

"Fugacity for trace components in landfill gas"

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1 **EVALUATING FUGACITY MODELS FOR TRACE COMPONENTS IN LANDFILL GAS**

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9
10 **Abstract** – A fugacity approach was evaluated to reconcile loadings of vinyl chloride
11 (chloroethene), benzene, 1,3-butadiene and trichloroethylene in waste with concentrations observed
12 in landfill gas monitoring studies. An evaluative environment derived from fictitious but realistic
13 properties such as volume, composition, and temperature, constructed with data from the
14 Brogborough landfill (UK) test cells was used to test a fugacity approach to generating the source
15 term for use in landfill gas risk assessment models (*e.g.* GasSim). SOILVE, a dynamic Level II
16 model adapted here for landfills, showed greatest utility for benzene and 1,3-butadiene, modelled
17 under anaerobic conditions over a 10 y simulation. Modelled concentrations of these components
18 ($95\ 300\ \mu\text{g m}^{-3}$; $43\ \mu\text{g m}^{-3}$) fell within measured ranges observed in gas from landfills ($24\ 300\text{-}180$
19 $000\ \mu\text{g m}^{-3}$; $20\text{-}70\ \mu\text{g m}^{-3}$). This study highlights the need (i) for representative and time-referenced
20 biotransformation data; (ii) to evaluate the partitioning characteristics of organic matter within waste
21 systems and (iii) for a better understanding of the role that gas extraction rate (flux) plays in
22 producing trace component concentrations in landfill gas.

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1 **Keywords** – landfill gas risk assessment fugacity emissions modelling

2

3 **INTRODUCTION**

4

5 *Background*

6 Waste management technologies are increasingly subject to environmental risk assessments
7 that inform operational practice, environmental permitting and regulatory intervention. The quality
8 of any environmental risk assessment is influenced by the input data for the distribution and
9 dispersion of potentially harmful substances, and by the exposure models that support an analysis of
10 the probability and consequences of exposure. Landfills pose a hazard to workers and to local
11 communities because of the landfill gas (LFG) they generate. Considerable literature exists on the
12 hazards of bulk LFG (mainly CH₄ and CO₂) and, more recently, on the gas phase concentrations of
13 trace hazardous components in untreated LFG (Allen *et al.*, 1997; Scheutz and Kjeldsen, 2003;
14 Environment Agency 2003a; 2004). Risk assessment models used to evaluate the nature and
15 significance of exposure risks are now instrumental in improving landfill siting, operation, and some
16 aspects of design (Pelt *et al.*, 1998; Environment Agency, 2002a). The GasSim model (Environment
17 Agency, 2002a), for example, generates a source term for bulk gases using a first order rate equation
18 for the biodegradation of the organic component of the waste, and uses default values for trace
19 components based on concentrations in the bulk gas reported in the literature. In GasSim, the source
20 term gas is partitioned between two fates: (i) combustion in an engine or flare; and (ii) passive loss
21 of untreated gas through the landfill cap or sidewall. The latter is the most important when
22 considering potential exposures of human or ecological receptors to harmful components.

23 Whilst progress has been made in modelling the distribution of potentially harmful
24 components around a site (and hence an approximation of exposure) using standard air dispersion
25 models, risk estimates are constrained by the absence of a credible source term relative to waste

1 input. In practice, concentrations of trace components are generated by the loading of chemicals in
2 the initial waste mass (the source term) and the fate processes, including biotransformation, which
3 deliver measurable concentrations in the gas phase. Risk analysts are keenly aware of the need for
4 improved source term models that, it is hoped, will engender greater confidence in risk assessments
5 and risk management measures (El-Fadel *et al.*, 1997a; 1997b; Pollard *et al.*, 2006). In this paper, an
6 attempt is made to reconcile measured concentrations of four priority trace components in LFG,
7 with potential source term loadings estimated retrospectively using fugacity modelling. The
8 potential for the fugacity approach to improve current risk assessment models for landfill, e.g.
9 GasSim (Environment Agency, 2002a), is introduced, reviewed and critically appraised.

10

11 *Rationale*

12 Fugacity modelling (Mackay, 1979; 2001) has received a comprehensive treatment in a recent
13 special issue of a peer-reviewed journal (Gobas and Muir, 2004). Among its uses from global-scale
14 to *in vivo* modelling, its application to waste problems is increasing, albeit with an attending need to
15 address the gross heterogeneity and multiphase character of wastes. Applications include its use for
16 directing site remediation decisions (Pollard *et al.*, 1993; She *et al.*, 1995), in quantifying vapour
17 emissions at contaminated sites (Mills *et al.*, 2004) and in assessing the environmental fate of
18 hydrophobic compounds in landfills (Kjeldsen and Christensen, 2001).

19 Three models are worthy of review and establish the context of our work. The SOIL model
20 (Mackay, 2001) comprises four environmental compartments: air, water, soil mineral matter and
21 soil organic matter. Densities, volumes, areas and depths of soil are user-specified, enabling total
22 volumes and masses to be calculated, from which individual fugacities and environmental
23 concentrations are derived. Other input parameters include densities and volume fractions, of air,
24 water, organic and mineral matter, the mass of total soil, dry soil and organic carbon, a water-
25 leaching rate and mean diffusion distance. With regards to chemical input data, an original mass in

1 the soil needs to specified, along with physicochemical data on molecular weight, aqueous solubility
 2 vapour pressure (K_{ow}), and first-order reaction half-life ($t_{1/2}$). The model accounts for losses from
 3 degrading reactions, leaching (D_w) and volatilisation (D_A) by the designation of ‘D values’
 4 (Mackay, 2001). An adaptation of SOIL, SOILFUG (DiGuardio *et al.*, 1994) has been designed for
 5 pesticide application to soil with subsequent surface water runoff. Adaptations include incorporating
 6 the effects of sequential rainfall events with input parameters that include inflow and outflow rates.
 7 Leaching is replaced by run off (D_{roff}) taken from the amount of water flowing out of the system,
 8 here a river basin. The authors attempted verification by comparing the predicted concentrations of
 9 pesticide in the outflow with environmental monitoring data (DiGuardio *et al.*, 1994). SOILFUG
 10 may have relevance for a landfill environment, given the flushing of landfill cells and where
 11 leachate recirculation events might be considered analogous to successive ‘rainfall’ events. Finally,
 12 She *et al.* (1995) describe a fugacity approach (SOILVE) to predicting the efficiency of soil vapour
 13 extraction (VE) in removing volatile organic compounds (VOCs) from the unsaturated zone of a
 14 contaminated soil; a situation physically analogous to modern landfill sites where gas is actively
 15 extracted. SOILVE accounts for degradation, volatilisation and leaching and includes a term for gas
 16 phase extraction. The extraction is designated a D value, D_X , determined by a gas flow rate ($G_X \text{ m}^3$
 17 h^{-1}), combined with the fugacity capacity ($Z_G, \text{ mol m}^{-3}\text{Pa}$):

$$18 \quad D_X = G_X Z_G \quad (1)$$

19 The model accounts for the non-uniform distribution of VOCs in soil and introduces the concept of
 20 a ‘sweep efficiency’ E; a ratio of the effective air extraction rate (G_E) to the applied airflow.

$$21 \quad E = G_E / G_X \quad (2)$$

22 The effective D value (D_E) is then:

$$23 \quad E D_X = E G_X Z_G \quad (3)$$

24 Here, D values for D_E , D_A and D_w are calculated as with the SOIL model, but with the substitution
 25 of gas phase diffusion in the soil (D_G), for the air in soil (D_A);

$$D_G = B_{EG} A Z_G/Y \quad (4)$$

Where B_{EG} is gas phase diffusion ($\text{mol Pa}^{-1} \text{h}$), A the area m^2 and Y the path length (m)

The 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. This is given by:

$$E = E_f = E_i e^{-k_3 t} \quad (5)$$

Where E_f is at infinite time, E_i is at time 0 and k_3 is a decay constant. The presence of the decay term makes application of SOILVE particularly applicable to the landfill environment.

Trace components in landfill gas

The composition of LFG is dominated by the bulk gases methane, CH_4 (40 – 70 % v/v) and carbon dioxide, CO_2 (30 - 60% v/v) with smaller concentrations of hydrogen, hydrogen sulphide and other trace components (Table 1). Despite their low concentrations, hazardous trace components may pose a potential risk to human health where exposure is either acute, repeatedly episodic or prolonged (Brosseau and Heitz, 1994; Allen *et al.*, 1997; El-Fadel *et al.*, 1997a; Zou *et al.*, 2003). Due to its heavy reliance on landfill, many of the more significant studies have been undertaken in the UK. Early work on the trace composition of LFG (Young and Parker, 1983; Allen *et al.*, 1997; Eklund *et al.*, 1998) identified 100-140 trace components of concern, typically constituting < 1% v/v of the gas (Young and Parker, 1983). Some authors believe these constituents to be ubiquitous, regardless of whether the site operated a co-disposal (hazardous and municipal) or municipal waste-only disposal strategy (USEPA, 1997).

A study looking at the composition of trace gases from six different landfill sites revealed approximately 80 trace components (Meynell, 1983). Further trace components were characterised in the late 1980s following monitoring at three UK-based landfill sites over a period of three years (Dent *et al.*, 1986; Department of Environment, 1988). In this case, 136 organic compounds or

1 isomeric groups were identified. A 1997 study of seven landfill sites in the UK observed 140 trace
2 components, 90 of which were common to all seven sites (Allen *et al.*, 1997). Concentrations of
3 volatile organic carbon (VOCs) were closely related to methane production rates and displayed
4 variation (although not significant) with ambient temperature and atmospheric pressure. The VOCs
5 identified included vinyl chloride (chloroethene) (Young and Parker, 1983; Allen *et al.*, 1997),
6 tetrachloroethene, 1,1-dichloroethane, 1,2-dichloroethane, benzene, chlorobenzene,
7 trichloroethylene (TCE), ethylbenzene, xylene and toluene, amongst others. A similar UK-based
8 study identified 550 trace components (Environment Agency, 2003a).

9 The Environment Agency of England and Wales (EA) have published a list of priority
10 components requiring monitoring in LFG defined by their typical concentrations and published
11 toxicological and odour properties (Environment Agency, 2004; Tables 10.1, 10.2 and 10.3). The
12 list includes chloroethane, 1,1-dichloroethane, vinyl chloride, trichloroethylene, 1,1-dichloroethene,
13 1,2-dichloroethene and tetrachloromethane. The list was compiled acknowledging the toxicity,
14 known or potential carcinogenicity and physical characteristics of these substances (Environment
15 Agency, 2002b; 2003a; 2003b; Table 2). The Environment Agency (Environment Agency, 2003b)
16 monitored the concentrations of trace components in LFG at six sites during 2002 - 2003 for the 26
17 highest priority substances (Table 2). Analysis of the data by reference to landfill type, age of gas
18 and environment allows a summary, for selected chlorinated components, of the concentration
19 ranges generated by different landfill environments (Table 3). Still unknown, however, are the
20 initial waste loadings that could generate these concentrations. This, and the rate at which bulk
21 gases are generated, affects the measured concentrations of trace components generated in the
22 landfill. Addressing this knowledge gap was the starting point for this work.

23

24 *Study aims*

1 This study sought to build an evaluative environment (derived from fictitious but realistic
2 properties such as volume, composition, and temperature) within which to back-calculate the
3 potential source terms (loads) that could generate typical concentrations of trace components
4 reported in LFG studies. Our study focussed on benzene, vinyl chloride, trichloroethylene (TCE)
5 and 1,3-butadiene as representative of the main types of priority trace component, with a view to
6 providing a source term for risk assessment models such as GasSim (Attenborough *et al.*, 2002;
7 Environment Agency, 2002a). The objectives were to (i) apply fugacity concepts to the partitioning
8 of trace components within the landfill environment; (ii) test and select the most applicable
9 approaches to an evaluative landfill environment; and (iii) compare observed concentrations of trace
10 components with those modelled in the study.

11

12 **MATERIALS AND METHODS**

13

14 *Evaluative landfill environment*

15 The evaluative environment selected was a single cell of waste, rather than an entire landfill
16 (Figure 1), this choice influenced by the availability of data from the Brogborough (UK) landfill test
17 cells (Fletcher, 1989; Croft *et al.*, 2001; Blackmore *et al.*, 2003). Our evaluative environment allows
18 for three phases: gas, water, and waste, and for the processes of water and gas flux through the
19 system being represented. The Brogborough test cells were constructed during 1986-88 and were set
20 up to evaluate the effects of pre- and post-emplacement management techniques on methane
21 production rates (Croft *et al.*, 2001). Six cells were constructed each with a different management
22 technique such as leachate re-circulation, air injection and sewage sludge addition. A single cell
23 contained a mix of domestic waste and non-hazardous commercial waste. Our study has adopted the
24 design data from cell 1, the control cell, containing domestic waste placed in thin layers (Blackmore
25 *et al.*, 2003). The dimensions and characteristics of cell 1 are reported in Table 4. Leachate, gas and

1 solid waste were monitored at Brogborough between 1986 and 2000, making it the longest field
2 scale landfill study in the world (Blcakmore *et al.*, 2003). The cells have produced limited data on
3 the concentrations of trace components in the gas, but the gas production data and physical
4 characteristics of the cells (Table 5) provide a valuable base for this study. Test cell 1 was taken as
5 being typical of most UK landfill sites accepting domestic waste. The evaluative environment
6 remained constant for the fugacity studies that follow.

7

8 *Chemical input*

9 A recurrent issue for modelling landfills is the uncertainty associated with the composition of
10 incoming waste. Understanding the load and characteristics of the waste is important if generalised
11 findings are to be extrapolated between sites with comparable operational histories. However,
12 selecting values for chemical input parameters for a model is challenging without detailed
13 information on the chemical composition of the wastes under study, which are universally absent.
14 Due to these difficulties, a scalable initial value of 10 mg kg⁻¹ for all of the chemicals was initially
15 selected (Pollard *et al.*, 1993). This represented a load to the cell of 160 kg. Having generated an
16 initial set of gas concentrations, this enabled review and then back-extrapolation to determine
17 possible initial inputs of the chemical to the landfill. Molecular mass (g mol⁻¹), temperature (°C),
18 water solubility (g m⁻³), vapour pressure (Pa), log K_{ow}, melting point (°C) and the Henry's Law
19 constant (Pa.m³ mol⁻¹) were required for each substance in order to parameterise Equations 1 – 5.
20 All parameter values were derived from those reported in Mackay (2001).

21

22 *Gas and water regimes*

23 Gas flow through landfills is highly variable and dependant on a number of factors such as
24 atmospheric pressure, design and operational parameters (Young, 1992; Croft *et al.*, 2001;

1 Christopherson and Kjeldsen, 2001; Kjeldsen and Christensen, 2001). Historic data from
2 Brogborough test cell 1 shows gas production rates varying between 5-15 m³ t⁻¹ waste yr⁻¹ (Croft *et*
3 *al.*, 2001). A mean of 10 m³ t⁻¹ yr⁻¹ represents a gas extraction rate of *ca.* 20 m³ h⁻¹ from each cell. A
4 log mean diffusion path of 4.55 m was adopted from a diffusion path of 12.5 m, judged as the
5 maximum distance between gas extraction points at Brogborough and typical of a large, modern,
6 engineered landfill in the UK. Finally, rather than set a leachate head for this study, a water flow
7 rate though the cell was applied using an infiltration rate of 0.14 mm d⁻¹ adopted from GasSim
8 (Environment Agency, 2002a). This flow rate assumes the input of water into the system is constant
9 and derived from limited infiltration through a clay cap alone (Environment Agency, 2002a).

10

11 *Fugacity modelling*

12 Level I fugacity calculations illustrate general partitioning behaviour and preferential
13 partitioning to the organic fraction in the waste environment. Level II calculations account for
14 advection and reactions in the form of residence time and half-lives respectively (D values). The
15 calculations assume an environment in equilibrium, but under steady state flow; *i.e.* the amount
16 entering the environment is mass-balanced by the amount lost to flow, reactions or degradation. The
17 Level II model (Figure 2) allows the estimation of a residence time for a substance within the
18 system. The characteristics of the system are presented in Table 6. Reaction half-lives for each
19 chemical in air, water and waste were required and aerobic values were adopted from Mackay
20 (2001). Anaerobic conditions were subsequently modelled using degradation rates obtained from
21 aquifer studies (Aronson and Howard, 1997). Control runs set the degradation term to zero.

22 An adapted level II fugacity model, SOILVE is dynamic, in that time and extraction rates can
23 be specified. The model (She *et al.*, 1995) was re-coded using Model Maker 4™ (Modelkinetix,
24 2000). In concept, SOILVE has many similarities to the processes of LFG extraction.
25 Parameterisation is complex and includes concentrations in various phases, as well as D values

1 (transport parameters). To obtain these, a level II calculation was conducted prior to the SOILVE
2 run. Table 7 displays the additional parameterisation required for SOILVE and Table 8 lists the
3 series of model runs undertaken to evaluate the fate of trace components in LFG (Christopherson
4 and Kjeldsen, 2001). The selection of runs reflects the acknowledged (Kjeldsen and Christensen,
5 2001) importance of (i) the free organic carbon phase (represented by f_{oc}) (ii) the gas extraction rate;
6 and (iii) the redox status to estimating the concentration of trace components in LFG.

7

8 **RESULTS AND DISCUSSION**

9

10 *Level I and II fugacity modelling*

11 Here, discussion is reserved for the results offering greatest insight. (Shafi (2005) presents a
12 comprehensive analysis). Level I modelling (Figure 3) illustrates the role of organic matter (f_{oc}) in
13 determining the partitioning of trace components in the landfill system. Organic carbon can be
14 represented by conventional soil organic (humic) matter or by the presence of a free organic phase
15 common to many hazardous waste systems (Pollard *et al.*, 1993; Kjeldsen and Christensen, 2001).
16 Level II modelling has improved utility, producing illustrative data on persistence, losses due to
17 advection and reaction and other dynamic trends. Again, it highlights the influence of organic
18 carbon in the waste matrix on the mass of chemical in the gaseous phase and the residence time of a
19 chemical, given the flux (Figure 2) in the landfill (Figure 4). The concentrations of trace
20 components in each phase using a 10 mg kg^{-1} input, compared with the observed ranges in
21 monitoring studies, are presented in Table 9. Observed benzene concentrations are between 3500-
22 $150\,000 \mu\text{g m}^{-3}$. Modelled concentrations range between $32\,700$ - $139\,000 \mu\text{g m}^{-3}$ suggesting that,
23 assumptions holding, a 10 mg kg^{-1} (160 kg) input of benzene may be a good first approximation of
24 the source term. The modelled concentrations for vinyl chloride, trichloroethylene and 1,3-butadiene

1 were elevated above the observed ranges, although vinyl chloride was of the same order of
2 magnitude as the observed concentrations. One approach to estimating the initial load is to back-
3 extrapolate, taking the model assumptions as valid and the observed concentrations for each
4 component as input (Table 10). This provides a set of candidate loads that can be re-assessed with
5 anaerobic degradation rates to generate a new set of phase distributions (Table 11), the air phase
6 concentrations for which may be compared with the observed ranges of trace components in LFG.
7 One must be cautious as to the utility of this approach. The absence of representative anaerobic
8 degradation rates within landfills is a serious constraint. Further, it is clear from the analysis that the
9 complexities of the landfill environment stretch the capabilities of Level II fugacity modelling.

10

11 *Dynamic fugacity modelling*

12 Landfill processes (*e.g.* redox status, settlement, gas and leachate generation and chemical
13 composition) develop over decades. Exploratory SOILVE model runs were performed (data not
14 shown; see Shafi, 2005) (i) for *ca.* 1 year (8000 h) under aerobic and zero degradation conditions;
15 (ii) for individual components at gas extraction rates of 10, 20 and 40 m³ h⁻¹; and (iii) for the first
16 year, aerobically, at f_{oc} values of 0.05, 0.25 and 0.40. D values, along with other input parameters,
17 were derived from a prior set of Level II calculations (note limitations above), using an illustrative
18 10 mg kg⁻¹ input concentration (Table 8). Of specific interest is the effect of the gas extraction rate
19 on the long-term concentrations of trace components presented in LFG. A set of SOILVE model
20 runs was performed for a *ca.* 10 yr period (90 000 h) using zero and anaerobic degradation rates at
21 gas extraction rates of 10, 20 and 40 m³ h⁻¹. For the anaerobic simulations, trace component
22 concentrations in the gas phase were inevitably higher than for aerobic degradation. Predicted
23 concentrations of vinyl chloride appeared to be too low for all three extraction rates (Figure 5).
24 Once extrapolation to 160 kg input is considered, a 10m³ h⁻¹ extraction rate produces an order of
25 magnitude concentration for vinyl chloride akin to that observed in recent field investigations

1 (Environment Agency, 2003b) between 0.3 - 4.1 years. There is no information on the age of the
2 field data, however and no conclusive correlations can therefore be made. Figure 5 illustrates the
3 impact that degradation and extraction rates have on the concentration of trace components in LFG.
4 These factors change throughout the lifetime of a landfill (bi-, tri-phasic behaviour) generating
5 additional complexity.

6 Vinyl chloride behaviour is recognisably complex given its generation in landfill as a
7 biotransformation product of chlorinated organics (Vogel and McCarty, 1985). A more appropriate
8 assessment of the utility of the SOILVE approach may be achieved using less complex substrates.
9 The trace components 1,3-butadiene and benzene might be expected to exhibit more straightforward
10 characteristics, being resistant to biotransformation (Figure 6). Figure 6 exhibits near linearity for
11 benzene and an exponential decrease for 1,3-butadiene, becoming more pronounced at rapid
12 extraction rates. In both cases, the concentrations achieved are within the observed range (Table 11).
13 For these less complex substrates, modelled without the complexities of biotransformation, data that
14 are more representative can therefore be achieved. Overall, however, the results produced with
15 SOILVE illustrate the importance of using appropriate biotransformation rates.

16 17 *Study limitations and utility as a source term generator for risk assessments of landfill gas*

18 This study illustrates the complexities of LFG modelling under dynamic conditions even for a
19 well characterised conceptual model. One of the major limitations for all three models is the
20 requirement for site-specific data regarding input parameters. This is especially important in terms
21 of input concentrations, but also for the volumes of waste and air that are required to characterise
22 the evaluative environment. Representative mean values from the literature were used here, but site-
23 specific information is necessary for precision in model output beyond the order of magnitude data
24 presented here. A significant assumption is that the organic matter is the major partition medium for
25 organic contaminants in waste, as it is in soil. It is widely accepted that in most waste-soil systems,

1 free phase organic liquids, rather than soil humic matter, dominate the partitioning behaviour of
2 hydrophobic contaminants (Boyd and Sun, 1990; Young, 1992; Zemanek *et al.*, 1997). In addition,
3 for simplicity, water has been substituted for leachate in the models and leachate will in practice
4 express its own bulk density and possible co-solvency effects as it migrates through waste (Rao *et*
5 *al.*, 1990).

6 A further and influential limitation is the lack of representation of a leachate hydraulic head in
7 the models used. This may further account for some of the discrepancies between the observed and
8 predicted concentrations. The fact that a low-flow water regime has been applied in this study is a
9 consequence of the clay capping that is assumed in the evaluate environment. In practice of course,
10 gas and leachate flow rates fluctuate resulting in temporal variation in concentrations of trace
11 components.

12 An underlying challenge with the application of fugacity to landfill modelling is the reliance
13 on the physicochemical characteristics at standard values for 25 °C. Landfills undergo diurnal,
14 seasonal and microbiologically induced temperature changes through the various stages of their
15 lifetime, a feature that fugacity cannot address without running coupled simulations. This becomes
16 particularly significant for factors such as vapour pressure and solubility, which are also effected by
17 the changing pressure of the environment. Level II calculations have the limitation of requiring an
18 emission source to be presented as an input rate (kg h^{-1}). In this study, this was estimated using
19 Brogborough waste loading rates, whereas the observed monitoring data are sourced from landfills
20 of very different ages and loading rates. Finally, a common source of uncertainty is the paucity of
21 degradation rates for components of concern within the landfill environment and, as we have seen
22 here, the referencing of waste monitoring data to input load, time of emplacement and landfill redox
23 status.

24

25

1 **CONCLUSIONS**

2 Can fugacity models be used to generate source term concentrations of trace components in
3 landfill gas? There are clearly substantial constraints as presented by the poor referencing of
4 observed trace component data noted above. Back-extrapolation of waste inputs may assist, but
5 there are substantial variables in the system. In GasSim (Environment Agency, 2002a), trace
6 component concentrations are estimated (a) using distributed literature data using a uniform or
7 triangular distribution, as appropriate; or (b) from site-specific data. The evaluative environment
8 used in this study is similar to GasSim, the waste being considered a cuboid mass with vertical sides
9 from which characteristics such as volume and area are deduced (Environment Agency, 2002a). If a
10 site-specific fugacity model were constructed and applied, informed by an estimated inventory of
11 solvent mass in the landfill, then a more representative source term might be produced and
12 subsequent estimates of exposure and risk made more representative. SOILVE has the potential for
13 producing meaningful concentrations for the GasSim source module, the system is more dynamic
14 and there is an increased capacity for the propagation of error in the absence of better-characterised
15 sites. There is an explicit need for precise degradation data and firm evidence for the bounded
16 ranges of key variables that influence the concentrations of trace components in landfill gas. Further
17 work needs to be undertaken on the influence of successive redox regimes on trace component
18 biotransformation. Notwithstanding these limitations, we believe to have illustrated the potential
19 application of dynamic fugacity modelling and propose that this approach may have use for the
20 generation of a better, time-dependent source term for regulatory LFG risk assessments tools such
21 as GasSim.

22
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11

1 Table 1 Generic classes of trace components in landfill gas with concentration ranges (El-Fadel *et*
 2 *al.*, 1997a)

Chemical class	Typical concentration (mg m⁻³)
alcohols	2-2500
ketones	0-50
aldehydes	0-200
organosulphur compounds	3-240
hydrocarbons	
alkanes	20-4500
alkenes	6-1100
cycloalkanes	1-1000
cycloalanes	8-600
aromatics	30-1900
halogenated hydrocarbons	1-2900
esters	0-1300
ethers	0-250

3

1 Table 2 Environment Agency priority trace components (Environment Agency, 2003b)

Priority trace component	Analytical method	Detection limit (mg m ⁻³)	Component concentration [x]			[x] _{mean} P1-438 c.f.
			[x] _{min}	[x] _{max} (mg m ⁻³)	[x] _{mean}	[x] _{mean} P1-491 (mg m ⁻³)
1,1-dichloroethane	ATD	0.02	<0.02	3.90	0.57	-477
1,1-dichloroethene	ATD	0.03	<0.03	19.0	2.24	+2.10
1,2-dichloroethene	ATD	0.07	0.13	46.0	5.71	-10.5
1,3-butadiene	ATD	0.02	<0.02	<0.02	<0.02	-0.11
1-butanethiol	ATD	0.08	<0.08	<0.08	<0.08	->0.09
1-pentene	ATD	0.16	0.24	21.0	5.49	+3.80
1-propanethiol	ATD	0.04	<0.04	0.09	<0.05	-0.43
2-butoxyethanol	ATD	0.04	<0.04	<0.05	<0.05	no change
arsenic	arsenic tube	<0.01	<0.01	0.43	0.05	+0.05
benzene	ATD	0.03	3.10	73.0	18.4	+13.5
butyric acid	ATD	0.08	<0.08	17.5	1.85	-7.00
carbon disulphide	ATD	0.10	0.90	170	34.0	+34.0
chloroethane	ATD	0.02	<0.02	5.30	0.49	-76.4
chloroethene	ATD	0.30	1.10	730	102	+35.7
dimethyl disulphide	ATD	0.03	<0.03	12.0	1.02	+1.00
cimethyl sulphide	ATD	0.03	<0.03	24.3	3.69	->0.37
ethanal	DNPH	0.01	0.08	2.55	0.43	-2.60
ethanethiol	ATD	0.08	<0.08	<0.08	<0.08	no change
ethyl butyrate	ATD	0.09	0.41	42.0	7.22	-25.7
furan	ATD	0.07	0.02	6.20	1.23	+0.50
hydrogen sulphide	Lab GC	0.15	2.40	580	111	no change
methanal	DNPH	0.01	0.03	0.19	0.07	-2.90
methanethiol	ATD	0.30	<0.30	<0.30	<0.30	->6.00
tetrachloromethane	ATD	0.02	<0.02	<0.02	<0.02	->5.20
trichloroethene	ATD	0.04	0.25	88.0	8.59	-6.40

2 Key: ATD: automated thermal desorption; Lab GC: laboratory gas chromatograph; and DNPH: 2,4-dinitrophenyl-
3 hydrazine derivatised aldehydes

4

1 Table 3 Selected trace component concentrations (mg m^{-3}) in landfill gas in different MSW landfill
 2 environments (Environment Agency, 2003b)

Category of waste	Large component of commercial & industrial	Domestic site with leachate	High Ash Content
recent gas			
chloroethene	17.6 ^a	7.70	2.30
chloroethane	<0.03	<0.02	<0.03
tetrachloromethane	<0.02	<0.02	<0.02
1,1-dichloroethene	0.28	2.80 ^a	0.08
trichloroethene	0.90	7.30 ^a	0.04
recent gas with leachate			
chloroethene	9.00	55.0	17.0 ^a
chloroethane	<0.03	<0.03	<0.03
tetrachloromethane	<0.02	<0.02	<0.02
1,1-dichloroethene	1.98	2.80	0.14 ^a
trichloroethene	2.45	8.00	0.55
mature gas			
chloroethene	1.10 ^a	100	31.0 ^a
chloroethane	<0.03	<0.03	<0.03
tetrachloromethane	<0.02	<0.02	<0.02
1,1-dichloroethene	<0.03	1.88	<0.03
trichloroethene	0.25 ^a	3.50	0.33

3 ^a Sample volume of 100 ml, else 400 ml standard.

4

5 Table 4 Dimensions of the landfill evaluative environment

Parameter	Value
cell length	40m
cell width	20m ^a
cell depth	25m
cell volume	20 x10 ³ m ³
cell mass	16 x10 ⁶ kg ^b
waste density	830 kg/m ^{3,c}

6 ^aBrogborough test cell 1 (Blackmore *et al.*, 2003)

7 ^bCalculation $m=pv$

8 ^cCroft *et al.*, 2001

1

2 Table 5 Volumetric composition of the landfill evaluative environment

Parameter	Volume fraction	Justification/reference	Mass (kg)	Volume (m ³)
LFG/air	0.10	10% effective porosity of waste ^a	2.20 x10 ³	2000
Water	0.25	Estimated water content ^{a, b}	5.00 x10 ⁶	5000
Waste				
organic	0.25	Estimated from type of waste input. Similar mean reported by Schwarze ^c		
inorganic	0.40	Remaining volume		
Waste total	0.65	Accumulative	1.15 x10 ⁷	13000

3 ^aBlackmore *et al.*, 2003 ^bCroft *et al.*, 2001 ^cSchwarze, 2001

4 Table 6 Parameters for Level II fugacity calculation

Parameter	Value	Justification/reference
Emission rate of chemical into environment	0.05 kg h ⁻¹	Calculated using 10ppm (160 kg) of chemical with filling time 4.5 months ^a
Gas flow rate	20 m ³ h ⁻¹	Adapted to evaluative environment ^b
Leachate flow rate	6 x10 ³ m h ⁻¹	Calculated from water infiltration rate of 0.14 mm d ⁻¹ through environment
Advective residence time for LFG	100 h	Calculated using gas flow rate and level one calculation; assumes chemical concentration in incoming gas of zero
Advective residence time for leachate	833333 h	Calculated using leachate flow rate as above

5 ^aFletcher, 1989 ^bCroft *et al.*, 2001

1 Table 7 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 (m ³ h ⁻¹)	Gas flow rate	20 m ³ h ⁻¹
E (unitless)	Sweep efficiency	She <i>et al.</i> , 1995
k ₃	Rate constant for decay	She <i>et al.</i> , 1995
t _{1/2} (h)	Half life of chemical in soil	Aerobic ^a ; anaerobic ^b
k _r (h ⁻¹)	Rate constant for degrading reactions	0.693/t _{1/2}
Z _T (Pa)	Total fugacity	
V _T (m ³)	Total volume	
D _R (mol Pa ⁻¹ h)	D value for degrading reactions	DR = KrZ _T V _T
D _L (mol Pa ⁻¹ h)	D value for water leaching	Water flow rate/Z _{water}
D _X (mol Pa ⁻¹ h)	D value for gas phase advection	Gas flow rate/Z _{gas}
K _v (m s ⁻¹)	Mass transfer coefficient	From diffusivity calculation ^c
D _E (m s ⁻¹)	Diffusion across a stagnant boundary layer	DE=kv Az _{gas}
B _{EG} (mol Pa ⁻¹ h)	Gas phase diffusion	
D _G (mol Pa ⁻¹ h)	Gas phase diffusion in soil	
B _{EW}	Water phase diffusion	
D _W (mol Pa ⁻¹ h)	D value water phase diffusion	

Comment: Units?

2 ^aMackay, 2001 ^bAronson and Howard, 1997 ^cLyman *et al.*, 1982

1 Table 8. Range of adapted SOILVE model runs

trace component	load (kg)	duration (y)	redox status	f_{oc}	gas extraction rate (m³ h⁻¹)
vinyl chloride	160	1.00	aerobic	0.05	20.0
				0.25	
				0.40	
	16.0			0.25	10.0
					20.0
					40.0
benzene	160	1.00	aerobic	0.05	20.0
				0.25	
				0.40	
trichloroethylene	160	1.00	aerobic	0.05	20.0
				0.25	
				0.40	
1, 3-butadiene	160	1.00	aerobic	0.05	20.0
				0.25	
				0.40	
vinyl chloride benzene trichloroethylene 1, 3-butadiene	160	1.00	aerobic and no deg. comparison	0.25	20.0
vinyl chloride	16.0	10.0	aerobic	0.25	10.0
					20.0
					40.0
benzene	16.0	10.0	aerobic	0.25	10.0
					20.0
					40.0
trichloroethylene	16.0	10.0	aerobic	0.25	10.0
					20.0
					40.0
1, 3-butadiene	16.0	10.0	aerobic	0.25	10.0
					20.0
					40.0
vinyl chloride	16.0	10.0	anaerobic and no deg. comparison	0.25	10.0
					20.0
					40.0
benzene	16.0	10.0	anaerobic and no deg. comparison	0.25	10.0
					20.0
					40.0
trichloroethylene	16.0	10.0	anaerobic and no deg. comparison	0.25	10.0
					20.0
					40.0
1, 3-butadiene	16.0	10.0	anaerobic and no deg. comparison	0.25	10.0
					20.0
					40.0

2

- 1 Table 9 Level II fugacity calculations. Modelled and observed concentrations of priority components in LFG assuming a 10 mg kg⁻¹ waste
 2 input (all data in µg m⁻³)

foc	Benzene			vinyl chloride			trichloroethylene			1,3-butadiene		
	air	water	soil/waste	air	water	soil/waste	air	water	soil/waste	air	water	soil/waste
0.05	1.39x10⁵	6.19x10 ⁵	1.42x10 ⁶	1.05x10⁶	3.20x10 ⁵	1.23x10 ⁵	5.34x10⁵	1.12x10 ⁶	6.46x10 ⁶	1.65x10⁵	1.98x10 ⁴	3.29x10 ⁴
0.10	9.49x10⁴	4.22x10 ⁵	1.94x10 ⁶	1.03x10⁶	3.19x10 ⁵	2.43x10 ⁵	3.17x10⁵	6.65x10 ⁵	7.67x10 ⁶	1.63x10⁵	1.96x10 ⁴	6.51x10 ⁴
0.25	4.86x10⁴	1.26x10 ⁵	2.48x10 ⁶	9.95x10⁵	3.07x10 ⁵	5.85x10 ⁵	1.43x10⁵	3.00x10 ⁵	8.64x10 ⁶	1.58x10⁵	1.90x10 ⁴	1.58x10 ⁵
0.40	3.27x10⁴	1.45x10 ⁵	2.67x10 ⁶	9.59x10⁵	2.96x10 ⁵	9.03x10 ⁵	9.20x10⁴	1.93x10 ⁵	8.92x10 ⁶	1.53x10⁵	1.84x10 ⁴	2.45x10 ⁵
observed: 3.50x10² - 1.50x10⁵			2.43x10⁴ - 1.80x10⁵			1.95x10³ - 7.01x10³			<2.00x10¹ - <7.00x10¹			

- 3
 4 Table 10 Back-extracted estimates of trace component load to evaluative landfill cell

trace component	mean observed gas concentration (µg m ⁻³)	estimated input to cell (kg)
vinyl chloride	8.70x10 ⁴	14.0
benzene	4.86x10 ⁴	160
trichloroethylene	4.53x10 ³	5.00
1,3-butadiene	4.50x10 ¹	0.05

- 5
 6 Table 11 Estimating LFG concentrations with anaerobic degradation rates (Level II)

trace component and input (kg)	input (kg/h)	gas concentration (µg m ⁻³)	observed range in LFG (µg m ⁻³)
vinyl chloride (14)	5.00x10 ⁻²	4.92x10 ⁵	3.50x10 ³ - 1.50x10 ⁵
benzene (160)	4.30x10 ⁻²	9.53x10 ⁴	2.43x10 ⁴ - 1.80x10 ⁵
trichloroethylene (5)	1.50x10 ⁻³	1.30x10 ⁴	1.95x10 ³ - 7.10x10 ³
1,3-butadiene (0.045)	1.30x10 ⁻⁴	4.30x10 ¹	2.00x10 ¹ - 7.00x10 ¹

7

1 **List of Figures**

2

3 Fig. 1. An evaluative landfill environment

4 Fig. 2 Evaluative environment for Level II model

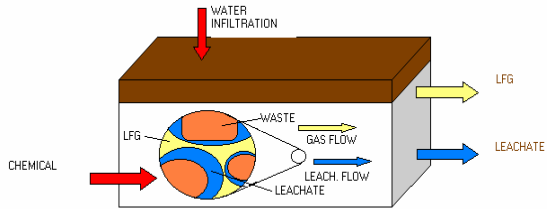
5 Fig. 3 Illustrative mass contributions (%^w/_w) of vinyl chloride (VC) to landfill gas (LFG), water and
6 waste phases contingent on the fraction of organic carbon (f_{oc}) in the system

7 Fig. 4 Residence time of trace components in landfill as a function of the fraction of organic carbon
8 (f_{oc}) using Level II fugacity modelling

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

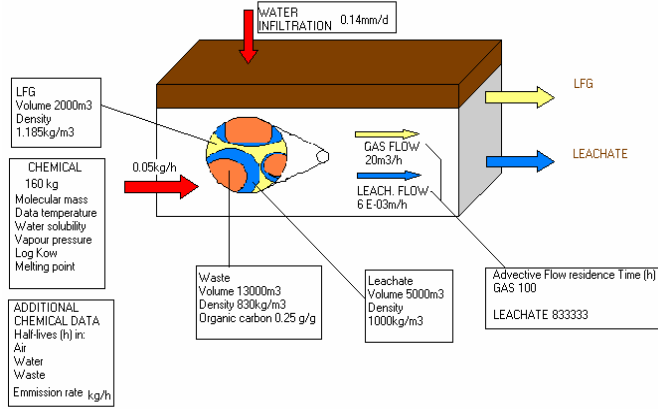
11 Fig.6 Illustrative SOILVE simulations (10 y) showing the effect of 10 (solid), 20 (dotted) and 40
12 (dashed) $m^3 h^{-1}$ gas extraction rate on (a) benzene; and (b) 1,3-butadiene concentrations in LFG,
13 assuming no biotransformation.

14

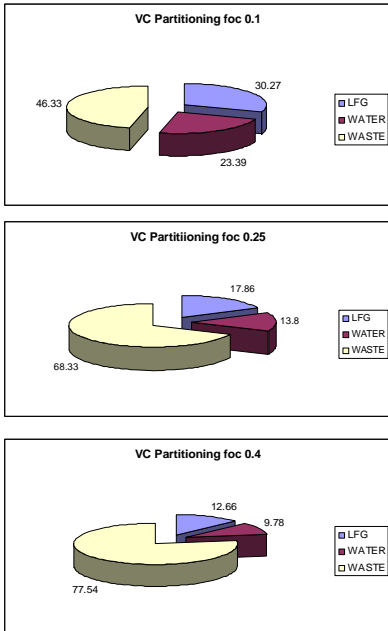


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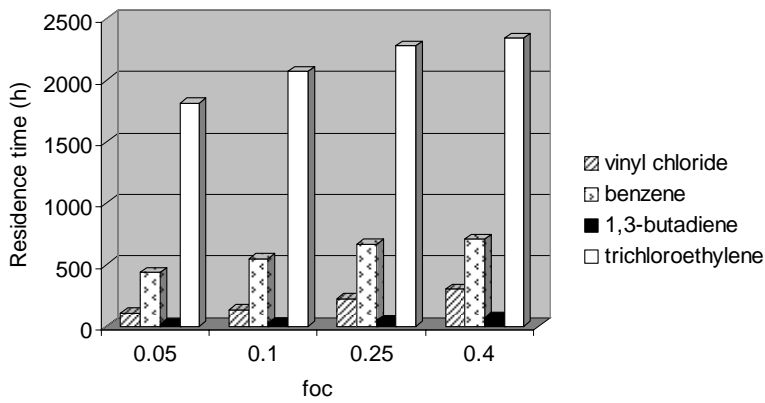


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 7 (f_{oc}) using Level II fugacity modelling

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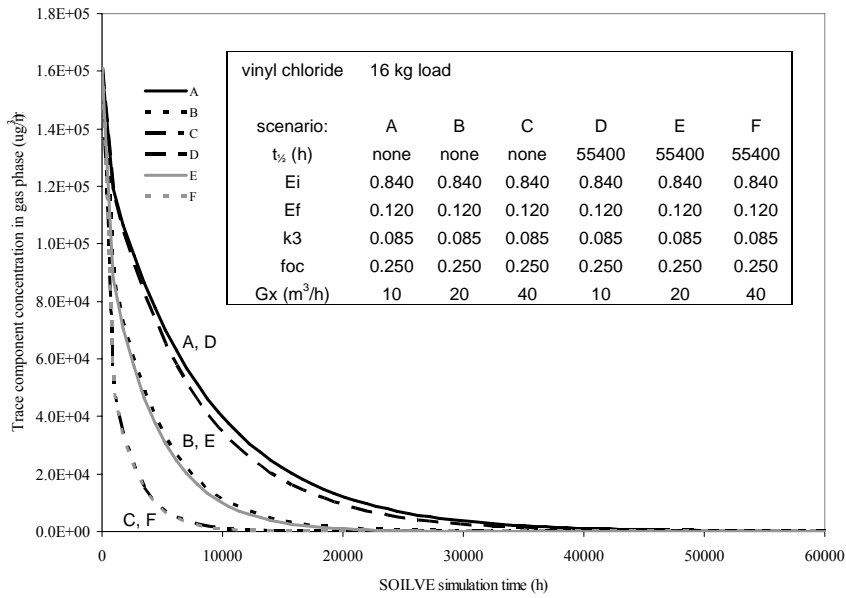
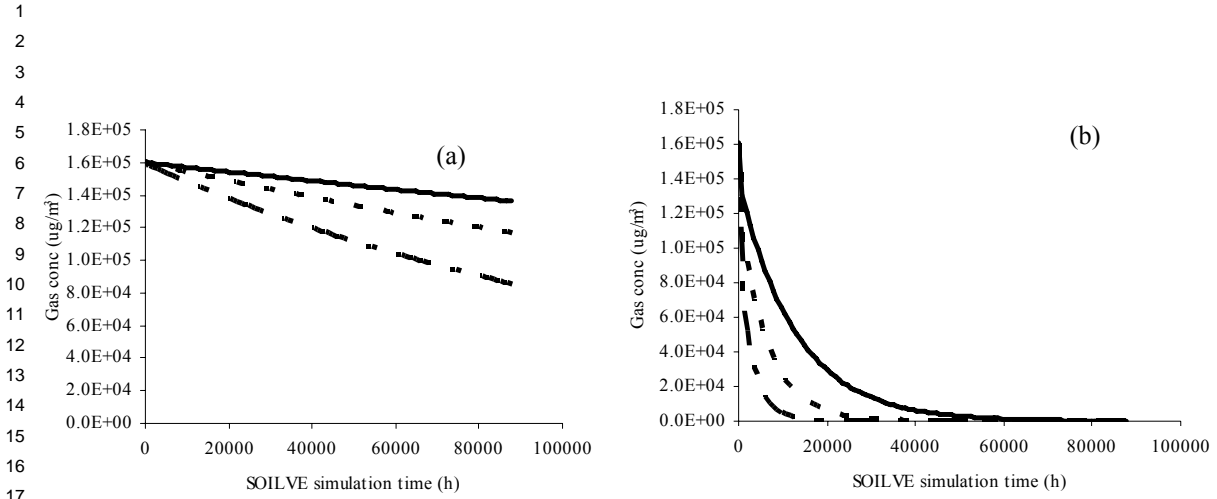


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