A FUGACITY APPROACH FOR GENERATING A LANDFILL GAS TRACE COMPONENT SOURCE TERM

S. SHAFI*, S.J.T. POLLARD*, R. SMITH*, A. SWEETMAN** AND A. ROSEVEAR °

*Integrated Waste Management Centre, Cranfield University, Bedfordshire MK43 0AL, UK
** Department of Environmental Science, Lancaster University, Lancaster LA1 4YQ, UK
° Science Group - Waste and Remediation, Environment Agency, Reading RG1 8DQ, UK

SUMMARY: The quality of risk assessment output is determined by the input data used in environmental distribution, dispersion and exposure models. Whilst recent focus has been on the development of regulatory exposure assessment models for landfills, risk analysts are keenly aware of the need for improved source term models in order to improve confidence in risk assessments and allow better targeting of risk management actions. This research sought to reconcile measured concentrations of selected priority trace components in landfill gas with potential source term loadings that could be generated within landfilled waste. A fugacity approach estimated the loadings of four priority trace components required to generate the source-term for landfill gas risk assessment models; vinyl chloride (chloroethene), benzene, 1,3-butadiene and trichloroethylene. Three fugacity models, coded originally for soils, were adapted for an evaluative landfill environment, developed using data from the Brogborough (UK) test cells. Modelled concentrations were within the range of those observed in the field.

1. INTRODUCTION

1.1 Background

Waste management technologies are increasingly subject to environmental risk assessments that inform operational practice, environmental permitting and regulatory intervention. The quality of any environmental risk assessment is influenced by the input data for the distribution, dispersion and exposure models that support an analysis of the probability and consequences of exposure. Improved source-term models will engender greater confidence in risk assessments and risk management measures (El-Fadel *et al*., 1997a, 1997b and Pollard *et al*., 2005). Considerable literature exists on the hazards of bulk landfill gas (LFG) *i.e.* CH_4, CO_2 and, more recently, on

the gas phase concentrations of trace components in untreated LFG (Allen *et al.*, 1997 and Environment Agency, 2003, 2004). GasSim (Environment Agency, 2002) is a probabilistic Monte Carlo UK regulatory LFG model that generates a source term for bulk gases using a first order rate equation for the biodegradation of the organic component of the waste and uses default values for trace components based on concentrations reported in the literature or preferably single time point ('snapshot') monitoring data from the specific site. The inventory of trace components is allowed to decay and does not take into account partitioning into other phases. Here, we attempt to reconcile measured concentrations of four priority trace components in LFG with potential source term loadings that we estimate retrospectively using fugacity modelling.

1.2 Rationale and fugacity model selection

Fugacity modelling studies adopt a reasonably uniform methodology (Mackay, 1979, 2001, 2004) and the approach has been applied to many different environmental applications ranging from global-scale to *in vivo* modelling. Its application to waste problems is increasing. Soil fugacity models, or adaptations of them, are routinely used to represent environmental systems. They are useful starting points as source term generators for LFG risk assessment. The rationale for three such models used in our study is reported elsewhere (Shafi, 2005). The SOILVE model recognises that the effectiveness of gas extraction declines exponentially as a result of removal of the gas from more permeable areas, followed by extraction from areas where the permeability is lower. The presence of a decay term also makes application of SOILVE particularly attractive for the landfill environment. A conceptual, representative 'evaluative environment' is established, in our case a landfill. The evaluative environment is constructed with volumetric proportions of environmental compartments (air, water, soil), and chemicals of concern are then allowed to distribute themselves between these compartments with varying degrees of sophistication, as the available data to populate the model and the model complexity allows (*e.g.* steady-state equilibrium; introducing flux; flux with loss terms (Mackay, 2001).

1.3 Trace components in LFG

LFG composition is dominated by the bulk gases methane (40 - 70 $\%^v/_v$) and carbon dioxide (30 - 60$\%^v/_v$) with smaller concentrations of hydrogen, hydrogen sulphides and other trace components that may make up 1% $^v/_v$. The toxicological characteristics of the trace components are such that despite their low environmental concentrations, they may pose a potential risk to human health where exposure is either acute, repeatedly episodic or prolonged (Allen *et al.*, 1997, Brosseau & Heitz, 1994, El-Fadel *et al.*, 1997a, Zou *et al.*, 2003). Trace composition of LFG is variable temporally, spatially and on an inter- or intra- cell or site basis, making it very difficult to predict. There is considerable prior art, however with UK research into LFG trace components beginning in the early 1980s. A UK study identified 550 trace components (Environment Agency, 2003). As part of a LFG emissions reduction strategy, regulators have sought to prioritise the monitoring of these trace components by reference to the hazards they pose and on account of their typical concentrations and published toxicological and odour properties of individual components (Environment Agency, 2004). The list includes chloroethane, 1,1-dichloroethane, vinyl chloride, trichloroethylene, 1,1-dichloroethene, 1,2-dicholoroethene and tetrachloromethane, most of which are present on the national pollution inventory as substances hazardous to health.

2. MATERIALS AND METHODS

2.1 An evaluative landfill environment

Landfill is a complex heterogeneous environment. The evaluative environment was a single cell of waste, rather than an entire landfill (Figure 1), this choice being influenced by the availability of data from the Brogborough (UK) landfill test cells (Fletcher, 1989, Croft *et al.*, 2001, Blackmore *et al.*, 2003). Our evaluative environment allows for three phases; gas, water and waste, and for the processes of water and gas flux through the system to be represented.

The Brogborough test cells were constructed during 1986-88 at the Shanks and McEwan landfill (Brogborough, Bedfordshire, England). The site is situated on the Oxford clay and naturally contained. Waste was deposited between July and October 1988 (4½ months). The test cells were set up to evaluate the effects of pre and post-emplacement management techniques on methane production rates (Croft *et al.*, 2001). Six cells were constructed each with a different management technique such as leachate re-circulation, air injection and sewage sludge addition. A single cell contained a mix of MSW and non-hazardous commercial waste (control cell). Our study has adopted the design data from cell 1 containing MSW placed in thin layers (Blackmore *et al.*, 2003). The dimensions and characteristics of cell 1 are reported in Table 1. Leachate, gas and solid waste were monitored at Brogborough between 1986 and 2000, making it the longest field scale landfill study in the world (Blackmore *et al.*, 2003). The cells have produced limited data concerning the concentrations of trace components in the gas but the gas production data and physical characteristics of the cells (Table 2) provide a valuable base for this study. Here, test cell 1 was taken as being typical of most UK landfill sites accepting MSW. The evaluative environment remained constant for the fugacity studies that follow.
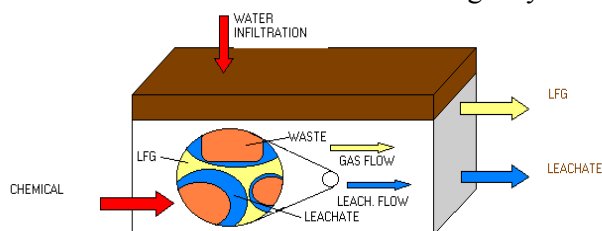

Figure 1. An evaluative landfill environment

Table 1. Dimensions of the landfill evaluative environment

Parameter	Value	Justification/reference
Cell length	40m	
Cell width	20m	Brogborogh test cell 1 (Blackmore *et*
Cell depth	25m	*al.*, 2003)
Cell volume	$20 \times 10^3 m^3$	
Cell mass	$16 \times 10^6 kg$	Calculation (m=ρv)
Waste density	$830 kg/m^3$	(Croft *et al.* 2001)

Table 2. Volumetric composition of the landfill evaluative environment

Parameter	Volume fraction	Justification/reference	Mass (kg)	Volume (m³)
LFG/air	0.10	10% effective porosity of waste (Blackmore *et al.*, 2003)	2.20×10^3	2000
Water	0.25	Estimated water content (Croft *et al.*, 2001, Blackmore *et al.*, 2003)	5.00×10^6	5000
Waste				
organic	0.25	Estimated from type of waste input, similar mean reported by Schwarze (2001)		
inorganic	0.40	Remaining volume		
Waste total	0.65	Accumulative	1.15×10^7	13000

2.2 Chemical input

A recurrent issue for modelling landfills is the uncertainty associated with the composition of incoming waste. Understanding the load and characteristics of the waste is important so that generalised findings can be extrapolated between sites with similar operational histories. However, devising an input of chemical for a model is always challenging without precise waste receipt, composition and analytical records. A scalable initial value of 10 mg/kg for all of the chemicals (Pollard *et al.*, 1993) was used here in the first instance. This represents a load to the cell of 160 kg and, having generated an initial set of gas concentrations, allowed a subsequent back-extrapolation of possible initial inputs of the chemical to the landfill. Molecular mass (g/mol), temperature (C), water solubility (g/m^3), vapour pressure (Pa), log K_{ow}, melting point (C) and the Henry's Law constant (Pa.m^3/mol) were required for each substance and adopted from those reported in Mackay (2001).

2.3 Gas and water regimes

Gas flow through landfills is highly variable, dependant on a number of factors such as atmospheric pressure, design and operational parameters and fluctuates daily and monthly (Kjeldsen & Christensen, 2001, Croft *et al.*, 2001, Young, 1992, Christopherson & Kjeldsen, 2001). The historic data from Brogborough test cell 1 shows gas production rates varying between 5-15m^3/tonne of waste/yr (Croft *et al.*, 2001). A mean of 10m^3/t/yr represents a gas extraction rate of *ca.* 20m^3/h from each cell. A log mean diffusion path of 4.55m was adopted from a diffusion path of 12.5m, judged as the maximum distance between gas extraction points at Brogborough and typical of a large, modern, engineered UK landfill. Rather than set a leachate head for this study, a water flow rate though the cell was applied using an infiltration rate of 0.14mm/d adopted from GasSim (Environment Agency, 2002). This flow rate assumes that water input into the system is constant, and derived from limited infiltration through a clay cap alone (Environment Agency, 2002).

2.4 Fugacity modelling

Level 1 fugacity calculations illustrate general partitioning behaviour and preferential partitioning to the organic fraction in the waste environment, which we know is an important and frequently misrepresented aspect of modelling hazardous waste problems (Kjeldsen & Christensen, 2001, Young, 1992). Level II calculations account for advection and reactions in the form of residence time and half lives respectively (D values). The calculations assume an environment in equilibrium, but under steady state flow *i.e.* the amount entering the environment is mass balanced by the amount lost to flow, reactions or degradation. The Level II model (Figure 2) allows the estimation of a residence time for a substance within the system. The characteristics of the systems are presented in Table 3.

Table 3. Parameters for Level II fugacity calculation

Parameter	Value	Justification/reference
Emission rate of chemical into environment	0.05kg/h	Calculated using 10ppm (160kg) of chemical with filling time 4.5 months (Fletcher, 1989).
Gas flow rate	20m3/h	Adapted to evaluative environment (Croft *et al.*, 2001)
leachate flow rate	6 x103 m/h	Calculated from water infiltration rate of 0.14mm/d through environment.
Advective residence time for LFG	100h	Calculated using gas flow rate and level one calculation; assumes chemical concentration in incoming gas of zero.
Advective residence time for leachate	833333h	Calculated using leachate flow rate as above.

Reaction half-lives for each chemical in air, water and waste were required. Aerobic values were adopted from Mackay (2001). A further set utilised anaerobic degradation rates obtained from aquifers studies (Aronson & Howard, 1997). Control runs set the degradation term to zero. An adapted level II fugacity model, SOILVE is dynamic, in that time and extraction rates can specified. The model (She *et al*., 1995) was recoded using Model Maker 4™ for the purposes of this study. In concept, SOILVE has many similarities to the processes of LFG extraction. Parameterisation is complex and includes concentrations in various phases, as well as D values (transport parameters). To obtain these, a level II calculation was conducted prior to the SOILVE run. Table 4 displays the additional parameterisation required for SOILVE. The series of model runs undertaken to evaluate the fate of trace components in LFG (Christopherson & Kjeldsen, 2001) is reported elsewhere (Shafi, 2005). The selection of runs reflects the acknowledged (Kjeldsen & Christensen, 2001) importance of (i) the free organic carbon phase (represented by f_{oc}) (ii) the gas extraction rate; and (iii) the redox status to estimating the concentration of trace components in LFG.
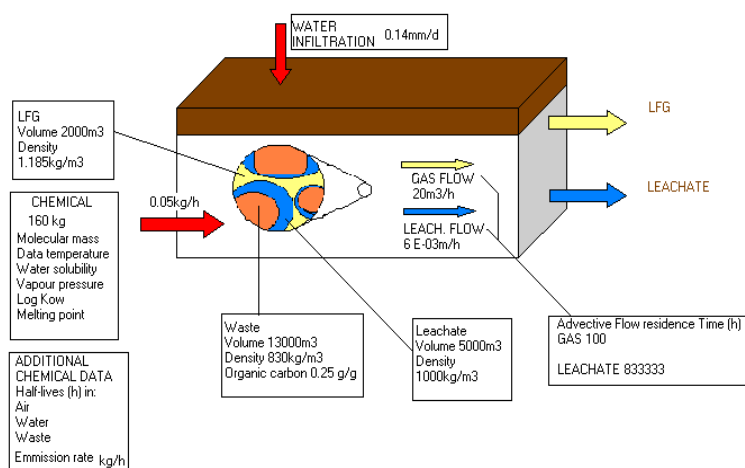

Figure 2. Evaluative environment for Level II model

Table 4. Parameterisation of SOILVE

Parameter/unit	Explanation	Justification/calculation/derivation
Chemical input	Amount of chemical in kg	160 kg
Z values	Fugacity capacity of each phase	Generated from level II calculation
G (m³/h)	Gas flow rate	20 m³/h
E (unitless)	Sweep efficiency	(She *et al*., 1995)
k_3	Rate constant for decay	(She *et al*., 1995)
t½ (h)	Half life of chemical in soil	Aerobic (Mackay, 2001); anaerobic (Aronson & Howard, 1997)
k_r(h⁻¹)	Rate constant for degrading reactions	$0.693/t_{1/2}$
Z_T (Pa)	Total fugacity	
V_T (m³)	Total volume	
D_R (mol/Pa h)	D value for degrading reactions	$DR = KrZ_TV_T$
D_L (mol/Pa h)	D value for water leaching	Water flow rate/Zwater
D_X (mol/Pa h)	D value for gas phase advection	Gas flow rate/Zgas
K_v (m/s)	Mass transfer coefficient	From diffusivity calculation (Lyman *et al*., 1982)
D_E (m/s)	Diffusion across a stagnant boundary layer	DE=kv Azgas
B_{EG}	Gas phase diffusion	
D_G (mol/Pa h)	Gas phase diffusion in soil	
B_{EW}	Water phase diffusion	
D_W(mol/Pa h)	D value water phase diffusion	

3. RESULTS

In GasSim (Environment Agency, 2002), trace component concentrations are estimated (a) using distributed literature data using a uniform or triangular distribution, as appropriate; or (b) from site-specific data. The evaluative environment used in this study is similar to GasSim, the waste being considered as a cuboid mass with vertical sides from which characteristics such as volume and area are deduced (Environment Agency, 2002). If a site-specific fugacity model were constructed and applied, informed by an estimated inventory of solvent mass in the landfill, then a more representative source-term might be produced and subsequent estimates of exposure and risk made more representative.

3.1 Level I and II fugacity modelling

Here, discussion is reserved for the results offering greatest insight. A comprehensive analysis is presented by Shafi (2005). Level I modelling (Figure 3) illustrates the role of organic matter (f_{oc}) in determining the partitioning of trace components in the landfill system. Organic carbon can be represented by conventional soil organic (humic) matter or by the presence of a free organic phase common to many hazardous waste systems (Pollard *et al.*, 1993, Kjeldsen & Christensen, 2001).
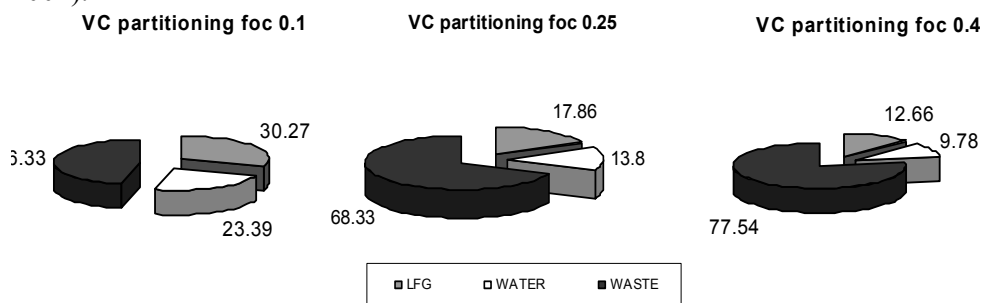

Figure 3. Illustrative mass contributions (%^{w}/w) of vinyl chloride (VC) to LFG, water and waste phases contingent on the fraction of organic carbon (f_{oc}) in the system

Level II modelling has improved utility, producing illustrative data on persistence, losses due to advection and reaction and other dynamic trends. It again highlights the influence of organic carbon in the waste matrix on the mass of chemical in the gaseous phase and the residence time of a chemical, given the flux (Figure 2) in the landfill (Figure 4).
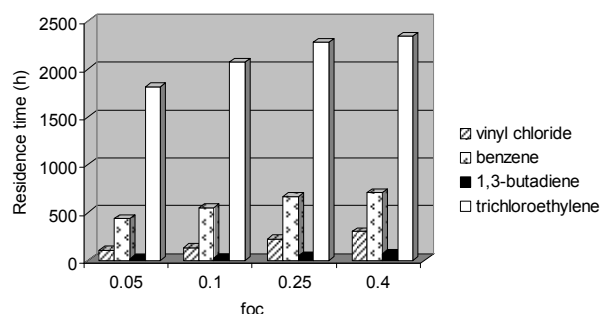

Figure 4. Residence time of trace components in landfill as a function of f_{oc} using Level II fugacity modelling

The concentrations of trace components in each phase using a 10 mg/kg input are presented in Table 5 and compared with the observed ranges in monitoring studies. Observed benzene

concentrations are between 3500-150 000 $\mu g/m^3$. Modelled concentrations range between 32 700-139 000 $\mu g/m^3$ suggesting that, assumptions holding, a 10 mg/kg (160 kg) input of benzene may be a good first approximation. The modelled concentrations for vinyl chloride, trichloroethylene and 1,3-butadiene were elevated above the observed ranges, although vinyl chloride was of the same order of magnitude as the observed concentrations. One approach to estimating the initial load is to back-extrapolate, taking the model assumptions as valid and the observed concentrations for each component as input (Table 6). This provides a set of candidate loads that can be re-assessed with anaerobic degradation rates to generate a new set of phase distributions (Table 7), the gas phase concentrations for which may be compared with the observed ranges of trace components in LFG. Level 2 fugacity calculations achieved realistic estimates for the compounds of concern and may prove a beneficial source term generator.

Table 5. Level II fugacity calculations. Modelled and observed concentrations of priority components in LFG assuming a 10 mg/kg waste input (all data in $\mu g/m^3$).

foc	Benzene			vinyl chloride			trichloroethylene			1,3-butadiene		
	gas	water	soil/waste	gas	water	soil/waste	gas	water	soil/waste	gas	water	soil/waste
0.05	**139000**	619000	1420000	**1050000**	320000	123000	**534000**	1120000	6460000	**165000**	19800	32900
0.1	**94900**	4.22E+05	1.94E+06	**1033100**	3.19E+05	2.43E+05	**317100**	6.65E+05	7.67E+06	**163000**	1.96E+04	6.51E+04
0.25	**48600**	126000	2480000	**995000**	307000	585000	**143000**	300000	8640000	**158000**	19000	158000
0.4	**32700**	145000	2670000	**959000**	296000	903000	**92000**	193000	8920000	**153000**	18400	245000
Observed: 3500-150000				**24300-180000**			**1950-7100**			**<20-<70**		

Table 6. Back-extracted estimates of trace component load to evaluative landfill cell

Trace component	Mean observed gas concentration ($\mu g/m^3$)	Estimated input to cell (kg)
Vinyl chloride	87000	14
Benzene	48600	160
Trichloroethylene	4525	5
1,3-butadiene	45	0.045

Table 7. Estimating LFG concentrations with anaerobic degradation rates (Level II) (after Environment Agency, 2003)

Trace component and input (kg)	Input rate (kg/h)	Gas concentration ($\mu g/m^3$)	Observed range in LFG ($\mu g/m^3$)
Vinyl chloride (14)	0.05	492000	3500-150000
Benzene (160)	0.043	95300	24300-180000
Trichloroethylene (5)	0.0015	13000	1950-7100
1,3-butadiene (0.045)	0.00013	43	20-70

The absence of representative anaerobic degradation rates within landfills is a considerable constraint. Further, it is clear from the analysis that the complexities of the landfill environment stretch the capabilities of Level II fugacity modelling.

3.2 Dynamic fugacity modelling

Landfill processes (e.g. redox status, settlement, gas and leachate generation and chemical composition) develop over decades. Exploratory SOILVE model runs were performed (Shafi, 2005) (i) for ca. 1 year (8000 h) under aerobic and zero degradation conditions; (ii) for individual components at gas extraction rates of 10, 20 and 40 m^3/h; and (iii) for the first year, aerobically, at f_{oc} values of 0.05, 0.25 and 0.4. D values, along with other input parameters, were derived from a prior set of Level II calculations (note limitations above), using an illustrative 10 mg/kg

input concentration (Table 7). Of specific interest is the effect of the gas extraction rate on the long term concentrations of trace components present in LFG. A set of SOILVE model runs was performed for a ca. 10 yr period (90 000 h) using zero and anaerobic degradation rates at gas extraction rates of 10, 20 and 40m^3/h. For the anaerobic simulations, trace component concentrations in the gas phase were inevitably higher than for aerobic degradation. The vinyl chloride concentrations predicted appeared to be too low for all three extraction rates (Figure 5).

Once extrapolation to 160 kg input is considered, a 10m^3/h extraction rate produces an order of magnitude concentration for vinyl chloride akin to that observed in recent field investigations between 0.3- 4.1 years. There is no information on the age of the field data, however and no conclusive correlations can therefore be made. Figure 5 illustrates the impact that degradation and extraction rates have on the concentration of trace components in LFG. These factors change throughout the lifetime of a landfill (bi-, tri-phasic behaviour), generating additional complexity.

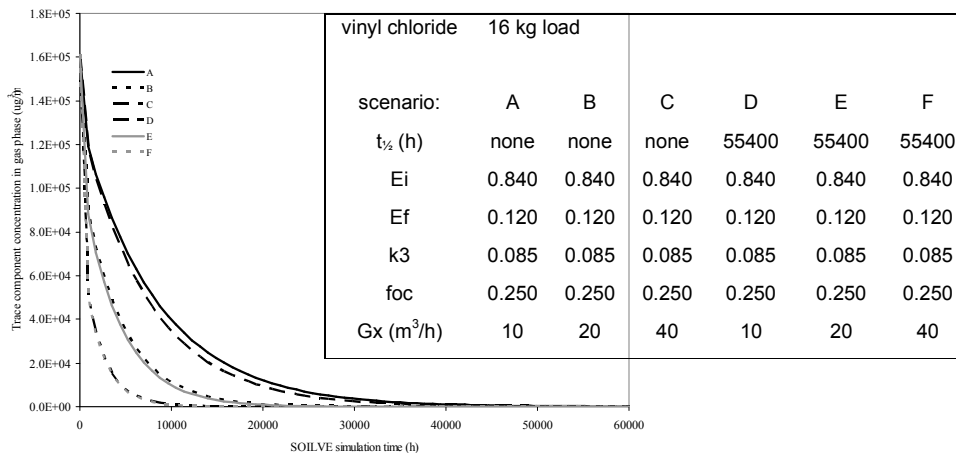| vinyl chloride	16 kg load					
scenario:	A	B	C	D	E	F
$t_{\frac{1}{2}}$ (h)	none	none	none	55400	55400	55400
Ei	0.840	0.840	0.840	0.840	0.840	0.840
Ef	0.120	0.120	0.120	0.120	0.120	0.120
k3	0.085	0.085	0.085	0.085	0.085	0.085
foc	0.250	0.250	0.250	0.250	0.250	0.250
Gx (m^3/h)	10	20	40	10	20	40

Figure 5. Illustrative SOILVE simulations illustrating effect of gas extraction rate and varying degradation rates on vinyl chloride concentrations in LFG (16kg input).

Vinyl chloride behaviour is recognisably complex given its generation in landfill as a biotransformation product of chlorinated organics. The utility of the SOILVE approach might be better assessed using less complex substrates. The trace components 1-3 butadiene and benzene might be expected to exhibit more straightforward characteristics, being resistant to biotransformation (Figure 6). Figure 6 exhibits near linearity for benzene and an exponential decrease for 1-3 butadiene, becoming more pronounced at rapid extraction rates. In both cases, the concentrations achieved are within the observed range (Shafi, 2005). For these less complex substrates, modelled without the complexities of biotransformation, more representative data appear to be obtained. Overall, however, the results produced with SOILVE illustrate the importance of using appropriate biotransformation rates. The data obtained shows huge variations depending on this variable and more appropriate rates are required to achieve more representative data.
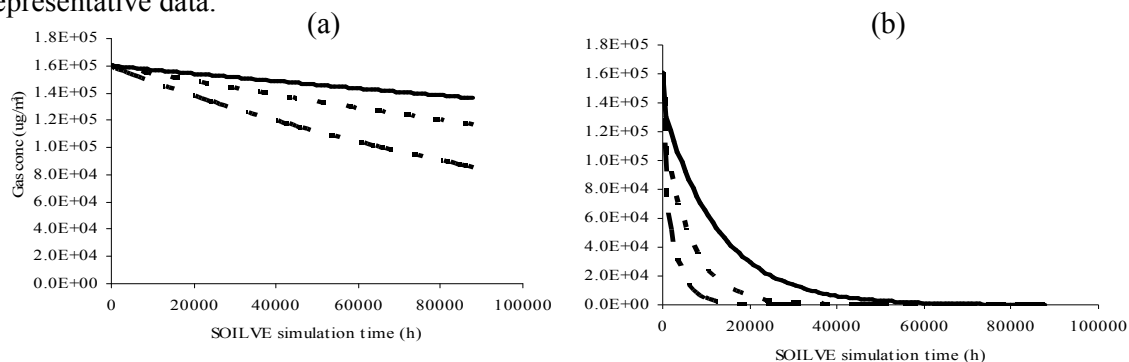
Figure 6. Illustrative SOILVE simulations (10y) showing the effect of 10 (solid), 20 (dotted) and 40 (dashed) m³/h gas extraction rate on (a) benzene; and (b) 1,3-butadiene concentrations in LFG, assuming no biotransformation.

4. DISCUSSION

This study illustrates the complexities of LFG modelling under dynamic conditions even in the presence of a reasonably well-characterised conceptual model. One of the major limitations for all three models is the requirement for site-specific data regarding input parameters. This is especially important in terms of input concentrations, but also for the waste and air volumes that characterise the evaluative environment. Representative mean values from the literature were used here, but site-specific information is necessary for precision in model output beyond the order of magnitude data presented here. A significant assumption is that the organic matter is the major partition medium for organic contaminants in waste, as it is in soil. It is widely accepted that in most waste-soil systems, free phase organic liquids, rather than soil humic matter, dominate the partitioning behaviour of hydrophobic contaminants (Young, 1992, Boyd & Sun, 1990). Also, for simplicity, water has been substituted for leachate in the models and leachate will in practice express its own bulk density and possible co-solvency effects as it migrates through waste (Rao *et al*., 1990).

A further and influential limitation is the lack of representation for a leachate hydraulic head in the models. This may account for some of the discrepancies between the observed and predicted concentrations. The fact that a low-flow water regime has been applied in this study is a consequence of the cap that is assumed in the evaluate environment. In practice of course, gas and leachate flow rates fluctuate and effect concentrations considerably. The degree and nature of gas production from saturated waste needs establishing *i.e.* inhibition or enhancement.

An underlying challenge with the application of fugacity to landfill modelling is the reliance on the physicochemical characteristics at standard values for 25°C. Landfills undergo diurnal, seasonal and microbiologically-induced temperature changes through the various stages of their life-time; a feature that fugacity cannot address without running coupled simulations. This becomes particularly significant for factors such as vapour pressure and solubility, which would also be effected by the changing pressure of the environment. Level II calculations have the limitation of requiring an emission source to be presented as an input rate (kg/h). In this study, this was estimated using Brogborough waste loading rates, whereas the observed monitoring data are sourced from landfills of very different ages and loading rates. Finally, a common source of concern is the paucity of degradation rates for components of concern within the landfill environment and, as we have seen here, the referencing of waste monitoring data to input load, time of emplacement and landfill redox status.

ACKNOWLEDGEMENTS

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