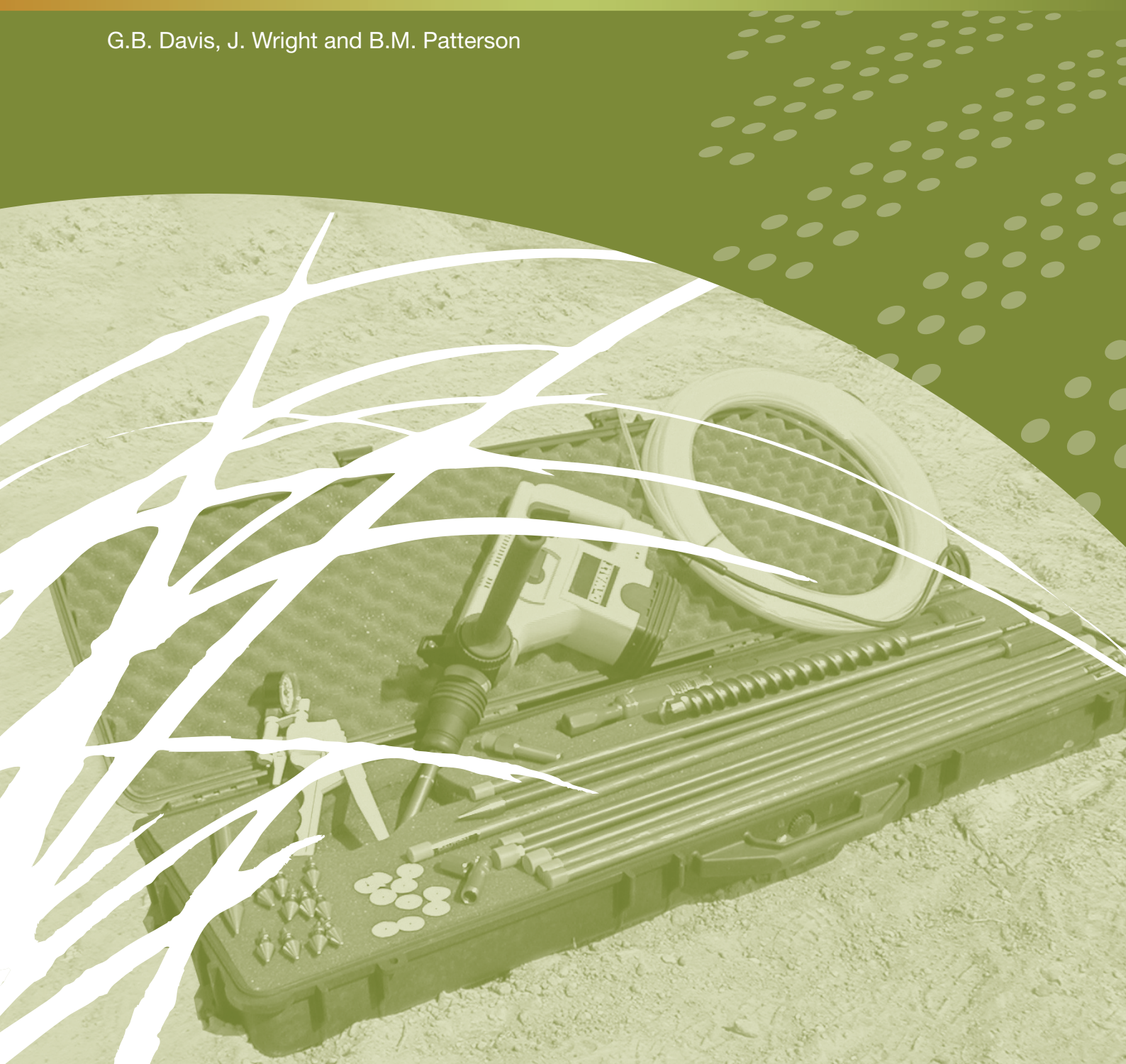


no. 13  
**technical**  
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## Field assessment of vapours

G.B. Davis, J. Wright and B.M. Patterson





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G.B. Davis<sup>1</sup>, J. Wright<sup>2</sup> and B.M. Patterson<sup>1</sup>

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# Executive summary

Australia has no current guidance on the field assessment of volatile compounds for sites where vapours have the potential to migrate into buildings and pose risks to human health. There are recommendations to provide such national guidance. This report updates knowledge available internationally related to guidance and methods of vapour assessment. It is intended to be used with other documentation to inform the variation of the Australian *National Environment Protection (Assessment of Site Contamination) Measure* (NEPM) currently underway.

In this report:

- the processes underlying vapour behaviour are described
- available guidance is reviewed
- a framework for vapour assessment and screening is suggested
- design issues for field assessment of vapours are described
- investigation and sampling techniques are compared, and
- observations from the work are summarised.

It is found that a well-described conceptual site model (CSM) of vapour risk embodies understanding of site conditions, potential vapour behaviour, and priorities for investigation. It serves as the basis for vapour risk assessment along with data quality objectives (DQOs).

Extensive vapour intrusion and assessment guidance documentation has been developed within the United States of America and by industry, but limited guidance is available for other countries. A staged approach (Tier 1, 2, 3 or 4) for vapour assessment is generally adopted across nearly all guidance, however, the breadth of investigation required in each stage is not consistent across the available guidance. The stages of investigation for vapour assessment do not always align with accepted stages of a more general site investigation (Phase I or Phase II environmental site assessments – ESAs, or preliminary/detailed site investigations – PSIs/DSIs).

There is substantial information that would support an exclusion distance approach applicable at a Tier 1 screening level, whereby if a property or building is beyond a set distance to the edge of a vapour source, then it could be excluded from further investigation. Consideration of the use of soil gas vapour concentrations (representative of the direct pathway of exposure), rather than soil concentrations alone, for comparison to health-based investigation level (HIL) screening values seems warranted. In Australia, this may require the development of soil gas HILs for volatile compounds. Where soil vapour assessment techniques are not used at Tier 1, then soil and/or groundwater investigations will be required to assist in the definition of the exclusion distance or to provide data for comparison to HIL screening values.

A variety of vapour assessment techniques are available. Advantages and disadvantages of many are tabulated. Choices of vapour investigation approaches should target improvement and modification of the CSM. Guidance documents recommend a number of approaches. Common elements are, where required and practical, (i) subsurface soil gas samples should be taken no shallower than 1 m, unless adequately justified, (ii) to determine maximum vapour concentrations in the subsurface, samples should be recovered as close as possible to the source (it is acknowledged that this may be particularly difficult for groundwater sources and may not be warranted for very deep sources), and (iii) depth profiles can be useful. Seasonal and short-term atmospheric changes (barometric, etc.) can influence vapour concentrations but this effect decreases rapidly with depth depending on the period of the transient disturbance and the re-equilibration time of the vapour concentrations through the soil profile. Vapour behaviour may need to be assessed over time where shallow sampling is undertaken and where transient behaviour might be expected to occur.

Most experience and investigations have been carried out for petroleum hydrocarbons and chlorinated solvent vapours. Whilst the techniques and approaches may be valid for use for other volatile compounds, for some compounds (e.g. mercury, butadiene) there is limited experience, and hence careful adoption of field approaches would be required.



# 1. Introduction

## 1.1 Background

The risks posed by volatile contaminants in soil and groundwater remain uncertain but a large number of investigations over the last decade have provided greater surety around the behaviour of vapours. Volatile compounds, as vapours, can migrate into buildings and pose a risk to residents or workers. Because of previously high uncertainty in quantifying vapour exposures, conservative assumptions have been adopted. Because of this, the potential for vapours to accumulate in indoor air often became the dominant driver of health risk for an impacted site and thus affected the extent of remediation required (API 1998; Sanders & Stern 1994).

The difficulties associated with assessing such risks across a number of sites in a consistent and uniform manner led to the adoption of risk-based decision making (RBDM) and risk-based corrective action (RBCA) methodologies (US EPA 1995). These methodologies have since been adopted by many nations, and a range of assessment tools have become available to support environmental management and remediation activities within the RBDM and RBCA frameworks.

Understanding of vapour behaviour, techniques for vapour measurement, and design principles for field assessment of vapours at potentially impacted sites are evolving continuously. Internationally (e.g. ASTM 2008; ITRC 2007a; US EPA 2002) and in Australia (NEPC-ASC 2006; NSW DECC 2009) jurisdictions are recognising this and are issuing or planning to issue guidance on vapour assessment.

Currently no national guidance is available in Australia, and a variety of methods and approaches are adopted and used. Review and compilation of approaches and techniques used for vapour assessment seems warranted. Beyond the initial Australian review compiled by Davis, Trefry and Patterson (2004) and guidance from the US EPA (2002), there is a large body of additional research and issued guidance to draw upon (e.g. API 2005; ASTM 2008; ITRC 2007a, 2007b; Golder Associates 2007; GWMR 2009; McHugh & Nickels 2008; NEPC-ASC 2006; NSW DECC 2009; US DoD 2009).

## 1.2 Australian context and scope of report

Recommendation 16 from the *National Environment Protection (Assessment of Site Contamination) Measure* (NEPM-ASC) variation team states (NEPC-ASC 2006):

'Update the Western Australian Department of Environment and Conservation review of models and field methods on the assessment of volatiles. Select and adopt as interim guidance in the NEPM a model(s) and field methods most suited to Australian conditions'.

The Western Australian Department of Environment and Conservation (WA DEC) review (Davis, Trefry & Patterson 2004) provided a status report on vapour behaviours, vapour data observed under Australian conditions, some discussion of vapour assessment techniques, and an overview of available models. To address the 'modelling element' of Recommendation 16, Davis, Trefry and Patterson (2009) reported on a comparative review of two vapour modelling approaches. Based on a variety of criteria, they recommended the Johnson and Ettinger (1991) modelling approach, as applicable to Australian conditions for development of Tier 1 health-based screening levels (HSLs). HSLs using this approach were subsequently reported in Friebe and Nadebaum (2009).

This report does not address vapour modelling *per se*, although some references deal with modelling. In this report we address the other element of Recommendation 16 – field methods for assessment of vapours specifically for Australia. Primarily the methods discussed are targeting chronic low levels of vapour concentrations, but some mention is made of methane which can sometimes be at percent by volume levels in soils.

This report does not explicitly distinguish, but does refer to two types of vapour compounds:

1. those that biodegrade under oxygenated (aerobic) soil conditions, such as petroleum hydrocarbons like benzene, ethylbenzene, toluene and the xylene isomers (BTEX), or some other halogenated organic vapours such as vinyl chloride, and
2. those that do not readily biodegrade under aerobic conditions, such as tetrachloroethene (PCE) or trichloroethene (TCE).

## 1. Introduction

The distinction is made to allow consideration of biodegradation as an amelioration process when considering vapour risks. As such, the measurement of oxygen (and perhaps other major gases) may be required. Risk reduction due to biodegradation has not been generally adopted in the past, but increasingly this is occurring – as reported across a number of jurisdictions in the United States of America and in Canada (Golder Associates 2008). They have mostly adopted a tenfold reduction in risk due to biodegradation of petroleum hydrocarbons. Davis, Trefry and Patterson (2009) suggested that aerobic biodegradation be considered as part of a screening (Tier 1) assessment for petroleum hydrocarbon vapours, and recently Davis, Patterson and Trefry (2009a) recommended how this might be implemented. Additionally, ASTM (2008) specifically provides guidance that distinguishes degradable from non-degradable vapours.

Here we largely focus on hydrocarbon and halogenated (e.g. chlorinated) hydrocarbon vapours. The majority of the discussion pertains to organic vapours. It is noted however, that many of the issues for organic vapours are common to those observed for radon (apart from biodegradation phenomena and the typical distribution of vapour sources), and perhaps mercury vapour. There is a large body of literature related to radon behaviour and exposures that can be used to assess aspects of organic vapour exposures. Some of the radon literature is referenced in Davis, Trefry and Patterson (2004). Further discussion of radon is excluded from this report.

This document provides information on vapour fate processes and behaviour, available vapour assessment guidance, a vapour assessment framework, guiding principles for assessment, and assessment techniques for vapours to help define exposures and risk. Gaps in understanding of vapour-related processes are mentioned.



## 2. Conceptual site model and vapour behaviour

Fundamental understanding of the potential behaviour of vapours in the subsurface and in close proximity to buildings, and the development of a sound conceptual site model (CSM), are important in framing the approach to assessing vapour issues and where required, what and where to measure during a vapour field assessment.

Overall, it is important to identify what is to be evaluated or protected. Is it (i) inhalation exposure targeting chronic (long-term) low levels of vapour concentrations, (ii) potentially higher concentration acute (short-term) exposures, (iii) potential accumulation of explosive/flammable levels of vapours in enclosed spaces, or some other aspect? Here the issue of chronic (long-term) low levels of vapour concentrations is the main focus, but the methods presented may be applicable to alternate foci. In addition, the approach taken may differ if a site is to be assessed where buildings are present and will remain on a site compared to the case where redevelopment is planned and land use and building configurations change.

### 2.1 Conceptual site model

To frame a CSM, historical information about a site use and landform and basic hydrogeological/soil conditions are required, along with climatic conditions, the regional setting, water table levels, potential chemical storage and use, and surface features. Many of these aspects should be determined as part of a preliminary (site) investigation (PSI) or Phase I environmental site assessment (Phase I

ESA). For vapour intrusion assessment, additional details about buildings or planned buildings may be important – including building plans that may define subsurface utilities, the foundation construction, and the ventilation and heating capacity. These should also be considered as part of a Phase I ESA where vapours are to be assessed at a screening level.

CSMs can be expressed in writing or as a diagram, both of which commonly contain:

- assumptions about a source and nature of the vapours
- a pathway through the soil profile (usually driven by diffusion at deeper depths and possibly convection at shallower depth)
- the types and number of buildings or planned buildings on a site
- various exchanges with a building or planned building from sub-foundation to air exchange above ground, and
- in some cases the receptor.

Figures 1–6 are all schematics that have been developed to represent vapour intrusion scenarios and CSMs. Some depict the source-pathway-receptor approach explicitly (see Figures 2 and 5).

Figure 1 emphasises the multiple residential dwelling construction types (slab-on-ground, crawl-space, basement) above vapour sources that might be mobile or residual non-aqueous phase liquid (NAPL), or groundwater. Note that all dwellings depicted are single storey houses.

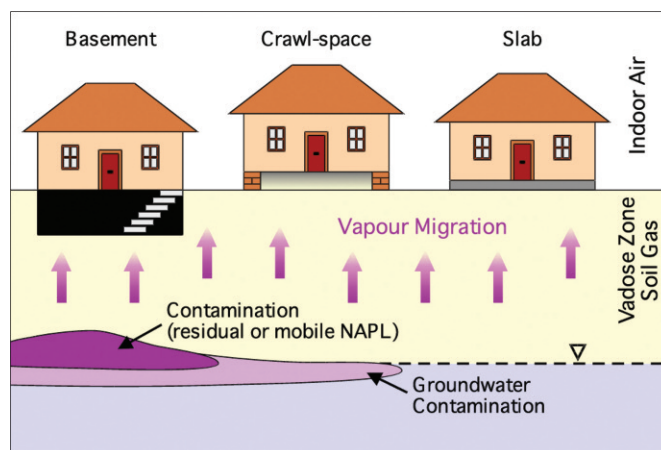


Figure 1. Conceptualisation – modified after US EPA (2002) schematic of vapour intrusion.

## 2. Conceptual site model and vapour behaviour

Figure 2 depicts two storey dwellings and a building, includes receptors (but not children), and the depiction seems to imply that the source is mostly below the water table.

Figure 3 incorporates many more processes, and alerts the viewer to the possibilities when dense NAPLs (DNAPLs) are present leading to deeper groundwater impacts, to recharge processes that may influence vapour fluxes from groundwater, and to lateral vapour movement. The depiction more directly implies an influence of buildings

on vapour behaviour, and suggests that commercial and multi-story buildings should also be considered. It also depicts a buried drum scenario whereby vapours and/or leachate may migrate and subsequently impact groundwater or a soil gas phase. Additionally, it indicates the potential for the attenuation of vapour impact on nearby buildings due to lateral separation of a property some distance from the original vapour source. This aspect is gaining increasing attention (see e.g. ASTM 2008 and later discussion).



Figure 2. Conceptualisation – modified from ITRC (2007a), and used as logo for the US EPA National Forum on Vapor Intrusion held in Philadelphia, PA on 12–13 January 2009.

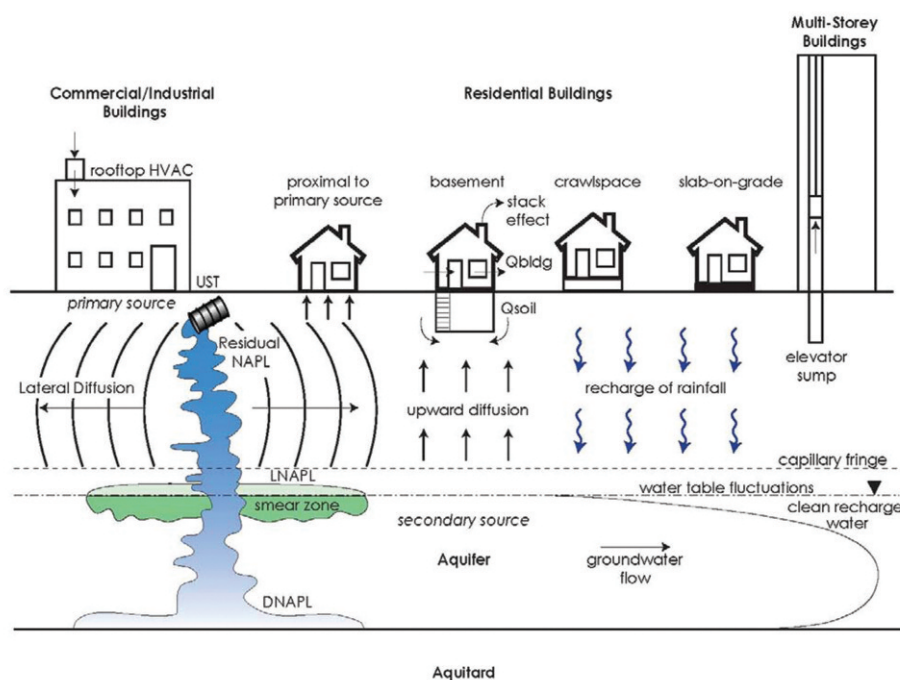


Figure 3. Conceptualisation – from Abreu and Ettinger ('Understanding the Conceptual Site Model for Vapour Intrusion into Buildings', US EPA National Forum on Vapor Intrusion, 12–13 January 2009, Philadelphia, PA).



Figure 4 is a focused depiction of processes and zones or pathways of vapour migration, with some added detail around processes. This figure will be discussed in some detail in Section 2.2.

Figure 5 shows highly sensitive receptors such as a child and baby, but also in this depiction the receptors dominate the graphic, along with the leaking drums – both features that might evoke a greater perception of a threat to receptors.

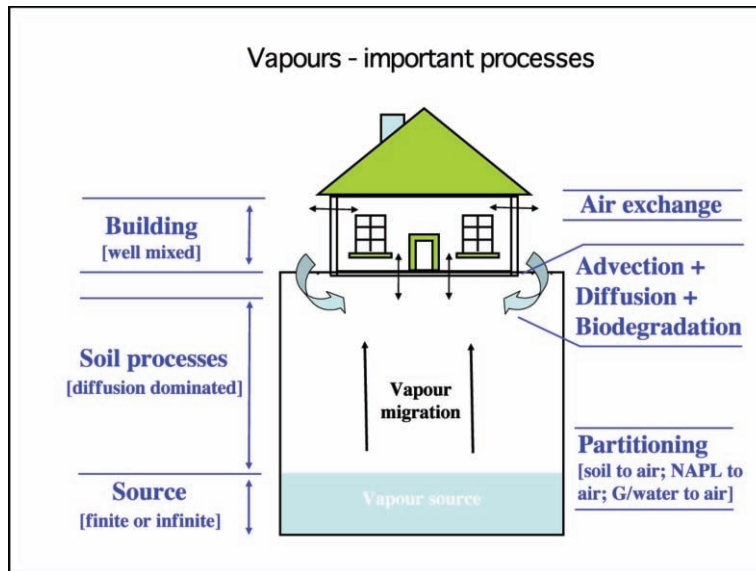


Figure 4. Conceptualisation – modified after a graphic produced by Professor Paul Johnson.

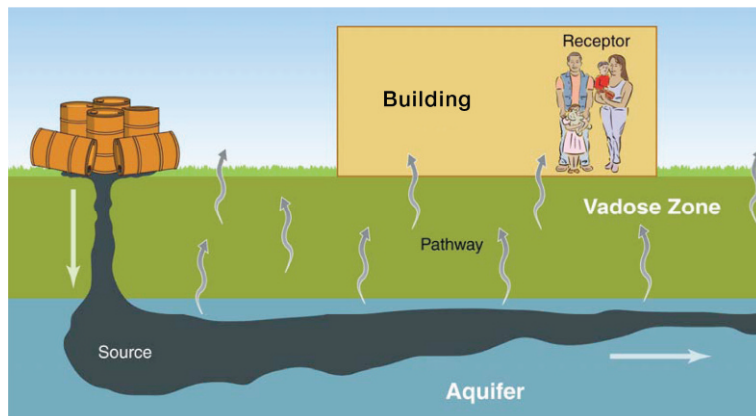
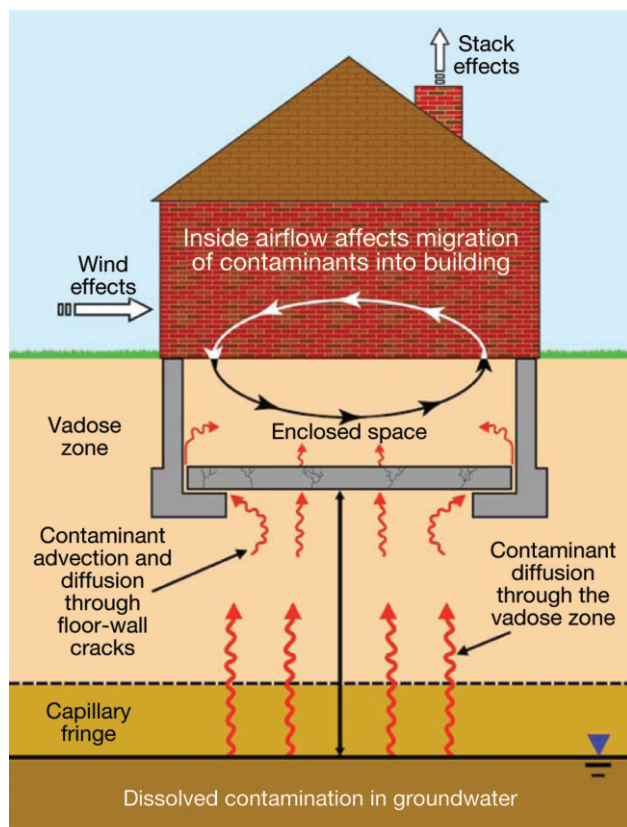


Figure 5. Conceptualisation – from ITRC (2007a).

Figure 6 provides even greater detail of physical processes – focusing on vapours emanating from groundwater through a capillary fringe, and movement through foundation structures such as cracks and foundation gaps, and possibly diffusion through the foundation, with circulation occurring between areas internal to the house.



**Figure 6. Conceptualisation – from ITRC (2007a).**

For a CSM all aspects depicted here could be important at a site. Note that Figures 1–6 are all depicted as two-dimensional depth sections. Consideration should be given to the proximity of the site to other features, such as other buildings, vacant land, vegetated areas, pathways, industrial activities, parking areas, or other topographical features such as roads, wetlands or topographic high points. These could be depicted in a complementary plan sketch or plot. Transient effects may also play a role, so some sense of the scale of such influences may be important to consider in a CSM word or graphical sketch.

Note too that no depiction presented in Figures 1–6 considers utilities and services to the buildings, such as sewer lines, electricity, plumbing, etc. These can play a critical role as conduits for vapours, especially where volatile chemicals have been discharged to sewer lines,

and where such lines leak and where sewer lines and conduits connect to adjoining or multiple buildings. The potential for such aspects should be incorporated into CSM depictions.

Once a CSM is developed, additional data collection and interpretation should be targeted at validation and/or refinement of the CSM.

## 2.2 Vapour behaviour

In establishing a CSM for vapours, and in devising any sampling plan for vapours, it is useful to understand key vapour behaviours and regions or zones of the soil/building continuum in which vapours may behave differently. Roggemans et al. (2001) and Davis, Patterson and Trefry (2006) describe typical depth profiles of vapours that they observed. Figure 4 shows some of the zones of interest (source zone, soil zone and building zone) that may need to be considered for assessment of vapour risks. Here we summarise the primary active processes that transport vapours from a subsurface source towards the ground surface, and ultimately lead to concentration estimates in buildings. A number of models of vapour behaviour embody these main processes. Note that vapour model estimates have typically been shown to be quite conservative, in that models largely overestimate the concentration of vapours, particularly petroleum vapours in buildings. This suggests the need to better understand the underlying processes governing vapour behaviour and the soil/building/atmosphere parameters that may be applicable in models.

We provide example data to illustrate potential vapour behaviour. Greater detail can be found in Davis, Trefry and Patterson (2004) and other references.

### 2.2.1 Source zone

Vapours emanate from source zones at some depth below ground surface in groundwater or the soil profile (see Figure 4). This zone can extend from the ground surface, may have multiple layers if the soil profile is layered, and may contain multiple compounds. There may also be multiple source zones present within the profile, in groundwater or spread across a site.

Vapours partition from sources into an air phase either:

- by desorption from soil organic matter, based on the sorption coefficient and the fraction of organic carbon in the soil

- 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 – see e.g. Barber et al. 1990), and/or
- 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 other factors).

The partitioning processes can all occur concurrently. In addition, further sorption and desorption of vapours to soil organic matter can occur as vapours migrate within a soil profile. Details on these processes can be obtained elsewhere, some of which are described in Davis, Trefry and Patterson (2004).

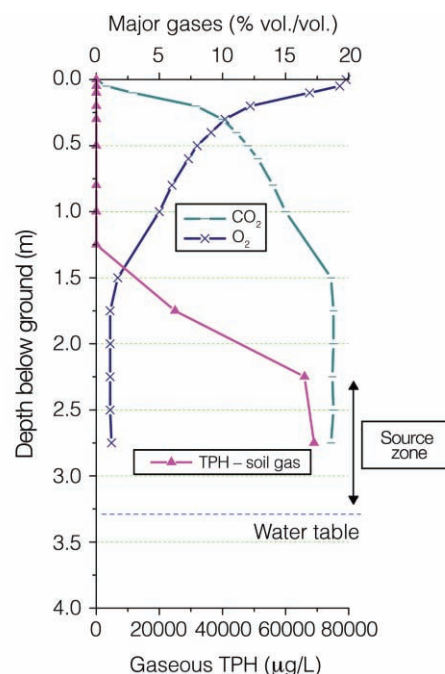
The source type (e.g. fuels like gasoline, crude oil, diesel; or solvents like tetrachloroethene (PCE), trichloroethene (TCE)) and the partitioning processes govern the final vapour concentration (and composition) observed in the air phase near the source zone. This source vapour concentration can be 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. Either approach to determining the source vapour concentration has advantages and disadvantages. Equations and example calculations are given in Appendix A.

For vapours emanating from a groundwater source, vapour fluxes through an overlying soil profile may be much reduced. Diffusion through a water phase is 1000 – 10,000 times less than in an air phase. Davis and Barber (1989) and Barber et al. (1990) document such transitions for methane and other compounds as they move from a dissolved plume below the water table, through the capillary fringe and through the overlying soil profile towards ground surface. Recently, the much reduced vapour fluxes from groundwater sources have been emphasised when considering distances to vapour sources as screening criteria (e.g. ASTM 2008, and see Section 3). Consequently, dissolved groundwater sources may be at much closer distances to a property or building and not pose an unacceptable human health risk, compared to soil or NAPL sources of vapours. This is particularly true for petroleum hydrocarbons that biodegrade aerobically.

To distinguish between groundwater and other vapour sources in applying screening criteria, additional investigations may be required to have enough certainty of subsurface conditions, and the source distribution.

### 2.2.2 Deep soil profile zone

Primarily, transport of vapours from the source zone (see Figure 4) vertically upwards through the bulk of the soil profile is dominated by diffusion processes. During transport the vapours will continue to partition between water, air and soil organic matter phases and will tend towards the establishment of equilibrium concentrations in all phases. Concurrently, atmospheric gases and gases produced from biological processes (e.g. nitrogen, oxygen, carbon dioxide, methane) will also move via diffusion in this zone. Figure 7 shows an example depth profile for petroleum hydrocarbon vapours and major gases through a sandy soil where the only vapour source is deeper than 2.25 m below ground.



**Figure 7. Example depth profiles of total petroleum hydrocarbon (TPH) vapours and major gases (oxygen and carbon dioxide) with a vapour source zone at 2.25–3.25 m below ground.**

### 2.2.3 Shallow near-surface soil zone

In the shallow near-surface zone advection, diffusion and aerobic biodegradation are all probable transport and attenuation mechanisms for vapours (see Figure 4). Advection occurs due to (usually small) pressure differences between that found in the soil and that 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, and positive pressure differences may impede movement of vapours into buildings. 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. Figure 7 shows oxygen ingress over a shallow depth of 1.25–1.50 m, and petroleum vapours decreasing to non-detectable concentrations at this same depth in the soil profile. These observations and carbon dioxide accumulation in the soil profile are all indicators of petroleum vapour biodegradation.

Chlorinated hydrocarbon vapours will not necessarily behave in the same way, however some, like vinyl chloride, may biodegrade aerobically (e.g. Davis & Carpenter 1990). Figure 8 shows tetrachloroethene (PCE) vapour concentrations penetrating to ground surface, while petroleum hydrocarbons (TPH) in the same profile decrease to below detectable concentrations at depths of 1.5–2 m below ground surface due to aerobic biodegradation – even though source concentrations for the TPH are 30 times greater than those for PCE. PCE at this site could be inferred to have a greater potential for accumulation in buildings and posing risk at ground surface despite the source concentration contrast.

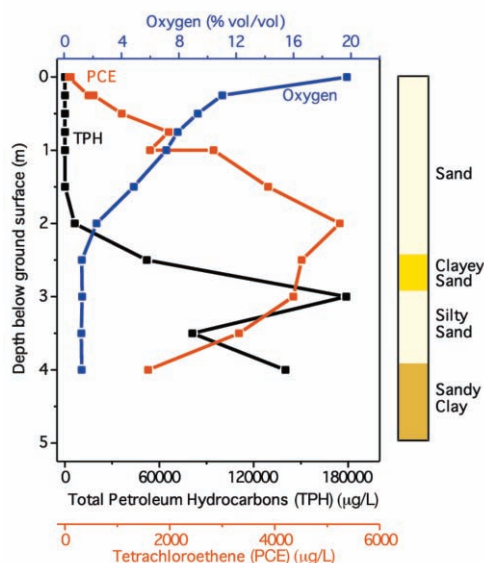


Figure 8. Example PCE and TPH vapour, and oxygen depth profiles.

Additionally, in this shallow near-surface zone the building itself may influence the distribution of vapours. If the ground surface is well sealed from the atmosphere it may increase the potential for vapour accumulation at shallow depths in the soil profile. Hydrocarbon vapour data from beneath a slab-on-ground building shows this effect (Figure 9). At the edge of the structure oxygen penetrates and/or vapours escape through the ground surface. Near the centre of the building vapours accumulate beneath the underside of the slab where vapours can potentially move into and out of the building (due to transient pressure changes) through cracks in the building's foundations. Details can be found in Patterson and Davis (2009) and also some discussion of the effects of buildings on petroleum hydrocarbon biodegradation can be found in Davis, Trefry and Patterson (2009).

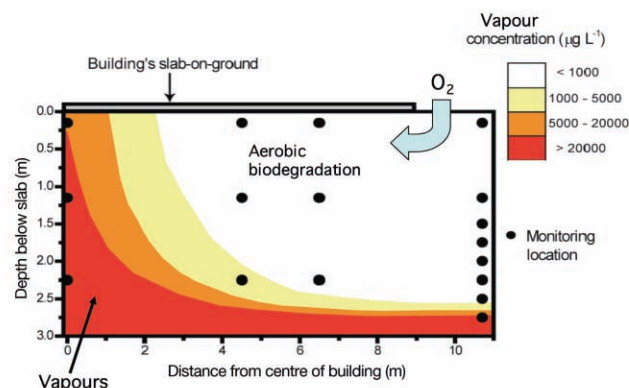


Figure 9. Petroleum hydrocarbon vapour depth cross-section section beneath a slab-on-ground building. The vapour data are contoured based on concentrations determined at each of the monitoring locations. Overlain are a depiction of potential oxygen ingress and the potential zone of aerobic biodegradation.

#### 2.2.4 In the building

Vapours that migrate into the building (see Figure 4) 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). Mostly, buildings are assumed to be well mixed environments, and as such concentrations throughout a building may be assumed uniform. In multi-storey buildings this may not be the case, or where the building is compartmentalised.



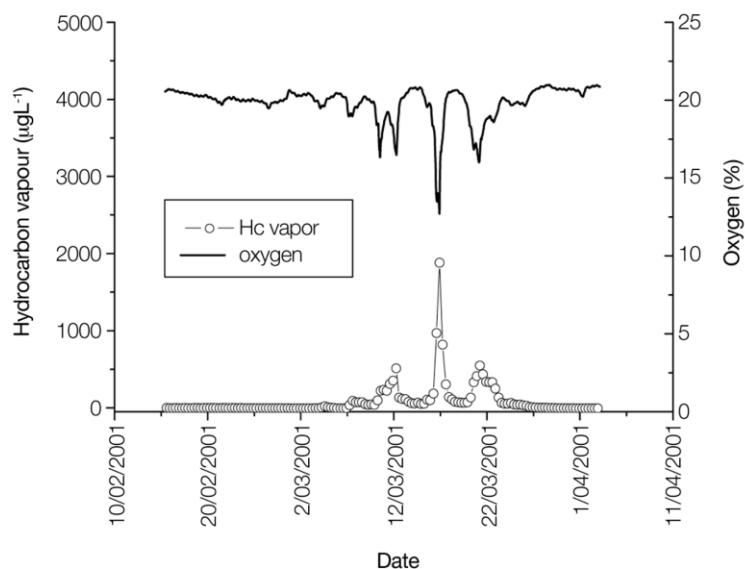
### 2.2.5 Additional zones

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 air 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 at deeper depths (0–1.5 m in Figure 7), and through an anaerobic zone nearer the source of vapours (1.5–3.25 m in Figure 7).

### 2.2.6 Other considerations

Transient issues may be prominent at shallow depths. Vapour and gas profiles can be influenced by daily and diurnal changes in barometric pressures, temperature etc. and seasonal effects – an example is given in Figure 10. When sampling in the subsurface, most guidance (see Section 3) advises sampling below 1 m and sometimes 5 feet (~1.5 m) to avoid biasing samples due to such transients. Shallower sampling points (< 1 m deep) may be warranted to determine if the vapour intrusion pathway is complete, but sampling over time may be required to confirm data.

API (2005, p. 6) also discusses the characteristic time it takes for a soil gas profile to reach steady state (equilibrium) from a step change in the source concentration. The time scale is proportional to the square of the depth to the source of the vapours and linearly proportional to the inverse of the diffusion coefficient (see Appendix A for example calculations). Times may range from days for a high (0.4) air-filled porosity soil with a shallow depth to the source (1 m), up to ~3.5 years for a low (0.1) air-filled porosity soil with a deeper depth to the source (say, 4 m). Higher retardation coefficients will increase these times proportionally. Such characteristic times are useful to estimate the time to equilibration from an initial release of a vapour source, but overestimation may occur due to seasonal effects. Distinct seasons may lead to wetting and drying of the soil profile, inhibiting vapour movement when wet and allowing shallower penetration of vapours when drier (see, for example, Davis et al. 2005), but are unlikely to create a step change in vapour source concentrations – a gradual change may be expected. As such, times estimated using the approach in Appendix A could be overestimates of the time for gradual transition to a new steady state (equilibrium).



**Figure 10. Temporal variations in oxygen and total petroleum hydrocarbon vapour (Hc) concentrations determined using oxygen and VOC probes buried 0.5 m below ground.**



## 3. Guidance documents

There are several guidance documents available for evaluating the vapour exposure pathway and related to vapour assessment, however most have been developed overseas and in particular in the United States of America. The documents discussed here are only representative of a wide range of similar documents now used by regulators, industry and consultants around the world. They reflect the present scientific understanding of subsurface vapour behaviour, assessment and risk processes. Some are also summarised in Table 2.

### 3.1 Australian guidance

There is limited Australian guidance on the field assessment of vapours.

#### 3.1.1 *National Environment Protection (Assessment of Site Contamination) Measure*

The *National Environment Protection (Assessment of Site Contamination) Measure* (NEPM-ASC) was formed in December 1999 (NEPC-ASC 1999). This is currently being varied (revised). It has no specific sections devoted to the investigation of vapours, but the overlying principles of staged site investigation apply.

The NEPM includes two Schedules – Schedule A which gives a general strategy for site investigation, and Schedule B which provides particular sub-schedules containing detailed guidance for site assessment. Schedule A indicates that site assessment should progress in a staged way, from a preliminary (site) investigation (PSI) involving data quality objectives (DQOs), site history, review of local geology and hydrogeology, and establishing a sampling strategy and sampling pattern for soil and groundwater contamination. The PSI also may commonly involve some preliminary intrusive sampling of a site, since such site data are compared to investigation levels (IL) defined in the NEPM-ASC. If soil or groundwater concentrations determined from the site exceed the health, groundwater or ecological investigation levels (HILs, GILs, EILs), then a next stage of detailed site investigation (DSI) is required.

Schedule B includes guidance on investigation levels, data collection and sampling, laboratory analysis, ecological and health risk assessments, community consultation and more. Schedule B (2) documents guidelines for data collection and in particular sample design and reporting for soil and groundwater, but not soil gas. A weighting towards shallow soil sampling is advised where ecological and health risk assessments are required. Deeper soil sampling to determine the nature and potential longevity of a source of vapours moving through the soil profile is noted.

As indicated earlier, the current variation of the NEPM will consider in greater detail vapour risk and assessment (NEPC-ASC 2006).

#### 3.1.2 *NSW DECC*

In February 2009, the New South Wales Department of Environment and Climate Change issued a 'Draft for consultation only' *Guidance Note on Vapour Intrusion* (NSW DECC 2009). This was drafted to address the gap seen in advice to consultants around field assessment of vapours. It is currently being updated and finalised.

It points to the US EPA (2002) and ITRC (2007a, 2007b) guidance, notes the importance of a conceptual site model, provides descriptions of sampling methods, and provides indications of the scope of sampling (number, locations, depths, timing) that may be warranted in a vapour assessment. It suggests that attention be paid to subsurface barriers and conduits, hot spots, sub-slab sampling and multi-slab conditions, internal house structures and seasonal sampling. It promotes a weight-of-evidence approach – suggesting the recovery of a range of samples from multiple locations.

This Guidance Note was only issued as draft and for consultation purposes. It is cited and summarised here with permission from the NSW DECC, and as noted above, it is currently being updated and finalised.



#### 3.1.3 Standards Australia

AS (1999) provides some detail on the precautions and methods for reliable sampling of volatile compounds in soils, including an overview of soil gas sampling protocols. It emphasises that soil type may play a significant role in design and practice of soil gas sampling – it raises issues such as recoverable soil gas volumes during sampling in tight soils, sealing of permanent boreholes to avoid short-circuiting and leakage and the use of inert sampling materials.

## 3.2 Overseas guidance, standards and information

#### 3.2.1 US EPA

The US EPA (US EPA 2002) developed *Draft Guidance for Evaluating the Vapor Intrusion to Indoor Air Pathway from Groundwater and Soils (Subsurface Vapor Intrusion Guidance)*. This contains screening level assessments and was not initially recommended for assessment of underground storage tank sites, because it contained conservative assumptions not necessarily applicable to petroleum hydrocarbons, e.g. no biodegradation.

It explicitly outlines a three Tier (Tier 1, 2 and 3) structure for investigation and assessment of potential vapour intrusion at a site – Tier 1 being an initial screening stage, where little or no quantitative site information is required.

It proceeds to lead the user through a series of questions related to the assessment process and leads through the three Tier approach based on answers to the questions. Sampling and measurement techniques are included in appendices to the draft guidance.

For Tier 1, three questions in the draft guidance focused on identifying (US EPA 2002, p. 14):

- if chemicals of sufficient volatility and toxicity are present or reasonably suspected to be present
- if inhabited buildings are located or are planned to be located above or in close proximity to subsurface contamination, and
- if current conditions warrant immediate action.

Interestingly, US EPA (2002, p. 8) recommends:

‘you consider the possibility of exposure by this pathway if you have or suspect the presence in soil or groundwater, of volatile chemicals (Henry’s Law Constant  $> 10^{-5}$  atm m<sup>3</sup>/mol) at your site as follows:

- located 100 feet or less in depth; or
- located in close proximity to existing buildings or future buildings; or
- to the expected footprint of potential future buildings.’

Close proximity (related to the statements on pages 8 or 14) was stated to be within 100 feet (~30 m) in the vertical or laterally.

This page 8 statement implies a pre-Tier 1 step whereby a site or building can be excluded from further investigation when it is beyond a specified distance from a vapour source. ASTM (2008), described in this Section, formalises this approach.

US EPA (2008) outlined vapour intrusion considerations for redevelopment of brownfield sites. It describes the importance of a conceptual site model, and itemises some sampling strategies for soil gas largely pointing to ITRC (2007a), US EPA (2002) and other guidance for general approaches and methods. It provides a tabulation of state regulatory guidance.

#### 3.2.2 ASTM International

Note that ASTM was formerly the American Society for Testing and Materials (ASTM). It is now ASTM International. ASTM (1992) provides guidance on soil gas monitoring in the vadose zone. This was re-approved in 2001. This provides guidance on ‘sample recovery and handling, sample analysis, data interpretation and reporting’. Previous general guidance was published by ASTM, such as ASTM (1995 and re-approved in 2002) which is the US standard guide for risk-based corrective action applied at petroleum release sites (RBCA). It was developed by ASTM in response to the need to prioritise action at petroleum release sites. The guidance sought to establish a tiered approach to site characterisation and possible remediation based on the use of threshold values that may dictate additional or no further action at an impacted site.

The approach sought to account for all potential exposures and risks, and so eliminate some sites from further investigation while focusing efforts where threshold values and risks were exceeded and unacceptable. This was termed risk-based corrective action since the risk became the driver of the decision for further action and possibly remediation rather than default values for soils and groundwater. In essence the approach required the development of alternate and more specific (although not

necessarily site-specific) threshold values for action based on modelled exposure pathways, default parameters, aquifer/soil type, land use and other assumptions.

More recently ASTM (2008) was developed which provides guidance on vapour assessment at sites of real estate transfer. It defines a procedure rather than technical methods that should be adopted. It points to ASTM (2005) which describes phased investigations at sites for more detail on methodologies.

ASTM (2008) defines a vapour intrusion condition (VIC), and the standard provides guidance on defining if a VIC occurs on a parcel of real estate through vapour intrusion assessment procedures. The standard also defines a potential VIC (pVIC), where there is:

‘the potential for the presence or likely presence of any chemical of concern in the indoor air environment of existing or planned structures on a property caused by the release of vapor from contaminated soil or groundwater either on the property or within close proximity to the property, at a concentration that presents or may present an unacceptable health risk to occupants.’

This definition would seem to equate with common understanding of a potential vapour risk.

ASTM (2008) discusses the information stream required to assess if a site has a VIC or pVIC at a Tier 1, Tier 2, Tier 3 and Tier 4 (mitigation) level. At Tier 1, it describes a ‘critical distance’ assessment, and states:

‘If the lineal distance in any direction from the nearest edge of a contaminated plume to the nearest existing or planned structure on the target property, or to the nearest target property boundary if there are no planned structures on the target property, is less than 100 feet, except for dissolved petroleum hydrocarbon chemicals of concern in which case if the lineal distance is less than 30 feet, then it is presumed that a pVIC exists.’

Based on the level of confidence in site conditions and information available on chemical distributions in the subsurface, this provides a Tier 1 exclusion/screening criterion for sites that are beyond these distances. The standard prescribes screening or exclusion distances that are different for dissolved or light NAPL (LNAPL) vapour sources, and are different for aerobically biodegradable (e.g. petroleum hydrocarbons) and non-degradable vapour sources. A summary is given in Table 1.

**Table 1. Summary of ‘critical distances’ beyond which a site may be excluded from further assessment under ASTM (2008).**

Vapour source	Critical distance	Comments
Dissolved plume – non-degradable	100 feet (or ~30 m)	
Dissolved plume – petroleum hydrocarbon (biodegradable)	30 feet (or ~9 m)	Aerobic biodegradation is assumed to occur in the vadose zone above the source
NAPL – petroleum hydrocarbon (biodegradable)	100 feet (or ~30 m)	Aerobic biodegradation is assumed to occur in the vadose zone above the source
NAPL – non-degradable	Not specified at Tier 1	

If a property is within the critical distance and a pVIC is deemed, then a Tier 2 Risk-Based Concentration Test is recommended – whereby concentrations at the site are compared to regulatory RBC levels which are like HILs in Australia. If the site concentrations are below the RBCA levels then a pVIC is presumed not to occur at the site, and no further action is warranted. Tier 3 and 4 assessments are also described in ASTM (2008).

Throughout, the ASTM standard provides caveats and warnings related to situations that may warrant exceptions to these rules, but in all cases the standard requires clear documentation of decisions in assigning or not assigning a pVIC or VIC to a site. It also defines the minimal information requirements for each Tier assessment.

#### 3.2.3 ITRC

ITRC is the Interstate Technology and Regulatory Council, made up of member states of the United States of America. The reports they produced in 2007 (ITRC 2007a, 2007b) provide a practical approach to assessment of the vapour intrusion pathway. They present a 13-step approach that progresses from ‘Is there an acute exposure?’ to ‘Is mitigation warranted?’.

It describes a screening process to define if the vapour pathway is incomplete, and for comparison to screening level criteria (such as Australian HILs). This allows screening of sites that do not pose a risk. Beyond that ITRC (2007a, 2007b) provide guidance on subsequent stages of assessment including vapour intrusion investigative techniques, and if required, mitigation options.

Comprehensive documentation is provided of sampling methods and techniques for soil gas, groundwater plume delineation and indoor air. In addition, analytical approaches are discussed, along with quality assurance/quality control (QA/QC) and data reporting suggestions.

For soil gas, they suggest sampling at 5 feet (~1.5 m) or deeper, and if shallower, that repeat samples are taken. A minimum of one sample per building on a site is suggested. If a basement is present, measuring a vapour depth profile adjacent to the basement wall is recommended. Depth profiles are noted as requiring a minimum of three sampling depths (fewer for shallower aquifers), and that depth profiles are useful for determining source (maximum) vapour concentrations and for determining attenuation potential. They note that sample density is a site-specific issue – ‘sufficient soil gas samples ... to make appropriate decisions’. The

guidance suggests sampling beneath (and/or within) a structure if the vapour source is beneath the structure, if feasible to do so, but sampling beside and away from the structure if the vapour source is located some distance laterally. It suggests not sampling soil gas immediately after precipitation.

For indoor air sampling in a standard house, one sample per storey of the house is recommended to be taken at breathing height about 3–5 feet (~1–1.5 m) above the floor. They recommend that additional samples be taken in basements or crawl-spaces.

The ‘preliminary screening phase’ (Tier 1) in the ITRC guidance suggests that some sites will be removed from further assessment if it is demonstrated that:

- the exposure pathway is and will remain incomplete
- the chemicals of concern are not deemed sufficiently volatile (as defined by the regulatory agency) to pose a hazard, or
- the concentrations of the volatile chemicals fall below generic screening levels.

These are variants of the screening criteria described in US EPA (2002).

#### 3.2.4 Canada

Golder Associates Ltd (2007) developed draft guidance for Health Canada to assist with environmental site characterisation for human health risk assessment. This contains significant material devoted to vapour assessment procedures and methods, both subsurface sampling and indoor sampling advice.

The report outlines the need for a CSM and study objectives that drive a sampling approach and design. It outlines soil gas probe construction and sampling/analysis procedures, quality assurance and quality control guidelines, and data validation and interpretation.

On sampling, the guidance suggests samples should be taken on at least two sides of a building and within 10 m of the building, that samples should be collected  $\geq$  to 1 m below ground and the mid-point from the foundation to the vapour source, but 0.5–1 m above a water table (to avoid inundation and to maximise vapour concentration data), and that sampling should be repeated. It also indicated that soil depth profiles may be obtained at selected locations for increased confidence and if the vapour source is laterally removed some distance from the site.

### 3.2.5 United Kingdom

There appears to be limited guidance on vapour assessment in the United Kingdom, although there is a VOCs handbook that was released in July 2009 (CIRIA 2009). There has been a strong emphasis on ground gas hazards (CIRIA 2007) in the United Kingdom – which relate primarily to methane in soil gas that may be an explosive hazard, but also carbon dioxide, hydrogen sulphide and carbon monoxide risks. CIRIA (2007) refers to vapours, but directs further investigations to the US EPA (2002) draft and UK EA (2005). The UK has well developed guidance on vapour intrusion modelling (Evans et al. 2002).

In CIRIA (2009) a three-tiered risk assessment approach is described. It includes: (i) a preliminary risk assessment effectively based on a Phase I ESA, (ii) a generic quantitative risk assessment based on site investigation data and possible use of generic screening criteria, and (iii) a detailed quantitative risk assessment based on further intrusive site investigations and data. It outlines a vapour investigation strategy, and a broad range of exploratory and analytical techniques. CIRIA (2009) stresses the need to consider site-specific issues, and to be guided by the CSM and DQO developed for the site. For soil gas sampling, they recommend targeting potential hot spot locations, points of potential exposure, and uncontaminated areas to obtain soil gas background. API (2005) is referenced for guidance on locations and sampling systematics.

### 3.2.6 Other jurisdictions of the United States of America

US EPA (2008) tabulates state regulatory guidance – 21 states are listed as having vapour intrusion guidance as at the publication date of March 2008. These are collated in Appendix B.

Eklund et al. (2007) summarised vapour intrusion approaches across many states of the United States of America. They included 23 states – 17 of which had individual guidance documentation, and six of which largely deferred to the US EPA (2002) draft guidance. Since that time, additional guidance has appeared for Kansas (and others – see e.g. US EPA 2008), which were not included in the 23 states reviewed. Eklund et al. (2007) notes that a number of states (California, Colorado, New Hampshire, New Jersey, Pennsylvania) use the distance from a source to potentially exclude sites from further assessment (as per the later ASTM 2008 standard). Kansas and Minnesota have recently adopted this exclusion distance approach (Kansas DHE 2007; Minnesota PCA 2008). Soil, soil gas or groundwater concentration screening criteria developed across these States are also summarised by Eklund et al. (2007), with states having screening concentrations for between 5 and >130 volatile organic compounds.

At a regional governmental scale, a number of other jurisdictions in the United States of America developed vapour guidance. For example, the County of San Diego Department of Environmental Health (2004) developed a Site Assessment and Mitigation (SAM) Manual, which outlines soil vapour sampling guidelines. DTSC (2005, 2009) also describes vapour guidance developed for California, most recently related to vapour risk mitigation.

Table 2. Compilation of aspects from guidance documents.

Reference	Strategy (S) and/or Techniques (T)	CSM	DQO	Sampling guidance	Techniques
US EPA (2002)	S mostly	Y	Y	• Take soil gas or groundwater samples $\geq 5$ feet (1.5 m) below foundation	Largely references other guidance
ASTM (2008)	S	Y	Y	References other guidance	References other guidance
Golder Associates Ltd (2007)	S and T	Y	Y	<ul style="list-style-type: none"> <li>• Take samples on <math>\geq</math> two sides of a building and within 10 m of the building</li> <li>• Sample <math>\geq 1</math> m below ground and <math>\geq</math> the mid point from the foundation to the vapour source, but 0.5–1 m above a water table</li> <li>• Sampling should be repeated</li> <li>• Soil depth profiles should be obtained</li> <li>• Possibly two sub-slab samples if required</li> <li>• Indoor air strategies</li> </ul>	<ul style="list-style-type: none"> <li>• Soil gas probes</li> <li>• Sample containers and devices</li> <li>• Sampling procedures</li> <li>• Analysis techniques</li> <li>• Background for indoor air</li> <li>• Low detection levels</li> </ul>
ITRC (2007a, 2007b)	S and T	Y	Y	<ul style="list-style-type: none"> <li>• Sampling at 5 feet (~1.5 m) or deeper. If shallower repeat sampling</li> <li>• <math>\geq</math> one sample per building on a site is suggested</li> <li>• Measure a vapour depth profile adjacent to the basement wall if present</li> <li>• If required, depth profiles require <math>\geq</math> three sampling depths (fewer for shallower aquifers)</li> <li>• Depth profiles useful to find maximum vapour concentrations and to assess attenuation potential</li> <li>• If feasible sample beneath a structure if the vapour source is beneath it</li> <li>• Sample beside/away from a structure if the vapour source is otherwise</li> <li>• Sample indoors from each storey, and at 3–5 feet height</li> </ul>	<ul style="list-style-type: none"> <li>• Soil gas probes</li> <li>• Sample containers and devices</li> <li>• Sampling procedures</li> <li>• Analysis techniques</li> <li>• Background for indoor air</li> <li>• Detection levels</li> <li>• Advantages and disadvantages of measurements</li> </ul>
API (2005)	T	Y	Y	<ul style="list-style-type: none"> <li>• Consider site-specific issues</li> <li>• Sample at two or more depths</li> <li>• Transects and vertical profiles can be useful</li> <li>• Sample immediately above the vapour source</li> <li>• Sample adjacent to the building foundation</li> <li>• Sample <math>\geq 3</math> feet (about 1 m) below ground</li> </ul>	<ul style="list-style-type: none"> <li>• Soil gas probes</li> <li>• Sampling procedures</li> <li>• Analysis techniques</li> <li>• Some alternates – passive samplers</li> </ul>
CIRIA (2009)	S and T	Y	Y	<ul style="list-style-type: none"> <li>• Consider site-specific issues</li> <li>• Be guided by CSM and DQO</li> <li>• Hot spots, points of exposure, and background</li> <li>• ‘Adequate’ spatial coverage</li> <li>• Refers to API (2005) for location and systematic sampling</li> </ul>	<ul style="list-style-type: none"> <li>• Soil gas probes</li> <li>• Sample containers and devices</li> <li>• Sampling procedures</li> <li>• Analysis techniques</li> <li>• Background for indoor air</li> <li>• Low detection levels</li> </ul>



## 3.3 Industry guidance and procedures

### 3.3.1 American Petroleum Institute

The American Petroleum Institute (API) developed an initial guidance document in 1998 (API 1998), on *Assessing the significance of subsurface contaminant vapor migration to enclosed spaces – site-specific alternative to generic estimates*. Subsequently, API published API (2005) which specifically looks at soil gas sampling from the vadose zone in relation to assessing the vapour intrusion pathway. The documents specifically focus on petroleum hydrocarbon vapours.

API (2005) discusses petroleum vapour behaviour, transport and typical subsurface depth profiles; conceptual understanding based on this; sampling locations, depths and frequency; sample installations and sampling methods along with analytical methods and data interpretation.

In terms of sampling strategies, API (2005) emphasises the need to consider site-specific issues. It suggests sampling at two or more depths will increase data confidence, transects and vertical profiles can be useful especially if the vapour source is distant from the site, that a soil gas sample should be collected immediately above the vapour source to obtain the highest concentration of the chemical of concern, and that a sample be obtained adjacent to the building foundation.

Some more specific recommendations presented in the API (2005) document include:

- the shallowest sampling depth is recommended to be no less than 3 feet (about 1 m)
- a lateral separation distance of 100 feet (~30 m) is likely to be sufficient for petroleum hydrocarbon impacted sites provided the vapour source edge is well defined
- soil gas data collected immediately above the source can be useful in screening sites including those open sites where future buildings may be constructed, and
- sufficient time must be allowed to pass following a spill to enable vapour concentrations to establish an equilibrium prior to sampling.

### 3.3.2 Petroleum industry in Australia

The sampling and assessment of vapours derived from petroleum hydrocarbon sources is undertaken by a range of consultants on behalf of major petroleum companies in Australia.

The petroleum industry in Australia adopts approaches and methods available in guidance, predominantly from the US (as summarised in Sections 3.2 and 3.3.1). Some companies provide information and guidance on approaches to the assessment of petroleum vapour issues such as the Technical Position Paper available from Shell Global Solutions (2005, 2009) and Atlantic Richfield (2006). The level of detail provided varies widely, however there are many key areas that are consistent in the guidance provided. These include the following:

- a tiered approach to the assessment of petroleum hydrocarbon vapours is recommended
- acute issues should be identified and addressed first. Sampling is typically focused on high vapour concentrations, acute exposures and hazardous (flammable/explosive) issues
- other sites where acute issues are not present, are associated with long-term (chronic) issues and hence any sampling approaches focus on low level vapour concentrations
- the design of a sampling program for petroleum hydrocarbons is complex. The design should address site-specific issues identified in a conceptual model
- sampling of vapour on petroleum hydrocarbon sites should be (and generally is within the industry) undertaken using a tiered approach. A number of sampling techniques are available and recommended for the sampling and assessment of petroleum hydrocarbon vapours (initial sampling stages) without entering an existing building
- collection of indoor air data is not routinely undertaken, or recommended, due to the large range of indoor sources resulting in false positives and difficulty in interpretation. Sub-slab data can also be affected by the movement of indoor air beneath the slab
- the use of field screening methodologies such as photo ionisation detector (PID) or flame ionisation detector (FID) instruments or passive samplers may be beneficial in providing a qualitative evaluation, identifying hot spots for the collection of soil gas (using quantitative methods) or screening utility corridors/preferential pathways

- where soil gas data is collected, the collection of data from close to the source and (where possible) vertically through the profile is recommended, particularly where the data is being used to assess future buildings on an existing vacant site. Vertical profiles are recognised as useful in characterising attenuation through the profile
- soil gas data from shallower depths (typically 1–1.5 m depth or close to basement foundations) is suggested for the assessment of existing buildings
- assessment of shallow sources should be undertaken with care (particularly where there is ingress of groundwater into a basement), and where representative vapour data cannot be obtained, the assessment of vapour issues may need to rely on source (soil and/or groundwater) concentrations
- biodegradation is an important aspect of the assessment of petroleum hydrocarbon vapours. Data relevant to the assessment of biodegradation potential ( $O_2$ ,  $CO_2$  and  $CH_4$ ) is recommended to be collected during sampling
- the number of samples collected from a site is not fixed, however sample collection in the vicinity of source zones and existing buildings is typically suggested and undertaken
- consideration of exclusion factors, such as lateral separation distances are suggested.

#### 3.3.3 Consulting industry

The approach adopted by the consulting industry to the sampling and assessment of vapours is generally consistent with and follows guidance available from the US. Approaches to the assessment of petroleum hydrocarbon sites are addressed above. For the assessment of other sites where petroleum hydrocarbons are not present a similar approach is adopted, however the potential for degradation is generally of less importance (depending on the compounds of interest). Often, a wider range of sampling techniques and other considerations with respect to sampling depths is relevant for sites where degradation is not of importance. Sampling methods commonly adopted include soil gas sampling, sub-slab sampling, flux emissions sampling and indoor air sampling. These methods are commonly utilised with either active or passive sampling techniques. The commonly used methods are outlined in Section 6.



## 4. Framework for vapour assessment

US EPA (2002), ITRC (2007a, 2007b), ASTM (2008) and a number of other guidance documents suggest a staged or Tier approach to vapour assessment at a site. This is generally accepted for any site investigation (see, for example, NEPC-ASC 1999 or Davis, Merrick & McLaughlan 2006), although sometimes an accelerated site characterisation approach is adopted (e.g. ITRC 2003).

Generally, Tiers or stages of assessment may be described as:

- **Tier 1:** A screening level assessment, whereby via some criteria, sites or properties would be screened out as not having undue risks posed by vapours
- **Tier 2:** Usually involves an initial site investigative stage where additional site data are obtained to assess if a potential vapour risk is posed
- **Tier 3:** Additional detailed site-specific investigation, sampling and/or modelling might be carried out to determine site-specific risks
- **Tier 4:** Mitigation/remediation may occur.

Unfortunately, there are different understandings of what level of detail and investigation constitutes each Tier, and there are many guidance documents, especially for each of the states of the United States of America, and federally in the United States of America (e.g. US EPA, ASTM, ITRC, DoD). This then can lead to confusion when timely action may be required at a site.

Some of the confusion arises because a Tier 1 screening of vapour risk may only be possible after a site-specific Phase II ESA (or DSI – as per NEPC-ASC 1999) is conducted. Of course, in practice it may be easier to carry out vapour investigation at a site at the same time as a Phase II ESA site assessment rather than have separate cycles of activity.

In this section we provide a brief description of some of the Tiers/stages in a vapour assessment and how they link with Phase I (PSI) and Phase II (DSI) ESAs. We highlight common and differential aspects from prominent guidance documentation, and suggest an approach that may be applicable.

Typically for a Tier 1 screening assessment, ‘measured or reasonably estimated’ (US EPA 2002) soil, soil vapour or groundwater concentrations for a site are compared to risk-based criteria (RBC) (ASTM 2008) or HIL screening

levels (NEPC-ASC 1999). However, US EPA (2002) and ASTM (2008) introduce an earlier stage of screening. Here we describe both approaches as part of a Tier 1 assessment, and the information required for carrying out such screening assessments.

Note that if vapour intrusion is suspected to pose an existing or imminent threat to human health, then immediate mitigation strategies might be implemented, or bypassing of the staged (Tier) approach may be warranted.

### 4.1 Screening assessment (Tier 1): ‘Exclusion distance’ – little or no site vapour data

#### 4.1.1 ‘Exclusion distance’ understanding

The conditions under which the US EPA recommends you consider the vapour pathway/guidance are that (US EPA 2002, p. 8):

‘you consider the possibility of exposure by this pathway if you have or suspect the presence, in soil or groundwater, of volatile chemicals (Henry’s Law Constant  $> 10^{-5}$  atm m<sup>3</sup>/mol) at your site as follows:

- located 100 feet or less in depth or
- located in close proximity to existing buildings or future buildings or
- to the expected footprint of potential future buildings.’

Close proximity was stated to be within 100 feet (~30 m) in the vertical or laterally. The draft guidance then goes on to consider Tier 1 screening. As such, the exclusion criterion stated above is a pre-Tier 1 assessment compared to the terminology of the US EPA (2002) document.

ASTM (2008) codifies this approach. Tier 1 in ASTM (2008) is a screening assessment based on the ‘critical distance’ of a property or structure from a source of vapours – effectively equivalent to the ‘close proximity’ concept in the US EPA (2002) draft guidance.

In essence both the US EPA (2002) and ASTM (2008) guidance documents say that if the property or structure is beyond a prescribed distance from the source (and other criteria are satisfied), then effectively an unacceptable vapour intrusion risk (vapour intrusion condition) is

unlikely to occur on a site. As indicated earlier, ASTM (2008) prescribes screening or exclusion distances that are different for dissolved or LNAPL vapour sources, and are different for aerobically biodegradable (e.g. petroleum hydrocarbons) and non-degradable vapour sources.

### 4.1.2 Information requirements

ASTM (2008) lists the required information and caveats to this (additional) exclusion distance Tier 1 screening – which is largely based on a Phase I ESA – such as given in ASTM (2005).

ASTM (2005) states that a Phase I ESA will have four components:

- Records review – review of records
- Site reconnaissance – a visit to the property
- Interviews – including interviews with past or present owners, operators and occupants of the property, and local government officials
- Report – evaluation and report.

ASTM (2008) broadens this to require specific information on:

- existing/planned use of the target property
- types of structures existing or planned on the target property
- surrounding area description
- federal, state, local, and tribal government records that relate
- historical records of use
- physical setting – e.g. soil type, hydrogeology
- significant natural or man-made conduits – e.g. sewers, utility corridors, Karst terrain
- user (of the standard) specialised knowledge, experience and commonly known information.

This required information is largely equivalent to that suggested in a Phase I ESA or PSI (NEPC-ASC 1999), but excludes any invasive site investigation for vapours.

Critical to the use of such exclusion distance screening is the location of the vapour source and its possible movement over time relative to the property or building(s) under consideration. Based on a Phase 1 ESA (or PSI) and professional judgement it may be obvious that no further investigation is able to be recommended based on an exclusion distance approach.

However, uncertainties associated with the location and distribution of source mass in the soil or groundwater

may remain – so further definition of the distance from the vapour source to the building/property may be warranted. Such uncertainties need to be reduced to acceptable levels for the exclusion distance to apply. To achieve this, preliminary vapour or other site measurements may be carried out, or a Phase II ESA whole of site investigation may provide the required information on the subsurface distribution of the vapour source – with or without vapour-phase investigations. ASTM (2008) also mentions the possible use of Phase II ESA whole of site investigations to achieve this.

An issue here is what might be considered enough or adequate information to establish that an ‘exclusion distance’ screen can be employed. ‘Adequate’ may be deemed different if you are the owner of the site, the developer, the consultant to the owner, the auditor on a site, the regulator, the future inhabitants of buildings on the site, or the community nearby.

Regardless, it seems possible to apply such a screening depending on the level of confidence in the basis for the exclusion distance. Information pertaining to the exclusion distance is described below.

### 4.1.3 Basis for the exclusion distance estimates

US EPA (2002) draft guidance suggested a 100 feet (~30 m) exclusion distance. This was based on data from Colorado sites (including chlorinated hydrocarbons) where the vapour intrusion pathway had been evaluated. It was stated that ‘at these sites, no significant indoor air concentrations have been found in residences at a distance greater than one house lot (approximately 100 feet) from the interpolated edge of ground water plumes’.

Lowell and Eklund (2004) derived a depth-section, two dimensional analytical model to assess reductions in vapour fluxes and concentrations at ground surface with increasing lateral distances between a building and a source of vapours in the subsurface. They accounted for diffusive transport of vapours and assumed the building had little impact on vapour behaviour. They reported that if the depth to the vapour source was 5 m then the emission flux of vapours at ground surface at a lateral distance of 25 m would be  $7 \times 10^{-4}$  as a fraction of the emission flux located directly over the vapour source. At a lateral distance of 50 m the emission flux of vapours at ground surface would be  $2 \times 10^{-7}$  as a fraction of the emission flux located directly over the vapour source.

Similar fractional reductions in concentrations were reported.

Abreu and Johnson (2005) developed a three dimensional numerical model of vapour movement from subsurface sources to the interior of slab-on-ground buildings or buildings with basements. They assessed the effects of lateral separation of the vapour source from the location of the building with and without biodegradation. They accounted for advective movement of vapours from sub-foundation to the interior to the buildings by applying a pressure differential across the foundation. They also accounted for the dimensions of the building (footprint of 10 m x 10 m) and assumed a vapour source with lateral dimensions of 30 m x 30 m. Without biodegradation, they found that for a vapour source at a depth 3 m below ground and at a 20 m lateral separation distance from the nearest edge of a building, concentrations in the buildings were reduced by a factor of  $\sim 2 \times 10^{-5}$  compared to the vapour source being located directly under the building. Interestingly, they reported that if the vapour source was at a depth of 8 m below ground but at the same 20 m lateral separation from the building, the reduction factor was much less, being  $1 \times 10^{-2}$ . The shallower source appears to have a greater potential to move into the atmosphere above ground over the short 3 m depth interval of soil compared to the travel distance

and time it takes for vapours to move the lateral distance of 20 m to the building. In comparison, the source at 8 m depth has a much greater potential to move laterally before it is transported into the atmosphere through 8 m of overlying soil. Extrapolating the results in Abreu and Johnson (2005) to a separation distance of 30 m yields a fractional reduction in concentration of approximately  $1 \times 10^{-3}$  for a vapour source at 8 m below ground and  $2 \times 10^{-7}$  for a vapour source at 3 m below ground. With biodegradation, the fractional reductions in concentrations were a number of orders of magnitude lower.

DeVaul (2007) considered lateral distances of vapour impact, but for biodegrading (petroleum hydrocarbon) vapours. He reported that a lateral separation distance (or exclusion distance) was a more reliable measure of the assessment of petroleum hydrocarbon vapour intrusion than an attenuation coefficient (i.e. the ratio of the concentration in indoor air to that found at the source).

Prior to publication of ASTM (2008), Eklund et al. (2007) reported which US states had adopted exclusion distance criteria based on the distance to the receptor from the source of vapours. The information is summarised in Table 3 along with some additional information for other states published afterwards.

**Table 3. Summary of 'exclusion distances' adopted by some US states.**

USA state	Vapour source	Petroleum vapour source (biodegradable)	Reference
California	100 feet (or ~30 m)		Eklund et al. (2007)
Colorado	100 feet (or ~30 m)		Eklund et al. (2007)
New Hampshire	100 feet (or ~30 m)	30 feet (or ~9 m)	Eklund et al. (2007)
New Jersey	100 feet (or ~30 m)	30 feet (or ~9 m)	Eklund et al. (2007)
Pennsylvania	100 feet (or ~30 m)		Eklund et al. (2007)
Alaska	100 feet (or ~30 m)		Eklund et al. (2007)
Ohio	100 feet (or ~30 m)		Eklund et al. (2007)
Indiana	100 feet (or ~30 m)	50 feet (or ~15 m) for BTEX	Eklund et al. (2007)
Connecticut	30 feet (or ~9 m)		Eklund et al. (2007)
Massachusetts	30 feet (or ~9 m)		Eklund et al. (2007)
Kansas	100 feet (or ~30 m)	40 feet (or ~12 m)	Kansas DHE (2007)
Minnesota	100 feet (or ~30 m)		Minnesota PCA (2008)

The contention seems well founded that beyond a set distance from a source vapours attenuate significantly. The supporting evidence is substantial, and a range of jurisdictions have assessed the evidence and adopted such a criterion into guidance. The attenuation is strongest for petroleum hydrocarbons where aerobic biodegradation occurs. Attenuation can be so large that vapour concentrations near or in buildings on properties can be well below detection limits. Such distances could be considered for use in Australia (where relevant) as they span a range of climatic conditions and soil types.

The critical issue appears to be the certainty of investigation or knowledge required to determine the subsurface extent of the vapour source (and potential for migration) so the lateral distance between the exposure point or building and the edge of the source or plume can be accurately determined. It may be in applying such an approach that the edge of the vapour source is defined by soil or groundwater investigations, or by soil gas sampling or even modelling. Alternately, to apply such an approach, it may be acceptable to measure 'low' or non-detectable concentrations at a prescribed lateral exclusion distance away from the boundary of a property or building rather than by defining the vapour source dimensions more precisely.

## 4.2 Screening assessment (Tier 1): Comparison to health-based investigation levels (HILs) – little or no site vapour data

The 'preliminary screening phase' (Tier 1) in the ITRC (2007a, 2007b) guidance, suggests that some sites will be removed from further assessment if it is demonstrated that:

1. the exposure pathway is and will remain incomplete
2. the chemicals of concern are not deemed sufficiently volatile (as defined by the regulatory agency) to pose a hazard, or
3. the concentrations of the volatile chemicals fall below generic screening levels.

These are variants of the screening criteria described in US EPA (2002) – see Section 3. ASTM (2008) also itemises these issues for screening, but deems comparison to generic screening levels (Item 3 above) as Tier 2, after the 'critical distance' screening is carried out.

Regardless, all (and NEPC-ASC 1999) have an approach that compares concentrations in soil, groundwater or soil gas phases against generic screening levels – and if below these screening levels then no further investigation is required.

In Australia, criteria commonly used for the purpose of screening include soil concentration criteria (from various sources) and drinking water criteria. Where soil gas (or ambient/indoor air) data are available these are commonly screened (sometimes considering relevant attenuation from soil gas to indoor air) against available air guidelines from NEPC-AT (2004) and other international sources.

In NEPC-ASC (1999), no volatile compounds had screening (HIL) concentrations developed. However the current variation process for the NEPM (NEPC-ASC 2006) seeks to develop more screening concentrations for volatile compounds. For Australia, initial values for benzene were described by Turczynowicz (2003), and more recently a draft range of health-based screening levels (HSLs) were developed through Friebe and Nadebaum (2009). These consist of look-up tables of soil concentration screening levels for human health and other pathway risks.

To use the screening levels (HILs for Australia) a site-specific soil concentration is required. NEPC-ASC (1999 – Section B7A) states that there are two prerequisites. They are the use of:

1. uniform soil sampling methodology which provides an appropriate amount of information about the distribution and level of contaminants on a piece of land
2. uniform approach to data analysis to enable a meaningful interpretation of sampling results.

Clearly, this is beyond a PSI, but not as extensive a requirement as a DSI. The level of site investigation required remains ill-defined, except to be 'uniform' – in delivering an 'appropriate amount of information'. This is similar to the requirement for the exclusion distance, in that enough information is required to be comfortable that the source dimensions and distance from the property/building are defined.

Both the exclusion distance and HIL screening criteria require active site investigation – but may not require vapour investigations at a site. Soil (and/or groundwater) investigations may suffice. In Australia, this would typically proceed based on the NEPC-ASC (1999) guidance or the updated variation. For current HIL screening, acceptable soil data are those that address statistical and other (e.g. 'hot spot') criteria. Similarly,

targeted groundwater investigations can define groundwater vapour sources. In the US, screening criteria based on comparison to soil gas data are often preferred, as this is the phase that poses the risk to human health. In Australia, no soil gas screening criteria are currently available.

Where direct vapour measurements are required, or preferred, guidance on vapour investigation design and methods are given in Sections 5 and 6.

### **4.3 Tier 2 and Tier 3 – requires site vapour data**

Where the site under investigation fails to be screened out via the assessments indicated above, Tier 2 and Tier 3 assessments may be required. Such assessments may include a greater level of site-specific data collection, probably involving specific soil gas/vapour measurement. This may become part of a Phase II ESA or be a specific vapour investigation. Design issues for such investigations are considered in Section 5 and methods that may be used are considered in Section 6.

### **4.4 Tier 4 – mitigation**

This Tier is not considered further here. Details can be found in ASTM (2008) or other vapour mitigation documentation such as DTSC (2009).





## 5. Design issues for field assessment of vapours

As indicated above, what follows in this Section and Section 6 may only be required if Tier 1 screening does not exclude a site from further investigation, or if vapour assessment is deemed necessary at Tier 1 to be able to apply the available Tier 1 screening options.

The field assessment of vapours requires design of an appropriate sampling program to meet the project objectives and CSM. It is expected that a sampling plan would be prepared to ensure that the program undertaken meets the desired primary objectives – e.g. to assess potential human health exposures. In designing a sampling program, some additional issues that need to be considered are:

- knowledge and understanding of appropriate guidance documentation
- improvement of the conceptual site model (CSM)
- development and implementation of data quality objectives (DQOs)
- variability issues – spatial and temporal variability and indoor versus subsurface factors
- degradable and non-biodegradable vapours
- measurement options – reliability, representativeness, precision and accuracy
- use of data – e.g. in the context of the Australian audit process (level of conservatism).

Guidance documentation was largely summarised in Section 3, and the importance of the CSM was highlighted in Section 2 – neither are revisited in this section. Note however, that guidance may change on an ongoing basis, and although little Australian state government guidance was available at the time of preparing this report, it is likely that it will become available in the near future either because of variations to the NEPC-ASC (1999), or separately. In principle, design and planning for assessment of vapours should target improvement and/or validation of the CSM, and accommodate guidance that is available.

### 5.1 Data quality objectives

Data quality objectives (DQOs) establish arguments for collection of data, and hence guide investigations and planning of individual tasks that make up a site characterisation effort. DQOs appear in a number of guidelines (see e.g. AS 2005; US EPA 2006). It is argued by some (e.g. Crumbling 2002) that the emphasis has

been too much on ‘data quality’ and not enough on the ‘objectives’ when utilising the DQO approach. A challenge is defining the purpose (or objectives). A primary DQO would be one that evaluates what has been identified to be protected at the site – e.g. chronic (long-term) human health inhalation exposures to low vapour concentrations. This will help to identify exposure points, time periods of interest and concentrations of relevance at exposure points.

A soil vapour investigation needs to be adequate in extent and quality to meet the purpose of the investigation. How many samples and at what locations to provide adequate coverage needs to be defined by the CSM and DQO. The investigation also needs to be representative – that is, sampling strategies and techniques must provide data that are representative of the subsurface environment and site conditions. Crumbling (2002) asserts that data representativeness is fundamental to data quality. The data quality model for contaminant data can sometimes remain focused on analytical data quality methods to the neglect of strategies to accommodate sampling from a heterogeneous environment. Crumbling (2002) argues that for the same overall cost a greater spread of samples across a site with (even greatly) reduced analytical certainty from laboratory or field screening will have a lower uncertainty, and therefore be more representative than fewer samples analysed to a high degree of accuracy. Note though, that this was determined on soil samples primarily, and where concentrations were not close to detection limits. It may not apply as readily to soil vapour investigations.

The DQO adopted for a sampling program should be relevant for the sampling techniques and methods adopted to ensure that the target compounds can be adequately reported to a level required for the assessment of exposure and risk.

### 5.2 Variability issues

The variability of any vapour measurement is a function of how the sampling was collected, the analytical method used as well as the potential for temporal and spatial variability. These differ for the collection of different data and should be considered in any sampling design plan. Eklund (2007) provided a summary of the expected distribution of variabilities for different sample types. These are presented in Table 4.



**Table 4. Qualitative indication of the variability caused by the sampling process, chemical analysis, and temporal and spatial variations – for a range of sample types – from Eklund (2007).**

Sample type	Relative significance by type of variability			
	Sample recovery*	Chemical analysis	Short-term temporal	Spatial
Soil gas	Medium	Very low	Very low	High
Sub-slab	Medium	Very low	Medium	High
Emission flux	Medium	Very low	Medium	High
Indoor air	Low	Very low	High	Medium
Ambient air	Low	Very low	High	Low

\* Variability associated with the use of a selected sampling technique for collection of data, particularly when assessed using duplicates as part of a QA/QC assessment. It is noted that the potential variability of data collected using different sampling techniques (refer to Section 6 for discussion) may differ (e.g. different limits of reporting for different sampling media) and should be considered further where required. It is also noted that the types of variability are not necessarily independent of each other.

Spatial variability encompasses a multitude of issues. Interior to a building spatial and temporal variability may be closely linked, especially if short-term vapour concentration changes occur due to pressure differentials. The spatial density and frequency of sampling should be matched to the understanding of such variability. In the subsurface, spatial variability in soil gas and vapour concentrations may occur due to layering of fine and coarse soil horizons, high moisture content zones, or indeed gross features such as utility conduits, plumbing or sewer lines. These features can lead to enhanced lateral migration and unforeseen variability in vapour concentration measurements if not accommodated in planning a site investigation.

ITRC (2007a) discusses the variability in soil gas concentrations that may be associated with temporal effects. Based on studies undertaken short-term variations in soil gas at depths of 4 feet (~1.3 m) or deeper are less than a factor of 2. Seasonal differences in colder climates are less than a factor of 5. Other effects that may affect variability include rainfall and barometric pumping. The document suggests that if soil gas concentrations are less than a factor of 5–10 below adopted (screening) guidelines, additional sampling is not required to address temporal variation. ITRC (2007a) also note that temporal variability in indoor air quality shows concentrations within a range of 2–5 fold. This variability can be considered when screening limited data sets for the purpose of identifying if vapour risks exist and if additional sampling is required. It is noted that

additional sampling may be required if other key site conditions changed such as groundwater elevation or source concentration.

### 5.3 Biodegradable vapours

The biodegradation of vapours changes their distribution in the subsurface. As such determining maximum concentrations near sources of vapours would typically require sampling at deeper depths of the soil profile. Oxygen may inhibit the movement of degradable vapours to shallower depths. Aerobically biodegradable vapours include most volatile petroleum hydrocarbons, some light chlorinated hydrocarbons such as vinyl chloride (Davis & Carpenter 1990), and some ketone compounds such as diisobutylketone (DIBK) (Davis, Woodbury & Bastow 2004). In addition methane will readily biodegrade where oxygen is present (e.g. Lundegard et al. 2008).

Davis, Patterson and Trefry (2009a) recently recommended sampling for oxygen at a depth no shallower than 1 m (based on Davis, Patterson & Trefry 2009b), to avoid surface effects and transients. If the determined oxygen concentration was above 5% by volume (and other criteria were satisfied) then they argued that a 10–100 fold reduction in risk could be applied if the depth of the vapour source was 2–4 m below ground. This was recommended to be applied at the Tier 1 screening level to health-based screening levels derived by assuming vapours were not biodegrading.

## 5.4 Measurement options

The ITRC (2007a) developed a tabulation of possible vapour assessment methods and their applicability for a range of source conditions and building types. The matrix categorised some of the methods and strategies as primary, secondary, optional or 'not usually appropriate' as vapour assessment options. API (2005) provides a revised matrix that focuses on petroleum vapour methods. The matrix provided by ITRC has been reviewed to reflect approaches and methods commonly used and accepted in Australia for the purpose of assessing vapour issues. The revised matrix is provided in Table 5 and can be considered in the identification of suitable methods and options that may be considered for use in a field program. Refer to Section 6 for discussion on the sampling methods.

It is noted that the ITRC (2007a) matrix identifies a number of other measurement techniques such as tracer testing for alpha (attenuation) factors, tracer testing for ventilation rate and pressure differential monitoring. In addition the collection of methodological data and potential use of real-time analysers during the sampling methodologies listed may be relevant. These methods are not commonly used in Australia and are not discussed further. However, guidance from documents such as ITRC (2007a) is available, should these methods be required as part of a sampling program.

## 5.5 Data interpretation

The design of any sampling program needs to consider the suitability of the data for interpretation and quantification of exposure and risks to human health. Some issues that may need to be considered in the design of the sampling program include:

- methods adopted can meet required limits of reporting such that if analytes are not detected, no risk can be demonstrated
- adequate understanding of the uncertainties and variabilities that are associated with the sampling methods adopted
- samples collected can be appropriately used in the CSM to support the quantification of exposure and risk. This includes the consideration of how data collected from depth will be used (if necessary) to quantify exposures at ground level
- data collected is not affected by other sources that cannot be quantified (common problem in sampling indoor air where multiple indoor sources may be present)
- selection of sample collection methods/media that adequately address the range of target compounds. More than one sample collection method may need to be used to address the range of compounds required at some sites.

Table 5. Matrix of various assessment options to evaluate vapour intrusion (revised from ITRC 2007a).

Measurement approach	Source at depth (>1.5 m) under site/building#			Shallow source (<1.5 m feet) under site/building#			Source in vadose zone adjacent to site/building#			Special conditions		
	Undeveloped site	Building with basement or slab-on-ground floor	Building with dirt floor or crawl-space	Undeveloped site	Building with basement or slab-on-ground floor	Building with dirt floor or crawl-space	Undeveloped site	Building with basement or slab-on-ground floor	Building with dirt floor or crawl-space	Petroleum hydrocarbons	Vapour migration routes	Wet basement****
Deep (>1.5 m) soil gas	P	P	P	N	N	N	O	O	O	P	O	N
Shallow (1–1.5 m) soil gas	P	P	P	P	P	P	P	P	P	P	P	N
Sub-slab soil gas	N	O/S	N	N	O/S	N	N	O/S	N	O/S	O	N
Vertical profile of soil gas	O	O	O	N	N	N	O	O	O	O	O	N
Indoor air	N	S	S	N	S	S	N	S	S	S**	P**	S
Ambient (outdoor) air	O	O	O	O	O	O	O	O	O	O	O	O
Passive soil gas sampling	S	S	S	S	S	S	S	S	S	S	S	N
Emission flux chambers	O	O	S	O	O	S	O	O	S	N***	N	N

**Notes:**

The ratings presented in the table are associated with the range of options that could be used for the assessment of vapour intrusion. While some methods may be noted as more preferred than others, other methods (noted as secondary or optional) can be used as primary options provided they can address the CSM and DQOs. The rating presented includes:

P = Primary investigative option – can potentially be used as a principal option for assessing vapour intrusion.

S = Secondary investigative option – can be used as a line of evidence in support of another line of evidence, or as a primary option where relevant.

O = Optional investigative option – can be used as an additional line of evidence, as means to focus a primary investigation or as a primary/secondary option depending on the relevance in addressing the CSM and DQOs.

N = Not usually appropriate as an investigative option.

\* May be considered an option if the sampling is undertaken with appropriate methods to ensure representative sample is collected (refer to Section 6).

\*\* May not be an appropriate option if target compounds are common urban air contaminants or have a significant indoor/local source.

\*\*\* Not recommended as an option for assessing aerobically biodegradable vapours (e.g. petroleum hydrocarbons) due to the influence of oxygen near the surface, however applicability of method would depend on CSM and sample location.

\*\*\*\* Assessment of a wet basement requires consideration of relevant groundwater concentrations and potential for volatilisation (dependent on building design) in addition to any vapour data that may be collected.

**# 'Site/building' includes:**

Undeveloped site: A site with no existing buildings or structures present.

Building: Refers to the type of building constructions that may be assessed for residential and/or commercial/industrial use.

## 6. Vapour and gas sampling and monitoring techniques

This section provides a summary of the commonly used methods for the sampling and characterisation of vapour concentrations at a site. The methods presented provide a range of options that may be considered in the design of a sampling program. The methods used in any program should address the design issues identified in Section 5 as well as the CSM developed for the site.

### 6.1 Soil gas sampling methods

#### 6.1.1 Temporary spear probing

Spear probing, or driven soil gas probes, of soil involves driving a spear/rod into the ground to a shallow depth (e.g. 1.5–2.0 m below ground surface), extracting a soil gas sample for analysis of the vapours of concern and/or major gases (e.g. oxygen), and withdrawal of the spear probe. The probe can be decontaminated and reused for the sampling of soil gas at the next location (if required). Decontamination would need to be appropriate for the compounds expected; alternatively disposable implants can be used where cross-contamination is expected to be of concern. Spear probing can provide vapour and major gas concentration data at a series of locations and selected depths, but is not a survey technique designed to determine changes over time.

Spear probing is typically used in one of two ways: as a screening level assessment technique or for the quantitative sampling of soil gas.

As a screening level technique, spear probes are used with a field sampling method to identify the presence of vapours in the subsurface, and can assist with locating 'hot spots'. Recovery of the samples from the spear probe can be collected in a glass syringe (or container)

for vapours (to minimise loss of vapours due to sorption) or collected in a plastic syringe (or container) if collecting a gas sample for analysis of major or fixed gases such as oxygen. Analysis of the sample directly from the syringe (or container) is preferable to minimise air contact and vapour/gas loss and exchange with the atmosphere. A photo ionisation detector (PID) may be used in the field to analyse or screen the sample. Detailed analysis could be done on a portable or laboratory-based gas chromatograph (GC), or by GC- mass spectrometry (MS). The use of spear probes for a screening level assessment enables a large number of locations to be sampled in a cost-effective manner. This provides guidance for any additional more intensive investigations that may need to be conducted. To be effective as a survey technique, samples should be taken below the zone influenced by transients, which is likely to be at depths of 1.0–2.0 m or greater below surface. The sampling depth may also depend on the location of the vapour source. The method can also be used to collect samples from a vertical profile (from as shallow as 0.3 m) to assist in the identification of various vapour zones and to define the potential aerobic reaction zone.

As a quantitative technique the spear probe can be installed and sampled in the same manner as permanent probes/samplers. Sometimes it is more difficult to achieve an adequate seal on a temporary installation or spear rod – hence tracer methods are suggested by some (NYSDOH 2006). Additional considerations associated with the sampling of soil gas are noted in Section 6.1.6.

Based on industry experience and after Hartman (2002) and API (2005), Table 6 outlines a number of advantages and disadvantages of the temporary probe methods.

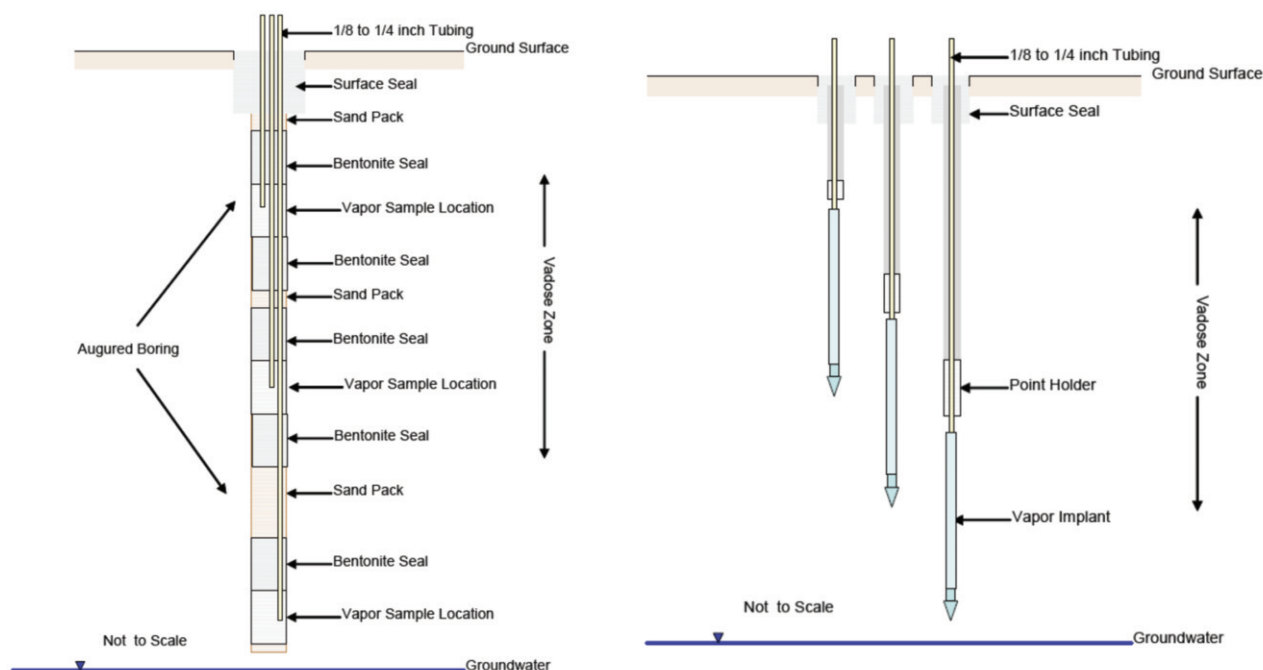
**Table 6. Advantages and disadvantages of the temporary probe methods.**

Advantages	Disadvantages
<ul style="list-style-type: none"> <li>Probes can be installed, sampled and removed with minimal surface disruption</li> <li>Useful for the sampling of shallow soil gas (where the source is shallow)</li> <li>Useful for screening where field monitoring or analytical techniques are incorporated to direct decisions on further sampling</li> <li>Can direct installation of permanent probes</li> <li>Can be used to assess vertical profiles (but depth limited due to practical depth of installations)</li> </ul>	<ul style="list-style-type: none"> <li>Additional costs associated with remobilisation if further sampling is required and permanent installations using spear probes are not possible</li> <li>Lower level of reproducibility (between events) as there is a higher degree of variability with the installation method</li> <li>Potential for cross-contamination between locations</li> <li>Harder to get good seal to minimise ambient air ingress</li> <li>Not usually used to collect samples from low permeability soil</li> </ul>

### 6.1.2 Permanent multi-level probes/samplers

Permanent subsurface soil gas/soil vapour monitoring locations can be installed to allow (i) depth profiling of vapour concentrations through the soil profile from near source to near the ground surface, and (ii) repeat sampling and monitoring over time at fixed locations. Guidance is available from API (2005), NYSDOH (2006), ITRC (2007a) and others that outline key aspects of installing soil gas probes/implants/samplers so that they can be used to collect a representative soil gas sample.

Single depth permanent probes can be installed, either at depth (close to the source) or shallow (particularly where the source is shallow). Multiple depth (or multi-level) gas sampling installations may be undertaken by installing multiple sample ports at different depths (separated by a bentonite seal) within the one sampling well (API 2005; Hartman 2002), or installing separate soil gas probes at different depths (separated by at least 2 ft or 0.6 m) (API 2005; NYSDOH 2006). Options are illustrated in Figure 11.

**Figure 11. Schematic of multiple depth soil gas sampling installations (after API 2005).**

There are a range of methods for installing permanent probes. DiGiulio et al. (2006) reported good agreement between installation/drilling methods. Essentially, they found that the variation in results was not significant by using different installation methods as long as installation was done correctly. Hence the probe installation method used should be determined based on site-specific factors including access and environmental conditions (e.g. soil texture or moisture conditions that may limit the usefulness of very narrow tubing and other effects). Correct sealing of the installations was seen as essential, especially in tighter fine-textured soils. Separate installations rather than multiple sampling points in one drilled hole are sometimes recommended for finer soils, to ensure a good seal is able to be achieved or where the upper sample is less than 1 m below the surface.

Care should be taken to construct installations from inert, non-sorbing and well flushed or 'tested' materials.

Sampling of the permanent probes and multi-level samplers can be carried out using a range of sampling methods. Typically, permanent probes would need to be left for a minimum of 24–48 hours prior to sampling

(DTSC 2009; NYSDOH 2006) depending on the installation method and the site conditions. Additional considerations associated with the sampling of soil gas are given in Section 6.1.6.

Additionally, during drilling to install the permanent probes and multi-level samplers, a log of soil types should be documented. Sometimes a soil core may also be recovered and be sub-sampled to determine organic carbon and soil parameters (e.g. bulk density, porosity), at the depths of the sampling ports, and for analysis of the soil for the chemicals of concern.

Data from depth profiling using multi-level samples can be used to calculate vapour fluxes to the ground surface and possibly infer degradation rates, where it occurs.

Hartman (2002), API (2005) and Atlantic Richfield (2006) outline a number of advantages and disadvantages of the permanent probe methods. Some of these are summarised in Table 7.

**Table 7. Advantages and disadvantages of the permanent probe methods.**

Advantages	Disadvantages
<ul style="list-style-type: none"> <li>Probes can be sampled over time allowing temporal variability to be assessed</li> <li>A number of methods are available for installation (augured or direct push) enabling flexibility for a range of sites where access may or may not be limited or where a range of lithologies are present</li> <li>Installation provides the opportunity to carefully seal each probe and sampling interval</li> <li>Deep probes, located just above the source, can be used to measure the maximum vapour source concentration – that can be used for screening purposes or for assessment of buildings on a vacant site</li> <li>Multilevel probes enable an assessment of attenuation through the vadose zone</li> <li>Can be used to collect samples in low permeable soil</li> </ul>	<ul style="list-style-type: none"> <li>If only deep probes are installed, the data may not be representative of soil gas at shallower depths due to overlying soil layers or degradation (particularly relevant for petroleum hydrocarbons)</li> <li>Depending on the lithology and installation the permanent probes may be affected by wet conditions (moisture in the vadose zone) or clogging over time preventing their re-sampling (requiring re-installation)</li> </ul>



6.1.3 On-line VOC and oxygen probe

Near-continuous measurement of total vapour (or volatile organic compounds – VOCs) and oxygen concentrations is possible using on-line VOC and oxygen probes (Patterson & Davis 2008; Patterson et al. 1999, 2000). These can be buried at multiple depths to give near-continuous measurements of total vapour and oxygen concentrations for extended periods (over months to years) – and indeed can be used for vapours or dissolved phase concentrations. Apart from providing vapour and oxygen depth profiles, the detailed information derived from these probes allows seasonal trends in vapour fluxes and other parameters such as degradation rates to be assessed. The probes can also provide an assessment of remediation progress where the adopted remediation impacts vapour concentrations.

Probes such as these have been used at a number of sites across Australia to measure total hydrocarbon and solvent compounds in soils and aquifers. In particular the probes have been used to measure vapours in soils beneath and in the vicinity of built structures (e.g. houses, Patterson & Davis 2009), and in sandy and heavier clay soil environments (Davis, Patterson & Trefry 2009b). The probes do not directly monitor individual compounds, such as benzene, but can be sub-sampled to obtain a gas sample, which can then be analysed by conventional means for component VOC and major gas concentrations.

6.1.4 Sub-slab sampling

This involves the collection of soil gas samples from directly under a building slab or foundation. The sampling requires drilling a hole through the building slab, including within the driveway or garage, or beneath a foundation. The rationale for this technique (as opposed to collecting soil gas data adjacent to a building, Atlantic Richfield 2006) is that the sub-slab region is in closest proximity to the potential access points to the built structure.

Sub-slab installations may be permanent, semi-permanent or temporary depending on access and the need to resample. Sampling of a sub-slab installation can be carried out using a range of sampling methods consistent with those used to sample soil gas from either temporary or permanent locations. Additional considerations associated with the sampling of soil gas are noted in Section 6.1.6.

API (2005) and Atlantic Richfield (2006) outline a number of advantages and disadvantages of the sub-slab methods. These are summarised in Table 8.

Table 8. Advantages and disadvantages of the sub-slab methods.

Advantages	Disadvantages
<ul style="list-style-type: none"><li>Provides a measure of soil gas directly beneath the slab which is closer to the point of exposure</li></ul>	<ul style="list-style-type: none"><li>No validated sampling method is available and hence the affect of environmental variables is less well understood</li><li>Large spatial variability at some sites</li><li>Highly intrusive method and as such is not a preferred method</li><li>Requires damage to building floors (and higher risk of damaging subfloor services)</li><li>If not installed correctly, can act as short-circuit for vapour intrusion</li><li>Data can be more difficult to evaluate as concentrations can be affected by indoor sources (vapour may move inward or outward through concrete depending on pressure differences)</li></ul>

### 6.1.5 Across the capillary fringe

It may not be commonly required, but if source conditions in groundwater near to the capillary fringe are critical to a vapour assessment, then measurement across this zone may be required. The near-capillary fringe zone is a region of rapid transition in soil moisture content, from water saturated conditions in groundwater to (usually) increasing air-filled porosity through a soil profile. The increased air-filled porosity allows vapour transport. Traditional sampling methods suggested in this zone include (i) recovery of gas samples as close to the top of the capillary fringe as possible (API (2005) recommend 0.5–1 m above the capillary fringe), and (ii) investigation of the distribution of the volatile compounds in the groundwater (the groundwater plume). Close to the capillary fringe determination of gas or groundwater concentrations becomes increasingly difficult.

Barber and Briegel (1987) reported on a diffusion cell technique that allowed fine-scale measurement of volatile compounds and gases across this zone. It entailed deployment of a bundle of coiled gas-permeable polymer tubing at defined depth intervals below ground. Sampling was carried out by passing a carrier gas through the coiled tubing. The gas sample was collected at ground surface, and the recovered sample would be sent for analysis or analysed on-site. Whether in a water-saturated or gas-filled environment, the recovered gas stream from the diffusion cells would be representative of conditions in the soil/water media adjacent to the diffusion cell, and be representative of the concentration that would partition to a gas phase, as per a vapour source. The probes reported in Patterson et al. (2000) used a similar technique to provide near-continuous total VOC measurements.

### 6.1.6 Factors that may be considered when sampling soil gas

The following factors may need to be considered in the design of a soil gas sampling program:

- *Location:* The number of locations sampled depends on the conceptual model developed, access and cost. There are a range of suggestions as to the location of soil gas samplers, however Hartman (2002) suggested that samples should be collected at the site of maximum source concentration near or under a building and at each corner or along each side (if practical).
- *Depths:* The depth of samples should be based on the conceptual model developed, in particular the depth of subsurface sources and the nature of the contamination. Where shallow sources are present or where deeper samples cannot be obtained the collection of soil gas from shallow depths (<1.0 m) may be appropriate. However, sampling from these depths may require justification. The installation and use of data from shallow wells should consider the potential for aerobic degradation of petroleum hydrocarbons, and potential transient influences.
- *Frequency:* A single sampling event may be sufficient; however, additional sampling events may be required in the event that (i) the first round of data shows high concentrations, (ii) if samples were collected from shallow depths (<1.0 m), or (iii) if sampling occurred in winter and large seasonal variations in temperature or soil moisture occur.
- *Probe integrity/seal:* Soil gas probes (temporary or permanent) should be installed to ensure that ambient air is not drawn into the sampling system and that any soil gas sample collected is representative. This may require an additional seal around the probe, even for temporary probes. An adequate seal may be particularly important for shallow probes or sub-slab probes. A number of tracer methods are outlined in guidance (API 2005; ITRC 2007a) that can be used to test the seal integrity. Hartman (2002) notes that tracer testing may only be necessary for shallow depths (<1 m depth), when large sample volumes (>0.5 L) are collected or there is a visibly poor seal at the surface. It may also be important where samples are collected from low permeable soils (McAlary, Nicholson et al. 2009).
- *Tubing type:* Tubing type is important as vapours may emanate from polymer tubing, especially flexible tubing, and can also adsorb to tubing providing false positives or negatives when samples are analysed (Hartman 2006). For more rigid tubing the tubing type is of less importance. When using more rigid tubing, handling and storage of samples becomes more critical. Improper handling and storage can also result in cross-contamination and false positives.
- *Sample volume:* The recovered size of the sample volume may be an important aspect. Hartman (2002) indicated that the larger the sampling volume the greater the uncertainty about the exact location where the soil gas came from. Near ground surface, recovering large sample volumes may result in the draw-in of ambient air from outside the annulus of the shaft of the probe. Large sample volumes increase the likelihood that the sample may be from different depths and locations. A review of available studies on sample volumes by Hartman (2006) suggested

that the sample volume is less important for coarse-grained soil, but in finer-grained soils large volumes may be difficult to collect due to the creation of vacuum conditions during sampling. The sample volume should be appropriate for the soil types and sampling/analytical method.

- **Purge volumes:** The sample probe, tubing and equipment have an internal volume that must be purged prior to sampling. This is undertaken to ensure that only soil gas is sampled and the data is representative. The volume of gas that is purged is subject to a range of opinions. Hartman (2002) and ITRC (2007a) suggested between one and five volumes should be purged prior to sampling. A study by Zimmerman and Schumacher (2004), McHugh (2008) and McHugh and Nickels (2008) showed that the soil gas concentration determined (using a number of methods) after a range of purge volumes did not vary significantly. Whatever calculation is used to estimate the volume purged, this should remain consistent for all locations sampled. It is noted that large purge volumes can result in low pressure/vacuum conditions that can result in contaminant partitioning from the soil to soil gas resulting in the sample not being representative (Hartman 2002). A recent study (Schumacher et al. 2009) recommended for temporary probe installations, that the purge volume be minimised to ensure the sample collected is representative.
- **Sample flow rates:** To minimise the potential for desorption of contaminants from soil to soil vapour in the sampling zone the sample flow rate should be appropriate for the soil type. In the US, guidance typically suggests a limit on the sample flow rate of <0.2 L/min. However, a study by McAlary and Creamer (2006) considered flow rates from 0.1 L/min to 100 L/min in coarse-grained soils and showed little difference in estimates of soil vapour concentrations. This is consistent with guidance provided by ITRC (2007a). A low sample flow rate is important where soil gas is collected from low permeable soil (McAlary, Nicholson et al. 2009). Low permeable or high-moisture content soils can induce greater suction pressures when sampling. This sometimes makes samples difficult to recover.
- **Environmental:** Temperature variations within a soil profile are generally low and decrease with depth. Temperature variations in Australia are typically not large (as occur in some parts of the US and Europe) and hence temperature variations are not expected to have a large influence on soil gas concentrations.

Changes in barometric pressure can result in a pressure gradient between the soil gas and ambient air increasing the flow of vapours in the subsurface. This effect is only of importance where sampling is shallow. Rainfall can affect the measurement of soil gas by changing the moisture content in the soil profile and creating a cap above the source area (Davis et al. 2005). Sampling of soil gas (particularly from depths shallower than 1–1.5 m) directly after significant rainfall events (>25 mm) should generally be avoided, unless the rainfall is representative of normal conditions. Soil gas samples collected from depth >1.5 m are unlikely to be significantly affected by rainfall events (Hartman 2002). There are no specific guidelines available on how long to wait before sampling shallow soil gas after a rainfall event as it is dependent on the soil type and other climatic conditions. If uncertainty remains as to the potential for a rainfall event to change the distribution of vapours in the subsurface, then repeat sampling may be warranted or measurements of soil moisture may be taken at the time of vapour sampling.

## 6.2 Flux chamber methods

A flux chamber (or a flux hood) is a device that is placed on a surface which enables a measurement of vapour/gas flux (or emission rate) discharging through that surface. The surface may be open ground or be part of a building foundation such as a concrete slab. There are two primary types of flux chamber methods: a static (closed) chamber method and a dynamic chamber method.

### 6.2.1 Static chamber

The static chamber method requires the placement of the flux chamber on the surface of the ground or building foundation, without any passage of air through the chamber. This allows vapours to be trapped and the stagnant chamber vapour concentration to build up over time. The method is described by Eklund and Schmidt (1990), Hartman (2003) and Heggie and Stavropoulos (2008). Active samples can be collected at discrete intervals through a time period, and at the end of a time period. Passive sampling methods are also being developed whereby a sorbent is left within a static chamber for a period of time (Heggie & Stavropoulos 2008). Table 9 outlines a number of advantages and disadvantages of this method.

Table 9. Advantages and disadvantages of the static chamber method.

Advantages	Disadvantages
<ul style="list-style-type: none"> <li>• Equipment and procedures are simpler and less expensive than the dynamic flux chamber method enabling more locations to be sampled</li> <li>• Can be used to provide a time integrated sample over long periods reflecting flux variations with temporal variability</li> <li>• Minimises disturbance of natural flux conditions</li> <li>• Method can be more sensitive than the dynamic flux chamber method (depending on the static flux method adopted) enabling the use of less expensive analytical techniques with a higher detection limit limiting false positives</li> </ul>	<ul style="list-style-type: none"> <li>• If concentration in the chamber builds up to a significant fraction of the subsurface concentration the flux will be impeded and the data collected will be underestimated. This is expected to be of issue where emissions are known to be high. For many applications the build-up is not expected to be significant</li> <li>• Small footprint of the chamber compared to heterogeneity of the ground/foundation</li> </ul>

### 6.2.2 Dynamic chamber

The dynamic chamber method (see e.g. Figure 12) is described in guidance developed for the US EPA (Eklund & Schmidt 1990; Kienbusch 1986; Reinhart et al. 1992). This method involves the use of an inert sweep gas which is continually introduced into the chamber with an

equivalent amount of gas allowed to escape. The system is allowed to reach steady-state, assumed to be four of five chamber volumes. Then the chamber is sampled. The sample can be a discrete sample or monitored continuously. Table 10 outlines a number of advantages and disadvantages of this method (Hartman 2003).

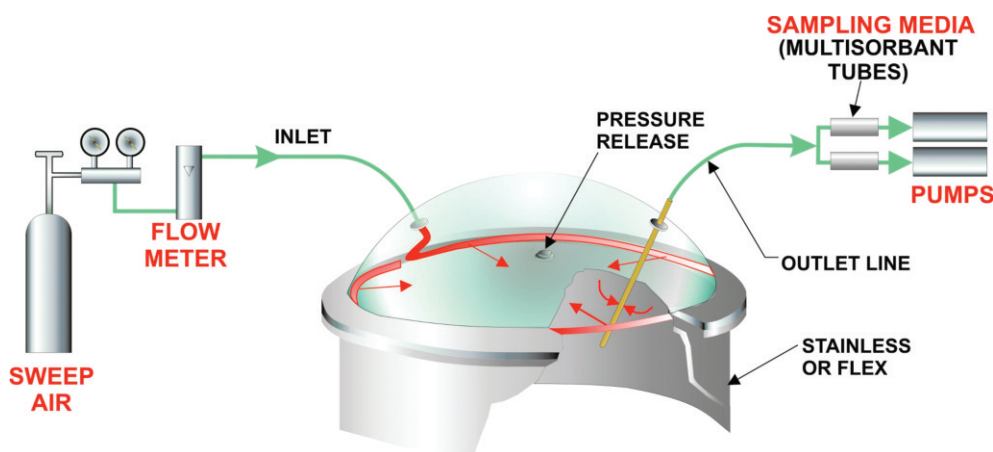


Figure 12. Schematic of the dynamic chamber method (after URS 2008).

**Table 10. Advantages and disadvantages of dynamic chamber method.**

Advantages	Disadvantages
<ul style="list-style-type: none"> <li>• Little chance of chamber concentration build-up and hence very little chance that the measured flux will be impeded</li> <li>• Validated method for sampling of emissions from landfill sites (or where active gas generation is expected)</li> </ul>	<ul style="list-style-type: none"> <li>• More complex and expensive method requires more experience and greater potential for QA issues</li> <li>• Dilution in the chamber results in loss of sensitivity and requirement for more expensive analytical techniques that have a low detection limit</li> <li>• Inflow and outflow of sweep gas has potential for disturbance of natural flux (e.g. creation of advective flow in chamber)</li> <li>• Temporal variations not easily captured due to the shorter duration of sampling events</li> </ul>

### 6.2.3 Factors that may be considered when using flux methods

The advantage of this technique is that it enables the direct measurement of a vapour flux from the surface of the ground or building foundation. This is somewhat of a direct estimate of the parameter of interest often close to the point of potential exposure (rather than calculating it from subsurface vapour distributions). It also does not require additional subsurface investigations. It effectively ‘integrates’ all subsurface processes (e.g. phase partitioning, bioattenuation, preferential pathways, advective and diffusive transport). The major disadvantages of this technique are the potential changes in fluxes that are induced by the device itself, and the small footprint of the chambers.

When designing a sampling program the following should be considered:

- *Coverage of the area of concern:* Hartman (2003) suggested targeting areas of possible vapour conduits, areas of maximum source concentrations and consideration of other site-specific building features.
- *Deployment period:* This refers to the period of time the chamber is deployed and sampled. This should be adequate to address the issues of concern and where possible enable temporal variability to be assessed.
- *Environmental conditions:* Emission rates from soil may be reduced immediately after rainfall. Kienbusch (1986) recommended waiting seven days after a rain event of greater than 7 mm. Barometric pressure may also have an effect with higher emissions during periods of low atmospheric pressure. Hartman (2003)

suggested avoiding deployment during extreme pressure conditions. Temperature effects have been found to be relatively minor except where the flux is from a source at (or very close to) the surface. If samples are collected in a building, heating and cooling may alter emissions. If sampling is undertaken to assess a landfill, these effects may be more significant and should be considered when deciding when to collect representative samples.

- *Petroleum hydrocarbons:* These compounds actively biodegrade in the presence of oxygen, particularly in the near-surface soil. If samples are collected from open ground the emissions may be reduced by biodegradation. The use of the data needs to be considered in the context of the site conceptual model.
- *Chlorinated solvents:* These compounds do not biodegrade readily in the vadose zone, potentially yielding higher mass fluxes at ground surface. As such, flux methods may be more usable for chlorinated hydrocarbons in open ground conditions than at petroleum hydrocarbon-impacted sites.
- *Basements:* Flux chambers may not be suitable for dwellings with basements because of additional potential fluxes from the basement walls to the interior of the dwelling.
- *Changed land form:* Flux chambers used on a bare soil surface may not reflect measurements obtained when a structure is in place.
- *Subsurface conditions:* This technique provides little information about the processes that may be occurring within the vadose zone such as oxygen penetration and hydrocarbon degradation. Longer-term controls



on emissions and hence potential changes in subsurface conditions may not be detected with such a device, unless long-term near-continuous emission monitoring is undertaken.

- **Buildings:** Because of the usually limited surface area of coverage, flux chambers may not measure the actual flux into a built structure especially if there is preferential access to the structure. Also, air-movement conditions within the chamber may not reflect 'natural' room conditions in a structure – leading to over- or under-estimation of fluxes depending on relative pressure differentials inside and outside a chamber.

### 6.3 Crawl-space and indoor/outdoor air sampling

Air samples can be collected from a crawl-space beneath a building to provide a more realistic measurement of a vapour concentration beneath the floor space of such a structure. Assumptions (or modelling) are required to estimate a concentration within the home; however the collection of data from a crawl-space provides a measure that is closer to the point of exposure (when compared with soil gas flux methods). Samples can be collected using simple methods (consistent with those used to sample indoor/ambient air). Atlantic Richfield (2006) suggests that samples be collected near the mid-point between the top and bottom of the crawl-space, near the centre of the building.

The sampling of indoor air provides a more direct measurement of potential exposure. Methods often use time-integrated sampling (e.g. over 24 hours). The collection of such data is intrusive and can be difficult to interpret; hence it is typically only undertaken after other methods of assessing vapour issues have been explored. Table 11 summarises some advantages and disadvantages of collecting air data from crawl-spaces and indoor air (some noted from Atlantic Richfield 2006 and ITRC 2007a).

Indoor air data are subject to large temporal variability. Meteorological and other conditions during sampling may be important. In addition the collection of indoor air data can be affected by significant ambient (outdoor) and indoor sources. This is particularly relevant to the sampling of petroleum hydrocarbons and some chlorinated solvents (commonly used in household products). A number of documents (Atlantic Richfield 2006; ITRC 2007a; NYSDOH 2006) provide detailed guidance protocols for the collection of indoor air data to assist in the identification (and removal prior to sampling) of indoor sources and interpretation of data collected.

Ambient (outdoor) air samples may also be collected to supplement other data collected from indoors or from a crawl-space. The data is collected to characterise background air conditions relevant to a specific site or area.

**Table 11. Advantages and disadvantages of collecting crawl-space and indoor air samples.**

Advantages	Disadvantages
<b>Crawl-space air:</b> <ul style="list-style-type: none"> <li>• Simple to measure</li> <li>• Does not require access into a building</li> <li>• Limited interference from indoor</li> </ul>	<ul style="list-style-type: none"> <li>• Background/ambient sources may affect data interpretation</li> <li>• Not a direct measure of exposure concentration indoors and further estimation (or modelling) of a concentration indoors is required</li> </ul>
<b>Indoor air:</b> <ul style="list-style-type: none"> <li>• Simple to measure</li> <li>• May provide data that residents can better understand</li> <li>• Provides measurement of potential exposure concentration</li> </ul>	<ul style="list-style-type: none"> <li>• Background/ambient and indoor sources complicate data interpretation and communication to the public</li> <li>• Requires access inside a building/home</li> <li>• Temporal variability large</li> <li>• Low reporting limits are often required</li> <li>• Sample control can be more difficult to manage</li> </ul>



## 6.4 Passive implant sampling

'Passive' implant sampling refers to the burial or placement of an adsorbent or other material in the ground, which would be recovered for analysis after an appropriate period of time (hours, days). It is termed passive because no gas sample is actively recovered from the soil profile. This technique generates a time-integrated total mass or a time-integrated equilibrated concentration (e.g. Laor et al. 2003), so uncertainties associated with temporal changes are reduced. The time-integrated mass cannot be equated to a concentration because the volume of air associated with the adsorbed mass is largely unknown. Also, passive samplers may desorb soil vapours from fine grained layers that are otherwise not mobile, thus overestimating the amount of soil vapours that are capable of being transported into overlying zones. The method however enables a screening level assessment of the presence of vapours in the vadose zone to identify if the vapour pathway is complete and to identify hot spot areas for further sampling using more quantitative methods.

Passive samplers may be of benefit in areas where soil gas probes cannot be installed, in areas where preferential pathways are suspected (or need to be assessed) or where very fine-grained soils limit the practicality and integrity of sampling from soil gas probes (API 2005).

## 6.5 Sample collection and analysis

The sampling methods discussed in Sections 6.1–6.4 can be used in conjunction with a range of active and passive sample collection methods and analytical methods. A range of methods/media are available to enable the analysis of a range of volatile organic compounds (VOCs), semi-volatile organic compounds (SVOCs), non-methane organic compounds (NMOC) and polycyclic aromatic hydrocarbons (PAHs).

Samples can be drawn through on-line detectors such as photo ionisation detectors (PIDs) and/or flame ionisation detectors (FIDs) to provide a screening level assessment of the vapour. In addition, other hand-held meters such as landfill gas detectors can be used to obtain field readings of key parameters such as O<sub>2</sub>, CO<sub>2</sub> and methane. Other real-time monitors (e.g. mercury vapour) can also be used depending on the compound of concern and required reporting limit.

Samples that need to be collected and sent to a laboratory (or field GC/MS) for analysis may be collected using a range of media that include tubes (charcoal or multisorbent), canisters, Tedlar bags, glass vials, and syringes. A number of analytical methods are available, particularly in the US, with a number listed in API (2005) and ITRC (2007a) guidance. The number of methods that are available in Australia is more limited and any method selected should be considered with respect to the sampling design objectives, conceptual model, availability of analysis, and the advantages/disadvantages of each method.

It is important to note that the specific method, list of analytes, QA/QC protocols vary among laboratories, so these should be reviewed and specified in the work plan prior to data collection.

The sample collection and analysis methods can be grouped into two categories: active and passive sampling methods. The commonly used methods are discussed further in the following sections.

### 6.5.1 Active methods

#### Sorbents

Sorbent materials, packed into tubes, typically comprise of activated carbon and/or a range of multi-sorbent materials (that can include one or more different sorbent media in each sample tube). Vapour samples are collected by drawing air (using pumps) at a calibrated rate through the tube over a specified period of time. The flow rate and sampling volume are dependent on the sorbent media used, the range of target chemicals and the required limit of reporting. The reporting limit is determined by the volume of air drawn through the sample tube, the adsorbent and analytical method used, and the potential for high concentrations (requiring dilution of the sample during analysis).

Figure 13 illustrates sorbent tubes that may be used for the purpose of sampling a range of compounds (includes some passive badges discussed further in Section 6.5.2).

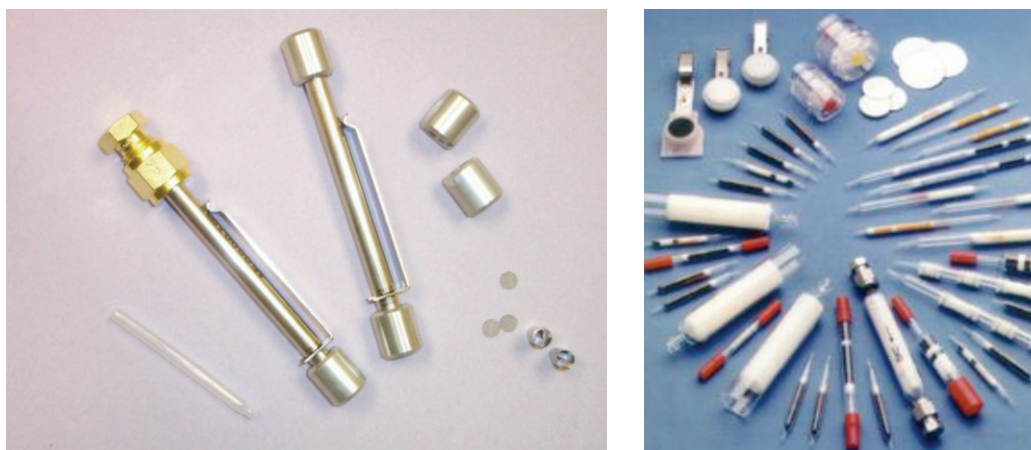


Figure 13. Example sorbent tubes (source: Air Toxics Ltd and SKC).

Once a sample is collected, the tubes are sent to a laboratory for analysis. Common methods used include the following:

- *Solvent extraction method:* A modified NIOSH method (1500 & 1501) is commonly used for the analysis of samples collected onto carbon adsorbent media. Other sorbent media can also be used for different ranges of compounds as required. This method is commonly used in occupational monitoring and is detailed in Australian Standard AS 2986.1-2003 (AS 2003a). Note that good quality control procedures should always be adopted including blanks etc. The method can be used to assess over 70 compounds that include alcohols, aliphatic and aromatic hydrocarbons, chlorinated hydrocarbons, esters, ketones and complex solvents with a limit of reporting ranging from 0.1 to 50 µg/tube (depending on target analytes).
- *Thermal desorption method:* US EPA TO-17 method (US EPA 1999) is used for the analysis of samples collected onto multi-sorbent media. The method describes sorbent tube/thermal desorption/gas chromatographic-based monitoring for VOCs in air with a limit of reporting ranging from 5 to 10 ng/tube or 0.4 to 20 µg/m<sup>3</sup> depending on the volume of gas drawn through the tube. The range of compounds reported with this method is the same as for the TO-15 method (canisters – see below).

Key aspects of the method relevant to use of sorbents in field sampling procedures are (i) the selection of sorbent materials to address the target compounds, (ii) screening expected concentrations (using a screening method such as carbon tube or data from previous work) to

assist in selecting the sampling duration and approach (to avoid saturation), (iii) sampling a range of volumes where expected concentrations are unknown, and (iv) collection of adequate QA samples. Table 12 summarises some advantages and disadvantages of the use of carbon and multi-sorbent media for the collection and analysis of gas (some noted from ITRC 2007a; US EPA 1999).

Other sorbents commonly used include:

- *Amberlite XAD-2 Resin Trap:* This polymeric resin (and glass fibre filter) is used to collect semi-volatile compounds from a variety of sources. Target compounds are removed using soxhlet extraction followed by a solvent exchange and concentration step. XAD-2 is specified in many testing methods as well as TO-13A.
- *PUF Cartridge:* Polyurethane foam (PUF) in conjunction with a glass fibre filter is used to collect organochlorine pesticides and polychlorinated biphenyls. Sampling is most often undertaken using a high volume sampler. Semi-volatile compounds are adsorbed on the surface of the foam; they are removed using soxhlet extraction. Often a filter is used to collect the particulates for TO-4A. Excessive exposure to organic solvents degrades the foam. PUF is specified in TO-4A, TO-10A and TO-13A. This method provides a limit of reporting ranging from 0.5 to 1.0 µg/sample for pesticides and 1 to 2 µg/sample for PCBs.
- *XAD-2/PUF Cartridge:* This combination is often used to collect ambient air semi-volatiles. Sampling is most often undertaken using a high volume sampler. The resin is placed between PUF plugs in a glass cartridge. The organic compounds are adsorbed onto the surface of either the PUF (if halogenated) or the XAD.

Often a filter is used to collect the particulates. The filter is extracted along with the PUF and XAD. This combination trap is specified in TO-13A. This method provides a limit of reporting that ranges from 5 to 10 µg/sample. A selective ion monitoring (SIM) method is also available that enables analysis of some

semi-volatile organic compounds (including polynuclear aromatic hydrocarbons – PAHs) to a lower limit of reporting (0.5–1.0 µg/sample). Note the limit of reporting relevant to the air concentration is dependent on the volume of air sampled.

**Table 12. Advantages and disadvantages of the use of carbon and multi-sorbent media.**

Advantages	Disadvantages
<b>Carbon (solvent extraction):</b> <ul style="list-style-type: none"><li>• Can be used to sample for longer periods of time (e.g. 8–12 hours) as method typically used in occupational environments</li><li>• Occupational monitoring pumps can be used – easy to set up and use</li><li>• Can be used to sample high concentrations</li><li>• Front and back portions of tube can be analysed to determine potential for breakthrough</li><li>• Lower cost</li></ul>	<ul style="list-style-type: none"><li>• High limit of reporting makes it unsuitable for some sampling methods and where public health issues need to be addressed (must be considered in conceptual model and sampling plan)</li><li>• Potential for saturation of media and breakthrough (resulting in loss of sample)</li><li>• Possible cross contamination due to nature of solvent used in analysis (needs to be reviewed prior to sampling)</li></ul>
<b>Multi-sorbent (TO-17):</b> <ul style="list-style-type: none"><li>• Low limit of reporting makes the method suitable for a wide range of sampling methods</li><li>• Lightweight and easy to handle</li><li>• A range of adsorbent materials can be packed into the tubes to address different target chemicals (e.g. petroleum versus chlorinated hydrocarbons). This may also include the inclusion of hydrophobic sorbents to assist in managing moisture in air samples</li><li>• Widely used method, evaluated for a range of conditions and compounds</li></ul>	<ul style="list-style-type: none"><li>• Requires use of calibrated pumps that can adequately draw air through the packed tube. The flow rate at the start, during and at the end of the sampling period must be monitored and recorded</li><li>• Potential for saturation of media and breakthrough (resulting in loss of sample). Sampling in series can be used to assess potential issues</li><li>• Tubes easily affected by moisture in air sampled resulting in loss of sample or highly elevated limit of reporting</li><li>• Photodegradation of samples may occur if exposed to light during transport and storage prior to analysis</li><li>• Short sampling time, typically 1–2 hours based on media used, how tight the tube is packed and limitations of pumps</li><li>• Cost can be an issue where multiple samples required (different time periods as well as samples collected in series)</li><li>• Thermal desorption of sample results in one chance for analysis. Elevated concentrations without dilution can damage analytical equipment and result in loss of sample</li></ul>

## Canisters

The use of canisters to collect an air sample is the most common method used to collect a whole air sample. Canisters that are specially prepared are sent to the field under vacuum and certified clean and leak-free. The canister is fitted with a calibrated regulator that, when opened, allows air to be drawn into the canister over a preset time period at a constant flow rate. Initial and final vacuums are recorded for each canister, as well as the vacuum when received at the laboratory. Figure 14 shows a range of canisters commonly used for the sampling of air from a range of sampling methods (source: Air Toxics Ltd website).



Figure 14. Canisters commonly used for the sampling of air (source: Air Toxics Ltd).

Samples collected using canisters can be analysed by a laboratory using a range of methods that include (check methods available with the selected laboratory to confirm analytical list and limits of reporting as these vary depending on the laboratory used):

- *US EPA TO-15*: The US EPA TO-15 analysis using GC/MS can be run in two modes (US EPA 1999). The Standard TO-15 method is run in full scan mode and provides a large list of approximately 70 compounds with a limit of reporting ranging from 0.4 to 20  $\mu\text{g}/\text{m}^3$ . Compounds detected include polar and non-polar VOCs. The SIM method (also noted as TO-15A) can be used to achieve a lower limit of reporting ranging from 0.005 to 0.02  $\mu\text{g}/\text{m}^3$  for a smaller list of 12–15 compounds.
- *US EPA TO-14A (GC/MS)*: This analysis using GC/MS (which can also be run in full scan or SIM mode) provides a list of approximately 40 compounds with a limit of reporting ranging from 0.4 to 20  $\mu\text{g}/\text{m}^3$ . Compounds detected are non-polar VOCs (US EPA 1999). This method is not as commonly used and is largely replaced by the TO-15 method.
- *US EPA TO-12 (GC/MS)*: This method provides analysis of non-methane organic compounds (NMOC), in particular hydrocarbons in the range C2–C12 (and C12+) with a limit of reporting ranging from 0.01 to 0.02 ppmv (US EPA 1999).

Table 13 summarises some advantages and disadvantages of the use of canisters for the collection and analysis of air (some noted from Atlantic Richfield 2006 and ITRC 2007a).



**Table 13. Advantages and disadvantages of the use of canisters.**

Advantages	Disadvantages
<ul style="list-style-type: none"> <li>• Low limit of reporting (0.4–20 µg/m<sup>3</sup> for TO-15 and TO-14A, and 0.005–0.02 µg/m<sup>3</sup> for TO-15A) makes the method suitable for a wide range of sampling methods</li> <li>• No pumps required and hence sampling procedure is straightforward</li> <li>• Sample can be collected over extended periods, up to 24 or 48 hours</li> <li>• Not subject to interference from moisture issues, saturation or breakthrough</li> <li>• Analysis only uses part of the air sample collected enabling re-analysis in the laboratory without the requirement to resample</li> <li>• Where chlorinated VOCs, particularly vinyl chloride is present the method is more reliable (achieving low limit of reporting) than tubes (Hayes et al. 2009)</li> </ul>	<ul style="list-style-type: none"> <li>• Can be expensive and bulky to ship to laboratory (however cost can be comparable to multi-sorbent tubes)</li> <li>• Recovery of analytes of higher molecular weight than naphthalene can be poor (McAlary, Groenevelt et al. 2009), hence the suitability of the method for these analytes (if required) needs to be checked with the laboratory</li> <li>• Care must be taken when using canisters to sample in low permeability soil to ensure sample flow rates are sufficiently low</li> <li>• Must be certified clean by laboratory</li> </ul>

## Other methods

Whole air samples can also be collected using Tedlar® bags, with smaller samples also collected using syringes and glass vials. The following methods are also available for the analysis of these samples (ITRC 2007a):

- VOCs can be sampled using Tedlar® bags, syringes and glass vials and analysed using method 8021B or 8260B (US EPA 1994). These methods can be used for on-site analysis (where available) and provide a limit of reporting that ranges from 10 to 100 µg/m<sup>3</sup>.
- Fixed gases (oxygen, carbon dioxide, nitrogen, carbon monoxide and methane) can be sampled using Tedlar® bags or canisters with analysis using US EPA 3C, ASTM D-1946 or ASTM D-1945 (depending on the gases required).
- TPH can also (in addition to the TO-12 method noted above) be sampled using Tedlar® bags or canisters with analysis using 8015 modified method (C4-C24) and 8260 (C4-C12) method (see US EPA 1994 for details of methods).
- Note that Tedlar® bags should not be stored for long periods, filled beyond half full or transported significant distances. As such, field sites may need to be in close proximity to analytical laboratories to allow extensive use.

## 6.5.2 Passive methods

Passive methods can involve the use of a wide range of sorbent materials. These materials are available in a range of forms (badges, canisters, tubes, strips) where the collection of compounds is based on the diffusion of the compound to the surface of the sorbent material. Common passive samplers used in Australia include badges provided by 3M and SKC (commonly used for occupational monitoring), Radiello samplers and Gore soil gas modules. Figure 15 shows examples of SKC and Radiello passive samplers. Other samplers/systems are also available and can be used depending on the target analytes, required use and reporting limits.

Common methods for the analysis of passive samples are the same as for the analysis of actively-sampled adsorbent media, namely solvent extraction and thermal desorption (depending on the passive sampler used), as outlined in Section 6.5.1. Passive sampling methods and media are commonly used in occupational monitoring and are detailed in Australian Standard AS 2986.2-2003 (AS 2003b).

The range of compounds that are commonly analysed with passive sorbents include petroleum hydrocarbons, chlorinated hydrocarbons, ammonia, aldehydes, phenols and creosols, hydrogen chloride, hydrogen fluoride,

hydrogen sulphide, ozone, nitrogen dioxide and sulphur dioxide. Other compounds can be targeted using passive methods depending on the sorbent materials/housings used, the ability to assess uptake (diffusion) rates, and analysis methods. The limit of reporting varies depending on the sampler (sorbent material) used, the analysis method and the sample time.

The use of a passive sampling system, selection of appropriate sampler (to adequately address the range of compounds required), sampling time and analysis method should be considered in the design of the sampling plan. Table 14 summarises some advantages and disadvantages of the use of passive sampling media for the collection and analysis of air (some noted from Hodny et al. 2007; ITRC 2007a).

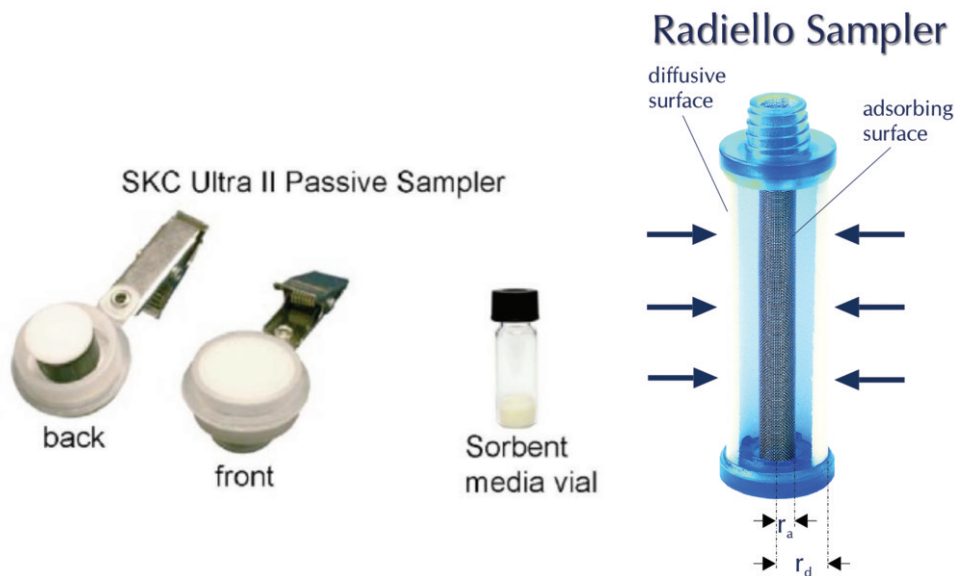


Figure 15. Examples of passive sampling devices (source: SKC and Radiello\*).

Table 14. Advantages and disadvantages of the use of passive sampling media.

Advantages	Disadvantages
<ul style="list-style-type: none"> <li>• Can be used to sample over a long period of time such as days and even weeks. This lowers the potential for sample variability</li> <li>• Can achieve low limit of reporting (dependant on sample time and sampling method used)</li> <li>• Simple to install, lightweight and easy to use</li> <li>• Can be used to sample soil gas in a wide range of conditions, including high soil moisture (provided appropriate media is selected)</li> <li>• No mechanical parts required such as pumps or calibrated flow controllers</li> <li>• Inexpensive to deploy and analyse making the method suitable for use in screening level assessments to identify hot spots</li> </ul>	<ul style="list-style-type: none"> <li>• Considered a qualitative method</li> <li>• In some circumstances, passive data can be used as a quantitative measure of concentration. However, this is dependent on concentration in air sampled, time sampled and for some samplers the movement of air past the sampler. The concentration based on diffusion principles (uptake rates) and reliability of quantifying should be assessed as part of the QA/QC for each sample</li> <li>• Potential for saturation of sorbent</li> <li>• Potential for desorbing gases off fine-grained materials</li> </ul>

\* Fondazione Salvatore Maugeri, Centro di Ricerche Ambientali, Padova, Italy: [www.radiello.it](http://www.radiello.it)



### 6.5.3 Summary of common methods

Table 15 presents a summary of the common active and passive sample collection and analysis methods used as part of a vapour sampling program. It provides, in relative terms, a comparison between methods based on Australian experience and information presented by Hodny et al. (2007) and Hayes et al. (2009). The use of any sample collection and analysis method should be considered within the scope and objectives of the sampling plan and site-specific requirements. There are a wide range of methods available. Target compounds and reporting limits should be considered in the process of selecting the most appropriate method(s) to be used on any particular site.

**Table 15. Overview of common sample collection and analysis methods.**

	Active methods			Passive methods
Sampling media	Activated carbon tubes	Multi-sorbent tubes	Canisters	Range of sorbents
Analytical method(s)	Modified NIOSH solvent extraction method	TO-17	TO-15, TO-14A, TO-12	Wide range including modified NIOSH and TO-17
Detection level	High	Low	Low	Low to high
Cost				
Analytical	Low	High	High	Moderate
Shipping	Low	Low	High	Low
Equipment	Moderate	High	Low	NA
Labour				
Field	Moderate to high	High	Low	Low
Evaluation	Moderate to high	Moderate to high	Low to moderate	High
Complexity				
Sampling	Low to moderate	High	Low to moderate	Low

## 7. Summary observations

1. *Conceptual site model (CSM)*: A conceptual site model (CSM) of vapour risk embodies a clear statement of what is to be evaluated or protected, and an understanding of site conditions, potential vapour behaviour and priorities for investigation. Along with data quality objectives (DQOs), it serves as the basis for vapour risk assessment (including identification of compounds of interest).
2. *Guidance documentation*: Extensive vapour intrusion and assessment guidance documentation have been developed within the United States of America, both federally and through individual states. Industry also has developed thorough guidance. This is in contrast to the limited vapour assessment guidance available for other countries, although some have been recently developed or are in preparation (e.g. Canada, UK).
3. *Staged approach*: A staged approach (Tier 1, 2, 3 or 4) for vapour assessment is generally adopted across nearly all guidance documentation. The breadth of work and/or investigation required in each stage is not uniform across the available guidance. The stages of investigation for vapour assessment do not always align with accepted stages of a more general site investigation (Phase I or Phase II ESAs, or PSIs and DSIs). For Australia, greater definition of the information required for a vapour assessment (such as building features, local utilities etc.) in a preliminary site investigation (Phase I ESA) would be an advantage.
4. *Screening, Tier 1 assessment*: There is substantiating information and adoption across some jurisdictions of an exclusion distance approach, whereby if a property or building is beyond a set distance to the edge of the vapour source, then it can be excluded from further investigation. An exclusion distance approach seems applicable at a Tier 1 screening level in Australia, provided the distance to the edge of the source can be adequately characterised. The approach could be applied as an initial screening option prior to comparison of site data to screening level HILs.
5. *Non-vapour investigation*: Where soil vapour assessment techniques are not used at Tier 1, then soil and/or groundwater investigations will be required to assist in the definition of the exclusion distance or to provide data for comparison to HIL screening values. Presently, in Australia, the definition of the level of site investigation required to apply Tier 1 screening (by exclusion distance or by comparison to HILs) is unclear. The NEPM-ASC requires the site investigation to be 'uniform' and delivering an 'appropriate amount of information'.
6. *Basis for HILs*: In the United States of America soil gas data are often preferred to soil data for Tier 1 screening criteria, since the soil gas (vapour phase) poses the direct inhalation risk to human health. Currently in Australia only soil concentrations are used to compare to HILs. Presuming sampling methods are reliable, soil gas concentration data would seem applicable in Australia for screening sites for vapour risk by comparison to soil gas HILs (as an alternate to soil concentrations).
7. *Vapour assessment techniques*: A variety of vapour assessment techniques are available. Advantages and disadvantages of many are tabulated. Choices of vapour investigation approaches should address the CSM and DQOs identified for the site, compounds of interest and target improvement and modification of the CSM.
8. *Locations and depths*: Guidance documents recommend a number of approaches. Common elements are, where required, (i) subsurface soil gas samples should be taken no shallower than 1 m unless adequately justified as appropriate, (ii) to determine the maximum vapour concentrations in the subsurface, samples should be recovered as close as possible to the source be it groundwater, NAPL or soil sources (it is acknowledged that this may be particularly difficult for groundwater or deep sources), and (iii) depth profiles can be useful. It is also acknowledged that subsurface utilities such as pipe and sewer lines can act as conduits for lateral and vertical transport of vapours, and in the case of sewer lines can act as a potential source of volatile compounds. Sampling plans should accommodate such site features, or be flexible enough to allow for them.

## 7. Summary observations

9. *Transients*: Seasonal and short-term atmospheric changes (barometric, etc.) can influence vapour concentrations but this effect decreases sharply with depth depending on the period of the transient disturbance and the re-equilibration time of the vapour concentrations through the soil profile. Vapour behaviour may need to be assessed over time where shallow sampling occurs.
10. *Vapour compounds*: Most experience and investigations have been carried out for petroleum hydrocarbons and chlorinated solvent vapours. Whilst the techniques and approaches may be valid for use for other volatile compounds, for some compounds (e.g. mercury, butadiene) there is limited experience and careful adoption of approaches would be required.



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# APPENDIX A. Parameter estimation techniques

(Parts are modified from Davis, Trefry & Patterson 2004)

## Volatilisation and partitioning from vapour sources

Vapours can emanate (partition) from (i) a NAPL phase, (ii) groundwater, or (iii) the soil profile itself if sorbed organic compounds are present.

### NAPL-air partitioning

Partitioning from a NAPL phase into an air phase can be described by Raoult's Law (Corapcioglu & Baehr 1987), which gives the concentration ( $C_{i,g}$  in  $\text{mg L}^{-1}$ ) of the  $i$ -th compound in a gas phase in equilibrium with a NAPL phase as:

$$C_{i,g} = \frac{M_i p_i x_i \gamma_i}{RT} \quad (1)$$

where  $M_i$  ( $\text{mg mole}^{-1}$ ) is the molecular weight of the compound,  $p_i$  (Pa) is the vapour pressure of the pure  $i$ -th compound (as a single component),  $x_i$  is the mole fraction of the  $i$ -th component in the NAPL,  $\gamma_i$  is the activity coefficient of the  $i$ -th component,  $R$  is the universal gas constant ( $8314 \text{ litres Pa K}^{-1} \text{ mole}^{-1}$ ) and  $T$  is temperature (degrees Kelvin).

Equation (1) allows calculation of likely (equilibrated) gas concentrations that may exist in the subsurface where NAPL is present and in direct contact with an air phase.

### Example calculations

For example if gasoline NAPL is present in the subsurface at a temperature of  $20^\circ\text{C}$  ( $293 \text{ K}$ ), benzene makes up 1% of the gasoline as a mole fraction ( $x = 0.01$ ), and the activity coefficient is assumed to be one, and given that  $M_{\text{benzene}} = 78,000 \text{ mg mole}^{-1}$  and that  $p_{\text{benzene}} = 11,700 \text{ Pa}$ , then  $C_{\text{benzene,g}} = 3.75 \text{ mg L}^{-1}$  or  $3,750 \text{ } \mu\text{g L}^{-1}$ . Where the gasoline NAPL has been aged through water washing, volatilisation and biodegradation processes over some period of time, the benzene concentration may be much reduced.

Under the same conditions, for a single phase chlorinated solvent DNAPL source, such as TCE,  $C_{\text{TCE,g}} = 532 \text{ mg L}^{-1}$  or  $532,000 \text{ } \mu\text{g L}^{-1}$ . In this case the mole fraction is one, and  $M_{\text{TCE}} = 131,400 \text{ mg mole}^{-1}$  and  $p_{\text{TCE}} = 9,870 \text{ Pa}$ . As a further example, vinyl chloride has

a vapour pressure approximately 30–40 times higher than TCE, and hence the vapour concentration of vinyl chloride would be 30–40 times higher under similar circumstances to those described here.

### Water-air partitioning

Partitioning from a water (groundwater) phase into air can be described at equilibrium by Henry's Law given by:

$$P_i = K_{H,i} C_{i,w} \quad (2)$$

where  $P_i$  is the partial pressure of a chemical in the air phase,  $C_{i,w}$  is the concentration in the water phase and  $K_{H,i}$  is the Henry's Law coefficient.

Since  $P_i = p_i x_i \gamma_i$ , then Equations (1) and (2) can be combined to give:

$$C_{i,g} = \frac{M_i K_{H,i} C_{i,w}}{RT} = H_i C_{i,w} \quad (3)$$

where  $H_i = \frac{M_i K_{H,i}}{RT}$  is referred to as the dimensionless Henry's Law coefficient.

### Example calculation

For example, if benzene is present in groundwater at concentrations of  $10,000 \text{ } \mu\text{g L}^{-1}$  ( $C_{\text{benzene,w}}$ ) the concentration in a gas phase in equilibrium with the groundwater ( $C_{\text{benzene,g}}$ ) would be  $2,250 \text{ } \mu\text{g L}^{-1}$ , where  $H_{\text{benzene}} = 0.225$ .

### Estimating a gas-phase concentration from groundwater data

Where a groundwater plume lies well below the water table, vapour migration may be altered and slowed. Barber et al. (1990) and Davis and Barber (1989) considered the movement of methane from groundwater plumes, across the capillary fringe and water table region, and then movement through the soil profile towards the ground surface. They found that the concentration of gas/vapours in the soil profile immediately above the water table for volatile chemicals with Henry's Law coefficients greater than  $0.025 \text{ kPa m}^3 \text{ mol}^{-1}$  was given by:

$$C_g = C_0 + \left( \frac{L D_2 C^*}{X D_1} \right) \quad (4)$$



where  $C_g$  is the gas/vapour concentration in the soil profile immediately above the water table,  $C_0$  is the concentration in gas near the ground surface,  $C^*$  is the dissolved concentration in groundwater at a distance  $X$  below the water table,  $L$  is the depth of the vadose zone, and  $D_1$  and  $D_2$  are the diffusion coefficients in the soil gas and groundwater phases respectively.

This equation can be used to estimate the likely concentration of vapours in soil gas near the water table where chemicals in groundwater pose a risk. Careful site characterisation would usually be required to carry out this style of assessment, especially in terms of measurement of  $C^*$  at a depth  $X$  below the water table. If  $C^*$  was underestimated due to dilution of concentrations by sampling from a long-screen borehole, for example, then  $C_g$  would be underestimated by a similar amount. Likewise, if the depth  $X$  below the water table were 1, 2 or 4 m the concentration  $C_g$  would change by a factor of 1, 2 or 4.

## Soil diffusion coefficient

Diffusion processes in the soil gas phase are typically slower than in gas-filled volumes. This is rationalised by a tortuosity model, essentially saying that the arrangement of microscopic pore spaces is so complicated in the soil that the effective path length of diffusing gas species moving between two locations is much longer than a direct line would give. Mathematically, this is incorporated by expressing the effective diffusion coefficient for a species in the soil gas,  $D_{eff}$ , as that species' free air diffusion coefficient,  $D_{mol}$ , multiplied by a tortuosity factor  $\tau$  (which is less than unity).

The Millington-Quirk (1961) empirical model (Equation (5)) uses measured data for the total porosity ( $\theta_T$ ), the air-filled fraction ( $\theta_a$ ), and the free-air diffusion coefficient for oxygen ( $D_{mol}$ ):

$$D_{eff} = \frac{\theta_a^{10/3}}{\theta_T^2} D_{mol} \quad (5)$$

Here the tortuosity factor  $\tau = \frac{\theta_a^{10/3}}{\theta_T^2}$ . The Millington-

Quirk formulation is widely used, but is not necessarily regarded as the most accurate equation over the full range of variation of  $\theta_a$  (e.g. see Davis et al. 2005; Jin & Jury 1996).

## Air-filled porosity estimation

The air-filled porosity is a critical parameter in estimating (oxygen and vapour) diffusion coefficients in soil.

Air-filled porosity can be determined from soil cores. A typical methodology to recover a soil core for such measurements might be to auger to just above (say 10 cm above) the depth of interest and push a thin-walled rigid tube another 20 cm into the soil. The drilling and coring could be carried out with a variety of drilling rigs, a cone penetrometer or via hand augering and manual insertion of the coring tube. The last 10 cm section of the tube/core can then be analysed to determine the bulk density and soil moisture content.

From this data, air-filled porosities can be estimated using Equation (6):

$$\theta_a = 1 - \left[ \frac{\rho_b}{\rho_m} + \rho_b \frac{\theta_g}{\rho_w} \right] \quad (6)$$

where  $\theta_a$  is the effective air-filled porosity ( $\text{m}^3 \text{m}^{-3}$ ),  $\rho_b$  is the bulk density ( $\text{kg m}^{-3}$ ),  $\rho_m$  is the free solid density (assumed equal to  $2650 \text{ kg m}^{-3}$ ; Rose 1966),  $\theta_g$  is the gravimetric moisture content ( $\text{kg kg}^{-1}$ ) and  $\rho_w$  is the density of water ( $\text{kg m}^{-3}$ ).

## Vapour and oxygen flux estimates

Equilibrium measurements of vapour and oxygen concentrations permit the inference of vertical fluxes,  $q$  (in units of  $\mu\text{g L}^{-1} \text{m s}^{-1}$ ) using the standard Fickian law:

$$q = D_{eff} \frac{\partial C}{\partial z} \quad (7)$$

$D_{eff}$  for the vapours and oxygen in the local porous medium can be estimated via the Millington-Quirk (1961) model of Equation (5). The estimated molecular diffusion coefficients for BTEX vapours is  $D_{mol} = 8 \times 10^{-6} \text{ m}^2 \text{s}^{-1}$  (Grathwohl 1998) and for oxygen is  $D_{mol} = 2.01 \times 10^{-5} \text{ m}^2 \text{s}^{-1}$  (Gliński & Stępniewski 1985).

## Characteristic time to equilibrium

The characteristic time for a vapour depth profile to reach equilibration ( $t_e$ ) over the depth of a soil profile ( $L$ ) can be estimated from Equation (8) (e.g. API 2005):

$$t_e = \frac{\theta_a \beta L^2}{D_{eff}} \quad (8)$$

where  $\theta_a$  is the effective air-filled porosity ( $\text{m}^3 \text{m}^{-3}$ ),  $L$  is the depth of the soil profile to the vapour source (m),  $D_{\text{eff}}$  is the effective diffusion coefficient in the soil profile ( $\text{m}^2 \text{s}^{-1}$ ), and  $\beta$  is the retardation coefficient of the vapour/gas based on the fraction of soil organic matter and the vapour/organic matter partitioning coefficient. Equation (8) assumes a step change concentration in source vapour concentrations and its propagation to a steady state depth profile throughout a soil profile. This occurs after an initial release into the subsurface, but may rarely occur at a later time.

Table A1 contains some estimates of such equilibration times, calculated based on Equations (5) and (8) and assuming  $D_{\text{mol}} = 8 \times 10^{-6} \text{ m}^2 \text{s}^{-1}$  (Grathwohl 1998). Based on these estimates the equilibration time for a ~2 m soil profile with an air filled porosity of 0.2–0.3 and a total porosity of 0.5 (as in Davis et al. 2005) would be 24–62 days. This is consistent with the time to re-equilibration reported in Davis et al. (2001) whereby in the same soil profile they flushed the vadose zone with nitrogen gas, and monitored vapour concentration increases over the depth profile. Note that for organic-rich soils the retardation coefficient may be greater than 1, and as such the time needs to be scaled linearly with the value of  $\beta$ .

**Table A1. Estimates of characteristic equilibration times (days) for a retardation coefficient,  $\beta=1$ .**

Equilibration times (days): Total porosity = 0.5					Equilibration times (days): Total porosity = 0.3			
Air-filled porosities (0.1 to 0.4)					Air-filled porosities (0.1 to 0.3)			
Depth (m)	0.1	0.2	0.3	0.4	Depth (m)	0.1	0.2	0.3
1	78	15	6	3	1	28	6	2
2	312	62	24	12	2	112	22	9
3	701	139	54	28	3	252	50	19
4	1247	247	96	49	4	449	89	35
5	1948	387	150	77	5	701	139	54
10	7792	1546	600	307	10	2805	557	216

## Converting soil gas concentrations

The ideal gas equation is written as:

$$PV = nRT \quad (9)$$

where

$P$  = ambient pressure (atm)

$V$  = gas volume (L)

$n$  = moles of gas

$R$  = universal gas constant ( $0.08206 \text{ L atm K}^{-1} \text{ mol}^{-1}$ )

$T$  = temperature ( $^{\circ}\text{K}$ )

### Converting soil gas concentrations from $\text{mg}/\text{m}^3$ to $\text{ppmv}$

Assuming a soil gas pressure of 1 atm, the ideal gas equation (Equation (9)) can be modified to convert soil gas concentrations from  $\text{mg}/\text{m}^3$  to  $\text{ppmv}$  according to:

$$\text{Concentration in ppmv} = (\text{Concentration in mg}/\text{m}^3) \times \frac{(273.15 + ^{\circ}\text{C}) \times 0.08206}{MW} \quad (10)$$

where

ppmv = ppm by volume (i.e. volume of gaseous concentration per 10<sup>6</sup> volumes of soil gas)

mg/m<sup>3</sup> = milligrams of gaseous concentration per cubic metre of soil gas

MW = molecular weight of the chemical (g/mol)

°C = soil gas temperature in degrees Celsius

### Example calculation

For a gas sample containing benzene (MW = 78.1 g/mol), convert 20 mg/m<sup>3</sup> to ppmv at 25°C.

$$\text{Concentration of benzene in ppmv} = \frac{20 \times (273.15 + 25) \times 0.08206}{78.1} = 6.27 \quad (11)$$

### Converting soil gas concentrations from ppmv to mg/m<sup>3</sup>

Assuming a soil gas pressure of 1 atm, the ideal gas equation (Equation (9)), can be modified to convert soil gas concentrations from ppmv to mg/m<sup>3</sup>.

$$\text{Concentration in mg/m}^3 = \frac{\text{Concentration in ppmv} \times \text{MW}}{0.08206 \times (273.15 + ^\circ\text{C})} \quad (12)$$

where

ppmv = ppm by volume (i.e. volume of gaseous concentration per 10<sup>6</sup> volumes of soil gas)

mg/m<sup>3</sup> = milligrams of gaseous concentration per cubic metre of soil gas

MW = molecular weight of the chemical (g/mol)

°C = soil gas temperature in degrees Celsius

### Example calculation

For a gas sample containing benzene (MW = 78.1 g/mol), convert 20 ppmv to mg/m<sup>3</sup> at 25°C.

$$\text{Concentration of benzene in mg/m}^3 = \frac{20 \times 78.1}{0.08206 \times (273.15 + 25)} = 63.8 \quad (13)$$

## APPENDIX B. Available US state guidance

(Primarily sourced from US EPA 2008. List current as at April 2007)

State	Available guidance
Alaska	<i>Evaluation of Vapor Intrusion Pathway at Contaminated Sites</i> (draft), 16 pp., 2006. <a href="http://www.dec.state.ak.us/spar/csp/guidance/draft_vap_intr_tm_6_28.pdf">http://www.dec.state.ak.us/spar/csp/guidance/draft_vap_intr_tm_6_28.pdf</a>
California	<i>Guidance for Assessing Exposures and Health Risks at Existing and Proposed School Sites</i> , excel spreadsheet for calculating risk updated July 12, 2006. <a href="http://www.oehha.ca.gov/public_info/public/kids/schools2604.html">http://www.oehha.ca.gov/public_info/public/kids/schools2604.html</a> <i>Use of California Human Health Screening Levels (CHHSLs) in Evaluation of Contaminated Properties</i> , 67 pp., 2005. <a href="http://www.calepa.ca.gov/Brownfields/documents/2005/CHHSLsGuide.pdf">http://www.calepa.ca.gov/Brownfields/documents/2005/CHHSLsGuide.pdf</a> <i>Guidance for the Evaluation and Mitigation of Subsurface Vapor Intrusion to Indoor Air</i> , 105 pp., 2004 (revised 7 February 2005). <a href="http://www.dtsc.ca.gov/AssessingRisk/upload/HERD_POL_Eval_Subsurface_Vapor_Intrusion_interim_final.pdf">http://www.dtsc.ca.gov/AssessingRisk/upload/HERD_POL_Eval_Subsurface_Vapor_Intrusion_interim_final.pdf</a> Advisory – Active Soil Gas Investigations, 25 pp., 2003. <a href="http://www.dtsc.ca.gov/loader.cfm?url=/commonspot/security/getfile.cfm&amp;pageid=94677">http://www.dtsc.ca.gov/loader.cfm?url=/commonspot/security/getfile.cfm&amp;pageid=94677</a> CalTOX: A Total Exposure Model for Hazardous Waste Sites <a href="http://www.dtsc.ca.gov/AssessingRisk/ctox_dwn.cfm">http://www.dtsc.ca.gov/AssessingRisk/ctox_dwn.cfm</a>
Colorado	<i>Policy on an Interim Risk Evaluation and Management Approach for PCE</i> , 3 pp., 2006. <a href="http://www.cdphe.state.co.us/hm/pcepolicy.pdf">http://www.cdphe.state.co.us/hm/pcepolicy.pdf</a> <i>Policy on an Interim Risk Evaluation and Management Approach for TCE</i> , 2 pp., 2006. <a href="http://www.cdphe.state.co.us/hm/tcepolicy.pdf">http://www.cdphe.state.co.us/hm/tcepolicy.pdf</a> <i>Draft Indoor Air Guidance</i> , 58 pp., 2004. <a href="http://www.cdphe.state.co.us/hm/indoorair.pdf">http://www.cdphe.state.co.us/hm/indoorair.pdf</a> <i>Guidance for Analysis of Indoor Air Samples</i> , 9 pp., 2000. <a href="http://www.cdphe.state.co.us/hm/airsmpl.pdf">http://www.cdphe.state.co.us/hm/airsmpl.pdf</a> <i>Petroleum Storage Tank Owner/Operator Guidance Document</i> , 45 pp., 1999. <a href="http://oil.cdle.state.co.us/OIL/Technical/Guidance%20Documents/guidancedoc.asp">http://oil.cdle.state.co.us/OIL/Technical/Guidance%20Documents/guidancedoc.asp</a>
Connecticut	<i>Significant Environmental Hazard Condition Notification Threshold Concentrations, Reference Table A: A Volatile Organic Substances</i> , 2005. <a href="http://ct.gov/dep/cwp/view.asp?a=2715&amp;q=324964&amp;depNav_GID=1626">http://ct.gov/dep/cwp/view.asp?a=2715&amp;q=324964&amp;depNav_GID=1626</a> <i>Connecticut's Remediation Standard Regulations Volatilization Criteria: Proposed Revisions</i> , 50 pp., 2003. <a href="http://ct.gov/dep/cwp/view.asp?a=2715&amp;q=325012">http://ct.gov/dep/cwp/view.asp?a=2715&amp;q=325012</a> <a href="http://ct.gov/dep/lib/dep/site_clean_up/remediation_regulations/RvVolCri.pdf">http://ct.gov/dep/lib/dep/site_clean_up/remediation_regulations/RvVolCri.pdf</a>
Delaware	<i>Policy Concerning the Investigation, Risk Determination and Remediation for the Vapor Intrusion Pathway</i> , 32 pp., March 2007. <a href="http://www.dnrec.state.de.us/dnrec2000/Divisions/AWM/sirb/policy%20concern07008.pdf">http://www.dnrec.state.de.us/dnrec2000/Divisions/AWM/sirb/policy%20concern07008.pdf</a>
Idaho	<i>Risk Evaluation Manual, Appendix C: Evaluation of the Indoor Air Inhalation Pathway</i> , woo4. <a href="http://www.deq.idaho.gov/Applications/Brownfields/download/appx_all.pdf">http://www.deq.idaho.gov/Applications/Brownfields/download/appx_all.pdf</a>

State	Available guidance
Indiana	<p>Indiana's pilot program guidance is intended to provide interim guidance, not requirements, for site investigation.</p> <p><i>Indiana Department of Environmental Management Draft Vapor Intrusion Pilot Program Guidance</i>, 90 pp., April 26, 2006.  <a href="http://www.in.gov/idem/files/la-073-gg.pdf">http://www.in.gov/idem/files/la-073-gg.pdf</a></p>
Louisiana	<p><i>Risk Evaluation/Corrective Action Program (RECAP)</i>, 119 pp., October 20, 2003  <a href="http://www.deq.louisiana.gov/portal/tabid/2929/Default.aspx">http://www.deq.louisiana.gov/portal/tabid/2929/Default.aspx</a></p>
Maine	<p><i>Edited/Adapted Field Guidelines for Protecting Residents from Inhalation Exposure to Petroleum Vapors</i>, 34 pp., 2000.  <a href="http://www.maine.gov/dep/rwm/sops/">http://www.maine.gov/dep/rwm/sops/</a></p> <p><i>Guidelines for Protecting Residents from Inhalation Exposure to Petroleum Vapors</i>, 271 pp., 1998.  <a href="http://www.maine.gov/dep/rwm/sops/">http://www.maine.gov/dep/rwm/sops/</a></p>
Massachusetts	<p><i>Indoor Air Sampling and Evaluation Guide</i>, WSC Policy #02-430, 157 pp., 2002.  <a href="http://www.mass.gov/dep/cleanup/laws/02-430.pdf">http://www.mass.gov/dep/cleanup/laws/02-430.pdf</a></p> <p><i>Guidelines for the Design, Installation, and Operation of Sub-Slab Depressurization Systems</i>, 15 pp., December 1995.  <a href="http://www.mass.gov/dep/cleanup/laws/ssd1e.pdf">http://www.mass.gov/dep/cleanup/laws/ssd1e.pdf</a></p> <p><i>Massachusetts Contingency Plan Numerical Standards: GW-2</i>  <a href="http://www.mass.gov/dep/cleanup/laws/gw2.htm">http://www.mass.gov/dep/cleanup/laws/gw2.htm</a></p>
Michigan	<p><i>RRD Operational Memorandum No. 1: Part 201 Generic Cleanup Criteria/Part 213 Risk Based Cleanup Levels</i>, 2004.  <a href="http://www.michigan.gov/deq/0,1607,7-135-3311_4109_9846_30022-101581--,00.html">http://www.michigan.gov/deq/0,1607,7-135-3311_4109_9846_30022-101581--,00.html</a></p> <p><i>RRD Operational Memorandum No. 2: Sampling and Analysis</i>, Attachment 3: Indoor Air Designated Methods and Target Detection Limits, 7 pp., 2004.  <a href="http://www.michigan.gov/deq/0,1607,7-135-3311_4109_9846_30022-101581--,00.html">http://www.michigan.gov/deq/0,1607,7-135-3311_4109_9846_30022-101581--,00.html</a></p> <p><i>Technical Memorandum: Residential Soil Volatilization to Indoor Air, Inhalation Criteria for Trichloroethylene (CAS# 79-01-65)</i>, 33 pp., 2004.  <a href="http://www.michigan.gov/documents/mshda_mf_tce_volatilization_114937_7.pdf">http://www.michigan.gov/documents/mshda_mf_tce_volatilization_114937_7.pdf</a></p> <p><i>Evaluation of the Michigan Department of Environmental Quality's Generic Groundwater and Soil Volatilization [sic] to Indoor Air Inhalation Criteria</i>, 67 pp., 2001.  <a href="http://www.michigan.gov/documents/iirept_3693_7.pdf">http://www.michigan.gov/documents/iirept_3693_7.pdf</a></p> <p><i>Part 201: Generic Groundwater and Soil Volatilization to Indoor Air Inhalation Criteria: Technical Support Document</i>, 39 pp., 1998.</p> <p><i>Part 213, Risk-based Screening Levels (RBSLs) for Groundwater and Soil Volatilization to Indoor Air</i>, Operational Memorandum No. 4, Attachment 8, 38 pp., 1998.  <a href="http://www.michigan.gov/documents/deq/deq-std-op4ATT8_250008_7.DOC">http://www.michigan.gov/documents/deq/deq-std-op4ATT8_250008_7.DOC</a></p>
Minnesota	<p><i>Indoor Air Sampling at VOC Contaminated Sites: Introduction, Methods, and Interpretation of Results</i>, 17 pp., 2004.  <a href="http://www.health.state.mn.us/divs/eh/hazardous/topics/iasampling.pdf">http://www.health.state.mn.us/divs/eh/hazardous/topics/iasampling.pdf</a></p> <p><i>Vapor Intrusion Assessments Performed During Site Investigations</i>, Guidance Documents 4-01a, 13 pp., 2005.  <a href="http://www.pca.state.mn.us/publications/c-prp4-01a.pdf">http://www.pca.state.mn.us/publications/c-prp4-01a.pdf</a></p>

State	Available guidance
Missouri	<p><i>Missouri Risk-based Corrective Action (MRBCA) Technical Guidance, Appendix H: Measurement of Soil Vapor Levels</i>, 16 pp., 2006.  <a href="http://www.dnr.mo.gov/env/hwp/mrbca/mrbca.htm">http://www.dnr.mo.gov/env/hwp/mrbca/mrbca.htm</a></p> <p><i>Missouri Risk-based Corrective Action (MRBCA) Process for Petroleum Storage Tank Sites, Appendix C: Evaluation of Indoor Inhalation Pathway</i>, 9 pp., 2004.  <a href="http://www.dnr.mo.gov/env/hwp/tanks/mrbca-pet/docs/mrbca-pet-appendix-c.pdf">http://www.dnr.mo.gov/env/hwp/tanks/mrbca-pet/docs/mrbca-pet-appendix-c.pdf</a></p>
Nebraska	<p>Nebraska has no individual guidance. However, the topic of vapour intrusion is discussed in <i>Riskbased Corrective Action (RBCA) at Petroleum Release Sites: Tier 1/Tier 2 Assessments &amp; Reports</i>, 2004 (now revised to May 2009 new PDF).  <a href="http://www.deq.state.ne.us/">http://www.deq.state.ne.us/</a></p>
New Hampshire	<p><i>Vapor Intrusion Guidance</i>, 44 pp., July 2006 (revised Feb 2007).  <a href="http://des.nh.gov/organization/commissioner/pip/publications/wmd/documents/wmd-06-1.pdf">http://des.nh.gov/organization/commissioner/pip/publications/wmd/documents/wmd-06-1.pdf</a></p> <p><i>GW-2 Methodology</i>, 2 pp., 2006.  <a href="http://des.nh.gov/organization/divisions/waste/hwrb/documents/revised_gw-2_methodology.pdf">http://des.nh.gov/organization/divisions/waste/hwrb/documents/revised_gw-2_methodology.pdf</a></p>
New Jersey	<p>New Jersey Johnson &amp; Ettinger Spreadsheets, 2006.  <a href="http://www.nj.gov/dep/srp/guidance/vaporintrusion/njje.htm">http://www.nj.gov/dep/srp/guidance/vaporintrusion/njje.htm</a></p> <p>Several reports at <a href="http://nj.gov/dep/srp/guidance/vaporintrusion/">http://nj.gov/dep/srp/guidance/vaporintrusion/</a> including:  <i>Vapor Intrusion Guidance</i>, 282 pp., 2005.  <a href="http://www.nj.gov/dep/srp/guidance/vaporintrusion/vig.htm">http://www.nj.gov/dep/srp/guidance/vaporintrusion/vig.htm</a></p> <p><i>Indoor Air VOC Sampling and Analysis Requirements</i>, 2 pp., 2003.  <a href="http://www.nj.gov/dep/srp/guidance/vaporintrusion/ia_sampling_req.pdf">http://www.nj.gov/dep/srp/guidance/vaporintrusion/ia_sampling_req.pdf</a></p>
New York	<p>Several reports at <a href="http://www.health.state.ny.us/environmental/indoors/vapor_intrusion/">http://www.health.state.ny.us/environmental/indoors/vapor_intrusion/</a> including:  <i>Guidance for Evaluating Soil Vapor Intrusion in the State of New York</i>, 2006.  <a href="http://www.health.state.ny.us/environmental/investigations/soil_gas/svi_guidance/">http://www.health.state.ny.us/environmental/investigations/soil_gas/svi_guidance/</a></p> <p><i>Strategy for Evaluating Soil Vapor Intrusion at Remedial Sites in New York (DER-13)</i>, 16 pp., 2006.</p> <p><i>Indoor Air Sampling and Analysis Guidance</i>, 4 pp., 2005.  <a href="http://www.health.state.ny.us/environmental/indoors/air/guidance.htm">http://www.health.state.ny.us/environmental/indoors/air/guidance.htm</a></p>
Ohio	<p><i>Methodology for Vapor Intrusion Assessment</i>, 4 pp., 2005.  <a href="http://www.epa.state.oh.us/derr/rules/vapor.pdf">http://www.epa.state.oh.us/derr/rules/vapor.pdf</a></p>
Oregon	<p>Screening Model for Volatilization from Soil to Indoor Air at Heating Oil Tank Sites (excel spreadsheet to be used with <i>Risk-based decision Making for the Remediation of Petroleum-Contaminated Sites</i>) at:  <a href="http://www.deq.state.or.us/lq/rbmd.htm">http://www.deq.state.or.us/lq/rbmd.htm</a>  <a href="http://www.deq.state.or.us/lq/tanks/hot/screeningmodel.htm">http://www.deq.state.or.us/lq/tanks/hot/screeningmodel.htm</a></p>
Pennsylvania	<p>Section IV.A.4, 'Vapor Intrusion into Buildings from Groundwater and Soil under the Act 2 Statewide Health Standard', (26 pp., 2002) in the <i>Recycling Program Technical Guidance Manual</i>.  <a href="http://www.dep.state.pa.us/dep/subject/advoun/cleanup/2002/BoldedVaporGuidance_100702.pdf">http://www.dep.state.pa.us/dep/subject/advoun/cleanup/2002/BoldedVaporGuidance_100702.pdf</a></p>
Wisconsin	<p><i>Chemical Vapor Intrusion and Residential Indoor Air: Guidance for Environmental Consultants and Contractors</i>, 16 pp., 2003. [Provided background on vapour intrusion but basically refers readers to EPA guidance and the Johnson and Ettinger (1991) model.]  <a href="http://www.dhfs.wisconsin.gov/eh/Air/fs/VI_prof.htm">http://www.dhfs.wisconsin.gov/eh/Air/fs/VI_prof.htm</a></p>



