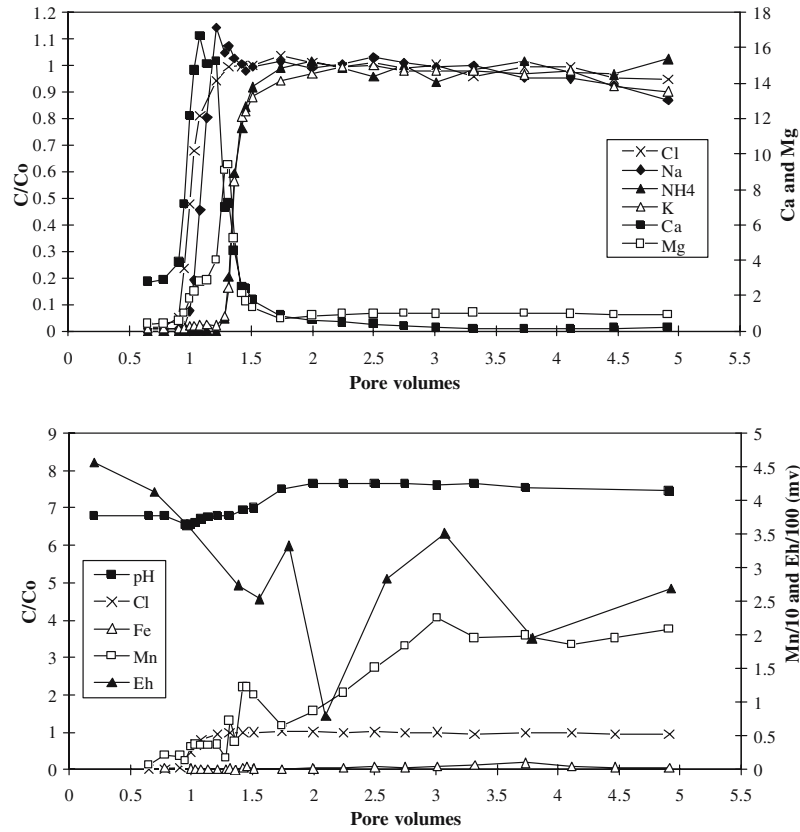


Figure 4. Breakthrough curves for inorganic solutes in M-phase leachate.

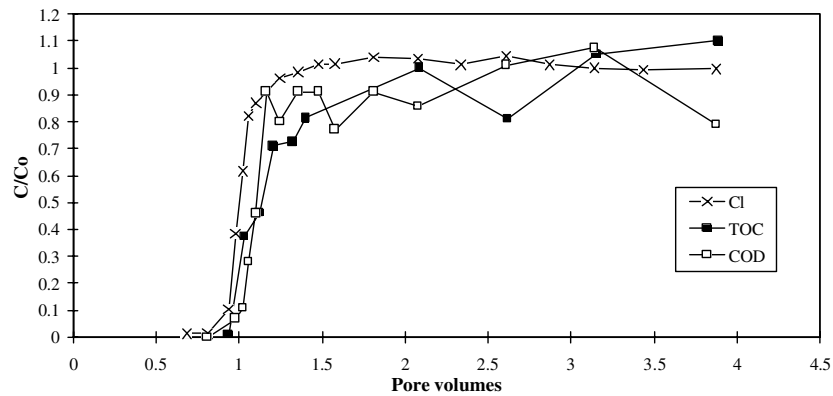


Figure 5. Breakthrough curves for organic solutes in M-phase leachate.

Despite the clearly complex (up to seven-way (Ca, Mg, Na, K, NH<sub>4</sub>, Fe, Mn)) ion exchange processes involved, the breakthrough pattern is such that NH<sub>4</sub> transport *in these systems* could be described using a simple partition coefficient ( $K_d^e$ ). Computed

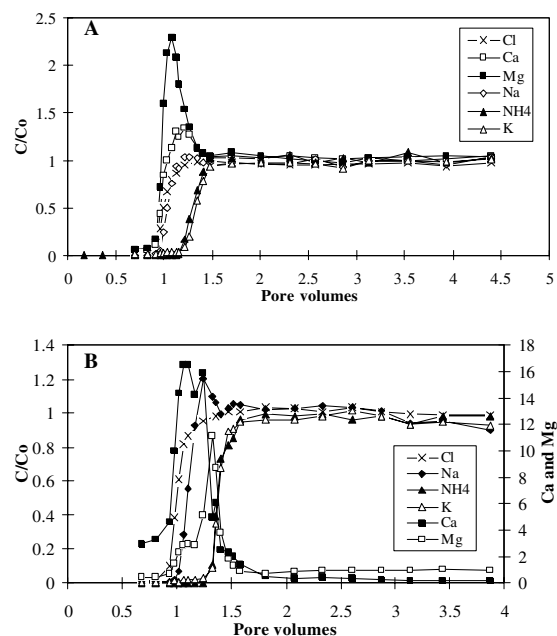
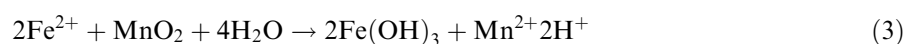


Figure 6. Breakthrough curves for selected solutes in duplicate experiments: (a) A-phase leachate, (b) M-phase leachate.

$K_d^e$  values for  $\text{NH}_4$  were found to be reasonably consistent for the different leachates. Unfortunately it was not possible in this study to explore the range of validity of this crude, but nevertheless, commonly applied approximation. Caution is therefore advised when extrapolating the results of this work to a description of leachate  $\text{NH}_4$  transport in other systems.

#### 4.1.2. Attenuation of heavy metals

Mn was eluted from the columns at concentrations significantly above those in each leachate and this coincided with the complete removal of the leachate Fe load. This feature lasted for approximately four pore volumes of the A-phase leachate flush, after which concentrations of Mn and Fe returned to input levels (Figure 2), but continued until the end of the experiment for the M-phase leachate flush (Figure 4). The masses of Mn and Fe involved are consistent with the stoichiometry of the following reaction (Postma, 1985; Thornton et al., 2000):



In this abiotic reaction Mn oxyhydroxides on the aquifer sediment are reduced by leachate  $\text{Fe}^{2+}$  which is oxidised and precipitated as an insoluble Fe oxyhydroxide. The Mn flush represents a redox front that is analogous in style to the Mn redox zones produced by microbial mediated reduction in groundwater contaminated by landfill leachate (e.g. Christensen et al., 1994). However, the Mn flush observed in the A-phase leachate-flushed experiments is produced by a chemical reaction, rather

than a microbially mediated reaction. The Mn flush observed in the M-phase leachate-flushed experiments exceeds that predicted by reaction 3, but the excess Mn can be accounted for by desorption of the exchangeable Mn fraction on the aquifer sediment (Thornton et al., 2000). Elevated Mn concentrations have also been recorded in the aquifer beneath the Burntstump landfill (Lewin et al., 1994).

The system redox status, represented by Eh, is also poised at a higher level during the Mn flush, suggesting that the former is influenced by the reduction of Mn oxyhydroxide fractions. In the A-phase leachate flush experiment the period of redox buffering and Fe attenuation continues until the Mn oxyhydroxide supply is exhausted, when Eh values return to that of the leachate. There is no subsequent mobilisation of native and/or freshly precipitated Fe oxyhydroxides and under these conditions the Mn oxide-based oxidation capacity of this aquifer sediment provides a sink for the leachate Fe load. The duration of the Mn flush depends upon the reservoir of reducible Mn oxyhydroxides and leachate Fe load. These results suggest that the high Fe load in A-phase leachates will quickly exhaust the Mn oxide reservoir on this aquifer sand, producing relatively short-lived Mn pulses. In contrast an extended Mn flush, and period of leachate redox buffering and Fe attenuation can be expected during contact with M-phase leachate.

#### 4.1.3. Attenuation of dissolved organic matter and XOMs

The sandstone was found to have limited capacity to sorb natural organic fractions (VFA, TOC, COD) in leachate and degradation of these components was minimal under the experimental conditions observed (Figures 3, 5 and Table 4). This observation is in agreement with the field data for the site, which shows that the

Table 4. Modelled sorption and degradation parameters estimated for organic solutes

Leachate	Solute	Sorption parameters		Degradation parameters	
		$R_f^c$	$K_d^c$	Lag phase (pv)	$T_{0.5}$ (days) <sup>a</sup>
A-phase	TOC	1.01	0.003	–	–
	COD	1.01	0.003	–	–
	Toluene	1.17	0.046	–	–
	TCE	1.26	0.07	–	–
	PCE	1.42	0.114	1.65	20
A-phase repeat	TOC	1.0	NA	–	–
	COD	1.0	NA	–	–
	Toluene	1.07	0.018	–	–
	TCE	1.11	0.028	–	–
	PCE	1.42	0.107	1.65	20
M-phase	TOC	1.05	0.013	–	–
	COD	1.09	0.024	–	–
M-phase repeat	TOC	1.03	0.008	–	–
	COD	1.08	0.023	–	–

<sup>a</sup> Determined for period of maximum degradation using the relationship  $T_{0.5} = \text{Ln}2/\lambda$ .

$R_f^c$  – Experimentally determined retardation factor;  $K_d^c$  – experimentally determined distribution coefficient in ml/g; NA – not applicable; pv – pore volumes.

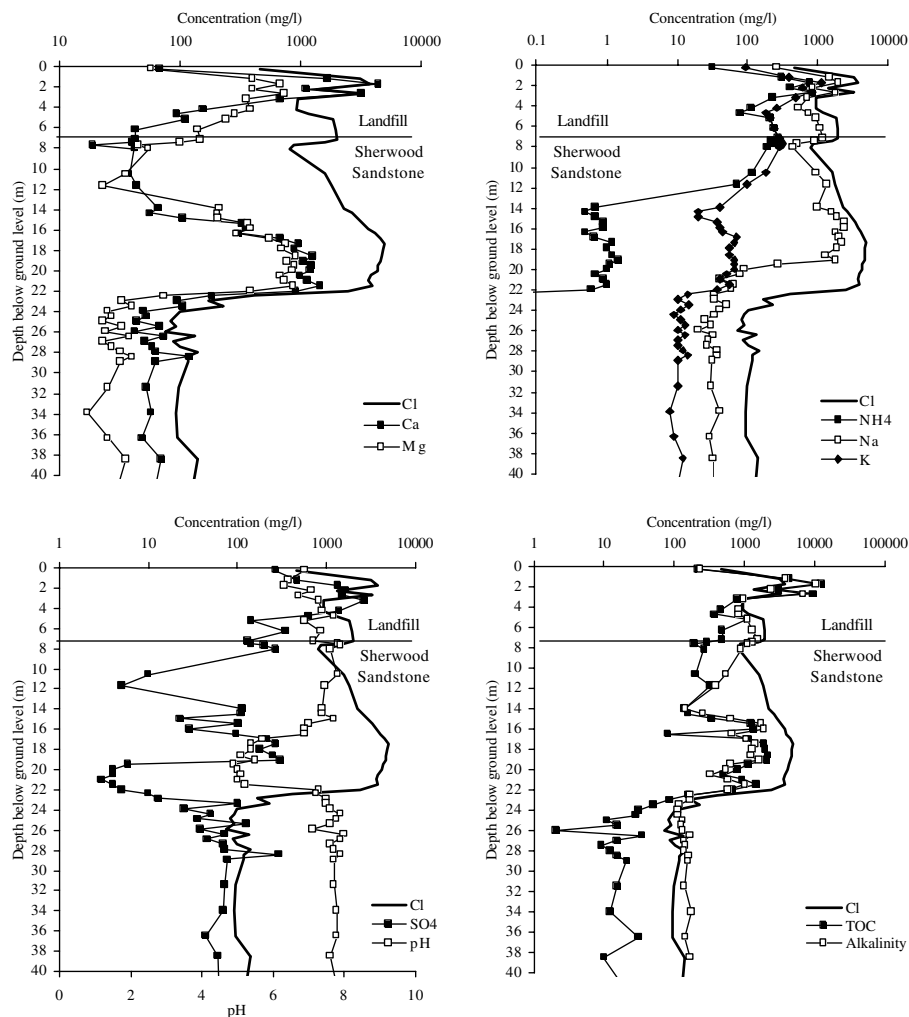


Figure 7. Unsaturated zone porewater major ion profiles at Burntstump landfill (from Lewin et al., 1994).

TOC fraction in leachate migrates at a similar velocity to the Cl front, indicating little attenuation by sorption (Figure 7). In contrast, although sorption of XOMs in the A-phase leachate was not significant (Table 4), the degradation of PCE was enhanced during the period of the Mn flush (Figure 3). This degradation occurred after a short lag phase and at the maximum rate of removal resulted in a half-life ( $T_{0.5}$ ) of 20 days (Table 4).

The limited sorption of natural organic matter in leachate by this Triassic sandstone is consistent with the results of related field studies which indicate that these fractions are highly mobile (cf. Figure 7) and migrate through the aquifer at velocities close to that of the groundwater (Lewin et al., 1994; Young et al., 1994).

Calculations show that the observed sorption of XOMs is less than that predicted from sorption theory (cf. Schwarzenbach et al., 1993). This is attributed to interactions with DOM fractions which result in enhanced solubility in the A-phase leachate.

The absence of significant degradation of the natural organic matter (e.g. VFAs) in the laboratory study contrasts with that observed in leachate plumes within the aquifer (e.g. Lewin et al., 1994). This difference may be partly related to the very high VFA load of the A-phase leachate which appears to exceed the low pH buffering capacity of these aquifer sediments (Table 2). This results in the suppression of pH values to those (pH 5.9) of the leachate (Figure 2), conditions which are known to suppress the activity of methanogenic bacteria responsible for VFA degradation (Christensen and Keldsen, 1989; Gurijala and Suffita, 1993). Beneath the landfill, pore water pH is also temporarily depressed to low values (pH 4–5) close to the leachate front, coincident with the presence of the highest TOC concentrations (Figure 7). This feature is consistent with the laboratory results for the A-phase leachate flush experiments. In addition, leachate transport through the laboratory columns has been necessarily accelerated over that within the aquifer, where a longer residence time may afford greater potential for degradation by a microbial consortia which is adapted to the ambient conditions. The absence of any significant toluene degradation in the laboratory columns is consistent with the lower potential for biodegradation of this aromatic XOM under the observed redox conditions (e.g. Acton and Barker, 1992; Christensen et al., 1994, 2001). The increased degradation of PCE during the Mn flush is consistent with that observed for this group of contaminants in the ferro-manganogenic zones of leachate plumes (Lyngkilde and Christensen, 1992; Christensen et al., 1994). PCE is usually biotransformed by reductive dechlorination to less oxidised daughter products (e.g. TCE) but there was no commensurate increase in TCE concentrations during the period of PCE degradation (Figure 3). Although the observed transformation of this XOM is linked to the abiotic redox reactions involving Fe and Mn in this system, the mechanism and pathway remains unclear.

#### 4.2. GEOCHEMICAL MODELLING

Modelled breakthrough profiles generated by the PHREEQM code for inorganic solutes in the A-phase leachate and M-phase leachate flush experiments are shown in Figures 8 and 9, respectively. The processes simulated include ion-exchange reactions between the major cations (Ca, Mg, K, Na,  $\text{NH}_4$ ,  $\text{Mn}^{2+}$ ,  $\text{Fe}^{2+}$ ), carbonate equilibria and a redox reaction involving the dissolution of  $\text{MnO}_2$  by  $\text{Fe}^{2+}$ . The modelled redox front has been generated from the total solid phase Mn mobilised by the A-phase leachate. This amount was obtained from a mass balance for the column experiment and is also assumed to be the total fraction of  $\text{MnO}_2$  available for reduction for the purpose of modelling the M-phase leachate flush column. In each case there is good agreement in the style and timing of contaminant breakthrough

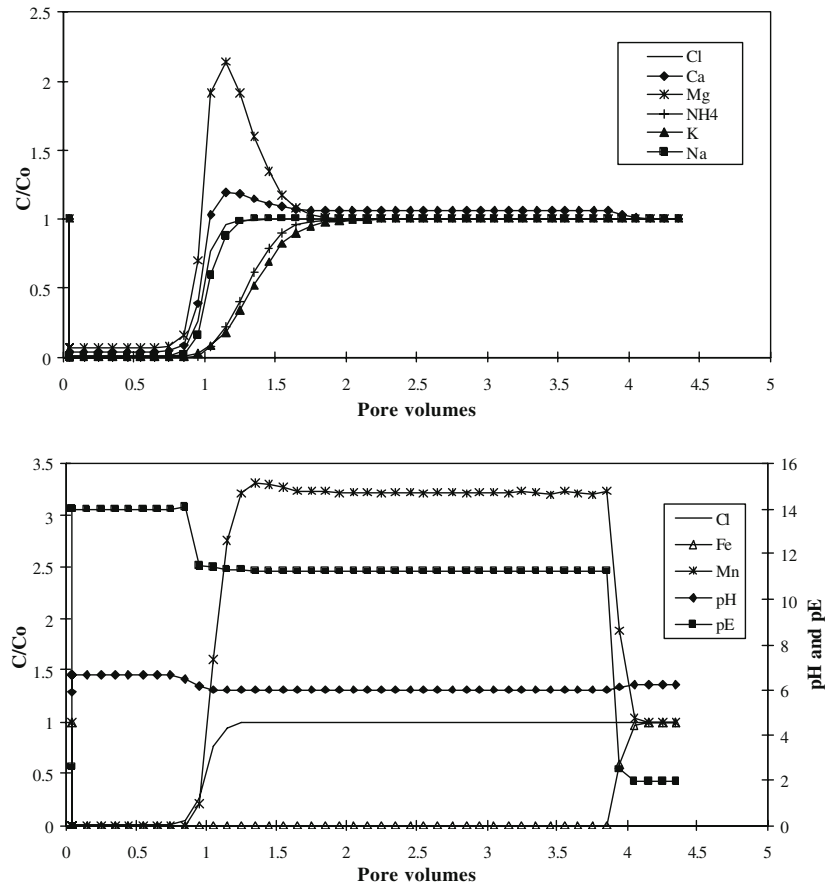


Figure 8. Simulated inorganic solute breakthrough curves for A-phase leachate.

between the simulated data and experimental results (Figures 2 and 4). Both the duration of the Mn flush and qualitative change in system redox status following its termination are adequately reproduced by the model for the A-phase leachate flush, as is the duration of the Mn flush (up to five pore volumes) for the M-phase leachate flush. Additional simulations have been performed to examine the contribution of other processes (e.g. rhodochrosite precipitation) on contaminant attenuation. These simulations are not shown but demonstrate that the high Mn concentrations produced during the Mn flush would be reduced below those of the input leachate in each experiment, suggesting that precipitation of  $\text{MnCO}_3$  is not important in the systems studied, at least over the timescale of the experiments. If precipitation of  $\text{MnCO}_3$  was occurring, it would provide a sink for the Mn produced by the chemical dissolution of Mn oxides and maintain the pore water Mn concentration at very low levels in the aquifer. The modelled results suggest that the three processes simulated adequately characterise the expected attenuation of these different leachates by the sandstone.

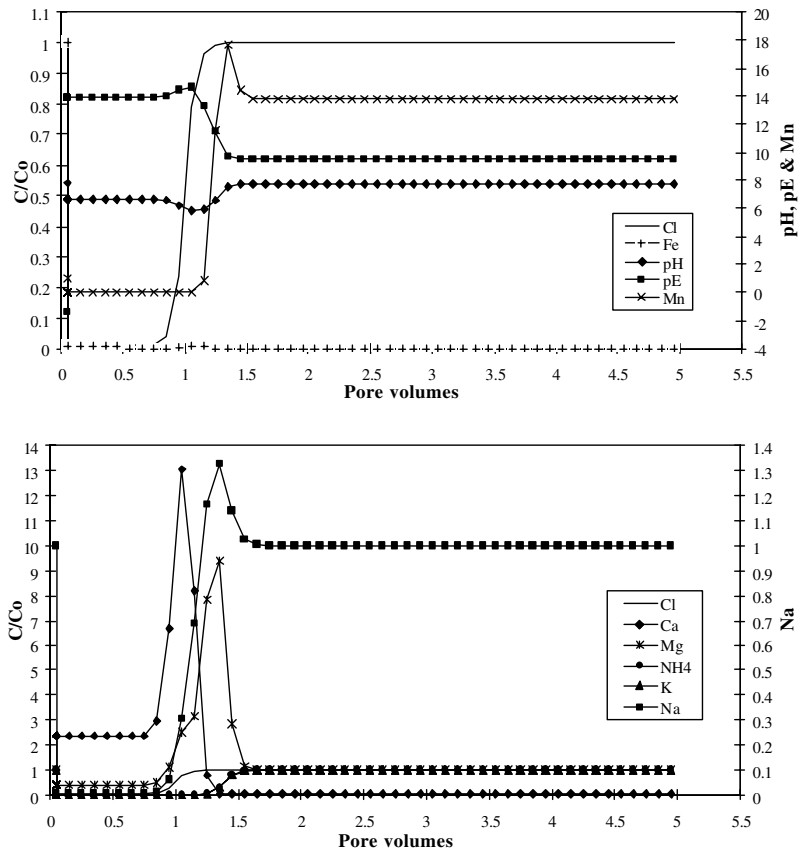


Figure 9. Simulated breakthrough curves for inorganic solutes in M-phase leachate.

## 5. Summary and Conclusions

The laboratory study has shown that many of the key features observed in the field system can be qualitatively replicated using column experiments. This experimental approach may therefore provide a useful means of investigating likely reactions at sites and collecting cost-effective data for assessing leachate attenuation. The modelling work is encouraging in that these complex systems can be described using leachates with very different but representative compositions. However, there is a need to obtain data from similar studies on other landfill sites on the aquifer to understand the broad applicability of the controlling processes, constrain the limits on the parameters describing these and to examine the range in validity of these for other systems. The geochemical transport code may be used to interpret laboratory or field data or to extrapolate laboratory data to field conditions, based on the results of this study. In combination the experimental and modelling approaches presented in this paper provide a powerful tool for risk assessment at both lined and unlined landfills.

The study has demonstrated that  $\text{NH}_4$  in leachate is attenuated by ion exchange with the aquifer sediment. This mechanism will delay the migration of  $\text{NH}_4$  in the aquifer, although concentrations of  $\text{NH}_4$  in groundwater may ultimately reach that of the leachate. Reduction of Mn oxyhydroxide coatings on the sandstone by leachate Fe may provide an effective sink for the leachate Fe load. The results suggest that the duration of the Mn flush, Fe attenuation and redox buffering produced by this mechanism will be much shorter during contact with A-phase leachate than M-phase leachate. This is due to the much higher  $\text{Fe}^{2+}$  load of acetogenic leachate, which results in a more rapid exhaustion of the aquifer Mn oxide-based redox buffering capacity by the chemical reaction observed, than that which is likely to occur for methanogenic leachate.

There is minimal sorption of organic contaminants in leachate by this aquifer material. Under the experimental conditions there was minimal degradation of natural DOM in leachate compared with that expected in the field system, but enhanced degradation of one XOM (PCE) during the period of Mn oxyhydroxide reduction. The Mn-reducing zones of leachate plumes in the aquifer may therefore have enhanced potential for the degradation of these (XOM) contaminants. However, as noted for  $\text{Fe}^{2+}$  attenuation, the duration of this attenuation could depend on the quantity of reducible Mn oxides on the aquifer sediment and leachate  $\text{Fe}^{2+}$  concentration.

Aquifer pH buffering capacity, reducible Mn oxyhydroxides and cation-exchange capacity are important geochemical properties which regulate leachate contaminant attenuation in this system. Based on these experimental results, contaminants in A-phase leachate will present a greater threat to groundwater in the aquifer than those in M-phase leachate. Leachate contamination of groundwater in this aquifer may be identified by increased concentrations of Cl, Ca, Mg, Mn, TOC and VFA relative to background levels. This 'hydrochemical signature' may assist the delineation of leachate plumes at unlined sites and provide a first indication of liner failure at monitored, lined sites on the aquifer.

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### References

- Acton, D.W. and Barker, J.F.: *In situ biodegradation* potential of aromatic hydrocarbons in anaerobic aquifers, *J. Contam. Hydrol.*, **9**, (1992), 325–352.

- APHA: *Standard Methods for the Examination of Water and Wastewaters*, American Public Health Association, 1985.
- Appelo, C.A.J. and Postma, D.: *Geochemistry, Groundwater and Pollution*, Balkema, The Netherlands, 1993.
- Bourg, A.C.M., Degranges, P., Mouvet, C. and Sauty, J.P.: Migration of chlorinated solvents through Coventry sandstone rock columns, *J. Hydrol.*, **149**, (1993), 183–207.
- Ceazan, M.L. Thurman, E.M. and Smith, R.L.: Retardation of ammonium and potassium through a contaminated sand and gravel aquifer: The role of ion exchange, *Environ. Sci. Technol.*, **23**, (1989), 1402–1408.
- Christensen, T.H. and Kjeldsen, P.: Basic biochemical processes in landfills. *Sanitary Landfilling: Process, Technology and Environmental Impact*, Academic Press, 1989, pp. 29–49.
- Christensen, T.H., Kjeldsen, P., Albrechtsen, H., Heron, G., Nielsen, P.H., Bjerg, P.L. and Holm, P.E.: Attenuation of landfill leachate pollutants in groundwater. *Crit. Rev. Environ. Sci.*, **24**, 1994, 119–202.
- Christensen, T.H., Kjeldsen, P., Bjerg, P.L., Jensen, D.L., Christensen, J.B., Baun, A., Albrechtsen, H.-J. & Heron, G.: Biogeochemistry of landfill leachate plumes. *Appl. Geochem.*, **16**, (2001), 659–718.
- Domenico, P.A. and Schwartz, F.W.: *Physical and Chemical Hydrogeology*, (2nd edn.), Wiley and Sons, 1998, p. 824.
- Gurijala, K.R. and Suffita, J.M.: Environmental factors influencing methanogenesis from refuse in landfill samples, *Environ. Sci. Technol.*, **27**, (1993), 1176–1181.
- Kjeldsen, P. and Christensen, T.H.: Soil attenuation of acid phase landfill leachate. *Waste Manage. Res.*, **2**, (1984), 247–253.
- Lewin, K., Young, C.P., Bradshaw, K., Fleet, M. and Blakey, N.C.: Landfill monitoring investigations at Burntstump Landfill, Sherwood Sandstone, Nottingham 1978–1993 (ENV 9003). *Final Report for the Dept. of the Environment*, CWM 035/94, 1994, p. 127.
- Lewin, K., Young, C.P., Sims, P., Blakey, N., Oakes, D., Reynolds, P. and Bradshaw, K.: Long term monitoring of non-contained landfills: Burntstump and Gorsethorpe on the Sherwood Sandstone. *Published DoE Report*, CWM 38/96, 1996.
- Lyngkilde, J. and Christensen, T.H.: Fate of organic contaminants in the redox zones of a landfill leachate pollution plume (Vejen, Denmark). *J. Contam. Hydrol.*, **10**, (1992), 291–307.
- McMahon, P.B., Vroblesky, D.A., Bradley, P.M., Chappelle, F.H. and Gullett, C.D.: Evidence for enhanced mineral dissolution in organic acid-rich shallow groundwater. *Ground Water*, **33**, (1995), 207–216.
- Ogata, A. and Banks, R.B.: A solution of the differential equation of longitudinal dispersion in porous media. *U.S. Geological Survey Professional paper*, 411-A, 1961, p. 7.
- Parkhurst, D.L., Thorstenson, D.C. and Plummer, L.N.: PHREEQE – A computer program for geochemical calculations. *US Geological Survey Water Resources Inventory*, 80–96, 1980, p. 210.
- Postma, D.: Concentration of Mn and separation from Fe in sediments-I. Kinetics and stoichiometry of the reaction between birnessite and dissolved FeII at 10 °C. *Geochim. Cosmochim. Acta*, **49**, (1985), 1023–1033.
- Robinson, H.D. and Gronow, J.R.: A review of landfill leachate composition in the UK. In: *Proceedings of the 4th International Landfill Symposium*, CISA, Environmental Sanitary Engineering Centre, Cagliari, Italy, 1993, pp. 821–832.
- Ross, C.A.M.: The unsaturated zone as a barrier to groundwater pollution by hazardous wastes. In: *Memoirs of the 18th Congress of the Int. Assoc. of Hydrogeologists*, 1985, pp. 127–141.

- Schwarzenbach, R.P., Gschwend, P.M. and Imboden, D.M.: *Environmental Organic Chemistry*. Wiley & Sons, 1993, p. 681.
- Thornton, S.F., Tellam, J.H. and Lerner, D.N.: Attenuation of landfill leachate by UK Triassic Sandstone aquifer materials: 1. Fate of inorganic pollutants in laboratory columns. *J. Contam. Hydrol.*, **43**, (2000), 327–354.
- van Reeuwijk, L.P.: *Procedures For Soil Analysis. Technical Paper no. 9*. International Soil Reference & Information Centre, Wageningen, The Netherlands, 1987.
- Young, C.P., Fleet, M., Lewin, K., Blakey, N.C. and Bradshaw, K.: Landfill monitoring investigations at Gorsethorpe landfill, Sherwood Sandstone, Nottinghamshire (1978-1992) (ENV 9003). *Final Report for the Dept. of the Environment*, CWM 034/94, 1994, p. 113.