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technical report

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

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Executive summary

The review of the Australian National Environment Protection (Assessment of Site Contamination) Measure (NEPM), and workshops in Australia over a number of years involving regulators, industry representatives, consultants and researchers, have motivated the need to review and recommend a model of vapour behaviour for use in the development of health-based screening levels (HSLs) in Australia. In particular, suggestions from a recent workshop held on the Gold Coast Queensland, Australia in February 2008 led to the development of this summary report.

Here, the processes underlying vapour behaviour are described and two models are compared for their utility in modelling petroleum vapours in soil profiles and as they move from the subsurface into built structures. In addition, the need for inclusion of biodegradation and finite lifetime sources in modelling approaches during the development of HSLs is considered.

Four primary recommendations are made concerning:

1. a model appropriate for immediate development of petroleum vapour HSLs in Australia
2. the need for additional National Workshops to develop the built environment scenarios that should be modelled for Australia and to agree the parameter values that will be used in the models
3. the need to include biodegradation in development of less conservative HSLs, and
4. the need to incorporate finite or infinite sources in vapour models.

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1. Introduction

1.1 Background and focus

On 26 February 2008 at Conrad Jupiters (Gold Coast, Queensland, Australia), CSIRO convened a Petroleum Vapour Modelling Workshop on behalf of the Cooperative Research Centre for Contamination Assessment and Remediation of the Environment (CRC CARE). This was part of a larger CRC CARE program of work that aims to generate health screening levels (HSLs) for volatile organic compounds (VOCs) in soil and groundwater environments in Australia.

The motivation for the project was the expressed need by the Australian National Environment Protection (Assessment of Site Contamination) Measure (NEPM) variation team to have vapour models reviewed and develop field assessment guidance specifically for Australia, and the broader desire to develop health investigation levels (HILs) for potentially hazardous volatile compounds.

The focus of the workshop was petroleum hydrocarbon vapours – although the larger CRC Project and the NEPM variation consider a broader range of vapours. Regardless, the outcomes of the workshop and this report, apart from those related to aerobic biodegradation, can also pertain to chlorinated hydrocarbon vapours. The specific aim of the workshop was to outline findings on vapour modelling of petroleum hydrocarbons, to workshop options, leading to a recommended model for use in Australia for development of HSLs. If the vapour model recommended here is adopted for use in development of HSLs in Australia – subsequently, a review of model parameter inputs and a parameter sensitivity analysis are planned to be undertaken.

Those who attended the workshop included representatives of state regulatory agencies in Australia (New South Wales Department of Environment and Climate Change, Western Australian Department of Environment and Conservation, Environment Protection Authority Victoria, Queensland Environmental Protection Agency, Environment Protection Authority South Australia), consulting companies (GHD, Coffey Environments, URS and ERM), industry (Shell, Exxon-Mobil, BP), CRC CARE, and CSIRO.

In Section 1.2, a listing of a fuller range of models is provided. For clarity, in this Section we outline the recommendations from the workshop which focused the scope for reporting.

From the meeting, it was recommended that:

1. A critical comparison of the attributes of two primary vapour models be conducted – the two primary vapour models being:

   a) Turczynowicz and Robinson (2003, etc.) and variants, and

   b) Johnston and Ettinger (1991, etc.) and variants.

   Such a comparison was to lead to a recommendation as to a vapour model that would be suitable to use in establishing human health screening levels – for possible adoption in the revised NEPM (Assessment of Site Contamination) guidelines in Australia.

2. Consideration be given to inclusion of biodegradation in the vapour model to avoid instances of undue conservatism apparent in many existing vapour models and assessments.
3. Consideration be given to inclusion of finite (versus infinite) sources into models of vapour behaviour and assessment.

It was also agreed that:

- as a part of the broader scope of work to develop HSLs, that it would be desirable to generate HSLs, with and without biodegradation, for each setting/scenario – to be applied in situations where there is confidence that biodegradation is occurring, and situations where there is little confidence that biodegradation is occurring
- it was desirable that whatever model is recommended that it be capable of further site-specific stages of assessment (Tier 2 etc.), not just a Tier 1 assessment, and
- it was desirable that the model be easily usable, have some record of application, and be available without undue delay.

This report provides an overview of the key processes that are important to consider in a vapour model, a comparison of two primary models, and recommendation of one that would be usable in the Australian context. There are a number of vapour migration models available for the generation of HSLs and undertaking higher-tier risk assessments. However, as suggested at the workshop, this report focuses on a comparison of only two models as this enables a suitable analysis of the key physical and model properties. Some comments and recommendations are also provided regarding inclusion of biodegradation processes, and the need for models to include finite (versus infinite) sources.

Firstly, in the following Section, a listing of available models and packages and some of the modelling comparison studies are summarised.

1.2 Other models

During the workshop it was recognised that many papers and reports related to the modelling of vapours have been published – some include:

- Ostendorf and Kampbell (1991)
- Johnson and Ettinger (1991) [denoted J&E hereafter]; Johnson et al*.* (1998, 1999)
- Little et al*.* (1992)
- Sanders and Stern (1994)
- Ferguson et al. (1995); Krylov and Ferguson (1998)
- Jeng et al. (1996)
- Waitz et al. (1996)
- Sanders and Talimcioglu (1997) [based on Jury et al. (1990) and Sanders and Stern (1994)]
- Ririe et al. (1998, 2002)
- Davis et al. (1998, 2005, 2009)

- Öhman (1999)
- Turczynowicz (and Robinson) (2001, 2003, 2007)
- Robinson (2000, 2003, 2005) (and earlier papers by Anderssen, Markey and others (1996, 1997))
- Trefry et al. (2000, 2001)
- Evans et al. (2002) and Hers et al. (2002)
- Parker (2003)
- Wright and Howell (2004)
- Abreu and Johnson (2005, 2006)
- Mills et al. (2007)
- DeVaull (2002, 2007).

Publicly available and packaged models are less numerous but include:

1. US EPA – Johnson and Ettinger (1991) [denoted J&E hereafter]
2. RISC (Risk Integration Software for Cleanup) – a compilation of J&E variants (see RISC 2006)
3. VAPEX3 (Env Systems and Technol. Inc. 1998) – based on J&E
4. GSI RBCA Toolkit (Groundwater Services Inc. 1995, 1998) – based on a J&E framework
5. British Columbia Model (Hers et al. 1997) – based on J&E
6. Canada – PHC CWS (2003) spreadsheet model – based on J&E
7. Orange County Health Care Agency (OCHCA) – Daugherty (1991)
8. VOLASOIL – Waitz et al. (1996) based on Jury et al. (1990)
9. Soil Risk – Behaviour Assessment Model based on Jury et al. (1990)
10. RISC-Human 3.1 (Risk Identification of Soil Contamination) – contains CSOIL and VOLASOIL.

Most of these packaged models are based on the J&E model (Items 1–6), with a number based on the Jury model (Items 8–10). In an Australian context, the Turczynowicz and Robinson (2001) and Trefry et al. (2001) models could also be included in the list, but neither appear to have publically available or packaged variants.

Reviews and descriptions of the range of models can be found in Evans et al. (2002)/Hers et al. (2002) and more recently in overview in Davis et al. (2004), Tillman and Weaver (2005) and Turczynowicz and Robinson (2007).

Evans et al. (2002) (also reported in part in Hers et al. (2002)), reviewed ten vapour transport models based on contents, benefits, limitations and suitability for UK conditions. Their aim was to recommend a vapour model as part of the multi-pathway **c**ontaminated **l**and **e**xposure **a**ssessment model (CLEA). Five models (GSI, British Columbia Model, VOLASOIL, RISC and Ferguson et al. (1995)) were shortlisted and compared using a common soil contamination scenario and a parameter sensitivity analysis. Except for VOLASOIL, calibration studies were carried out for these models against data from three field sites. They found that no one model satisfied all criteria, but they recommended RISC (2006). They also found that models incorporating diffusion and advection based on the J&E framework would in most cases result in predictions for petroleum hydrocarbons that are conservative by up to one or two orders of magnitude providing that appropriate input parameters are used.

Davis et al. (2004) referenced the comparative review of Evans et al. (2002), the model of Turczynowicz and Robinson (2001) and other models, but limited their detailed description to four main modelling tools – US EPA (2003) J&E spreadsheet model, an earlier version of RISC (2006), GSI RBCA Toolkit (2004) and the PHC CWS (2003). All embody variants of the J&E approach.

Tillman and Weaver (2005) provide a brief description of each of the models published by J&E (1991), subsequent refinements in Johnson et al. (1998, 1999), Little et al. (1992), Sanders and Stern (1994), Ferguson et al. (1995), Waitz et al. (1996), Jeng et al. (1996), Sanders and Talimcioglu (1997), Krylov and Ferguson (1998), Ririe et al. (1998), Olson and Corsi (2001) and Parker (2003). They do not recommend any one model, but stress the need to consider uncertainties and parameter sensitivities in any model used.

Turczynowicz and Robinson (2007) noted a range of models – providing descriptive discussion of the attributes of many of those listed above. They pointed to variability in field assessments of the J&E model, and compared that variability with the Jury et al. (1983) Behavioural Assessment Model (BAM). They concluded that 'vapor intrusion modeling reflects variability and uncertainty, and a significant need for complete field validation'.

2. Overview of primary petroleum vapour processes

Figure 1 shows some of the transport zones of interest (source zone, soil zone and building zone) that need to be considered in modelling petroleum vapours, and the primary active processes that transport vapours from a subsurface source towards the ground surface, and ultimately lead to concentration estimates in buildings. Greater detail can be found in Davis et al. (2004) and other references.

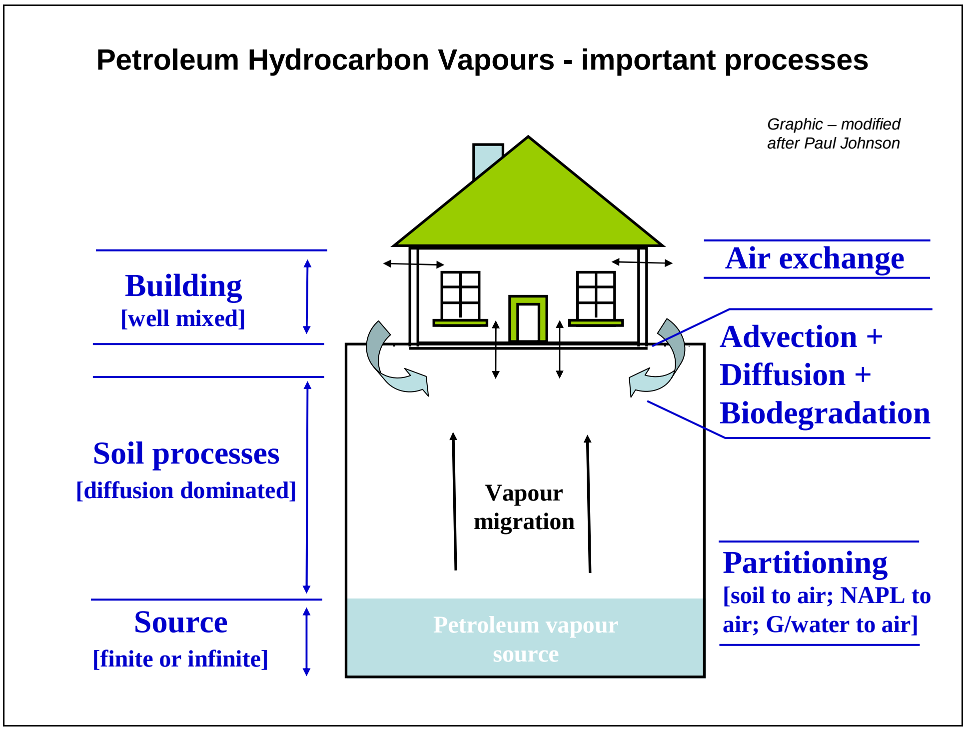

Figure 1. Zones (compartments) of vapour movement (source, soil, building) and prominent processes, in the vicinity of a building. A graphic produced by Paul Johnson was used as the basis for this figure.

2.1 Source zone

Hydrocarbon vapours emanate from petroleum source zones at some depth below ground surface in the soil profile (see Figure 1). This zone can extend from the ground surface. Vapours partition into an air phase either:

1. by desorption from soil organic matter, based on the sorption coefficient and the fraction of organic carbon in the soil
2. from groundwater plumes, based on the Henry's Law partitioning coefficient between water and air (and other factors, like the depth of the plume below the capillary fringe), and/or
3. from non-aqueous phase liquids (NAPL), based on the vapour pressure of the volatile compounds in the NAPL and the mole fraction of the compound of interest (and some other factors).

All partitioning processes can occur concurrently.

The different source types (e.g. gasoline, crude oil, diesel) and these partitioning processes govern the final vapour concentration (and composition) observed in the air phase near the source zone. This source vapour concentration can be estimated based on knowing the parameters that relate to the partitioning process and the source conditions, or can be measured more directly via soil gas sampling. Both approaches to determining the source vapour concentration have advantages and disadvantages.

2.2 Soil profile

Primarily, transport of hydrocarbon vapours from the source zone (see Figure 1) vertically upwards through the bulk of the soil profile is dominated by diffusion processes. During transport the hydrocarbons will continue to partition between water, air and soil organic matter phases and will tend towards the establishment of equilibrium concentrations in all phases.

2.3 Shallow near-surface zone

In the shallow near-surface zone advection, diffusion and aerobic biodegradation are all probable transport and attenuation mechanisms for hydrocarbon vapours (see Figure 1). Advection occurs due to (usually small) pressure differences between that found in the soil and that found above ground surface either in the dwelling, or in open ground conditions. The pressure difference may be due to activities within the building (e.g. heating/cooling, opening and closing of doors/windows, air conditioning), or climatic and other conditions external to the building (e.g. wind, barometric pressure changes, temperature changes). In this zone, advection can accelerate movement of persistent vapours into the building. Diffusion also continues to act as a transport mechanism in this zone. Aerobic biodegradation of petroleum hydrocarbons is most active in this zone because oxygen moves into the soil through the ground surface from the atmosphere above. Note that biodegradation needs to occur in an aqueous phase and as such is considered to occur in the soil water phase, rather than the soil gas phase.

2.4 In the building

Vapours that migrate into the building (see Figure 1) mix with air that is in the building. Air in the building may either be trapped or may be part of a gaseous exchange between the building volume and the external atmosphere (usually of lower chemical concentration). In most models, the assumption in the building is that it is a well mixed environment, and as such all concentrations throughout the building are the same.

2.5 Additional zones

In some models, additional zones might be included. For example, an additional crawl-space may be specified beneath the floor of the house and above the ground surface. In this case, the exchange of vapours is controlled by conditions at the ground surface, the exchange rate in the crawl-space, and the flux of vapours from the crawl-space to the interior of the house above the crawl-space. Another example of an additional zone is the transition zone in the soil profile within which biodegradation may vary from high to low. This sometimes corresponds with the zone over which oxygen concentrations transition from atmospheric at ground surface to low concentrations nearer the source zone of hydrocarbon vapours.

2.6 Key parameters

A range of physicochemical processes and characteristics govern vapour movement and the resultant concentration in a building. Key parameters include the source concentration and its depth below the foundation of the building, the source longevity, soil properties which generate the diffusion coefficient estimate such as soil moisture and air-filled porosity, the building type and size, the air exchange rate in the building, the advective soil gas inflow rate, sorption and partitioning processes if transient effects are of interest, and biodegradation in the soil profile. There are many studies of model parameter sensitivity, e.g. Evans et al*.* (2002) and Tillman and Weaver (2006). The source longevity, soil gas inflow rate and building ventilation rate have been reported to change potential exposures by up to tenfold, the soil properties may yield changes of ten to a hundred times, and biodegradation can change exposure estimates by over three orders of magnitude, depending on the depth to the source and the source vapour concentrations. For example, Tillman and Weaver (2006) show the importance of synergistic uncertainties in model parameters, and the effects on vapour exposure estimates.

3. Turczynowicz and Robinson (T&R) model

3.1 Background to the T&R model

In a series of papers, Len Turczynowicz and Neville Robinson reported on the development of a mathematical model to describe the behaviour of vapours as they move from a vapour source zone towards a building at ground surface. The aim of the papers was to develop health investigation levels (HILs) for Australian conditions.

The concepts for the modelling papers were based on earlier papers of Anderssen and Markey (see Anderssen et al*.* 1997; Anderssen & Markey 1997; Markey & Anderssen 1996), which were in turn based on the continuum Jury model (see Jury et al*.* 1983, 1990), first developed to describe the movement and volatilisation of pesticides in soils.

The T&R papers are listed separately in the Reference section (Section 7). There are likely to be other reports or technical documents not captured here – but it is believed that this list is a reasonable reflection of the T&R approach to vapour modelling. Listed are four published journal papers, a confidential technical report, and two papers in the proceedings of *The Fifth National Workshop on the Assessment of Site Contamination* held in Adelaide in 2002. There are an additional two CSIRO confidential technical reports not listed, as they appear to be embodied in the other papers referred to here – reference to them can be found in Robinson (2003). The T&R papers are cited in subsequent papers 12 times (based on a Google Scholar Search conducted in March 2008).

3.2 Features of the T&R model

The basic features and assumptions of the T&R model include:

- vertical one-dimensional model (infinite depth)
- equilibrium partitioning between water, soil (sorbed) and air (vapour) phases
- diffusive transport of vapours
- aqueous and gaseous phase advection may occur
- depleting (finite) source
- transient exposure to vapours
- a stagnant boundary layer at ground surface to transition vapours from the soil to the building
- first order biodegradation of the vapours in the soil and in the air of the crawl-space
- initially developed for a crawl-space house, and a source located from ground surface to some distance below ground.

The primary contribution has been to include a stagnant boundary layer at the soil surface to allow accumulation of vapours at the ground surface when a built structure is in place, and to be one of the first to consider in detail such behaviour for a crawl-space building. Of importance too is the collation of available Australian data to estimate parameter values in the model.

Robinson (2003) provides a theoretical description of boundary conditions for a wider range of scenarios (other than a crawl-space with shallow soil pollution). No outcomes from these scenarios seem to be available in the published papers or public reports.

More recent contributions expanded the model to radial coordinates (Robinson & Turczynowicz 2005) and allowed the initial distribution of vapours in the model to be located in a discrete interval below the ground surface (c.f. Turczynowicz & Robinson 2001 and Turczynowicz 2003, which had the source zones starting from the ground surface). The status of the work and possible further work was described in Turczynowicz and Robinson (2007).

3.3 Application of the T&R model and packaging

The main application of the T&R model has been to develop draft HILs for a crawl-space dwelling built immediately on top of petroleum-contaminated soil. These are reported in Turczynowicz and Robinson (2001) and Turczynowicz (2003) as draft HILs for potential exposure to benzene based on this scenario, and these are further referenced in T&R (2007). To develop the draft HILs, the model assumed a finite source distributed from ground surface to a prescribed depth of 3 m, which depleted over approximately two years for the parameter values taken for the model. Benzene half lives were taken to be 1.1 years in soil and 13 days in air in the crawl-space.

Mills et al*.* (2007) expanded the T&R approach to a crawl-space and basement structure, and compared their model estimates to field data from a trichloroethene (TCE) impacted site. A comparison with Turczynowicz and Robinson (2001) is included in the supporting information for Mills et al*.* (2007) and although boundary conditions and other factors required alteration, essentially identical results were obtained for time varying cumulative indoor air dose within a dwelling with a crawl-space.

No other applications to slab-on-ground or basement style buildings or use of the model for generating exposures are apparent for the T&R model.

The T&R model exists as executable Fortran code. Data are entered as data files (Robinson, pers. comm.).

No specific model validation and comparison with field data has been published, apart from the third-party work reported in Mills et al*.* (2007). In Mills et al*.* (2007) the comparison was to chlorinated solvent field data, rather than petroleum hydrocarbons.

4. Johnson and Ettinger (J&E) model

4.1 Background to the J&E model

Paul Johnson with Robert Ettinger developed and published a heuristic vapour modelling paper in 1991 (Johnson & Ettinger 1991), and then Paul Johnson published a series of papers on the application of the model, and most recently a three-dimensional numerical vapour model (Abreu & Johnson 2005, 2006) to test vapour exposure sensitivities to building dimensions, depth to source, source concentration and biodegradation. The original J&E (1991) model was largely based on understanding provided by field vapour data available at the time, and models developed for radon movement into buildings (see e.g. Nazaroff & Sextro 1989).

The J&E papers are listed separately in the Reference section (Section 7). There are likely to be other reports or technical documents not captured here – but it is believed that this list is a reasonable reflection of the J&E approach to vapour modelling. Listed are six published journal papers and a number of American Petroleum Institute (API) Bulletins. The J&E papers are cited in subsequent papers 161 times (based on a Google Scholar Search conducted in March 2008). The initial contribution by J&E (Johnson & Ettinger 1991) has been cited 94 times, and critically reviewed and commented on by a number of authors (e.g. Tillman & Weaver 2006, 2007). In addition, it has been compared against field data in numerous papers and reports (e.g. Hers et al. 2002, 2003).

4.2 Features of the J&E model

The basic features and assumptions of the J&E model include:

- vertical one-dimensional model (finite depth)
- contaminant vapours enter buildings primarily through cracks and openings in the walls and foundation
- advective transport is likely to be the most significant in the region very close to a basement or foundation, and vapour velocities decrease rapidly with increasing distance from the building
- vapour-phase diffusion is the dominant mechanism for transporting contaminant vapours from sources located away from the foundation to the soil region near the foundation
- all vapours originating from directly below the basement or foundation will enter the basement or foundation, unless the floors/walls are perfect vapour barriers
- the soil profile is homogeneous, or consists of multiple homogeneous layers
- the vapour source is constant (so infinite), and located some distance below the ground surface
- typically, the vapour distributions do not change with time (i.e. are steady state) – the original paper contains transient options as well
- mass loss due to biodegradation does not occur (later versions include first order biodegradation of the vapours, layered biodegradation, and oxygen-limited biodegradation).

The primary contribution has been to establish a model structure for vapour movement from the subsurface to the interior of slab-on-ground and basement buildings.

4.3 Application of the J&E model and packaging

The J&E model has been applied numerous times to assess vapour exposures, in many countries. The model has been applied to various soil types, building constructions (slab-on-ground, and basement mostly), and scenarios. It has rarely been applied to crawl-space dwellings – but suggestions on how to do so are available (Robbie Ettinger, pers. comm.), and Mills et al*.* (2007) compared a variant of J&E for both a basement and crawl-space building.

The model has been packaged in several ways – most significantly as a US EPA-approved spreadsheet (see http://www.epa.gov/oswer/riskassessment/airmodel/johnson_ettinger.htm) (see also US EPA 2002, 2003), and a number of other ways such as in the Risk Integrated Software for Cleanup package (RISC 2006).

The US EPA spreadsheet tool is commonly used to calculate risks and develop health protective screening levels for indoor air due to vapour intrusion. There are some distinctions between the J&E algorithm/model and the US EPA spreadsheet (see Johnson 2005). The US EPA developed and published guidance on the use of the spreadsheet (see http://www.epa.gov/oswer/riskassessment/airmodel/pdf/2004_0222_3phase_users_guide.pdf) (see also US EPA 2003) and also developed an uncertainty analysis (Tillman & Weaver 2006) and default parameter values and parameter ranges (Tillman & Weaver 2007) that would provide upper and lower bounds on parameters and predicted exposure concentrations.

The RISC package (see RISC 2006) embodies the J&E model in four forms – as indicated in Table 1. It is available at http://www.groundwatersoftware.com/risc.htm.

Table 1. Vapour model options in RISC – based on J&E model approach.

Assumption/fate and transport processes	Vapour model without degradation	Dominant layer model	Oxygen-limited model	Vapour model from groundwater
Source term	Soil gas or soil	Soil gas or soil	Soil gas or soil	Groundwater
Layering/ heterogeneity	May have two layers	May have three layers	Homogeneous	May have two layers plus cap. fringe
Degradation	No	Yes, in middle layer	Yes, if oxygen conc. high enough	No
Model oxygen conc.	No	No	Yes	No
Considers pressure driven flow by building	Yes	Yes	Yes	No

The model has been used and applied extensively, and has many variants. A comprehensive evaluation of the J&E model is included in Hers et al*.* (2003) including comparisons of model-predicted and measured vapour intrusion for eleven petroleum hydrocarbon and chlorinated solvent sites. They found that the J&E model was a conservative estimator of potential exposure – overestimating potential vapour concentrations in buildings. They also stressed the need for care in selecting appropriate model input parameters.

5. Synthesis

In recommending a petroleum vapour model for use in developing HSLs for Australia, a number of factors need to be considered, some of which were articulated at the Gold Coast Vapour Modelling Workshop on 26 February 2008. The main factors were:

1. Fit for purpose – will the model deal with Australian conditions?
2. Desire for one model that could possibly be used in Tier 1 or higher assessments.
3. Desire that the model be capable of including biodegradation – to avoid undue conservatism.
4. Desire that the model be capable of simulating transient conditions, e.g. including finite sources – to avoid undue conservatism if a source has a short lifetime.
5. Model be easily usable, having some public record of application, and be available without undue delay.

5.1 Fit for purpose – will the model deal with Australian conditions?

Both models are fit for purpose in terms of taking account of the key transport and attenuation processes that would govern vapour behaviour under Australian conditions. Both models allow for soil parameters that span the range seen in Australia, and they both allow for source conditions that may be observed in Australia, although building directly onto petroleum-impacted land as assumed in the T&R crawl-space model may require risk management of other more prominent exposure pathways (e.g. dermal contact or ingestion).

The two models have focused on different building construction types. At present the T&R model has focused on outcomes related to crawl-space houses and J&E has focused on slab-on-ground and basement buildings, although application of the J&E model to crawl-space buildings has been somewhat addressed by Ettinger (pers. comm.) and Mills et al. (2007).

Specific to Australian conditions are the parameters values that are suitable to go into the model – these include parameters such as the air exchange rate for buildings, moisture-filled and air-filled porosity of the soils, and the time of exposure in a building. In developing the HSL estimates for Australia, such parameter estimates need to be agreed between stakeholders at subsequent workshops.

5.2 Desire for one model that could possibly be used in Tier 1 or higher assessments

Greater sophistication in model processes may be warranted at complex sites or where greater realism is required in terms of Tier 2 (or higher) assessments. For example, neither model accounts for spatially variable soil parameters (e.g. air-filled porosity) although layering is allowed in J&E, and T&R suggest modifications that could account for layering. Neither also allow transients in terms of barometric or other advective forcing – all factors that can affect vapour behaviour.

In Table 2 we divide important features of soil vapour models into those characteristics of importance in a Tiered approach to exposure assessment. Tier 1 characteristics correspond to the minimum number of processes needed in order to perform a rapid screening of vapour exposure. Tier 2 and higher assessments may require the inclusion of additional processes and an increasing amount of site-specific data where the Tier 1 screening levels are exceeded. The table entries are populated largely based on T&R (Robinson & Turczynowicz 2005; Turczynowicz & Robinson 2003) and J&E (Johnson & Ettinger 1991; Johnson et al. 1999).

Table 2. Attributes of Tier 1 and Tier 2 (and higher) models, and assessments of the J&E and T&R model approaches against these.

Tier 1 Attribute	**J&E**	**T&R**
Steady source term	✔	✕
Depth to source	✔	✔
Diffusion	✔	✔
Advection	✔	?
Equilibrium sorption	✔	✔
Basement	✔	✕
Slab	✔	✕
Crawl-space	?	✔
Ingress pathways (cracks, holes etc)	✔	✔
Building dimensions	✔	✔
Multi-component	✔	✕
Ventilation	✔	✔
Partitioning from NAPL or groundwater	✔	✕
Biodegradation (first order)*	✔	✔
Oxygen-limited biodegradation*	✕	✕
Tier 2 or Higher Attribute	J&E	T&R
Layering	✔	✕
Transient source term	? ✔	✔
Soil saturation profile	✕	✕
Soil moisture advection	✕	✔
Climatic variations (temperature, pressure, soil saturation)	✕	✕
Building materials	✕	✕
Forced convection from volatilisation	✕	✕
Density effects	✕	✕
Capillarity	✕	✕
Coupled vapour degradation modelling	✕	✕

**Previously, most often considered a Tier 2 feature. Without including biodegradation processes, undue conservatism for petroleum hydrocarbons seems apparent.*

The table entries for Tier 1 characteristics show that the T&R model considers crawl-space dwellings, but not slab-on-ground or basement dwellings considered by J&E. J&E was not originally designed for crawl-space houses but has been used for such cases – hence the '?' in Table 1 against this attribute. T&R describe the expansion of their model to other building types (see Robinson 2003; Turczynowicz & Robinson 2007) but there are no available model outputs or example applications. Pressure-driven advection and multi-component data suites are handled explicitly by J&E but not by T&R, making practical use of the J&E results much simpler than T&R. Both models handle biodegradation simplistically, and do not include the understanding that oxygen availability is a limiting factor to biodegradation. This aspect is considered to be a pre-requisite of the model used to develop the HSLs where biodegradation is occurring (see Section 5.3 below).

Typically in Tier 2 assessments, site-specific data is used. In such cases, both models are applicable where they contain the processes that are still relevant given the extra conceptual understanding from site-specific data. For complex cases, neither model contains enough of the additional processes to be a strong candidate for higher order assessments, unless the focus for the higher order assessment is solely based on the availability of a greater intensity of site-specific data.

5.3 Desire that the model be capable of including biodegradation – to avoid undue conservatism

The T&R approach includes first order biodegradation of the vapours in the soil and in the air phase in the crawl-space. Johnson & Ettinger (1991) did not include biodegradation, but later modifications (e.g. Johnson et al*.* 1999) included first order biodegradation of the vapours in the soil (see also Table 1).

Field data and investigations suggest that the primary driver for biodegradation of petroleum hydrocarbon vapours is the presence of oxygen (see Davis et al*.* 1998, 2005, 2009). As such, petroleum hydrocarbon vapour biodegradation is believed to be limited by oxygen availability or be 'oxygen-limited' – see Davis and Ritchie (1986) as another example of oxygen limited bio-reactions. Hence, the transport and flux of oxygen into the soil and beneath the dwelling may be as equally important as vapour movement up through the soil profile from the petroleum vapour source zone. Combined consideration of oxygen transport downwards into the soil, and vapour transport upwards through the soil seems to be required in models if they are to adequately represent aerobic biodegradation processes and estimate potential rates of biodegradation of petroleum hydrocarbon vapours.

Typically, oxygen moves in the soil profile from the atmosphere above ground and is transported by diffusion through the soil and possibly advective processes (pressure differences). Abreu and Johnson (2005, 2006) embed such a process into a three-dimensional numerical model. Öhman (1999) also developed such a one-dimensional model, and compared it against field data (see also Trefry et al*.* 2000, 2001).

In a simple one-dimensional model, DeVaull et al*.* (2002) considered reducing the flux of vapours reaching the building based on the estimate of oxygen flux coming into the soil from above. DeVaull (2007) expanded this oxygen-limited approach. The DeVaull (2007) model in essence included all aspects of the J&E approach, but accommodated oxygen ingress via advection (air flow) and diffusion. A difficulty with the approach is the requirement for an estimate of the volumetric flow of air carrying oxygen into the soil – i.e. the rate of advective flow (or flux) of oxygen. Such estimates are available, but this approach may not lead to a 'conservative-enough' way of embodying oxygen-limited biodegradation into a vapour model.

Incorporation of appropriate oxygen-limited biodegradation is being actively considered by researchers and by other jurisdictions. Amongst other US State Agencies (e.g. New Jersey Department of Environmental Protection), the California Department of Toxic Substances Control (DTSC) is currently also considering how aerobic biodegradation can be included in petroleum vapour assessments.

Despite its absence in either of the current J&E and T&R models, further consideration of oxygen-limited biodegradation may be required to develop HSLs that remain protective of human health.

5.4 Desire that the model be capable of including finite sources – to avoid undue conservatism if a source has a short lifetime

Sources deplete over time, hence assuming an infinite source in a model of vapour exposure is a conservative assumption. *A priori*, it may be difficult to assess the life-span of a vapour source, even though depletion occurs on an ongoing basis. Often contamination instances are not characterised until years to decades after a release incident, and yet for significant releases vapours can still be present in the subsurface – especially for gasoline range fuels.

Turczynowicz & Robinson (2001) explicitly define a finite source in their vapour model. Their later papers describe other source scenarios, but do not publish vapour exposure estimates for those scenarios. J&E use a steady state approach assuming a constant (infinite) source, but also includes transient (finite) source approximations in the Johnson & Ettinger (1991) paper for situations where the source has a longevity much less than the exposure time (residence time in the building).

In Turczynowicz & Robinson (2001) and Turczynowicz (2003), vapour exposure estimates are provided for a source that effectively has a lifetime of two years. Where source configurations and subsurface conditions are uncertain, this may not be a conservative approach. This would be further exacerbated if non-aqueous phase liquid (as a mobile or immobile phase) were present at a site. Assuming a shortened source lifetime (e.g. two years) would need to be weighed against the intensity of characterisation data available for a site to ensure the assumption of a substantially shorter exposure time is valid (two years compared to perhaps 70 years if the default Australian resident lifetime exposure is used).

5.5 Model be easily usable, having some public record of application, and be available without undue delay

Sections 3.3 and 4.3 give information pertaining to aspects of this. The T&R model is available as executable Fortran code from Neville Robinson – the structure of the code appears to be described in a CSIRO Confidential Technical Report (see Robinson 1999). This report was not sourced for this review. There appears to be no publicly available code. It has been applied to a crawl-space building construction only, and for a finite source located at ground surface. Other applications are not apparent. The model has only had limited review and has not been widely assessed. However, note the recent adaptation by Mills et al*.* (2007). Also, the Jury BAM model which forms the basis of the soil transport aspect of the T&R model has been widely applied, but less so in vapour studies. Although other combinations/scenarios are described in Robinson (2003) and Turczynowicz & Robinson (2007), it is not clear what other embodiments of source/building types are available in code form. Any need for further code development could unduly delay the development of HSLs in the current time frames of interest to the NEPM variation team and CRC CARE.

The J&E model is available in spreadsheet form via the US EPA website, or in other packaged forms, such as RISC (RISC 2006). Data input is directly into the US EPA spreadsheet or via a user-friendly interface in RISC. It has been used and applied extensively, and critically evaluated against field data (see Hers et al*.* 2002, 2003, and earlier comments in this report).

6. Recommendations

6.1 Recommendation 1 – Which model?

Recommendation: Of the two models evaluated, the J&E model is recommended for use for development of HSLs in Australia.

Rationale: Both the J&E and T&R models could be used for modelling vapour behaviours, for development of HSLs in Australia. The model itself is simply a framework that incorporates the key physicochemical vapour transport processes. Parameter values that populate the model ensure it reflects Australian conditions (see Recommendation 2). As indicated in Sections 4 and 5, the J&E model has had widespread use and application, has been embodied in a US EPA spreadsheet, has been assessed in parameter sensitivity studies by the US EPA and others, and has been compared to field data. It is readily available in a number of forms. In the original Johnson and Ettinger (1991) paper an approximation for finite (transient) source conditions was also provided. In contrast, as indicated in Sections 3 and 5, currently there are a limited number of embodiments and applications of the T&R model, and it does not appear to be easily accessible or available for use.

6.2 Recommendation 2 – Model parameters

Recommendation: Workshops should be held between all stakeholders to agree the built environment/soil type model scenarios and parameter values that would be most applicable to Australian conditions – to be used in the vapour model to generate reliable HSL estimates for Australia.

Rationale: The recommended model should only be considered a framework in which to undertake the estimation of HSLs. The parameters that are used in the model are those that make it reflect Australian conditions. As such, scenarios and conditions specific to Australian soils and built environments need to be taken into account when developing HSLs applicable in Australia. This includes variables to be adopted for tabulation of HSLs, such as depth to source, building type, soil type, contaminant type and possible land use. Also parameter value estimates need to be agreed, such as soil air-field porosities and building ventilation rates amongst others. Importantly, T&R collate some of this data in developing draft benzene HIL values (Turczynowicz 2003; Turczynowicz & Robinson 2001). It is hoped that the recommended model parameter workshops will review what is known and update model parameters values to reflect current knowledge of Australian conditions.

6.3 Recommendation 3 – Biodegradation

Recommendation: For scenarios that are appropriate for the development of HSLs, biodegradation should be included in the modelling of petroleum hydrocarbon vapours. Further consideration should be given to how to adequately and conservatively incorporate oxygen-limited biodegradation into the J&E model for the purposes of HSL estimates. It is proposed that a program of development of HSL without biodegradation be progressed in parallel with further consideration of how best to incorporate oxygen-limited biodegradation.

Rationale: Petroleum hydrocarbon vapour biodegradation is reported to be limited by oxygen availability, and commonly, where oxygen is detected petroleum hydrocarbons are observed to readily biodegrade. A significant number of field investigations have been carried out overseas and in Australia (Davis et al*.* 2009), and a number of modelling papers have recently been published (Abreu & Johnson 2005, 2006; DeVaull 2007) that couple oxygen movement to petroleum hydrocarbon biodegradation. These studies provide a strong basis for considering incorporation of petroleum hydrocarbon biodegradation into a Tier 1 screening level assessment. This approach is not applicable to chlorinated compounds that are not susceptible to aerobic biodegradation.

6.4 Recommendation 4 – Finite or infinite source

Recommendation: It is recommended that further investigation and review be carried out that may assist with the definition of source lifetimes, which may allow finite sources to be incorporated in future HSL estimations. For now, it is recommended that a constant (infinite) source condition be adopted to develop the HSLs in order to ensure adequate conservatism in vapour model outputs and hence protection of human health.

Rationale: The distribution and lifetime of a source of petroleum hydrocarbon vapours is not always known *a priori* for a site, nevertheless depletion of a source will occur over time. Assuming a shortened source lifetime would need to be weighed against the experience available for similar site conditions and/or the intensity of characterisation data available for a site. Currently, no collation of information is available to CSIRO which could be used to support a finite-source approach. Further investigation and review should be carried out, and this should be a discussion point at stakeholder workshops.

7. References

This reference section has three parts:

1. General references (without the T&R and J&E papers)
2. T&R papers only
3. J&E papers only.

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