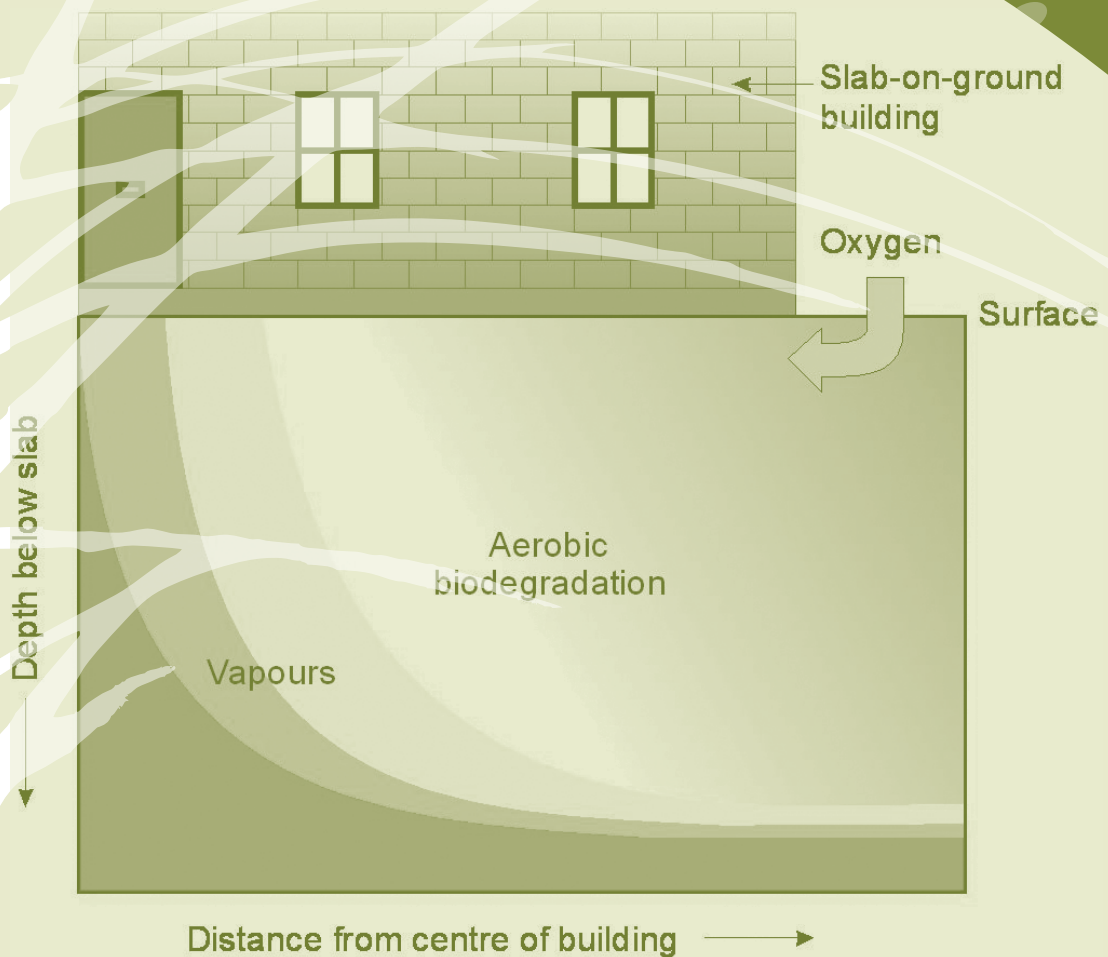


no. 12  
**technical**  
report

# Biodegradation of petroleum hydrocarbon vapours

G.B. Davis, B.M. Patterson and M.G. Trefry



CRC for Contamination Assessment and Remediation of the Environment

Technical Report no. 12

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CSIRO Land and Water

March 2009



National Research  
**FLAGSHIPS**



**Cooperative Research Centre for Contamination Assessment and Remediation of the Environment, Technical Report series, no. 12**

March 2009

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ISBN: 978-1-921431-09-8

Front cover image courtesy of CSIRO

**Enquiries and additional copies:**

CRC CARE, P.O. Box 486, Salisbury South, South Australia, Australia 5106

Tel: +61 (0) 8 8302 5038

Fax: +61 (0) 8 8302 3124

[www.crccare.com](http://www.crccare.com)

**This report should be cited as:**

Davis, GB, Patterson, BM & Trefry, MG 2009, *Biodegradation of petroleum hydrocarbon vapours*, CRC CARE Technical Report no. 12, CRC for Contamination Assessment and Remediation of the Environment, Adelaide, Australia.

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**Acknowledgement:**

This document was commissioned by CRC CARE from CSIRO Land and Water, and prepared by GB Davis, BM Patterson and MG Trefry. The work was carried out through the CSIRO Water for a Healthy Country National Flagship.

## Acknowledgements

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Many colleagues at CSIRO (John Rayner, David Briegel, Blair Robertson, Andrew Furness, Steve Fisher, Trevor Bastow, Robert Woodbury) assisted with collection of the Australian field data reported here. Over more than a decade, a number of agencies including the Western Australian Department of Environment and Conservation sponsored projects that allowed development of the understanding embodied in the report. Thanks too to Paul Johnson, Ian Hers, George DeVaul, Terry Walden and Jackie Wright for discussions regarding vapour behaviour.

## Executive summary

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In this report we review the role of biodegradation in reducing petroleum hydrocarbon vapour intrusion into slab-on-ground buildings for application at a Tier 1 or human health screening level. This work comprises part of the efforts through CSIRO and the Cooperative Research Centre for Contamination Assessment and Remediation of the Environment (CRC CARE) to provide technical input to the current review of the Australian National Environment Protection (Assessment of Site Contamination) Measure (NEPM).

Vapours emanate from subsurface spills and leaks of petroleum fuels such as gasoline, diesel and other petroleum products. Historic or recent events may lead to contamination, and investigation of vapour risks may be triggered by previous site investigations, knowledge of site history or use, or where land redevelopment is occurring. Vapours naturally attenuate or decrease in concentration as they move from the subsurface through the soil towards the ground surface and potentially into buildings. Here we consider the additional attenuation potential due to aerobic biodegradation of petroleum hydrocarbon vapours, and the consequent additional reduction in human health exposure that may be applicable at a Tier I or screening level. The report relates to the evaluation of long-term chronic low-level indoor air concentrations of petroleum hydrocarbon chemical constituents, rather than short-term concerns such as high-level explosive hazards or acute toxic concentrations.

Included in this report are: (i) published information on the biodegradation of petroleum hydrocarbon vapours; (ii) additional exposure reduction factors proposed by researchers and suggested by jurisdictions attributable to biodegradation of petroleum hydrocarbon vapours; (iii) data on petroleum hydrocarbon vapours and oxygen concentrations from four states of Australia along with an assessment of generalised trends; (iv) recommendations as to reduction factors that might be applied when oxygen is present in the subsurface and aerobic biodegradation of petroleum vapours is occurring; and (v) guidance on the application of such reduction factors.

The studies and modelling suggest that where oxygen was present petroleum vapours degraded rapidly. Where oxygen was absent little biodegradation was observed. Additional attenuation due to biodegradation of petroleum hydrocarbon vapours have been reported to vary from 1 (i.e., no change) to many orders of magnitude, depending on the depth to the source of vapours, the concentration resident in the source zone, and the potential for oxygen ingress. Australian and overseas data from studies in and beneath buildings show that significant biodegradation occurs, especially for modest sized buildings.

Four recommendations are made concerning:

1. the need for measurement and confirmation of the presence of oxygen in the subsurface
2. an exclusion/inclusion criterion related to depths to vapour sources
3. an exclusion/inclusion criterion related to the scale of the building foundations to which the recommendations apply, and
4. the magnitude of the additional exposure reduction that is applicable at a Tier 1 or screening level due to biodegradation of petroleum hydrocarbon vapours.

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# 1. Introduction

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## 1.1 Background and scope

The current review of the National Environment Protection (Assessment of Site Contamination) Measure (NEPM), and workshops over a number of years involving regulators, industry, consultants and researchers, have motivated the need to review health-based investigation levels (HILs) in Australia. The Cooperative Research Centre for Contamination Assessment and Remediation of the Environment (CRC CARE) is assisting with this review by development of health-based screening levels (HSLs) based in part on the assessment of petroleum hydrocarbon vapour risks in soil and groundwater environments.

The Western Australian Department of Environment and Conservation commissioned a review of vapour behaviour in 2004 (Davis et al. 2004). Recently, Davis et al. (2009a) described and compared two models for their utility in modelling petroleum hydrocarbon vapours in soil profiles and as they potentially move from the subsurface into built structures. In addition for the development of HILs, Davis et al. (2009a) considered the need for inclusion of biodegradation and finite life-time sources in vapour modelling approaches.

This report addresses the role of biodegradation as an attenuation process for petroleum hydrocarbon vapours as they migrate from the subsurface towards built structures. The type of petroleum hydrocarbon source will alter vapour composition and concentration, but the principles outlined here apply generally to all aerobically degradable vapour sources including gasoline, diesel, kerosene, crude oil and other petroleum fuels and oils. The report relates to the evaluation of long-term chronic low-level indoor air concentrations of petroleum hydrocarbon chemical constituents, rather than short-term concerns such as high-concentration explosive hazards or acute toxic concentrations.

The scope for application is essentially for residential scale buildings – for building slab sizes of less than 15 m width (see the Recommendations). The recommendations contained in this report primarily relate to slab-on-ground buildings, but could be applied to ventilated crawl-space buildings. The approach taken here is to consider biodegradation in the context of its applicability at a Tier 1, or screening level. This, *a priori*, requires recommendations that are supported by conservative assumptions; otherwise the guidance and application can become overly complex.

## 1.2 Premise and overview

Petroleum and chlorinated vapours attenuate, that is their concentration can reduce, as they travel toward building foundations from contaminant sources below ground surface (e.g. Johnson & Ettinger 1991). Utilising the Johnson and Ettinger (1991) modelling approach or via using measurements, an attenuation factor ( $\alpha$ ) can be estimated. This is the ratio of the vapour concentration in indoor air ( $C_{\text{indoor}}$ ) to the maximum hydrocarbon concentration found in the subsurface source zone ( $C_{\text{H,max}}$ ). This can be simply stated as:

$$\alpha = C_{\text{indoor}}/C_{\text{H,max}} \quad (1)$$

The processes that lead to this attenuation are diffusion outwards from the source zone towards the sub-slab region, concentration reductions due to boundary conditions, such as low vapour concentrations in ambient air in and outside of buildings at the ground surface, and due to pressure-driven air exchange in the near-surface zone of the soil profile or in the built structure (e.g. Hers et al. 2000, 2003).

For petroleum hydrocarbons, there is also the potential for significant additional attenuation due to aerobic biodegradation, because of the potential for oxygen to move into the subsurface from the atmosphere above ground (see e.g. Davis et al. 2005, 2009b; DeVaul 2007b; Franzmann et al. 1999; Hers et al. 2000; Roggemans et al. 2001; Patterson & Davis 2009). The scale of such biodegradation may reduce petroleum vapour concentrations by several orders of magnitude (Abreu & Johnson 2006). Therefore, excluding biodegradation from risk assessments for petroleum-impacted sites may lead to overly conservative protective measures. The US EPA (2002) acknowledged this when stating that the Johnson and Ettinger (1991) model may not be applicable to petroleum hydrocarbons since it did not account for biodegradation.

In this report we:

1. review scientific literature available on the biodegradation of petroleum hydrocarbon vapours
2. collate exposure reduction factors proposed by researchers and suggested by jurisdictions attributable to the biodegradation of petroleum hydrocarbon vapours
3. review data from seven field sites in Australia to compare trends with overseas data
4. provide recommendations on appropriate exposure reduction factors where biodegradation is deemed to be occurring, and
5. provide guidance on when such factors might be applied.

These reduction factors are in addition to attenuation estimated through the use of say the Johnson and Ettinger (1991) modelling approach, which, during standard application, does not include biodegradation.

## 2. Literature related to aerobic biodegradation of petroleum vapours

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A number of laboratory and field investigations, along with modelling studies, have observed and sought to quantify aerobic biodegradation of petroleum hydrocarbon vapours in shallow soil environments (Davis et al. 1998, 2005, 2009b; Fischer et al. 1996; Franzmann et al. 1999; Hers et al. 2000; Johnson et al. 1999; Ostendorf et al. 2007; Ostendorf & Kampbell 1991; Patterson & Davis 2009; Ririe et al. 2002; Sanders & Hers 2006). Some investigations have estimated vapour biodegradation based on oxygen concentration reductions and carbon dioxide production in the subsurface (Davis et al. 2005; Lahvis & Baehr 1996). Alternately, hydrocarbon concentration changes have been modelled to quantify attenuation processes without linkage to oxygen or other major gas concentrations (Ririe et al. 2002; Trefry et al. 2001; Turczynowicz 2003; Turczynowicz & Robinson 2001).

Increasingly, vapour biodegradation studies have focussed on coupled hydrocarbon vapours and gaseous oxygen transport to portray oxygen-dependent biodegradation conditions (Abreu & Johnson 2005, 2006; Davis et al. 2009b; DeVaul 2007b; Hers et al. 2000; Öhman 1999; Ostendorf & Kampbell 1991; Trefry et al. 2000). In contrast, Baehr and Baker (1995) report oxygen to be non-limiting where toluene was employed as a source in laboratory column experiments. This is at odds with most available field data, and subsequent studies in the field (Lahvis & Baehr 1996). It is reasonably accepted now that oxygen transport coupled to hydrocarbon biodegradation processes is of prime importance, and that biodegradation of petroleum vapours is limited by oxygen availability (e.g. Davis et al. 2009b).

Studies specific to petroleum vapour biodegradation in close proximity to building foundations or beneath buildings (or beneath covered ground) have been reported by Öhman (1999), Hers et al. (2000), Davis et al. (2001), Sanders and Hers (2006), Lundegard et al. (2008) and Patterson and Davis (2009). Abreu and Johnson (2005, 2006) also modelled these situations.

Studies related to Australian sites and conditions are reported in Trefry et al. (2001); Turczynowicz and Robinson (2001), Turczynowicz (2003), Davis et al. (1998, 2001, 2005, 2009b), Wright and Robinson (2009), Patterson and Davis (2009) and a number of other modelling papers.

These laboratory, field and recent modelling studies concur that where oxygen is present significant aerobic biodegradation of petroleum hydrocarbon vapours can occur, and that the rate of biodegradation is largely limited by oxygen availability.

### 3. Review of reduction factors due to aerobic biodegradation of petroleum vapours

Based on current scientific understanding, a Tier 1 or screening level reduction in exposure due to biodegradation of petroleum hydrocarbon vapours is under consideration by jurisdictions or has been incorporated into various vapour guidance documentation in the United States of America and Canada (Golder Associates 2008). In this section we provide an overview of the reduction or adjustment factors that have been proposed by others. Some have been obtained by comparing Johnson and Ettinger (1991) and other modelling estimates to site data and inferring the additional attenuation that is occurring due to biodegradation. Some estimates have been obtained by comparing chlorinated hydrocarbon vapour distributions against those for petroleum hydrocarbons. Some have been obtained from models that account for vapour biodegradation as discussed briefly in the review above.

#### 3.1 Golder Associates (2008) – Towards Guidance for Canada

Golder Associates (2008) have summarised a range of datasets from across the United States and Canada. They compared petroleum hydrocarbon vapour data to chlorinated solvent vapour data, and carried out modelling studies. The Golder Associates (2008) study was largely carried out by Dr Ian Hers who has published several refereed papers on vapour behaviour (see e.g. Hers et al. 2000, 2002, 2003).

**Table 1. Bioattenuation adjustment factors (BAF).**

Media	Contamination	Criteria	BAF
Groundwater	Dissolved – low	Benzene < 0.1 mg/L F1 < 5 mg/L F2 < 1 mg/L	100X for $D_s > 1$ m
	Dissolved – high	Benzene < 1 mg/L 5 < F1 < 15 mg/L 1 < F2 < 5 mg/L	10X for $D_s > 1$ m 100X for $D_s > 3$ m
	NAPL		10X for $D_s > 5$ m
Soil vapour	Dissolved	$C_g < 1$ mg/L	10X for $D_s > 1$ m 100X for $D_s > 1$ m, $D_p < 1$ m
	Transition dissolved & NAPL	1 < $C_g < 50$ mg/L	10X for $D_s > 2$ m
	NAPL	$C_g > 50$ mg/L	10X for $D_s > 5$ m
Soil	All		20X for $D_s > 1$ m

Notes:

- The adjustment factors should only be applied when there is no significant capping adjacent to the building.
- 100X means 100 times reduction
- $C_g = BTEX + F1$  (HC fraction  $C_6-C_{10}$ ) +  $F2$  (HC fraction  $>C_{10}-C_{16}$ ) +  $CH_4$
- $D_s$  = Separation distance between contamination source and building
- $D_p$  = Distance from contamination to soil gas probe

Golder Associates (2008) consolidated into one database the (i) US EPA Indoor Air Vapour Intrusion (IAVI) database, (ii) data from the State of Colorado, (iii) data from Utah Department of Environmental Quality, (iv) data from the New Jersey Department of Environmental Protection (NJDEP), and (v) data from 22 sites in Canada. Most data were from retail service station sites in Colorado, Utah, Massachusetts, New Jersey, California and British Columbia. The data were screened as a quality control measure and assessed for trends and modelling. The primary compounds assessed in this way were benzene, toluene, ethylbenzene and the xylene isomers (BTEX), MTBE, cyclohexane, and 2,2,4-trimethylpentane.

From this database, no trend or correlation was observed in scatter plots of measured indoor air concentrations of the petroleum compounds against groundwater concentrations or against the measured soil vapour concentrations. This is in contrast to positive trends observed for chlorinated compounds – this was also reported by Dr George DeVaul in his presentation at the Vapour Workshop on the Gold Coast, Queensland Australia in February 2008. The lack of correlation for the petroleum hydrocarbons is considered to be due to biodegradation process that are occurring in the soil profile, in contrast to many chlorinated vapour compounds which are less readily degradable under aerobic conditions.

Through assessment of depth profiles, oxygen and hydrocarbon vapour correlations, biodegradation rates and modelling, the overall assessment from Golder Associates (2008) was summarised in two tables – reproduced here as Tables 1 and 2. These suggest a minimum 10-100 fold adjustment factor – depending on the depth and concentration of the source of vapours. For all depths greater than 2 m to the source, and where no non-aqueous phase liquid (NAPL) exists, a general 10–20 fold adjustment factor was suggested.

**Table 2. Bioattenuation adjustment factor for soil.**

Contamination	Criteria	Bioattenuation Adjustment Factor <sup>1</sup>
No NAPL – Lower concentration	$C < C_{sat} * 0.1$	100X for separation distance > 1 m
No NAPL – Higher concentration	$C < C_{sat}$	10X for separation distance > 1 m 100X for separation distance > 3 m
NAPL	$C > C_{sat}$	10X for separation distance > 5 m

<sup>1</sup> Consideration could also be given to addition of a 2X factor to also account for non-equilibrium partitioning conditions. It was noted by Hers et al. (2002) that measured vapour concentrations were often much less than concentrations calculated via an equilibrium approach.

### 3.2 Utah Department of Environmental Quality (2008)

Utah Department of Environmental Quality (Davis 2008) compiled 243 soil vapour sampling events at 51 sites across the United States of America and Canada, and compared these with a case study in Utah. They found that results in the Utah study were comparable to general attenuation characteristics of the broader data set.

**Table 3. Reduction factors recommended by Davis (2008).**

<b>Situation</b>	<b>Reduction factor</b>	<b>Comment</b>
Very strong sources (e.g. benzene = 100–1,000 µg/L TPH = 100,000–200,000 µg/L) (Clean overlying soil)	100–100,000X	
Very strong sources (e.g. benzene = 100–1,000 µg/L TPH = 100,000–200,000 µg/L) (No clean overlying soil)	~1X	No oxygen
Very weak sources (e.g. benzene ≤10 µg/L TPH ≤ 2,000 µg/L) (Little hydrocarbon to attenuate)	~1X	Risk is small in any case

They found significant vapour biodegradation where 2–7 feet (0.7–2.2 m) of clean soil overlay a source zone, even with quite high source concentrations (e.g. benzene = 100–1,000 µg/L TPH = 100,000–200,000 µg/L). Weak sources with clean overlying soil also showed significant biodegradation. Davis (2008) also quantified biodegradation by comparing vapour measurements to models. It was not clear if ground coverage was considered in the assessment. A summary of the recommendations from the work is given in Table 3.

From this, Davis (2008) also suggested a 100 fold attenuation factor in coarse-grained soil and a 1–10 fold attenuation reduction factor for fine-grained soil.

### **3.3 Abreu and Johnson (2005, 2006)**

Abreu and Johnson (2005, 2006) reported numerical modelling of vapour ingress to a basement and a 10 m x 10 m slab-on-ground building. They incorporated aerobic biodegradation effects. This is discussed further in Section 5.

### **3.4 DeVaul (2002, 2007a, 2007b)**

In DeVaul et al. (2002), DeVaul (2007a) and DeVaul (2007b), models of biodegradation were presented along with selected summaries of data and rates of biodegradation for petroleum hydrocarbon vapours. In particular DeVaul makes the case that the separation distance from the source can be the key discriminator of risk for petroleum hydrocarbon vapours when oxygen-limited biodegradation is included. DeVaul includes convective transport of both vapours and oxygen.

With active biodegradation, DeVaul found that reduction factors are nearly always greater than ten-fold even for sources as close as 1 m below the building foundation.

### 3.5 Ririe et al. (2002) and Groundwater Services Inc (2003)

Ririe et al. (2002) used data from three field sites in California – one with NAPL as a source, one with dissolved benzene in groundwater, and one with gasoline impacted soil. They compared field vapour data to a model of vapour transport. Their assessment was that the additional reduction factor due to biodegradation was between 500 and 35,000.

Groundwater Services Inc (2003) used a database compiled by (McHugh et al. 2004) to estimate petroleum hydrocarbon attenuation factors, especially in comparison to chlorinated hydrocarbons. They surmised that ‘the attenuation factor for petroleum hydrocarbons should be 100 times greater than the attenuation factor used for chlorinated solvents’.

### 3.6 Other jurisdictions

The New Jersey Department of Environmental Protection (NJ DEP 2005) state:

*‘At the time this document was prepared, limited studies have been presented to support a biodegradation factor for these chemicals under aerobic conditions. However, as indicated in Section 4.2, Calculation of Ground Water Screening Levels for the Vapor Intrusion Pathway, several resources have suggested values for establishing a degradation factor for benzene, toluene, ethylbenzene, and xylenes ranging from 1 to 35,000. Until additional data is generated, the Department has selected an additional attenuation factor for benzene, toluene, ethylbenzene, and xylenes of 10 times the ground water to indoor air value calculated using the J&E model. Use of the additional attenuation factor assumes a minimum of 4% oxygen exists in the soil column beneath the structure. A biodegradation factor for MTBE, n-hexane, 1,2,4-trimethylbenzene, 1,3,5-trimethylbenzene, cyclohexane, 2,2,4-trimethylpentane, and tertiary butyl alcohol has not been included due to uncertainty over the rate of attenuation in the vapor phase.’*

The New Hampshire Department of Environmental Services (NH DES 2006) says that:

*‘The GW-2 groundwater screening values are intended to be used where VOCs (non-petroleum) are detected in groundwater above GW-2 levels within 100 feet (vertically or horizontally) of an occupied building. At petroleum hydrocarbon sites, the GW-2 screening values are intended to be used where petroleum VOCs are detected in groundwater above GW-2 levels within 30 feet (vertically or horizontally) of an occupied building.’*

This is an implicit recognition of the additional attenuation that occurs for petroleum hydrocarbons. In this case a factor of 3 applied within 9–10 m of the source.

The Hawaii Department of Health (2008) state that:

*‘To account for the potentially over conservative nature of the vapor intrusion model for non-chlorinated volatile chemicals, action levels generated by the model were adjusted upwards by a factor of ten ..... the use of soil gas data in combination with groundwater studies may be most*

*appropriate for evaluating sites where a more detailed evaluation of this issue is warranted.'*

The Tri-Services (2008) handbook, which is used by the US Air Force, Navy and Army for assessment of the vapour intrusion pathway, recognises that:

*'Since the J&E model does not account for degradation, modeling-based vapor intrusion risk assessments of petroleum hydrocarbon sites will often overestimate the long term exposure concentration, in turn overestimating the potential risk to receptors that may be present. However, not all states concur with this position. The Cal-EPA requires that petroleum hydrocarbons at sites in California be evaluated for the possibility of vapor intrusion' (DTSC, 2005).*

More recently, the DTSC have moved to consider a default ten-fold reduction due to the potential biodegradation of petroleum vapours.

### **3.7 Summary comment**

Many studies and jurisdictions recognise the additional reduction in hydrocarbon vapour concentration and exposures that can occur in buildings due to aerobic biodegradation. Most, too, recognise that the limitation to biodegradation is the availability of oxygen.

The studies quote a wide range of attenuation reduction factors. Most often they report at least a ten-fold reduction, although some quote values that are less.



## 4. Australian field data

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Wright and Robinson (2009) and Davis et al. (2009b) both report data across a number of field sites in Australia. Wright and Robinson (2009) compiled data from 47 petroleum-impacted sites. They highlighted the limitations of the data, but also stressed the need to consider aerobic biodegradation and source conditions when assessing vapour risks from such sites.

As reported in Davis et al. (2009b), in this section we compile petroleum hydrocarbon vapour data from four Australian states to assess:

- if biodegradation of petroleum vapours is occurring under a range of Australian conditions
- if so, under what typical conditions biodegradation occurs
- if so, provide a measure of the magnitude of biodegradation for estimating an exposure reduction factor.

### 4.1 Field sites

Petroleum hydrocarbon vapour and oxygen concentrations from thirteen depth profiles at seven sites on sandy and clay soils across four states of Australia were collated. Aspects and experimentation at two of the sites have been reported in Davis et al. (2001, 2005) and Patterson and Davis (2009). Three of the sites are located in Perth, Western Australia, on sandy soils, and four are located in Queensland, New South Wales and Victoria on finer textured soils. A summary of the characteristics of the sites is given in Table 4. In general the sites range from calcareous medium to coarse sands, to fine tight clay and silty sites, with petroleum sources ranging from near-pure compound releases (e.g. xylene) to kerosene and gasoline, and with varying vadose zone depths from 1.25 m to 10 m.

**Table 4. Summary of characteristics of the seven field sites.**

Site label	State of Australia	Site setting	Soil type	Source type	Vadose zone depth (m)	Organic carbon (% g/g)
A	Western Australia	Slab on ground, and open ground	Medium-course calcareous sand	kerosene	~3	0.16-0.97
B	Western Australia	Open ground	Medium-course calcareous sand	gasoline	2.6- 3.5	0.04-0.13
C	Western Australia	Asphalt cover and open ground	Silica sand and fill over clay	xylene, and BTEX	~3	0.05-1.0
D	Queensland	Open ground	Fill over clay or clay	gasoline	>4	<0.01-0.22
E	Queensland	Open ground near house	0.5 m of gravel fill over clay	gasoline	~1.5	0.1-0.47
F	NSW	Open ground near house	Tight brown clay and silty clay	gasoline	7	0.1-0.3
G	Victoria	Open ground near house	Brown clay sand	gasoline	10	<0.25-0.98

Note: Open ground refers to a site without a paved surface (i.e. vegetated or bare ground surface)

The field sites were instrumented with multilevel samplers (MLS) and in some cases with on-line volatile organic compound (VOC) probes (Patterson et al. 2000) and oxygen probes (Patterson & Davis 2008). This was to allow depth profile sampling of petroleum vapour and major gas concentrations in the subsurface, and to track changes over time. Samples were analysed for petroleum hydrocarbon vapours by gas chromatography mass spectrometry (GC-MS) and for major gases (i.e. oxygen, carbon dioxide, nitrogen and methane) using a GC with a thermal conductivity detector (GC-TCD).

## 4.2 Field data

Table 5 shows data from across the seven sites. The maximum total petroleum hydrocarbon (TPH) vapour concentration for any of the depth profiles was 180,000 µg/L at Site C, with 140,000 µg/L being m- & p-xylene isomers. The lowest maximum vapour concentration for any of the depth profiles was 130 µg/L at Site D. Total porosities ( $\theta_T$ ) were reasonably similar across the seven sites – ranging from 0.30 to 0.54 m<sup>3</sup>/m<sup>3</sup>, but with averages always greater than 0.38 m<sup>3</sup>/m<sup>3</sup> (Table 5). Air filled porosities ( $\theta_a$ ) were highly variable – ranging from effectively zero as a minimum at Sites E and F, up to 0.43 m<sup>3</sup>/m<sup>3</sup> on the sandy sites. For the clay/silty sites (E, F, G), the maximum  $\theta_a$  was 0.19 m<sup>3</sup>/m<sup>3</sup>, and the minimum average was 0.02 m<sup>3</sup>/m<sup>3</sup> at Site E. Diffusion coefficients calculated with a common tortuosity model (that of Millington & Quirk 1961) reflected this variability.

**Table 5. Characteristics for 13 depth profiles – including the maximum hydrocarbon vapour concentrations ( $C_{H,max}$ ), the depth at which this occurs ( $L_{max}$ ), total ( $\theta_T$ ) and air-filled ( $\theta_a$ ) porosities, and effective oxygen ( $D_{Ox,eff}$ ) and hydrocarbon vapour ( $D_{H,eff}$ ) diffusion coefficients.**

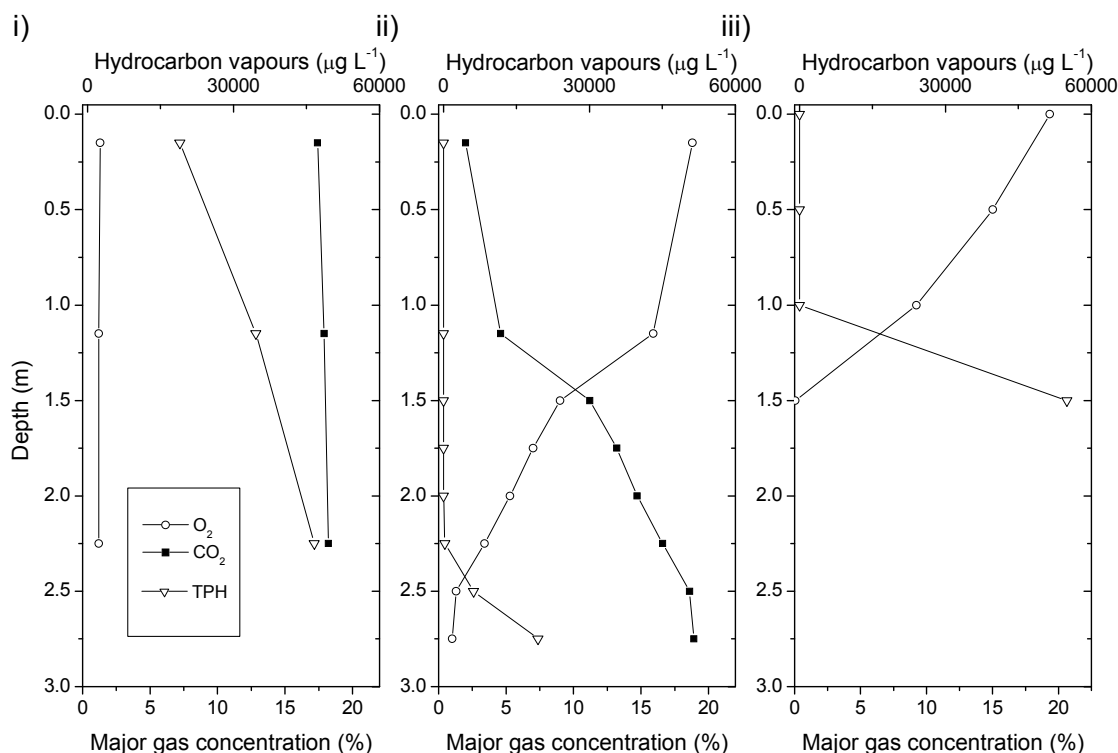
Site	Notes	$C_{H,max}$ ( $\mu\text{g/L}$ )	$L_{max}$ (m)	$\theta_T$ <sup>1</sup> ( $\text{m}^3/\text{m}^3$ )	$\theta_a$ <sup>1</sup> ( $\text{m}^3/\text{m}^3$ )	$D_{Ox,eff}$ <sup>2,3</sup> ( $\text{m}^2/\text{s}$ )	$D_{H,eff}$ <sup>2,3</sup> ( $\text{m}^2/\text{s}$ )	Depth profile shape
A	Open ground	19000	2.75	<b>0.51</b> <i>0.51</i>	<b>0.34</b> <i>0.34</i>	<b>2.1E-6</b>	<i>8.3E-7</i>	Near-linear oxygen. Linear HC.
A	Under building	47000	2.25	<b>0.54</b> <i>0.50</i>	<b>0.38</b> <i>0.39</i>	<b>2.6E-6</b>	<i>8.3E-7</i>	No oxygen. Linear HC.
B	Summer	66000	2.25	<b>0.52</b> <i>0.44</i>	<b>0.32</b> <i>0.38</i>	<b>1.2E-6</b>	<i>1.6E-6</i>	Non-linear oxygen. Linear HC.
B	Winter - wet layer	55000	2.0	<b>0.54</b> <i>0.48</i>	<b>0.26</b> <i>0.35</i>	<b>7.7E-7</b>	<i>1.0E-6</i>	Near-linear oxygen. Linear HC.
C	Open ground	140000 (xylene) 180000 (TPH)	3.0	<b>0.40</b> <i>0.43</i>	<b>0.30</b> <i>0.31</i>	<b>2.3E-6</b>	<i>8.7E-7</i>	Non-linear oxygen. Non-linear HC.
D	Fill - clay layer. Aug 2003	16000	3.5	<b>0.42</b> <i>0.50</i>	<b>0.30</b> <i>0.33</i>	<b>2.1E-6</b>	<i>7.7E-7</i>	Near-linear oxygen. Linear HC.
D	Fill - clay layer. May 2004	4000	3.5	<b>0.42</b> <i>0.50</i>	<b>0.30</b> <i>0.33</i>	<b>2.1E-6</b>	<i>7.7E-7</i>	Near-linear oxygen. Near-linear HC.
D	Open ground Aug 2003	12000	2.3	<b>0.48</b> <i>0.46</i>	<b>0.22</b> <i>0.26</i>	<b>6.0E-7</b>	<i>4.2E-7</i>	Near-linear oxygen. Two-point linear HC.
D	Open ground May 2004	130	1.3	<b>0.48</b> <i>0.46</i>	<b>0.22</b> <i>0.26</i>	<b>6.0E-7</b>	<i>4.2E-7</i>	Linear oxygen. Low $C_{max}$
E	Beside a building	55000	1.5	<b>0.46</b> <i>0.39</i>	<b>0.12</b> <i>0.02</i>	<b>8.3E-8</b>	<i>1.1E-10</i>	Linear oxygen. Two-point linear HC.
F	Apr 2002	6400	5.0	<b>0.43</b> <i>0.43</i>	<b>0.11</b> <i>0.15</i>	<b>6.6E-8</b>	<i>7.4E-8</i>	Non-linear oxygen. Two-point linear HC.
F	Oct 2002	170	5	<b>0.43</b> <i>0.43</i>	<b>0.11</b> <i>0.15</i>	<b>6.6E-8</b>	<i>7.4E-8</i>	Non-linear oxygen. Two-point linear HC.
G	Open ground	72000	8.7	<b>0.42</b> <i>0.38</i>	<b>0.14</b> <i>0.06</i>	<b>1.4E-7</b>	<i>4.7E-9</i>	Near-linear oxygen. Near-linear HC.

<sup>1</sup> **Bold values are averages for the shallow oxygenated zone of the vadose zone.** Italicised values are averages for the deeper vadose zone where hydrocarbon concentrations are highest.

<sup>2</sup>  $D_{Ox,eff}$  and  $D_{H,eff}$  are calculated using the Millington and Quirk (1961) approximation:  $D_{eff}=D_{free}\theta_a^{10/3}/\theta_T^2$ , where  $D_{Ox,free}=2.01 \times 10^{-5} \text{ m}^2/\text{s}$  (Gliński and Stępniewski 1985),  $D_{H,free}=8.0 \times 10^{-6} \text{ m}^2/\text{s}$  (Grathwohl 1998).

<sup>3</sup> **Bold values are calculated from bold values of  $\theta_a$  and  $\theta_T$ .** Italicised values are calculated from italicised values of  $\theta_a$  and  $\theta_T$ .

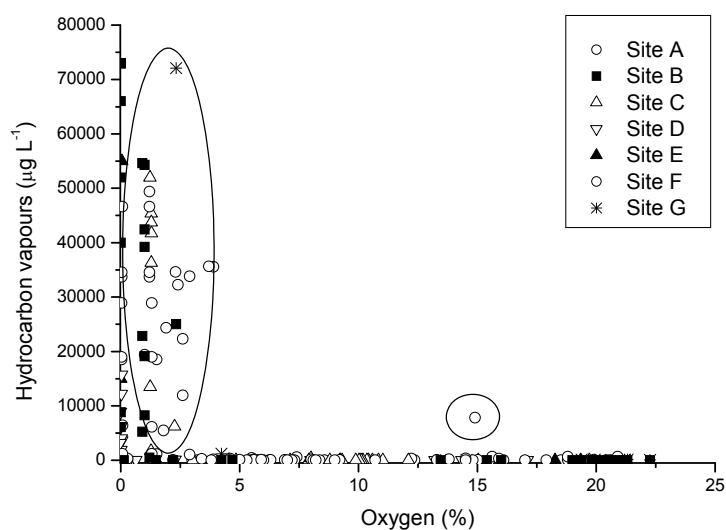
Figure 1 shows typical total hydrocarbon vapour and major gas concentration depth profiles for Site A and Site E. At Site A for open ground conditions (Figure 1(ii)), oxygen concentrations decreased to approximately 1% (effectively below detection limits) at a depth of 2.5 m below ground. Total hydrocarbon vapour concentrations were above detection limits at that depth and deeper. Carbon dioxide concentrations increased with depth, and showed an approximate volume for volume replacement of oxygen over the entire depth profile. This is consistent with the occurrence of microbial mineralisation (biodegradation) of hydrocarbon vapour in soils (Davis et al. 2005; Franzmann et al. 1999). Loss of carbon dioxide is only via diffusion through to the ground surface, hence the concentrations over the greater depths were very high. At the same site under the centre of a slab-on-ground building (Figure 1(i)) oxygen concentrations were below detection limits (approximately 1%). Carbon dioxide concentrations were uniformly high and hydrocarbon vapour concentrations were at elevated levels at the shallowest sampling port below the slab (0.15 m below ground). Note that this is only a single example of such a situation. Vapours were shown to be at elevated concentrations under the centre of a covered ground area at an adjacent site (Davis et al. 2001), but others have observed limited vapour concentrations beneath a slab-on-ground building (e.g. Lundegard et al. 2008). See Section 5 for further discussion of this. Figure 1(iii) shows an open ground depth profile in a heavy clay soil with 0.5 m of overlying gravel fill. In this case, the oxygen concentration was below detection limits at a depth of 1.5 m below ground meaning that oxygen had decreased to non-detect levels between 1 m and 1.5 m, and hydrocarbon vapour concentrations decreased from 55 000  $\mu\text{g/L}$  to below detection limits between 1 m and 1.5 m.



**Figure 1. Depth profiles for hydrocarbon vapour (TPH) and major gas concentrations for Site A for i) beneath the centre of a slab-on-ground building at Site A ii) open ground conditions beside the building at Site A, and iii) open ground conditions beside the building at Site E.**

Linear, or near-linear, oxygen and hydrocarbon concentration depth profiles were commonly observed (Table 5). At some sites data are limited and so linearity was difficult to confirm. For example, where only two data points were available a ‘two-point linear HC’ depth profile has been noted in Table 5 (e.g. see Site E data in Figure 1(iii)). At Sites B, C and F non-linear oxygen profiles were observed, and only at Site C was a non-linear vapour profile observed. Contrary to the general linear trends observed, under steady state conditions where zero- or first-order biodegradation kinetics is assumed, non-linear (i.e. quadratic or exponential) depth profiles would be predicted. Linear depth profiles are not able to be reconciled using such kinetics.

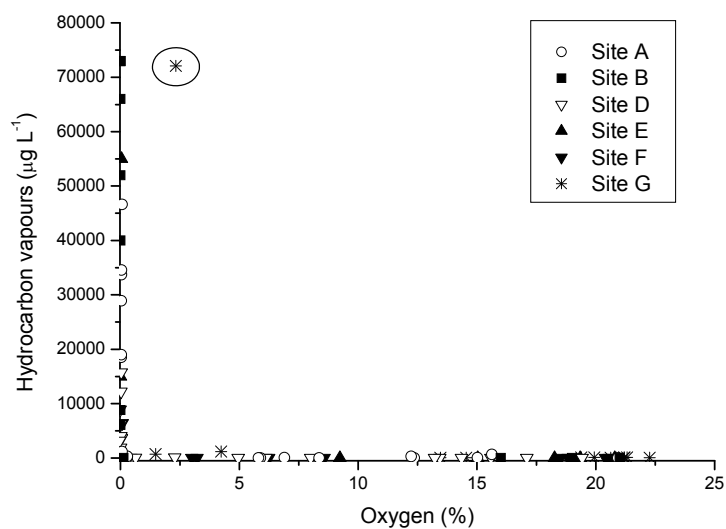
All oxygen and hydrocarbon vapour concentration data for all locations and depths at each site are shown in Figure 2. Data from both *in situ* probe measurements and conventional manual gas sampling and GC analysis are included. Note that data are from multilevel samplers located both in open ground conditions where profiles are like those displayed in Figure 1(ii), and from beneath the centre of a slab where profiles are like those displayed in Figure 1(i). For nearly all sites, when hydrocarbon vapour concentrations were above detection limits (i.e. > 200 µg/L for the *in situ* hydrocarbon probes; > 50 µg/L for the manual sampling and GC-MS analysis), oxygen concentrations were < 5 %. Further investigation of these data and subsequent sampling showed that only oxygen data obtained by conventional manual gas sampling with GC-TCD analysis gave oxygen concentrations between 0.5% and 6% (circled data in Figure 2) when hydrocarbon concentrations were above 200 µg/L.



**Figure 2. Total petroleum hydrocarbon vapour concentrations compared to oxygen concentrations for Sites A-G. Data from sites where oxygen and hydrocarbon vapours were coincident are circled.**

Comparing only *in situ* oxygen probe data to hydrocarbon data shows an even stronger relationship between the absence of oxygen and the presence of hydrocarbon vapours, and vice versa (Figure 3). Davis et al. (2009b) and Patterson and Davis (2008) provide information to support the argument that oxygen contamination of soil gas samples during manual collection, or permeation of oxygen through plastic sampling syringes during transportation to the laboratory, are the likely reasons for the change in the comparative data.

The only outlier was at one depth (8.7 m) at Site G where oxygen and hydrocarbon vapours were detectable (circled data point in Figure 3). On-line monitoring showed fluctuations in oxygen concentrations that were consistent with barometric pressure changes, due to a large 800 mm diameter bore being installed within 2–3 m laterally of this monitoring location. These results suggest that this outlier data point was a result of oxygen ingress to this location via advective barometric pumping. Similar results have been observed elsewhere in Australia where a borehole was screened in the same interval as soil gas sampling (Jackie Wright, personal communication 2009). Excluding this result in Figure 3 then provides good evidence that there was limited overlapping of oxygen and hydrocarbon concentrations under the field conditions across these thirteen depth profiles, and suggests aerobic biodegradation of the hydrocarbon vapours only occurs in a narrow depth interval where the two intersect.



**Figure 3. Total petroleum hydrocarbon vapour concentrations compared to oxygen concentrations – data from oxygen and VOC probes for all available sites.**

### 4.3 Implications

The absence of overlapping oxygen and vapour concentrations implies that transport to the zone of aerobic biodegradation is the rate-limiting process. Where oxygen transport is rate-limiting, other researchers (Davis & Ritchie 1986; Ritchie 1977) considered aerobic reactions to occur at a sharp interface, and described by an oxygen front moving into the porous media over time.

These data support the understanding that whenever oxygen and petroleum hydrocarbons are co-located in the subsurface they react and the location at which this occurs is only controlled by the transport to that location plus the stoichiometry of the reaction between the hydrocarbon vapours and oxygen. In addition, the data suggest that hydrocarbon vapour biodegradation rates are rapid when oxygen is present. These observations further suggest that under steady-state conditions, linear depth profiles would be typically observed. This is further described in Davis et al. (2009b).

Other oxygen consumption mechanisms in the soil such as natural organic matter and reduced inorganic species (e.g. sulphides – see DeVaul 2007b; Johnston & Desvignes 2003) may limit oxygen availability, and hence biodegradation. This would lead to non-linear oxygen depth profiles. Direct measurement can obviate the need to quantify all oxygen consumption processes, and provides surety that oxygen is present.

Based on these observations, Davis et al. (2009b) described a simple instantaneous model of petroleum vapour biodegradation for open ground conditions. It is also given in Appendix A. The model balances the flux of hydrocarbon vapours diffusing from a source at depth with the flux of oxygen diffusing from the ground surface. It provides an estimate of the depth at which the hydrocarbon vapours and oxygen meet, simply based on the ratio of the diffusion coefficients of oxygen and hydrocarbon vapours, the ratio of the maximum concentrations of oxygen and hydrocarbon vapours, the depth to the maximum hydrocarbon source concentration, and the stoichiometry coefficient. This model simply provides an estimate of the maximum depth to which oxygen can penetrate below ground surface, and hence the depth below which sampling for oxygen always yields a concentration that would be below detectable concentrations.

## 5. Biodegradation beneath a building

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The Johnson and Ettinger (1991) modelling approach, and those of many others (e.g. Davis et al. 2009b), are one-dimensional. They assume vapours are transported vertically upwards towards the base of a building by diffusion and convective processes. Additional attenuation due to biodegradation requires oxygen. Oxygen ingress from the atmosphere typically occurs through areas of open ground at the sides of buildings followed by lateral penetration beneath the building slab. This actually creates two and three dimensional transport processes.

Abreu and Johnson (2005, 2006) modelled the three-dimensional behaviour of vapours and oxygen beneath a basement and a slab-on-ground building. Patterson and Davis (2009) provided field data on the penetration of oxygen beneath a slab-on-ground building. Another recent study by Lundegard et al. (2008) carried out a nitrogen flushing experiment for vapours beneath a slab-on-ground house in the United States of America. Here we describe in some detail what additional exposure reduction factors due to biodegradation are estimated from these studies. First though, we describe a study by Sanders and Hers (2006) who measured vapour parameters near and beneath a series of buildings above a petroleum groundwater plume.

### 5.1 Sanders and Hers (2006)

Sanders and Hers (2006) report on vapour impacts near several buildings above a petroleum-impacted groundwater plume in a sandy aquifer with the typical depth to the water table of 3.3 m. BTEX concentrations in groundwater were up to 82 mg/L, but concentrations varied along the plume. Depth profiles were measured adjacent to several of the buildings, and hydrocarbon vapour concentrations were determined inside the buildings and beneath the floor (i.e. sub-slab or basement).

Three of the buildings had basements (two with partial crawl-spaces), one was a crawlspace building with an earthen floor and one was a slab-on-ground building. Those with basements had limited depths to the water table of ~1.6 m. Typically, the buildings were rectangular with footprint dimensions of approximately 10.3 m x 6.9 m, 8.3 m x 6.6 m, 15.2 m x 8.3 m, 9.7 m x 8.6 m and 13.8 m x 9.7 m (estimated from Figure 1 of Sanders & Hers 2006).

Sanders and Hers (2006) observed vapours in one of the basement buildings (10.3 m x 6.9 m) closest to the source zone of the plume. The slab-on-ground building (8.3 m x 6.6 m) was also close to the source but no vapour intrusion was detected. They noted significant biodegradation due to oxygen ingress at all depth-profile locations near to buildings.

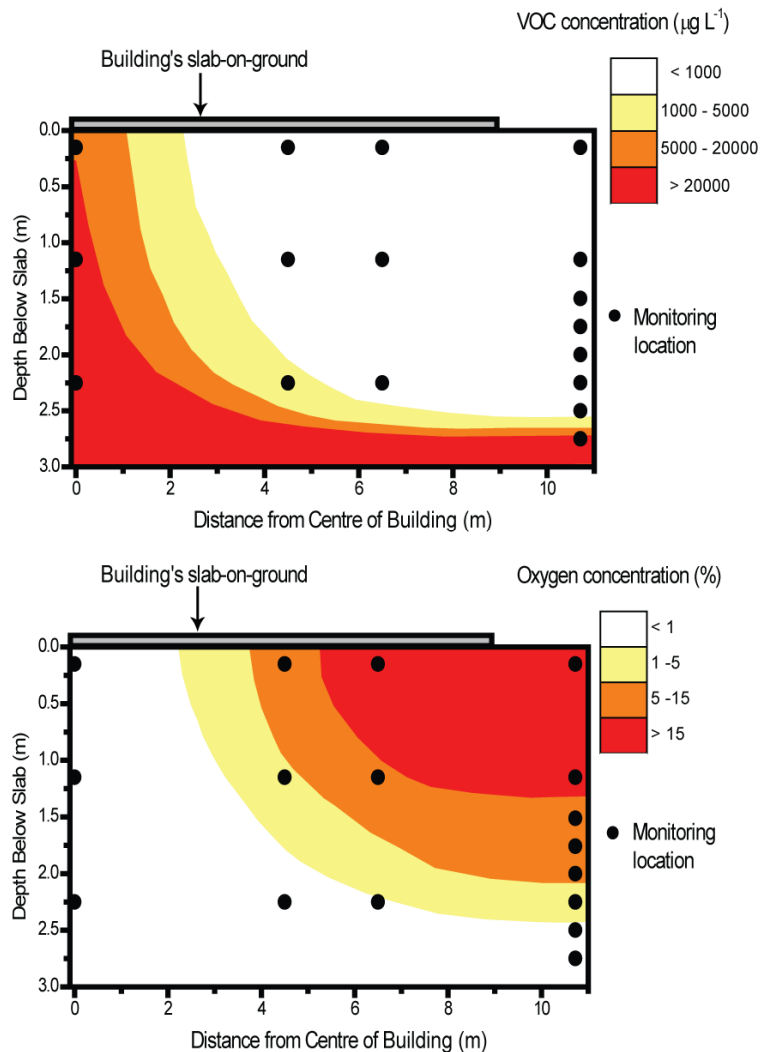
### 5.2 Patterson and Davis (2009)

Figure 4 shows a two-dimensional cross section of oxygen ingress beneath a slab-on-ground building, along with petroleum vapour concentration contours. The building slab was 18 m by 13.5 m, with a 10 m wide concrete apron on three sides. This is Site A in the data set described earlier, and is described in detail in Patterson and Davis (2009).



The oxygen and vapour concentrations do not display one-dimensional behaviour. Note that hydrocarbon vapours only penetrated to the base of the building at closer lateral distances than 3.0–4.5 m from the centre of the building. Oxygen is present at concentrations above 5% from at least a distance of 4.5 m from the edge of the slab. A one dimensional assessment might assume that the low (below detection limits) hydrocarbon vapour concentrations near the edge of the slab represent the entire slab area. Alternately, using a one-dimensional assessment, hydrocarbon vapour concentrations near the centre of the slab might be taken to represent the entire slab area. The two assessments would yield significantly different vapour exposures.

These data allow an areal assessment of the zone of the sub-slab region that is actually exposed to vapours. In this case, the area is approximately 27–60.75 m<sup>2</sup> (between 6 m x 4.5 m and 9 m x 6.75 m), assuming that oxygen penetrates to beneath the slab for a third, to a half, the slab width along all sides of the building. This compares to the total area of the slab of 243 m<sup>2</sup> (18 m x 13.5 m). Simplistically, taking the ratio of the actual area of the sub-slab that is exposed to above detection level vapour concentrations (27-60.75 m<sup>2</sup>) to the area of the entire slab would give 4-9 as an approximate additional exposure reduction factor due to biodegradation. However, the concentration observed immediately beneath the base of the slab is much lower than would be the case if no biodegradation was observed – by about a factor of two in the case presented by Patterson and Davis (2009). Together, this simple assessment would realise an overall exposure reduction factor of 8-18. Comparative modelling could help refine such estimates.



**Figure 4. Contour plots showing vadose zone soil gas concentrations of VOC (volatile organic compounds) vapours and oxygen. The plots show a cross section view through the centre line of the building from the centre of the building to the uncovered open space adjacent to one side of the building.**

Also, often in the United States of America the conceptual model for vapour intrusion assumes that cracks reside around the perimeter of a building, where external walls meet building foundations, and are the primary vapour entry points to buildings. If we accept this conceptual model, then the exposure reduction factor may be much greater. In fact, in the current case the exposure would be negligible, since below-detection level vapour concentrations are present around the building perimeter, and oxygen is abundant. However, more commonly in Australia, slab-on-ground buildings can have complete extensive slabs with walls constructed directly on top. In this case, adoption of a more general conceptual model of vapour ingress through cracks distributed across the slab may be appropriate.

### 5.3 Abreu and Johnson (2005, 2006)

Abreu and Johnson (2005, 2006) report numerical modelling of vapour ingress to a basement and for a 10 m x 10 m slab-on-ground building. They account for hydrocarbon vapour and oxygen transport via diffusion and convection, with an imposed pressure difference from sub-slab to in-building. They allowed for air exchange and other processes as in the earlier Johnson and Ettinger (1991) approach. In addition, they allowed for first-order biodegradation of the vapours due to the presence of oxygen.

They surmised that for a low concentration source (2 mg/L) located at a depth of 4 m below the base of a slab, biodegradation might reduce  $\alpha$  (effectively the exposure concentration in the building) by a factor from 10 to  $>10^7$  for first-order biodegradation rates of 0.018–1.8 hr<sup>-1</sup>. For a high concentration source (200 mg/L) located at a depth of 5 m below the base of a slab, biodegradation might reduce the concentration by a factor from 10 to  $>10^5$  for the same range of first-order biodegradation rates.

Davis et al. (2009b) and the Australian data in the body of this report suggest that reaction rates are rapid when oxygen is present. Table 6 is adapted from Abreu and Johnson (2006), for high degradation rates (but limited by oxygen availability). For a depth to source of 4 m, biodegradation is estimated to reduce  $\alpha$  by a factor of over 1000 for a 200 mg/L petroleum hydrocarbon vapour source and over 1,000,000 for a 2 mg/L petroleum hydrocarbon vapour source.

**Table 6. Exposure reduction factors for high biodegradation rates (but limited by oxygen availability) – extracted from Abreu and Johnson (2006).**

Exposure reduction factors		
	Maximum vapour concentration (mg/L)	
Depth (m)	2	200
2	1,000,000X	7.5X
3	>1,000,000X	50X
4	>1,000,000X	1400X
6	>1,000,000X	>1,000,000X
8	>1,000,000X	>1,000,000X

### 5.4 Lundegard et al. (2008)

Lundegard et al. (2008) reported an experiment to determine the transport of oxygen from the atmosphere to below a slab-on-ground building overlying petroleum-impacted soil. They flushed nitrogen gas beneath the slab and observed oxygen recovery over time. The house had an areal footprint of 200 m<sup>2</sup> with an adjoining garage of an additional 50 m<sup>2</sup>. Along one side of the house there was a 27 m long concrete driveway and walkway that was about 3 m wide for the bulk of its length. Importantly, because of the shape of the house, the maximum distance from the edge of the slab to any monitoring point beneath the slab was approximately 3.4 m (ignoring the concrete walkway). The primary hydrocarbon of concern was methane at a concentration up to 14% by volume at a depth of 1.5–1.8 m below slab or ground surface. In this interval TPH was 10,000–20,000 g-TPH/kg-soil.

Before flushing with nitrogen, Lundegard et al. (2008) consistently measured oxygen and no methane at depths shallower than 1 m beneath the slab. Flushing with nitrogen removed the methane and oxygen from beneath the slab, but after approximately 30 days oxygenated conditions returned to all locations across the sub-slab area. In this case, despite the very shallow source, oxygen ingress dominated methane flux. These data would imply a significant reduction in risk at this house due to aerobic biodegradation processes.

A similar occurrence has been observed in Queensland at Site E (see Table 1). At this site a gravel layer overlies a clay layer which contained the source of hydrocarbon vapours. Oxygen was always observed to be present in the shallow layer beneath the slab with no vapours present above detectable concentrations. The flux of oxygen through the shallow gravel layer and underneath the house slab seemed to dominate the flux of vapours upwards from the tighter clay materials below.

## **5.5 Implications**

Biodegradation can be significant when oxygen is present. For slab half-widths of less than 5 m, biodegradation can reduce petroleum hydrocarbon fluxes by a number of orders of magnitude even for modest depths to source zones ( $\geq 3$  m).

The dimensions of a slab can influence the extent of oxygen penetration and hence the biodegradation of petroleum hydrocarbon vapour.

If layering is apparent, then a coarse layer overlying a finer soil or clay can be advantageous for oxygen ingress and hence enhanced biodegradation of petroleum hydrocarbon vapour.

## 6. Recommendations

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The recommendations in this section are given in the context of the preceding information and discussion. They are framed to be protective of human health, to be simple to apply, and are based on the best available information to-date. It is likely that further application and information will bring to light refinements that should be adopted in the future.

The recommendations relate to slab-on-ground buildings, but could also be applied to ventilated crawl-space buildings. Although the underlying principles are applicable, to reduce complexity, buildings with basement have not been explicitly considered. The recommendations can relate to existing, or planned, slab-on-ground buildings. For planned buildings, if site soil conditions are not to be altered unduly during development, and proposed building slab sizes are approximately known, then the recommendations can be followed. Significant uncertainty regarding soil variability or heterogeneity (e.g. structured or fractured soils) may be an *a priori* condition that disqualifies a Tier 1 assessment regardless of the biodegradability of the vapours of concern.

### 6.1 Recommendation 1 – Primary criterion: the presence of oxygen

**Recommendation:** Subject to exclusions in Recommendations 2 and 3, to apply an exposure reduction factor based on aerobic biodegradation at a Tier 1 or screening level, it is recommended that oxygen be at a concentration above 5% by volume in a soil gas sample recovered in close proximity to the building (or in a similar nearby soil, soil moisture, soil coverage environment) or where building is planned. Because of sampling uncertainties at shallow depths and the need for oxygen to penetrate beneath a slab-on-ground building to apply a reduction factor, it is recommended that the sampled depth for oxygen be no less than 1.0 m below ground or the planned elevation of the ground where the elevation (or planned elevation) of the bottom of the building foundation (slab) is less than 0.3 m below ground. Where the slab penetrates the ground by more than 0.3 m, then the additional depth of penetration of the slab below 0.3 m should be added to the depth at which a sample will be recovered for analysis for oxygen.

**Rationale:** Where oxygen is present, biodegradation of petroleum vapours is observed. Hence, a primary requirement for aerobic biodegradation to occur is the presence of oxygen in the soil profile. Other factors such as nutrients, soil moisture, and appropriate microorganisms are less limiting. The requirement for a direct measurement of the oxygen concentration in the soil profile is because oxygen can otherwise be consumed by natural organic carbon or reduced inorganic chemicals (e.g. sulphides) in the topsoil, or by respiration associated with deeper rooted vegetation. Also, potentially, oxygen can be inhibited in its movement into the soil by elevated soil moisture or capping layers. Direct measurement removes those limitations. If this is not feasible at a site, then no default reduction factor is recommended for a site.

At depths shallower than 1.0 m, biodegradation can occur if oxygen is present. However, sampling for oxygen at shallow depths can be confounded by ground surface effects such as transient weather conditions or the presence of previously disturbed soils or heterogeneities. Also, to ensure oxygen can migrate laterally beneath a slab-on-ground structure, oxygen penetration at a concentration of 5% to a nominal depth of 1.0 m below ground seems appropriate, assuming the slab does not intrude significantly below ground. Note that, for variable slab sizes (lengths and widths), and variable depths to source and source concentrations, more detailed modelling would improve estimates of the depth of oxygen penetration into the soil, compared to lateral migration beneath a slab. No such modelling has been carried out for variable slab sizes.

The soil oxygen measurement(s) could be taken beneath an existing building but this is not a requirement. Such a measurement could be an advantage and may imply greater biodegradation. However, sampling beneath a slab may also be considered beyond a Tier 1 screening assessment.

## 6.2 Recommendation 2 – Exclusion/inclusion criterion: source depth

**Recommendation:** It is recommended that an exposure reduction factor due to biodegradation only be considered for soil profiles with a vapour source at a depth greater than or equal to 2.0 m below the base of a building.

**Rationale:** This Recommendation is largely based on modelling described in Davis et al. (2009b) and in Appendix A, which balances the potential for oxygen movement into a soil profile with the vapour flux upwards from a source located some depth below ground surface. For a low concentration vapour source at a depth of 2 m the theoretical maximum concentration of oxygen (by volume) at a depth of 1 m is approximately 10% (see estimates in Table 7, based on the approach in Appendix A). Recommendation 1 states that an oxygen concentration of 5% or greater be measured at a depth of 1 m or greater below ground surface for a biodegradation reduction factor to apply. Since oxygen consumption due to natural organic matter and other processes can occur in a soil profile, a theoretical maximum value of 10% is taken here to ensure that there is a high potential for measurement of an oxygen concentration of  $\geq 5\%$  by volume at a depth of 1 m or greater. Note that for very high vapour source concentrations (e.g. 200 mg/L) the theoretical maximum value of the oxygen concentration at a depth of 1 m is much less than 10% by volume (see Table 7 and Appendix A).

**Table 7. Theoretical total depth (m) of penetration of oxygen (and depth of 10% oxygen by volume), for different maximum soil vapour concentrations and source depths below ground surface, where the ground surface is open to the atmosphere (i.e. 20% oxygen in air).**

Theoretical depth of penetration of oxygen (depth of 10% oxygen by volume) in metres					
	Maximum vapour concentration in the source (mg/L)				
Depth of source below ground (m)	2	20	50	100	200
2	1.98 (0.99)	1.82 (0.91)	1.65 (0.83)	1.40 (0.70)	1.08 (0.54)
2.5	2.48 (1.24)	2.30 (1.15)	2.06 (1.03)	1.75 (0.88)	1.35 (0.68)
3	2.97 (1.49)	2.76 (1.38)	2.47 (1.24)	2.10 (1.05)	1.62 (0.81)
4	3.97 (1.99)	3.68 (1.84)	3.29 (1.65)	2.80 (1.40)	2.16 (1.08)
6	5.95 (2.98)	5.53 (2.77)	4.94 (2.47)	4.20 (2.10)	3.23 (1.62)
8	7.93 (3.97)	7.37 (3.69)	6.59 (3.29)	5.60 (2.80)	4.31 (2.16)

Note that the depths in Table 7 are calculated for open ground conditions, and do not represent the oxygen concentration depth beneath a building. Together with Recommendations 1 (depth of oxygen sample) and 3 (slab size), Recommendation 2 represents the potential for oxygen to move beneath certain sized buildings.

### 6.3 Recommendation 3 – Exclusion/inclusion criterion: foundation dimensions

**Recommendation:** It is recommended that a reduction factor due to biodegradation only be considered for slab lengths whereby the location of the furthest point of the house/building is no more than 7.5 m from the edge of the slab. If a slab is square this would imply a slab dimension of 15 m x 15 m (an area of 225 m<sup>2</sup>). Note that a rectangular house with one dimension less than or equal to 15 m would also fit this criterion.

**Rationale:** Extensive building foundation dimensions (e.g. slab lengths) seem to lead to restrictions to oxygen penetration from the ground surface to beneath a building. This can lead to potentially higher sub-slab vapour concentrations. The research discussed earlier by Patterson and Davis (2009) and Abreu and Johnson (2005, 2006) would imply that slab dimensions up to this scale would continue to allow oxygen ingress and petroleum hydrocarbon vapour concentration reductions of a scale that is equivalent to that in Recommendation 4. At least an equivalent amount of oxygen is likely to penetrate beneath ventilated crawl-space buildings, leading to aerobic biodegradation. It could be argued that even greater attenuation due to biodegradation may occur for such construction types, but no detailed evaluation has been carried out here for application to crawl-space constructions. It is noted that advective, pressure-driven air flow in the shallow zone may also deliver additional oxygen to the subsurface. This is not explicitly considered here. DeVaul (2007) allowed for this in his work.

It is recognised that the actual maximum slab size chosen as a cut-off point is somewhat arbitrary, and that oxygen penetration and the magnitude of biodegradation would be similar for slab sizes slightly greater or slightly smaller. Although Abreu and Johnson (2006) investigated the additional biodegradation that would be applicable for deeper sources or lower source concentrations, the scalability of reduction factors due to the size of the slab has not been considered in detail. Such modelling would enable better estimation of the extent of oxygen penetration laterally beneath slabs. Without such additional information, from either modelling or measurement, it is difficult to determine reduction factors for buildings of a greater slab size, especially for application at a Tier 1 or screening level. This would be a point of refinement as more investigations are carried out and other information becomes available.

#### **6.4 Recommendation 4 – Exposure reduction factor due to biodegradation**

**Recommendation:** It is recommended, that where oxygen is found at a site as per Recommendation 1 and that exclusions described in Recommendations 2 and 3 do not apply, then a reduction factor of ten-fold be applied at Tier 1 that is attributable to biodegradation for sources greater than 2 m deep. For sources greater than 4 m, a reduction factor of 100 should be considered for application, where the vapour source maximum is less than 100 mg/L.

**Rationale:** Previous studies have observed (attenuation) reduction factors due to biodegradation that range from 1 to many thousands. Typically, for greater depths to the source and/or low petroleum vapour source concentrations high vapour concentration reductions due to biodegradation are observed. For shallow depths to the source, and/or high petroleum vapour source concentrations, more modest reductions due to biodegradation are observed. A ten-fold reduction in risk seems conservative across most situations reviewed, given that Recommendations 1, 2 and 3 are adopted and applied. For depths to the source of 4 m, or greater, significant biodegradation has been observed and modelled. These warrant an exposure reduction factor of 100, if there is significant confidence in the measured oxygen concentration and the site is not overly complex. Table 7 indicates that even for the highest vapour concentrations considered here (e.g. 200 mg/L) the potential depth of penetration of oxygen (L) is greater than 2 m for depths to the source of 4 m and greater.

Note that this is a Tier 1 or screening level assessment and as such greater attenuation due to biodegradation may be applicable given more investigation at a site through Tier 2 or other assessments.



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## APPENDIX A.

### (Abridged from Davis et al. 2009b)

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Here we develop a simple model of oxygen diffusion into a soil profile open at ground surface balanced by the efflux of petroleum hydrocarbon vapours and biodegradation within the soil profile. The model is used to estimate the potential for oxygen to migrate into the subsurface and be available for aerobic biodegradation, beside or in the vicinity of a building.

### Model equations

For this approach, consider steady-state hydrocarbon vapour diffusion from a constant concentration source  $C_{H,max}$  at a depth  $z=L_{max}$  at the base of a soil profile. Consider also oxygen diffusion from a constant maximum concentration  $C_{Ox,max}$  at ground surface  $z=0$ . Assume that the hydrocarbon vapours instantaneously react with oxygen at the depth  $z=L$ , and also decrease to zero at this location. Under these assumptions the simple equations for oxygen,  $C_{Ox}(z)$ , and hydrocarbon vapour,  $C_H(z)$ , concentrations become:

$$C_{Ox}(z) = C_{Ox,max} (1 - z/L) \quad (1)$$

$$C_H(z) = C_{H,max} [1 - (L_{max} - z)/(L_{max} - L)] \quad (2)$$

The balancing of fluxes at  $z=L$  gives:

$$D_{Ox}C_{Ox,max}/L = \gamma D_H C_{H,max}/(L_{max} - L) \quad (3)$$

where  $D_{Ox}$  is the oxygen diffusion coefficient,  $D_H$  is the hydrocarbon vapour diffusion coefficient and  $\gamma$  is the stoichiometric mass of oxygen consumed per mass of hydrocarbon consumed in the biodegradation reaction. Rearranging, we can define the depth  $L$  as:

$$L = L_{max} / (1 + 1/\eta) \quad (4)$$

where  $\eta = D_{Ox}C_{Ox,max}/(\gamma D_H C_{H,max})$  measures the undersupply of oxygen flux ( $\eta < 1$ ,  $L/L_{max} \rightarrow 0$ ), or oversupply of oxygen flux ( $\eta > 1$ ,  $L/L_{max} \rightarrow 1$ ) with respect to the hydrocarbon flux.

If all assumptions are valid, the model only requires *a priori* knowledge of the maximum oxygen and hydrocarbon concentrations, their diffusion coefficients and the stoichiometry of the hydrocarbon biodegradation reaction. Note that the parameter values required to calculate  $L$  are simply obtained, or would normally be required for a conservative vapour modelling assessment as per the Johnson and Ettinger (1991) modelling approach. The maximum hydrocarbon vapour concentration can be measured directly, or can be estimated from soil or groundwater concentrations as per usual methods, and again is required to apply the standard Johnson and Ettinger (1991) modelling approach.

Note that for layered soils,  $D_{Ox}$  and  $D_H$  may be replaced with effective diffusion coefficients calculated according to the usual harmonic averaging method (e.g. Crank 1975, p.267).

## Example values for Australian field sites

Estimated values of L are given in Table A1.1, for the field sites described in Tables 4 and 5. In summary, Davis et al. (2009b) showed that the simple model was useful for estimation of values of L, when compared to measured values, besides situations where there is substantial layering in the soil profile. They also found that if the texture and soil moisture content of the soil profile were uniform, then the free air values of the diffusion coefficients for oxygen and hydrocarbon vapours could be used. This obviates the need to have knowledge of the total and air-filled porosity of the soil which would be needed otherwise to estimate the effective diffusion coefficients for oxygen and hydrocarbon vapours.

**Table A1.1. Estimated depths L for the depth profiles described in Tables 4 and 5.**

Site	Location or date	Estimated L from Equation (4) (m) <sup>3</sup>	
		Using D <sub>eff</sub> values <sup>1</sup>	Using D <sub>free</sub> values <sup>2</sup>
A	Open ground	2.5	2.5
A	Under building	N/A	
B	Summer	1.2	1.7
B	Winter - wet layer	1.0	1.6
C	Open ground	1.6	1.5
D	Fill - clay layer. Aug 2003	3.3	3.2
D	Fill - clay layer. May 2004	2.2	2.2
D	Verge Aug 2003	2.1	2.2
D	Verge May 2004	1.3	1.3
E	Beside a building	1.5	1.2
F	Apr 2002	4.6	4.8
F	Oct 2002	~5	5
G	Open ground	8.5	6.4

<sup>1</sup> Using D<sub>Ox,eff</sub> and D<sub>H,eff</sub> as shown in Table 5.

<sup>2</sup> Calculated using D<sub>Ox,free</sub>=2.01x10<sup>-5</sup> m<sup>2</sup>/s (Gliński and Stępniewski 1985), D<sub>H,free</sub>=8x10<sup>-6</sup> m<sup>2</sup>/s (Grathwohl 1998).

<sup>3</sup> Assumes γ = 3.5 g oxygen per g of hydrocarbon vapour.

## Generic estimates and application

Table A1.2 and Figure A1.1 provide generic estimates of L using free air diffusion coefficients for oxygen (2.01x10<sup>-5</sup> m<sup>2</sup>/s from Gliński and Stępniewski 1985) and benzene (8x10<sup>-6</sup> m<sup>2</sup>/s from Grathwohl 1998), a stoichiometry coefficient of 3, and the oxygen concentration in air of 279 mg/L.

As indicated, the value L is an estimate of the potential depth of penetration of oxygen into a soil profile open to the atmosphere (i.e. 20% oxygen in air). The value of L varies with the maximum petroleum hydrocarbon vapour concentration (C<sub>H,max</sub>) and its depth in the soil profile. Note that C<sub>H,max</sub> may be measured directly, or estimated from soil or groundwater concentrations as is commonly done when applying the Johnson and Ettinger (1991) model approach.

**Table A1.2. Theoretical values of L = total depth (m) of penetration of oxygen (and 50% of L = depth of 10% oxygen by volume), for different maximum soil vapour concentrations and source depths below ground surface.**

Theoretical depth of penetration of oxygen (depth of 10% oxygen by volume) in metres					
	Maximum vapour concentration in the source (mg/L)				
Depth of source below ground (m)	2	20	50	100	200
2	1.98 (0.99)	1.82 (0.91)	1.65 (0.83)	1.40 (0.70)	1.08 (0.54)
2.5	2.48 (1.24)	2.30 (1.15)	2.06 (1.03)	1.75 (0.88)	1.35 (0.68)
3	2.97 (1.49)	2.76 (1.38)	2.47 (1.24)	2.10 (1.05)	1.62 (0.81)
4	3.97 (1.99)	3.68 (1.84)	3.29 (1.65)	2.80 (1.40)	2.16 (1.08)
6	5.95 (2.98)	5.53 (2.77)	4.94 (2.47)	4.20 (2.10)	3.23 (1.62)
8	7.93 (3.97)	7.37 (3.69)	6.59 (3.29)	5.60 (2.80)	4.31 (2.16)

L is always less than the total depth of the soil profile and the depth to the maximum concentration of the vapour source ( $L_{max}$ ). At depths greater than L, the model suggests that the oxygen concentration will be zero, so there is little point sampling for oxygen at this depth in the profile. At a depth of 50% of L, theoretically, oxygen concentrations can be approximately 10% (i.e. > 5%) if no other oxygen consumption occurs in the soil. At depths between 50% of L and L, theoretically, the oxygen concentration can be above 5% but sampling at this depth has a greater likelihood of being less than 5% due to other potential oxygen consumption in the soil profile.

Recommendation 2 states that the vapour source must be no less than 2 m below a building. Estimates of L in Table A1.1 illustrate the reason for this exclusion distance. For a 2 m depth, and especially for high concentration vapour sources the 10% oxygen concentration is estimated to be at depths of 0.7 m for a source of 100 mg/L and 0.54 m for a source of 200 mg/L. For the 200 mg/L source, the oxygen concentration should not be found above 5% by volume at a depth of 1 m (which is a primary requirement as stated in Recommendation 1), and for the 100 mg/L source it would be highly unlikely (theoretically the 5% oxygen concentration would occur at a depth of 1.05 m). For lower source concentrations the potential is greater for oxygen concentrations to be above 5% at 1 m, but at a screening level it is not possible to distinguish all source concentration and depth to source combinations, whilst retaining a simple approach. Also, for lower source concentrations it may be that a standard conservative vapour intrusion assessment will yield a low exposure that would not warrant sampling for oxygen to qualify for adoption of an additional biodegradation reduction factor. If source vapour maxima are very high (e.g. 100–200 mg/L) then exclusions could also be applied for depths to the source zone even greater than 2 m. For example in Table A1.2, for a maximum vapour concentration of 200 mg/L at a depth of 2.5 m, 50% of L is 0.68 which would predict that the oxygen concentration at 1 m would be less than 5% – thus probably discouraging sampling as per Recommendation 1. But generally at this depth, for the broader range of vapour source concentrations there is potential for oxygen to be greater than 5% at a 1 m depth. An exclusion is not recommended for these possible variants, so as to retain a simple approach and since an oxygen measurement is required in any case to satisfy Recommendation 1.

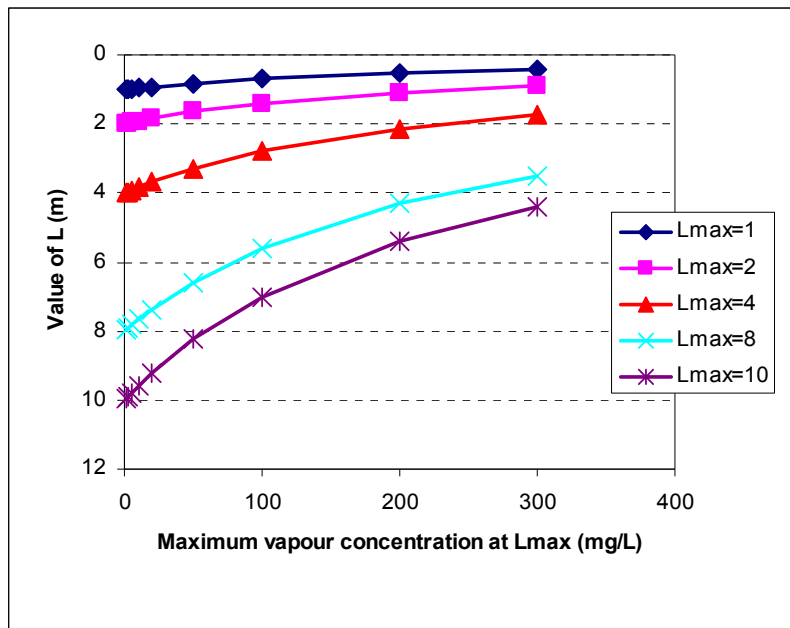


Figure A1.1. Calculated values of L from Equation (4) for free air diffusion coefficients for oxygen ( $2.01 \times 10^{-5} \text{ m}^2/\text{s}$  from Gliński and Stępniewski 1985) and benzene ( $8 \times 10^{-6} \text{ m}^2/\text{s}$  from Grathwohl 1998), a stoichiometry coefficient of 3, and the oxygen concentration in air of 279 mg/L.

Note that *a priori* calculation of L and 50% of L, may provide a guide to site owners, consultants and regulators that oxygen can theoretically be above 5% by volume at a 1 m depth, and hence that sampling for oxygen is worthwhile. Alternately, such a calculation can show that the oxygen concentration should not be above 5% by volume, in which case it can provide a quality control on oxygen data obtained at sites.

Note that the value of L is calculated for open ground conditions, and does not represent the oxygen concentration interface beneath a building. Together with Recommendations 1 (depth of oxygen sample) and 3 (slab size), Recommendation 2 represents the potential for oxygen to move beneath certain sized slab-on-ground buildings.





CRC CARE Pty Ltd  
ACN 113 908 044  
University of South Australia  
Mawson Lakes  
South Australia 5095

P.O. Box 486  
Salisbury South  
SA 5106  
Australia

**Tel:** +61 (0) 8 8302 5038  
**Fax:** +61 (0) 8 8302 3124  
**Email:** [admin@crccare.com](mailto:admin@crccare.com)  
**Web:** [www.crccare.com](http://www.crccare.com)



Established and supported  
under the Australian Government's  
Cooperative Research Centres Programme