CSIRO Land and Water

Petroleum and Solvent Vapours: Quantifying their Behaviour, Assessment and Exposure

A report to the Western Australian Department of Environment

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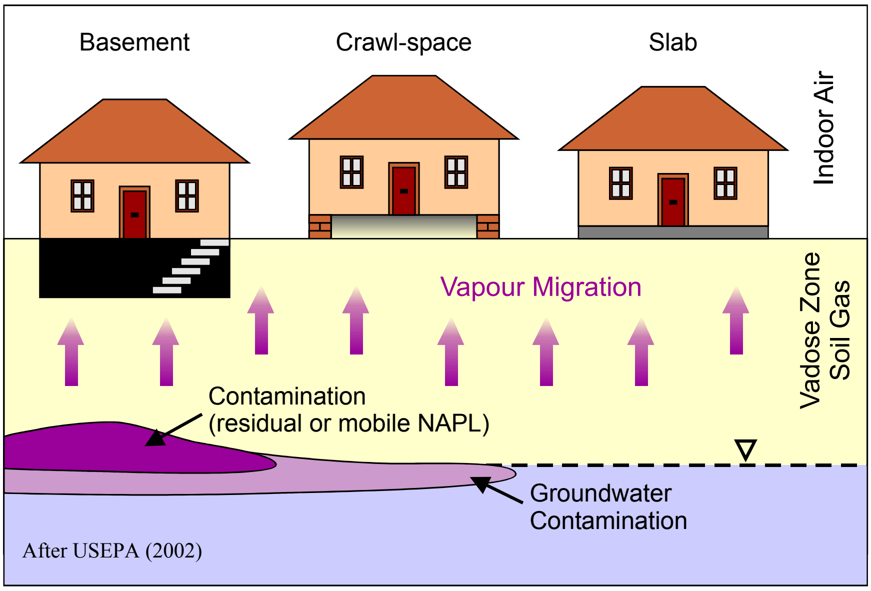

CSIRO Land and Water Report

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Important Disclaimer

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Executive Summary

Organic (petroleum and chlorinated solvent) contamination of soil and groundwater is common, and may lead to vapour migration and pose inhalation health risks to residents in buildings constructed on impacted land. Here the status of research and investigation techniques and knowledge in the area of vapour behaviour, potential exposures and the assessment of vapour risk is outlined.

In particular, this report includes,

(i) an overview of vapour literature and guidance documents;

(ii) a discussion of typical vapour behaviour and properties, and the influences and processes that govern vapour behaviour and risks;

(iii) the behaviour of vapours with respect to open-ground and built-ground environments including slab-on-ground, crawl-space and basement structures;

(iv) a description of vapour measurement, assessment and monitoring techniques; and

(v) modelling approaches that are commonly undertaken.

Vapour data collected from field sites in Australia are included in this report. The field data relate to sandy and clay soil environments, slab-on ground and open ground conditions, and conditions where petroleum hydrocarbon and chlorinated hydrocarbon vapours are present. These illustrate the variety of behaviours that vapours may exhibit, and provide data for model assessment and confidence in model prediction.

The contrasting response of vapours to open ground conditions and covered-ground conditions (such as slab-on-ground construction), and the contrasting behaviour of petroleum hydrocarbon vapours and chlorinated solvent vapours are highlighted.

A brief discussion of uncertainties and gaps in knowledge related to vapour assessment are outlined at the end of the report.

1 Introduction

Petroleum and solvent contamination in soil and groundwater may lead to vapour migration into built structures above ground and pose a risk of vapour exposure to residents or workers, as in Figure 1.1. The potential for vapours to accumulate in indoor air can be a significant driver of health risk and potentially affect the extent of remediation required at an impacted site (Sanders and Stern, 1994; API, 1998). The difficulties associated with assessing such risks across numbers 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 by the USEPA in 1995 (USEPA, 1995). These methodologies have since been adopted by many nations, and a range of assessment tools has become available to support environmental resource management and remediation activities within the RBDM and RBCA frameworks. This document provides a general overview of information on vapour fate processes, vapour properties, modelling of vapours in the subsurface, and assessment techniques for vapours to help define exposures and risk. In later sections various choices among RBCA-compliant modelling tools for assessing risks from vapour exposure pathways are noted and present gaps in understanding of vapour-related processes are mentioned.

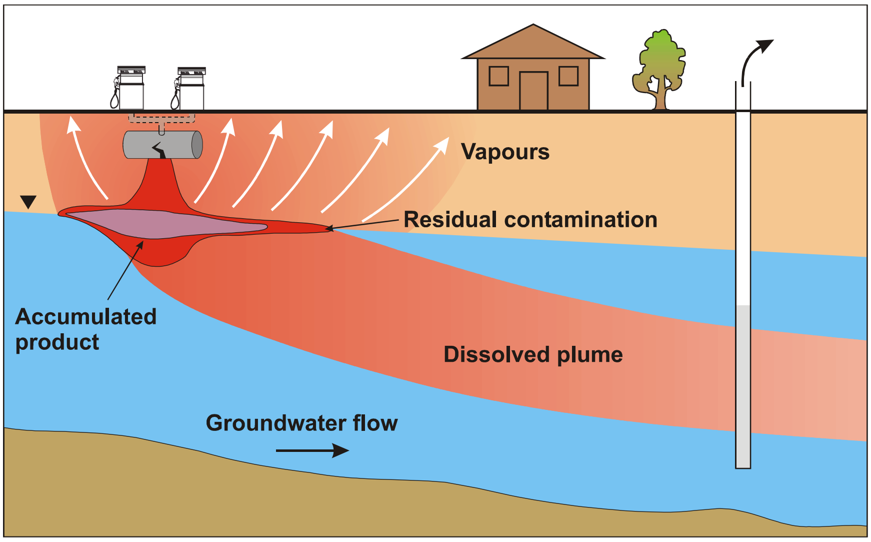


Figure 1.1 A leakage scenario leading to vapour release and potential exposure. The 'accumulated product' and 'residual contamination' in the schematic are non-aqueous phase liquids (or NAPLs), which can contain soluble and volatile contaminants that partition into the gas and aqueous phases.

Here we focus on petroleum hydrocarbon vapours, but in addition discuss solvent vapours and include some comment on other vapours that may pose risks. 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). 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 this literature is also referenced in this document.

1.1 Guidance Documents

Within the general RBDM and RBCA frameworks now used widely in environmental resource management and protection, there are several guidance documents available for evaluating the vapour exposure pathway and related to vapour assessment and modelling.

The USEPA (USEPA, 2002) has developed "Draft Guidance for Evaluating the Vapor Intrusion to Indoor Air Pathway from Groundwater and Soils (Subsurface Vapor Intrusion Guidance)" which was an update of earlier guidance developed in 2001 (see, USEPA, 2001; http://www.epa.gov/correctiveaction/eis/vapor.htm). This contains screening level assessments and was not initially recommended for assessment of underground storage tank sites. The USEPA has also developed on-line access to a screening model for a preliminary risk assessment of hydrocarbon vapour intrusion into buildings (http://www.epa.gov/athens/learn2model/part-two/onsite/JnE_lite.htm).

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 has published Bulletins on the Johnston and Ettinger (1991) model, its use and guidance on modifications to the model (API Bulletins 15 (2001); 16 (2002); and 17(2002)) – these are located at www.api.org/bulletins.

There is an American Society for Testing and Materials standard – which provides guidance on soil gas monitoring in the vadose zone (ASTM 1992). This guidance document was re-approved in 2001. This provides guidance on "sample recovery and handling, sample analysis, data interpretation and reporting.".

The New Zealand Ministry for the Environment (NZMfE, 1999) has compiled "Guidelines for Assessing and Managing Hydrocarbon Contaminated Sites in New Zealand", a comprehensive document on tiered risk-based approaches to assessing and managing contaminations of soil environments. The complete documentation set is freely available at http://www.mfe.govt.nz/publications/hazardous/oil-guide-jun99/oil-guide-jun99.zip.

The County of San Diego Department of Environmental Health (2004) developed a Site Assessment and Mitigation (SAM) Manual. Section 5 subsection IV outlines soil vapour sampling guidelines.
See http://www.sdcounty.ca.gov/deh/lwq/sam/manual_guidelines.html .

These documents are only representative of a wide range of similar documents now used by regulators around the world. They reflect the present scientific understanding of subsurface vapour contamination, remediation and risk processes. This report outlines the key scientific approaches to measuring and understanding these processes. In Sections 2 and 3 a short overview of soil vapour concepts and dynamics is presented, and then these are related to the impacts on built structures in Section 4.

Vapour sampling techniques are described in Section 5, and some popular modelling approaches and tools are discussed in Section 6, especially with respect to RBCA methodologies.

1.2 Basic Concepts of Spills

Before moving on to discuss vapour processes in detail, it is useful to introduce the general context of spills of organic liquids and how these liquids may potentially present risks via a variety of phases and exposure pathways in the environment.

1.2.1 General Scenarios

Spills and leaks of organic liquids (also known as non-aqueous phase liquids – NAPLs) such as petroleum hydrocarbons (e.g., gasoline), or industrial solvents (e.g., trichloroethene or methylethyl ketone) can lead to soil and groundwater contamination (see, for example, Figure 1.1). Organic chemicals can partition from the NAPL to the water, soil and air phases in the subsurface leading to off-site movement and potential exposures and risks.

Partitioning of organic chemicals into the air phase can occur either from the NAPL or groundwater phases in the subsurface, which act as sources of vapours. The vapours have the potential to migrate from the subsurface source zones through the soil profile to the ground surface. The rate and extent of movement depends on a range of factors – including the chemical and soil properties (these will be discussed in a later Section). Movement of the organic vapours is primarily governed by diffusion in the soil gas, although local wind (and other) conditions can also induce advective movement in the subsurface. Whether the vapours discharge to the atmosphere will depend on ground surface conditions and, in particular, the presence of built structures at the ground surface.

1.2.2 Sources of Vapours

The source of vapours can be either:

(i) NAPL that is resident in the subsurface

(ii) Groundwater that is contaminated with the volatile contaminant

(iii) Soil in the vadose zone that is contaminated with organic chemicals that will re-partition into a soil gas phase (the chemicals may be sorbed to the soil, for example, but not be present as a NAPL phase)

The situation of sorbed organics in a soil profile is not considered further in great detail, but can be investigated and assessed using the concepts and techniques described in this document.

NAPL as a source

The distribution of NAPL as a source of vapours may be variable dependent on its own physicochemical properties – for example a denser-than-water NAPL or DNAPL may penetrate to deeper depths in a soil profile and below the water table, whereas a lighter-than-water NAPL or LNAPL will typically only penetrate to the water table and pool there (as in Figure 1.1). In which case, NAPL acting as a vapour source may be distributed differently and non-uniformly depending on the properties of the NAPL and soil/aquifer media.

A common petroleum fuel LNAPL is gasoline, which acts as a source of vapours when present in the subsurface. Gasoline is a complex mixture of compounds – usually the dominant vapour of concern is benzene. Other common sources of petroleum hydrocarbon vapours are crude oil, aviation fuel, other specific blends, and single-component hydrocarbon liquids that are used as solvents (such as benzene or xylene). Diesel and kerosene fuels do not usually contain high concentrations of volatile compounds.

The chlorinated solvents (such as tetrachloroethene or PCE) are typically DNAPLs and can often be released to the environment as a pure phase, and although this is not always the case, they are not as commonly released as complex mixtures like gasoline. As dense liquids they can penetrate through the soil profile and water table and reside on top of low hydraulic conductivity layers either within the soil profile or possibly at the base of the aquifer. The DNAPL may be present in the soil profile as ganglia or stringers (rather than as with gasoline NAPL pooling at the water table), and as such may give rise to variable vapour concentrations in the soil profile. The groundwater may be the dominant source of vapours in such a case.

Groundwater as a source

Where spills and leaks have occurred, groundwater can contain chemicals of concern that may volatilise to the soil profile above. This may be of particular concern where groundwater has migrated off-site to beneath houses or built structures, or where redevelopment is intended on-site above impacted areas of a site. An additional concern may be where basement-type constructions are built below the water table, and where the groundwater is impacted with volatile chemicals.

Where groundwater is the source of vapours, the depth interval of the groundwater (saturated zone) over which the chemicals of concern are distributed is critical. If the groundwater plume is at or near the water table then volatilisation of the chemicals of concern to the air phase from groundwater readily occurs. If however, the groundwater plume is at some depth below the water table with ‘clean’ water between the source plume and the water table, then migration of the chemicals of concern to the water table and to the soil gas phase above the water table is slowed and controlled by diffusion and dispersion in the ‘clean’ (water-saturated) groundwater. Diffusion in water is typically four orders of magnitude slower than in a gas phase. Given enough time (i.e., under steady state conditions), the chemicals of concern will diffuse/disperse from the groundwater source zone to the soil profile above. Under transient conditions of, for example, continual seasonal inputs of rainfall recharge then the time to diffuse from the source zone at depth may be longer than the seasonal periodicity of recharge, resulting in limited vapour migration into the soil profile above. These issues will be further discussed in a later section.

2 Overview of Vapour Literature

There is a large body of information and active research related to vapour behaviour, and its modelling in soil and groundwater environments – the research is being carried out both within Australia (e.g., Markey and Anderssen, 1996; Davis *et al.*, 2000; Turczynowicz and Robinson, 2001; Wright and Howell, 2004; Davis and Johnston, 2004) and internationally (e.g., Johnson and Ettinger, 1991; Hers *et al.*, 2000; 2003). Despite this, current risk assessments for human exposure to soil vapours use simplified models of indoor air pathways and soil vapour dynamics, and rely on limited data sets regarding actual pathways into build structures. Some trends and consequences of the currently available data and models are apparent.

2.1 Petroleum Vapours

Issues of hydrocarbon contaminations in soil profiles and their remediation have been of concern for some time (see Morgan and Watkinson, 1989 for a useful review), but scientific field studies of petroleum vapour migration and fate are still relatively rare. Ostendorf and Kampbell (1991) carried out an initial field study of the behaviour and biodegradation of petroleum vapours in soil impacted with petroleum NAPL. There were earlier studies by Karimi *et al.* (1987) who carried out laboratory experiments, and Barber *et al.* (1990) who looked at a range of volatile contaminants in soil profiles near landfill leachate plumes. There have been several studies since looking specifically at gasoline-range vapours above petroleum-impacted soil and groundwater (Fischer *et al.*, 1996; Laubacher *et al.*, 1997; Davis *et al.*, 1998; Franzmann *et al.*, 1999; Hers *et al.*, 2000; Davis *et al.*, 2000; Davis *et al.*, 2001; Wang *et al.*, 2003).

2.2 Chlorinated Solvent Vapours

Whilst there is a body of literature on the fate of chlorinated DNAPLs in groundwater (Rivett *et al.*, 1990; Burston *et al.*, 1993; Pankow and Cherry, 1996; Jackson, 1998), research on the behaviour of chlorinated solvent vapours is less extensive (but see, for example, Conant *et al.*, 1996; Wright and Howell, 2004). Conant *et al.* (1996) carried out field experiments with a shallow emplaced finite-mass trichloroethene (TCE) source and generated transient depth data on vapour concentrations. Wright and Howell (2004) reported groundwater data and related model results (based on groundwater concentrations as the lower source boundary conditions) to observed emission data for chlorinated solvent and BTEX compounds measured at ground surface at a range of field sites. The models were found to over predict measured values by up to 5 orders of magnitude, but typically 2-4 orders of magnitude. This was also observed by Hers *et al.* (2003).

There appear to be few studies that show the natural depth distribution of chlorinated solvent vapours in vadose zone soils – to assess natural fate and potential risks, and few for extensive DNAPL source areas.

Typically a DNAPL that acts as a source of vapours may be less extensive aerially than LNAPL that pancakes across a water table. DNAPL would tend to penetrate through the water table possibly leaving residual ganglia in the vadose zone. In which case, natural profiles of solvent vapours related to DNAPL ganglia may be variable in three dimensions due to the possible limited volume of NAPL impact. In contrast, where an LNAPL spill is distributed extensively along the water table or where monitoring is carried out in the central area of a spill, the transport of vapours is likely to be effectively vertical and one-dimensional.

In some circumstances, petroleum hydrocarbons and chlorinated solvents may reside in the subsurface as a mixed NAPL, giving rise to a mixture of vapour types, concentrations and behaviours. This aspect is discussed later in Section 3.3.

2.3 Radon Gas

Radon entry studies are pertinent to the hydrocarbon context for several reasons. Firstly the radon is produced continuously within the soil column, much as a large NAPL source may produce hydrocarbon vapours for a long time via simple volatilisation. Secondly, radon is continuously undergoing (radioactive) decay at a time scale not significantly different to hydrocarbon biodegradation rates, and finally the mathematical equations governing radon transport are reasonably similar to the hydrocarbon equations. However, the differences between radon and hydrocarbon soil gas processes are important too. Radon decays regardless of its chemical environment – the presence or absence of oxygen or microbial agents has no effect on the decay rate. Also, Ra-222 does not sorb to natural organic carbon in the same way that hydrocarbons do, hence the potential for transport retardation to be different for radon and organic vapours. Nevertheless, some broad conclusions are transferable. First, that building type, construction and condition may be important factors in determining gas entry flux. Second, that soil characteristics may either promote or reduce soil vapour migration according to moisture state and permeability distribution, and thirdly, that climatic and barometric variations may induce significant time-dependent variations in gas entry fluxes, even if all other factors are held constant.

Radon gas is a natural product of radioactive decay of uranium species found, in varying concentrations, in most rock and soil types. Radon itself is chemically unreactive, but it also decays radioactively to produce daughter species that are highly reactive. Specifically, U-238 decays through several steps to Ra-226 (half-life 1600 years), which then decays to Ra-222 (half-life 3.82 days) via α-particle release. Daughter products of Ra-222 are a succession of polonium, bismuth and lead species before finishing with the stable Pb-206. The health risk associated with radon exposure is dominated by the combination of radioactivity and chemical reactivity exhibited by the polonium and lead daughter products.

In the early 1980s it was recognized that there was potential for natural radon concentrations in soil gas to be magnified within some classes of built structures, posing a risk to building inhabitants (Nero and Nazaroff, 1984). In particular, where building heating systems established convective circulation patterns, mean air pressures in basements and lower floors of the buildings could be lower than pressures in the nearby soil gas (see Figure 2.1). Other mechanisms for depressurization include wind loading and temperature imbalances (Garbesi and Sextro, 1989). There have been many studies of radon migration from the soil gas phase into buildings with increasing levels of theoretical and computational sophistication, ranging from lower dimensional approaches (e.g., Cripps, 1999) to fully three-dimensional fluid dynamic simulations (e.g. Louriero *et al.*, 1990; Wang and Ward, 2000). Even so, discrepancies between measured data and theoretical predictions of an order of magnitude or more were common, most probably influenced by the difficulty of characterizing the variability of soil and building material properties (Garbesi *et al.*, 1993). In particular, fluid transfer properties of cracks in concrete and other building materials are significant controls to radon entry and continue to provide research challenges (Etheridge, 1998; Liu and Nazaroff, 2001). One method of assessing crack influences is to perform inverse calculations based on gas entry observations – these yield effective ratios of crack size to solid area between 0.0001 and 0.001. Also, seasonal and other transient effects must be taken into account in assessing radon exposure (Chen, 2003; Karpinska *et al.*, 2004).

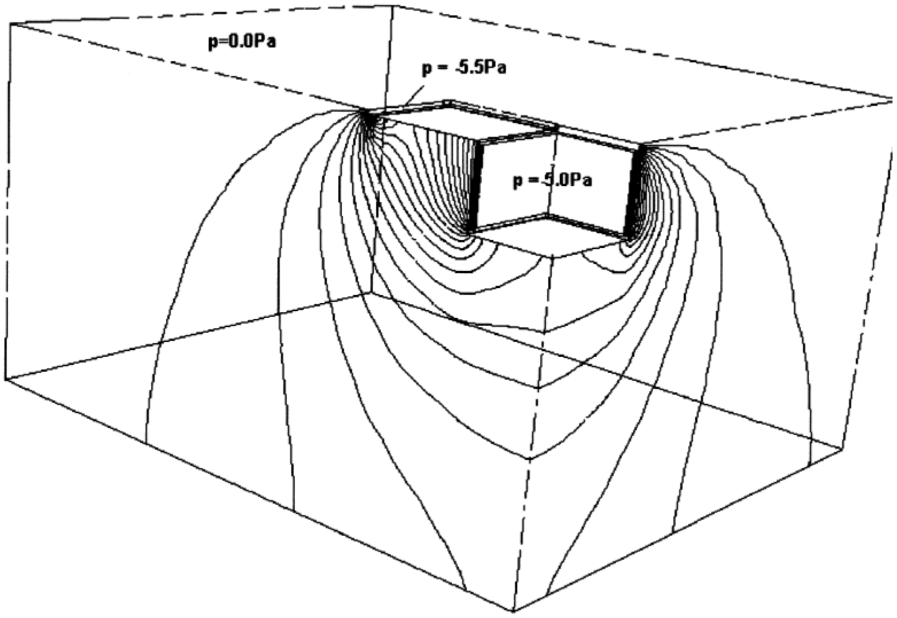


Figure 2.1 Three dimensional soil gas pressure distribution near a built structure with complex below-ground geometry (from Wang and Ward, 2000), showing how in-building ventilation can attract soil gases.

3 Typical Vapour Properties and Behaviour

3.1 Vapour Properties

Keys to the hazard posed by chemicals in a vapour phase are its physical and chemical properties. Properties for a range of chemicals that may be of concern in a vapour phase are given in Table 1.1. The range of chemicals listed in Table 1.1 is by no means exhaustive, nor is it meant to imply that these chemicals will always pose a vapour risk.

Further discussion of typical vapour behaviour is given in later Sections. Here some brief definitions and observations are made.

'Density' here is defined as the liquid phase density. This is important in assessing if chemical releases are LNAPLs or DNAPLs and as such where they may reside in the subsurface relative to low conductivity layers and the water table. Note that the petroleum hydrocarbons and the ketones are less dense than water (LNAPLs) and the halogenated solvents (chlorinated and brominated solvents) are all DNAPLs except vinyl chloride, which as a pure liquid would act as an LNAPL.

The 'Aqueous solubility' is the amount of a chemical that will dissolve into a water phase when in equilibrium with a separate pure NAPL of that chemical.

'Henry's Law constants' describe the propensity of a chemical to partition to an air phase from a neighbouring water phase. This is critical where groundwater is contaminated with a volatile chemical and NAPL is not present. It is akin (although not in absolute terms) to the ratio of vapour pressure and the solubility of the chemical of interest. The USEPA (2002) suggest use of its guidance document when the source of volatile chemicals is less than 100 feet (or ~ 30.5 m) below ground surface and the Henry's law constant of the chemicals of concern are > 0.001 kPa m^3 mol^{-1}.

The 'Octanol-water partitioning coefficient' is the propensity for a chemical to partition from a water phase to an organic phase here represented by an octanol NAPL, as a standard. The octanol-water partitioning coefficient is often directly proportional to the sorption coefficient for a chemical, which quantifies the sorption of organic compounds onto organic matter in soils and aquifers.

'Vapour pressure' is the pressure observed in a gas phase when in equilibrium with a pure NAPL phase. A higher vapour pressure for a chemical means it has a greater propensity to partition to a gas phase.

The values of 'Vapour density relative to air' are all much greater than one. This implies that in an air-filled gas phase with no other transport mechanisms operating, that the chemical as a vapour would sink to the base of an air phase – which may be the base of the soil profile (i.e., the water table) or possibly some low permeability layer in the soil profile. Note that where biodegradation is occurring a soil profile may have zero oxygen but 20% carbon dioxide and possibly some methane. In any case, nitrogen will continue to make up the bulk of the soil gas atmosphere (~80%) and as such the density of air would not change substantially – and hence the relative density to these chemical as vapours would not be likely to change. However, although commonly dense as vapours, these compounds will not remain at the base of the air phase, but will migrate vertically as well as horizontally through the soil profile due to diffusion.

Table 1. Chemical and physical properties of selected organic compounds

Compound	CAS number	Molecular weight ($g\ mol^{-1}$)	Density ($g\ cm^{-3}$)	Aqueous solubility ($mg\ L^{-1}$)	Henry's Law constant, H_c ($kPa\ m^3\ mol^{-1}$)	Henry's Law constant at 25 ^{0}C, K_{gw} (dimensionless)	Octanol-water partitioning coefficient (K_{ow}) (dimensionless)	Vapour pressure (kPa)	Vapour density relative to air (air =1)
Petroleum Hydrocarbons									
pentane	109-66-0	72.15	0.626	40.0 [f]	128 [c]	56.3	2450[d]	68.4[f]	2.5 [e]
hexane	110-54-3	86.18	0.655	12.4 [f]	131 [c]	57.6	7940 [d]	20.2 [f]	3.0 [e]
cyclohexane	110-82-7	84.16	0.779	57.5 [f]	19.5 [c]	8.58	2750 [d]	12.7 [f]	2.9 [e]
benzene	71-43-2	78.12	0.8787	1790[a]	0.564 [c]	0.225	138 [a]	11.7 [g]	2.77 [e]
toluene	108-88-3	92.15	0.8669	469 [a]	0.644 [c]	0.257	436 [a]	3.75 [g]	3.14 [e]
ethylbenzene	100-41-4	106.17	0.867	140 [a]	0.815 [c]	0.325	1480 [a]	1.30 [g]	-
m-xylene	108-38-3	106.17	0.8642	197 [b]	0.675 [c]	0.269	1100 [b]	1.13 [g]	3.66 [e]
p-xylene	106-42-3	106.17	0.8611	198[h]	0.614 [c]	0.270	1410	1.19 [g]	3.66 [e]
o-xylene	95-47-6	106.17	0.8802	176 [b]	0.424 [c]	0.169	1100 [b]	0.912 [g]	3.66 [e]
1,3,5-trimethylbenzene	108-67-8	120.2	0.8652	97.5 [b]	0.803 [c]	0.320	2880 [b]	0.345 [g]	4.15 [e]
naphthalene	91-20-3	128.19	1.0253	29.4 [a]	0.125 [c]	0.0496	2090 [a]	0.011 [g]	4.42 [e]
1-methylnaphthalene	90-12-0	142.20	1.0202	28.4 [a]	0.0365 [c]	0.0145	6610 [a]	0.008 [g]	-
Chlorinated Solvents									
tetrachloroethene	127-18-4	165.83	1.6227	150 [a]	2.72 [c]	1.08	1050 [a]	2.5 [f]	5.8 [e]

(PCE)									
trichloroethene (TCE)	79-01-6	131.39	1.4642	1360[a]	1.18[c]	0.472	186[a]	9.87[f]	4.53[e]
1,1-dichloroethene (1,1-DCE)	75-35-4	96.94	1.213	400[f]	2.32[c]	1.02	135[d]	79.3[f]	-
vinyl chloride (VC)	75-01-4	62.50	0.9106	1100[e]	2.27[c]	0.999	41.7[d]	344[f]	2.2[e]
carbon tetrachloride	56-23-5	153.82	1.594	1160[f]	2.98[c]	1.31	676[d]	15.06[f]	5.3[e]
chloroform	67-66-3	119.38	1.498	7950[e]	0.411[c]	0.181	93.3[d]	26.3[e]	4.1[e]
1,1,2,2-tetrachloroethane	79-34-5	167.850	1.595	3000[f]	0.033[c]	0.014	245[d]	0.867[f]	5.8[e]
1,1,2-trichloroethane (TCA)	79-00-5	133.41	1.4411	4420[f]	0.097[c]	0.043	77.6[d]	4.04[f]	4.6[e]
Other compounds									
1,1,2,2 tetrabromoethene	79-27-6	345.65	2.966	678[d]	0.0014[d]	0.0006	355[d]	0.0026[d]	-
tribromoethene	598-16-3	264.74	2.71	1000[i]	0.0495[d]	0.022	1590[d]	0.066[d]	-
1,2-dibromoethene	540-49-8	185.85	2.246	8910[d]	0.086	0.038	60[d]	4.2[d]	-
vinyl bromide	593-60-2	106.95	1.4933	7600[d]	1.216	0.55	37[d]	137[d]	-
Methyl ethyl ketone (MEK)	78-93-3	72.107	0.805	256000[e]	0.00569[d]	0.0025	1.9[d]	121.1[d]	2.5[e]
Methyl isobutyl ketone (MIBK)	108-10-1	100.16	0.7978	19000[e]	0.0138[d]	0.0061	20.4[d]	2.65[d]	3.5[e]

[a]Muller and Klein, 1992
[b]Suzuki, 1991
[c]Yaws *et al*., 1991
[d]SRC PhysProp Database, 2004
[e]ChemFinder, 2004
[f]Mackay and Shiu, 1981
[g]Mackay *et al*., 1992
[h]Hine and Mookerjee, 1975
[i]Patterson, 2004

3.2 Influences and Processes

Vapour behaviour is influenced by a range of processes, including:

- Volatilisation and partitioning from source regions such as NAPL and water phases into the soil gas phase
- Diffusion
- Sorption onto organic matter in the soil
- Biodegradation
- Soil properties such as soil moisture
- Soil stratigraphy and layering
- Transient influences such as temperature and barometric effects.
- Pressure effects – due to winds etc
- Density differences

The processes that will dominate vapour behaviour in the subsurface and its migration into built structures depend on the properties of the vapour itself, source conditions, building features and the soil type.

Built structures and subsurface utilities can significantly alter vapour behaviour – this aspect and the pathways of indoor air exposure are discussed in Section 4. The features of built structures that are in contact with the soil and may alter vapour behaviour and ultimately exposure through the indoor air pathway include:

- Slab on ground construction
- Crawl space construction
- Structures with basements

Such structures change the exchange processes between the bulk of the soil profile and the near ground surface and atmosphere, and where subsurface utilities are present, may re-direct vapours along preferred (or non-preferred) pathways of gas migration.

For Australian domestic housing conditions, structures with basements would be uncommon compared to slab on ground and crawl space constructions. Basements are more common in the USA and Europe. However it is common in Australia for commercial premises such as Hotels and Office blocks to have basements.

3.2.1 Volatilisation and Partitioning

As indicated in Section 1.2.2, vapours can emanate 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 and Baehr, 1987), which gives the concentration ($C_{i,g}$ in mg L^{-1}) of the i-th compound in a gas phase in equilibrium with a NAPL phase as:

$$C_{i,g} = M_{\mathrm{i}} \, p_{\mathrm{i}} \, \chi_i \, \gamma_i \, / \, (RT) \tag{1}$$

where M_i (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), χ_i is the mole fraction of the i-th component in the NAPL, γ_i is the activity coefficient of the i-th component, R is the universal gas constant (8314 litres Pa K^{-1} 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 °C (293 K), benzene makes up 1% of the gasoline as a mole fraction ($\chi = 0.1$), and the activity coefficient is assumed to be one, and given that $M_{\text{benzene}} = 78{,}000$ mg mole^{-1} and that $p_{\text{benzene}} = 11{,}700$ Pa from Table 1.1, then $C_{\text{benzene,g}} = 3.75$ mg L^{-1} or 3,750 µg 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, $C_{\text{TCE,g}} = 532$ mg L^{-1} or 532,000 µg L^{-1}. In this case the mole fraction is one, and $M_{\text{TCE}} = 131{,}400$ mg mole^{-1} and $p_{\text{TCE}} = 9{,}870$ Pa from Table 1.1. As a further example, vinyl chloride has a vapour pressure 30-40 times higher than TCE (see Table 1.1), 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:

$$P_i = K_{H,i} \, C_{i,w} \tag{2}$$

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

$$C_{i,g} = M_i \, K_{H,i} \, C_{i,w} \, / \, (RT) = H_i \;\; C_{i,w} \tag{3}$$

where H_i 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 µg L^{-1} ($C_{\text{benzene,}\mathbf{w}}$) the concentration in a gas phase in equilibrium with the groundwater ($C_{\text{benzene,}\mathbf{g}}$) would be 2,250 µg L^{-1}, where $H_{\text{benzene}} = 0.225$ (Table 1).

Estimating a gas-phase concentration from groundwater data

As indicated in Section 1, where a groundwater plume lies well below the water table, vapour migration may be altered and slowed. Research carried out in Perth considered this issue with respect to methane degassing from groundwater at landfill sites. In particular, 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 kPa m^3 mol^{-1} was given by:

$$C_g = C_0 + (L\, D_2\, C^*/X\, D_1) \tag{4}$$

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.

3.2.2 Diffusion

Diffusion occurs where a concentration difference or gradient exists. The magnitude of diffusion is govern by the effective diffusion coefficient (D_{eff}) and the concentration gradient of the chemical of concern (C), and is described by Fick's Law as:

$$q = D_{eff} \frac{\partial C}{\partial z} \tag{5}$$

where q is the mass flux (in units of μg L^{-1} m s^{-1}).

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 that 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 τ (which is less than unity).

The Millington-Quirk (1961) empirical model (Equation (6)) uses measured data for porosity (n), air-filled fraction (θ_a), and the free-air diffusion coefficient for oxygen (D_{mol}):

$$D_{eff} = \frac{\theta_a^{10/3}}{n^2} D_{mol} \tag{6}$$

Here the tortuosity factor $\tau = \theta_a^{10/3}/n^2$. The Millington-Quirk formulation is widely used, but is not necessarily regarded as the most accurate equation over the full range of variation of θ_a (e.g. see Jin and Jury, 1996; Őhman, 1999; Davis *et al.*, 2004).

3.2.3 Pressure-Driven Flows (Advection/Convection)

Advective or convective flow of air can occur where pressure gradients are present or are induced – possibly by temperature differences, wind effects, barometric pressure changes, or air conditioning and ventilation of buildings.

In such a case, the flow of air can be described by Darcy's Law, whereby:

$$u_v = -\frac{k_v}{\mu} \frac{\partial P}{\partial z} \tag{7}$$

where u_v is the vapour phase mass average velocity (cm s^{-1}), k_v is the intrinsic soil permeability (in this case to air flow) (cm^2), μ is the vapour viscosity (g cm^{-1} s^{-1}), P is the pressure in the gas phase (g cm^{-1} s^{-2}) and z is the spatial dimension (cm).

The soil permeability can vary by several orders of magnitude even within a small area. For clean sands or sands and gravel soils, like those of the Swan Coastal Plain the permeability may vary from 10^{-8} to 10^{-5} cm^2.

3.2.4 Sorption

Organic vapours typically sorb strongly to soil natural organic matter (NOM). The local relationship between equilibrium hydrocarbon concentrations in the water phase and the equilibrium sorbed concentration on the NOM phase is called a sorption isotherm. Whilst the sorption capacity of most soils is finite, leading to non-linear isotherms (Xia and Pignatello, 2001) or even non-equilibrium relationships, in the absence of site-specific data to the contrary it is usual to model the sorption process by a simple linear isotherm.

$$C_s = K_d \, C_w \tag{8}$$

where the sorbed concentration C_s is proportional to the water phase concentration C_w. The proportionality constant K_d is called the distribution coefficient and can be written as

$$K_d = K_{oc} \; f_{oc} \tag{9}$$

where K_{oc} is the organic carbon soil water adsorption coefficient and f_{oc} is the fractional organic carbon content in the dry soil, typically ranging between 0.0001 and 0.02. K_{oc} values also range over several orders of magnitude with simple alcohols displaying low sorption rates (ethanol K_{oc} = 1.6) and some carbazoles and pyrenes showing extremely high sorption rates (7H-dibenzo[cg]carbazole $K_{oc} = 10^6$), but these values can be affected by soil chemical factors (Meylan *et al.*, 1992). For BTEX compounds, K_{oc} ranges between 60 (benzene) and 600 (ethylbenzene). Higher vapour sorption rates tend to retard the migration of the vapour through a soil profile.

Note, however, that given enough time and vapour movement, the sorption capacity of the organic matter would be exceeded and a stable (steady state) vapour distribution would be established in the subsurface.

3.3 Typical Behaviour

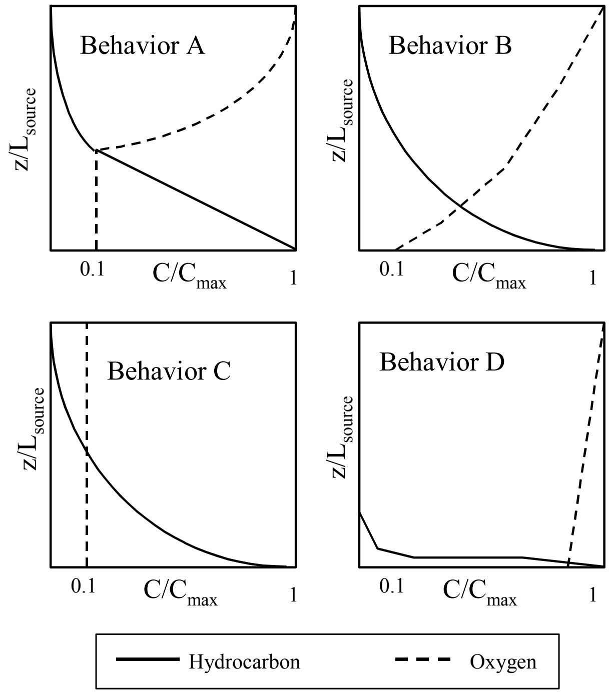
A review of vapour data by Roggemans *et al.* (2002) described 'typical' vertical distributions of petroleum hydrocarbon vapours (and oxygen profiles) as one of four Behavioural categories, depicted approximately in Figure 3.1. The data were collated from several sites and under grass or open ground conditions and in some cases under covered ground conditions (e.g., pavements or basements). The four Behaviours are described briefly in the caption to Figure 3.1. In particular, Behaviour A is typical of petroleum vapours where the vapours biodegrade under aerobic (oxygenated) conditions.

A petroleum hydrocarbon vapour depth profile for the shallow sand aquifer in Perth is given in Figure 3.2. In this case:

- The NAPL (source of the vapours) was distributed over a depth interval of 2.25 to 3.25 m below surface.
- The total petroleum hydrocarbon (TPH) vapours decreased from 70,000 µg/L at ~2.75 m below ground surface (within the zone of the NAPL) to effectively zero at 1.25 m below ground surface. Benzene was only a small fraction of the total vapour concentration (a maximum of a few hundred µg/L).
- Oxygen concentrations decreased from atmospheric concentrations at the ground surface (21% by volume) to effectively zero at 1.25 m below ground surface (the same depth that the vapours decreased to zero).

- Carbon dioxide concentrations increased to approximately 20% from less than 1% naturally in the atmosphere.
- The total porosity was very high at 40-50% throughout the soil profile.

At the end of summer (April) the soil moisture in the bulk of the soil profile was low (less than 10%) and the air-filled porosity was 28-40% over most of the profile.



Note: C_{O2}/C_{max} = 0.1 corresponds to C_{O2}? 2% v/v

Figure 3.1 Categories of typical petroleum hydrocarbon vapour behaviour (from Roggemans *et al.*, 2002). Behaviour A depicts a sharp decrease in vapour concentration up from the source zone with a concurrent decrease in oxygen concentration from the ground surface to a similar depth where the oxygen is <5%. Behaviour B depicts a more uniform decrease in vapour concentrations and oxygen concentrations with depth – in this case oxygen is always > 5%. Behaviour C depicts a steadily decreasing vapour concentration with shallower depth, but with oxygen concentration always less than 5% through the soil profile. Behaviour D depicts a rapid decrease in the vapour concentration deep in the vadose zone, but with oxygen concentrations much greater than 5% everywhere in the soil profile.

The decreasing oxygen concentrations and increasing carbon dioxide levels in the soil profile indicate that natural biodegradation is occurring (in analogy with the saturated-zone study by Kerfoot, 1994). For this profile, biodegradation was confirmed using microcosm studies on soils recovered from different depths of the soil profile (see Franzmann *et al.*, 1999).

Note that for these open/bare ground conditions, biodegradation appears to restrict the migration of vapours to the ground surface, limiting exposures and risks. In Section 4 we explore the effects of buildings on these distributions.

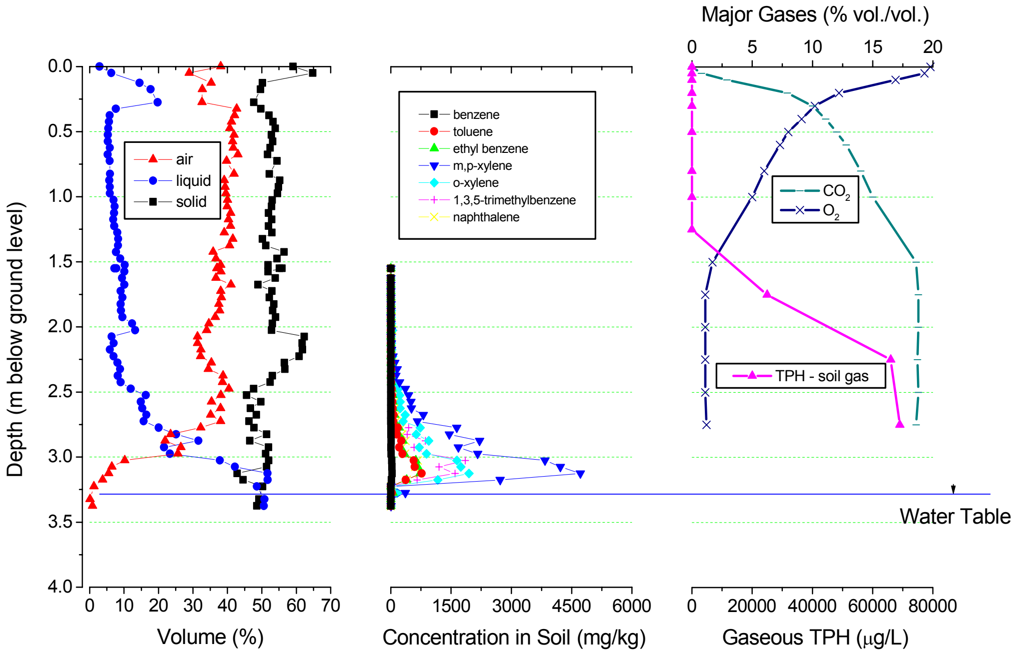


Figure 3.2 Depth profiles of soil volumes (left) and NAPL contents (middle) determined from soil cores, and soil (total petroleum hydrocarbon – TPH) vapour and major gas measurements (right) determined from multiple depth gas samplers installed in the sand aquifer underlying Perth. Data are for April 1999. Note that for soil volumes (left) – 'air' = air-filled porosity of the soil; 'liquid' = the total of water and NAPL filled porosity of the soil (note that below the water table this equals the total porosity of the soil/aquifer, and above the zone impacted by NAPL the liquid volume equals the water filled porosity); 'solid' = the volume of the soil made up of solid soil material.

Solvent vapours may behave differently to those proposed in Figure 3.1 and the petroleum hydrocarbon example in Figure 3.2. Some of the chlorinated compounds (e.g. PCE and TCE) do not degrade readily under aerobic conditions. In such a case another Behavioural category may be proposed – which is a soil profile with high vapour concentrations decreasing gradually from the subsurface source zone to effectively zero at the ground surface where the surface is open to the atmosphere. Without aerobic biodegradation, oxygen would remain plentiful within the soil profile typical of atmospheric concentrations unless other reducing reactions were occurring to consume the oxygen (such as oxidation of natural organic matter in the soil profile). This is like Behaviour B in Figure 3.1. In this case biodegradation may not be readily operating leading to increased concentrations of solvent vapours at shallow depths of the soil profile. In contrast, where soils are rich in organic matter, oxygen may be consumed readily. In addition in such soils, if anaerobic (reducing) conditions prevail, then anaerobic biodegradation of some of the chlorinated solvent vapours may occur (see Wiedemeier *et al.*, 1999).

The different behaviours of the petroleum hydrocarbon and chlorinated solvent vapours are shown in Figures 3.3 and 3.4. These vapour data relate to a mixed petroleum hydrocarbon and chlorinated solvent spill site in the shallow sand aquifer in Perth. In this case:

- The petroleum hydrocarbon vapours (predominantly the xylene isomers) decreased from a very high concentration of 180,000 µg/L at ~3 m below ground surface to effectively zero at 1.5-2.0 m below ground surface. Benzene was below detection limits.
- PCE vapour concentrations decreased from a concentrations of over 5,000 µg/L at ~2 m below ground surface and continued to decrease but at detectable concentrations throughout the shallow zone of the soil profile to ground surface.
- Oxygen concentrations decreased from atmospheric concentrations at the ground surface (21% by volume) to effectively zero at 2.0-2.5 m below ground surface (a similar depth where the vapours decreased to zero).
- Carbon dioxide concentrations increased to approximately 20% from less than 1% naturally in the atmosphere.

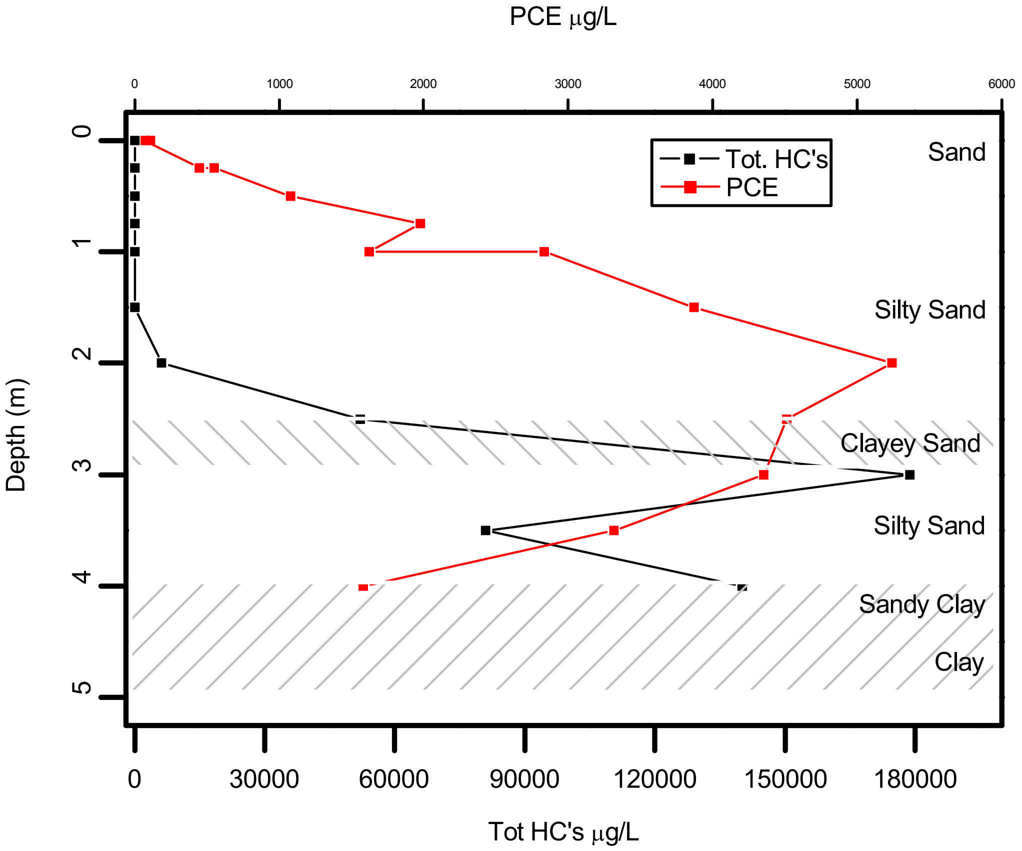


Figure 3.3 Depth profiles of the total volatile petroleum hydrocarbon (Tot. HC's) and PCE vapour concentrations determined from multiple-depth gas samplers installed in the sand aquifer underlying Perth. Data are for May 2004.

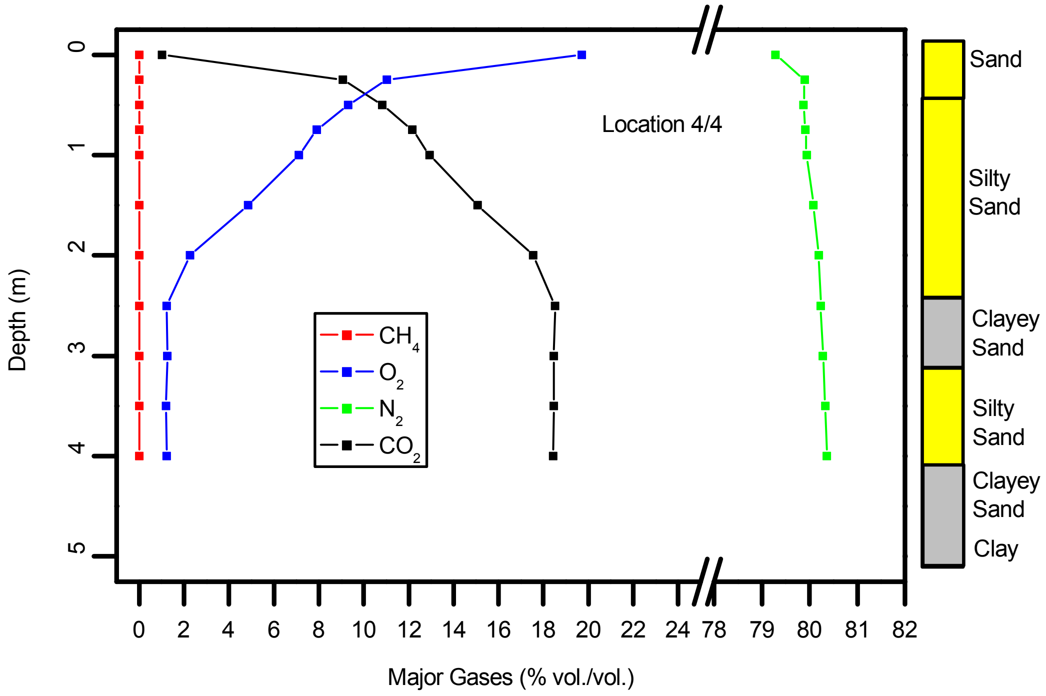


Figure 3.4 Depth profiles of the major gas concentrations determined from multiple-depth gas samplers installed in the sand aquifer underlying Perth. Data are for May 2004.

In this case, the chlorinated solvent (PCE) persisted to shallow depths in the soil profile and was not degraded aerobically. In such an instance, PCE has the potential to accumulate under covered ground conditions (such as beneath a house slab). In contrast, the petroleum hydrocarbon vapours apparently degraded aerobically over a very short vertical interval of the soil profile.

3.4 Biodegradation and Effects of Oxygen

Biodegradation of organic compounds occurs on soil/water surfaces where micro-organisms grow and respire. As such, it is only when organic vapours partition from an air phase into a soil water phase that biodegradation occurs. In essence then ‘vapour biodegradation’ is a misnomer, as degradation does not actually occur in the gas phase. Nonetheless, the result of partitioning of the organic vapours to the soil water phase and their subsequent biodegradation, is to reduce vapour concentrations in the gas phase (or air-filled pore space of the soil), which is effectively equivalent to vapour biodegradation.

Not all organic compounds degrade at similar rates, and not all have similar oxygen demands. It is well established that volatile petroleum hydrocarbons readily degrade aerobically – i.e., where oxygen is present. Lightly chlorinated or brominated hydrocarbons (mono and di halide hydrocarbons) are also susceptible to aerobic biodegradation. Compounds such as PCE and TCE (tetra and tri halide hydrocarbons) however, do not degrade readily under aerobic conditions. In contrast, PCE and TCE do degrade under reducing (anaerobic) conditions. Information on the degradability of some of the petroleum compounds and chlorinated solvents can be found in Wiedemeier *et al.* (1999).

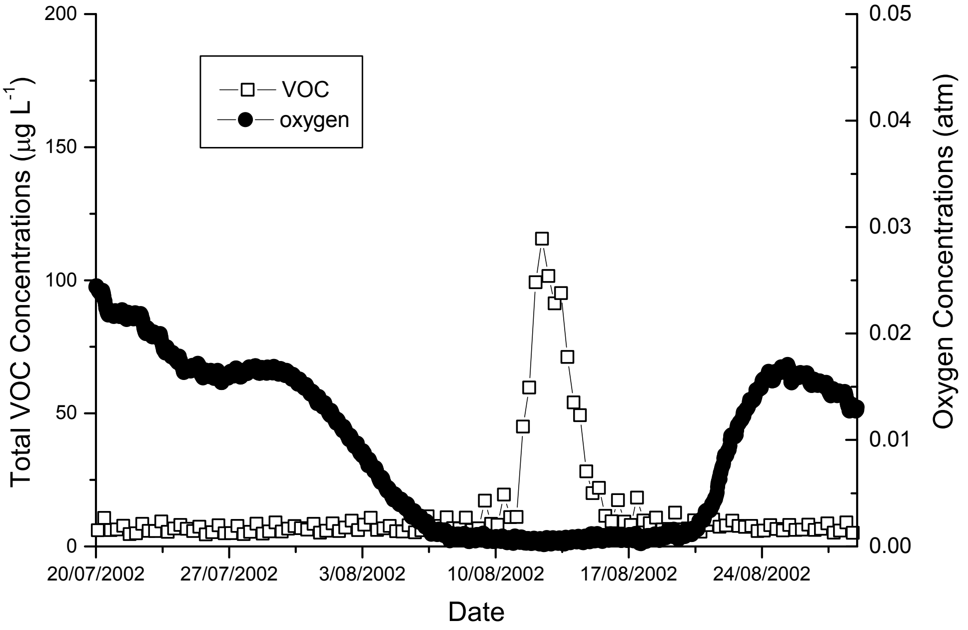


Figure 3.5 Oxygen and total VOC vapour concentrations in a clay soil (5.0 m below ground), during a period when oxygen concentration reduced below detection limits. The data were obtained from oxygen and VOC probes developed by CSIRO (see Patterson *et al.*, 1999; 2000)

Field data at a number of sites in Australia confirm that petroleum vapours biodegrade. Figure 3.2 depicts a static vapour/oxygen profile showing that where oxygen was present in the soil profile, petroleum hydrocarbon vapours were absent, due to aerobic biodegradation. At these sites, the oxygen diffusion influx (and biodegradation processes) seemingly dominated the potential for petroleum hydrocarbon vapour diffusion through to the ground surface. Transient oxygen and vapour (total volatile organic compound - VOC concentration) data in Figure 3.5 again depicts this distinct separation between the presence of oxygen and vapours.

3.5 Possible Transient Influences on Vapour Behaviour

Possible transient influences on vapour behaviour include:

(i) Barometric pressure changes

(ii) Temperature fluctuations

(iii) Rainfall and soil moisture changes

(iv) Gravitational effects due to earth tides

(v) Wind effects

3.5.1 Barometric pressure changes

Barometric pressure changes can lead to a pressure differential between the ground surface and the subsurface soil profile, potentially leading to enhanced gas exchange – effectively compacting or expanding the gas phase. The effects of this compaction/expansion decrease with depth below ground surface and also the effects are much reduced within a thinner vadose zone, compared to a deeper vadose zone. Theoretically, a marginal daily change in barometric pressure of say 4-5% would give rise to a 4-5% change in the volume of air contained in the soil profile. This amounts to an influence of 4 cm over a 1-m deep soil profile or possibly 20 cm over a 5-m deep soil profile.

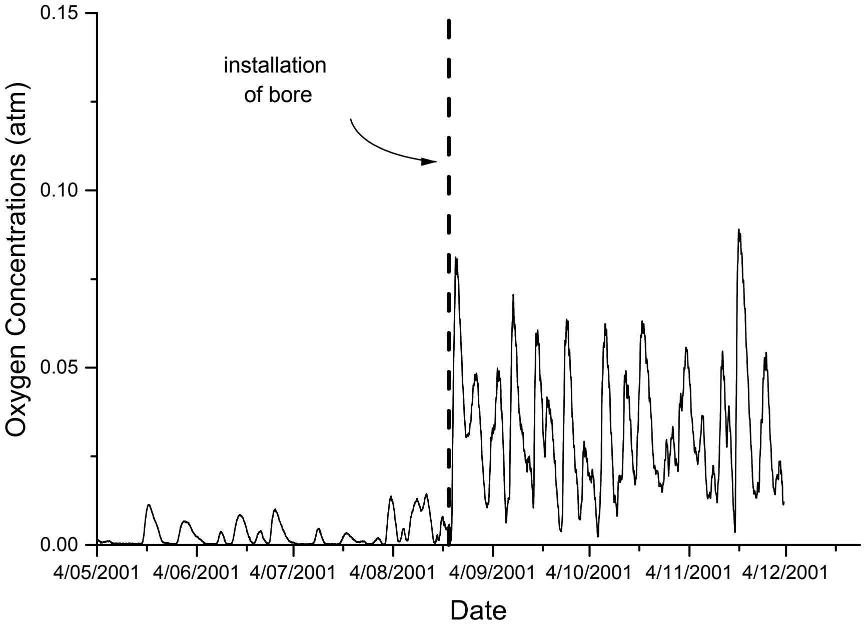


Figure 3.6 Oxygen concentrations measured by an oxygen probe in a sandy/gravely vadose zone layer overlayed by a tight clay, before and after the installation of a large diameter bore near this monitoring location.

The potential for enhanced exchange and ingress of oxygen into the vadose zone via barometric pumping may be possible under certain circumstances, for example, when a relatively impermeable tight clay layer overlaying a permeable sand/gravely layer is penetrated via the installation of a bore. The screened interval of the bore in the sandy/gravely vadose zone layer may provide a conduit for enhanced ingress of oxygen into the vadose zone via barometric pumping. This effect is shown for a field site in Australia in Figure 3.6. In this case, Figure 3.7 shows a good correlation of oxygen concentration fluctuations to barometric pressure data, suggesting oxygen ingress and fluctuations are due to barometric pumping.

Barometric variations have also been shown to affect groundwater levels (Rojstaczer, 1988), with a barometric efficiency of $\Delta h/\Delta P$ = -1 mm/mbar estimated for the superficial aquifer (in Safety Bay Sand) on Garden Island (Trefry and Bekele, 2004). While this relatively small amplitude is unlikely to affect vapour behaviour significantly in vadose zones several meters deep, it will contribute to the smearing of LNAPL sources as the water table fluctuates up and down in response to the passage of weather systems.

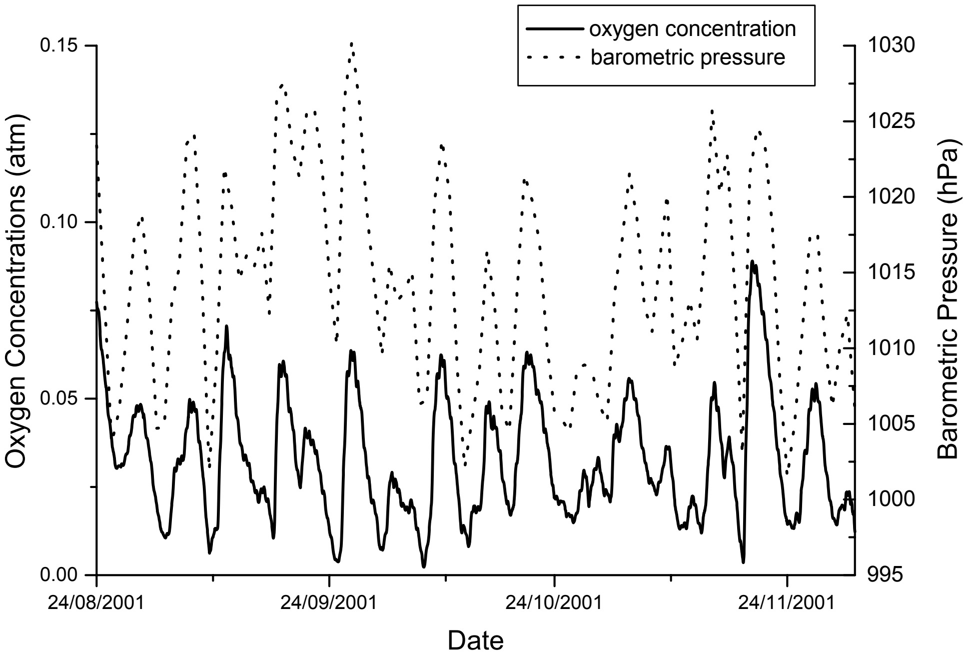


Figure 3.7 Barometric pressure data and oxygen concentrations in a sandy vadose zone layer overlain by a tight clay near a large diameter bore.

3.5.2 Temperature fluctuations

Variations in soil temperature results in the expansion and contraction of soil air, leading to partial exchange with the atmosphere. Hence vapour measurements may change from season to season, or daily. However, temperature effects decrease with depth below ground and typically show minimal variation much below 1 m below ground. For example, according to the Gas Law a 20 °C change in temperature (from 300 to 280 Kelvin) of the top 20-50 cm of a soil would lead to a 7% contraction of the soil gas. This implies, in reality, that only a few centimetres (1.4-3.5 cm) of soil gas would be exchanged with the atmosphere by contraction and expansion of the soil gas.

3.5.3 Rainfall and soil moisture changes

Soil moisture increases due to rainfall infiltration may inhibit gas exchange processes, and in particular vapour movement towards the ground surface, and oxygen ingress from the atmosphere. Increases in moisture contents decreases air-filled porosities resulting in lower vapour and gas diffusion rates in the vadose zone. This is likely to be particularly the case for heavier textured soils (e.g., clay soils).

The intermittent effect of increased soil moisture on gas distributions can be seen in Figure 3.8. This is data from oxygen and total volatile organic compound (VOC) probes (see Patterson *et al.*, 1999; 2000 for details) buried at multiple depths in a sandy vadose zone soil in Perth. Gasoline NAPL was present in the zone of water table fluctuation over a depth interval of approximately 2.25-3.25 m below ground (as in Figure 3.2). Following 17 mm of rainfall on 14 and 15 January 2000, the oxygen concentration decreased sharply at 0.5 and 1.0 m depths, but recovered to pre-rainfall conditions by late March 2000. It is surmised that the rainfall temporarily increased soil moisture contents in the shallow soil zone, decreasing the oxygen flux from the atmosphere, and that in February and March (summer dry) the soil moisture contents decreased again allowing increased oxygen fluxes from the ground surface. The oxygen concentrations did not decrease to zero at the 0.5 or 1.0 m depths, and no effect on total vapour VOCs was observed. This is consistent with the trend observed at a number of other sites - that wherever oxygen was present, vapours were apparently readily biodegraded, i.e., there remained a relatively sharp separation between the presence of oxygen and the presence of petroleum vapours.

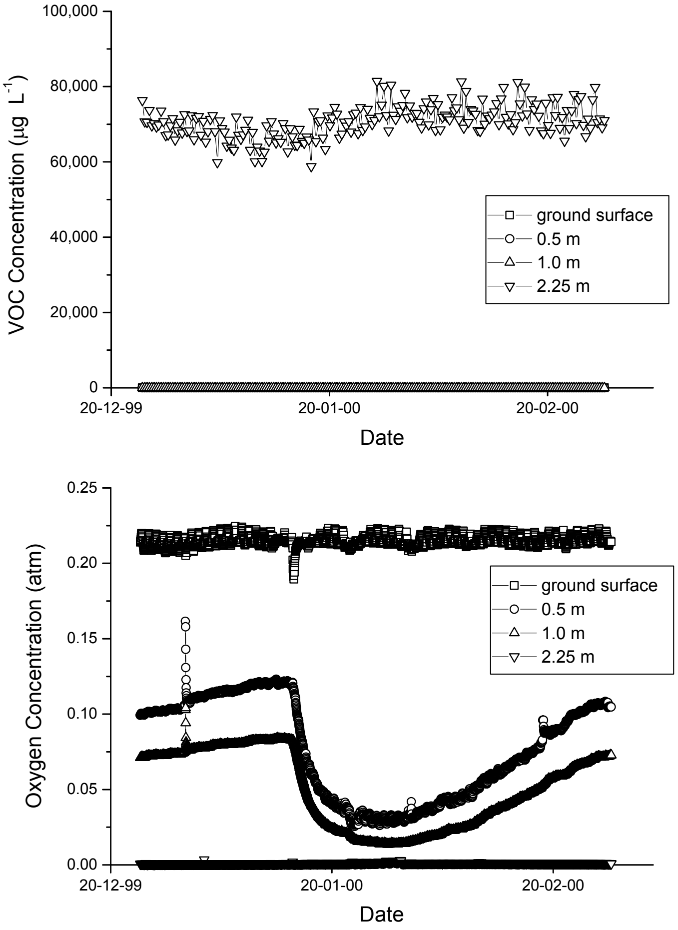


Figure 3.8 Continuous monitoring data from oxygen and total VOC probes buried at several depths above a gasoline NAPL at a sandy soil site from 24 December 1999 to March 2000. A 17 mm rainfall event occurred on 14-15 January 2000.

Measurement of soil moisture may be warranted during a site investigation to calculate the air-filled porosity of the soil, and allow calculation of vapour fluxes if required. Further discussion of the effects of soil moisture changes on vapour distributions and concentrations is contained in Davis *et al.* (2000, 2004). Measurement techniques are further discussed in Section 5.

Of course seasonal changes in groundwater levels may also be considerable (0.5 m to several metres depending on aquifer hydrogeology), in which case variations in the vapour profile may be induced. For the case of very large groundwater fluctuations, inundation and exposure of the vapour source zone may occur, requiring additional investigation. Induced, temporal changes in vapour concentrations could be significant.

3.5.4 Gravitational effects due to earth tides

Earth tides (created by gravitational pull of the moon and deformation of the Earth crust) are known to change water levels (Bredehoeft, 1967). These effects are greatest for deep hard-rock aquifers where water-filled porosities are low. Typically, for the Swan Coastal Plain superficial sand aquifer, changes induced by earth tides are small and may only change water table elevations by a few centimetres at most. This is unlikely to significantly alter vapour concentrations in an impacted soil profile, although LNAPL sources may potentially experience smearing at the water table as for the barometric variation case.

3.5.5 Wind effects

In some cases wind effects may have a significant effect on the exchange of gases between the soil and the atmosphere, particularly at shallow depths. For surfaces open to the atmosphere, however, the effect of wind is limited to a very shallow surface horizon. Kimball and Lemon (1971) indicate that the contribution of wind to gas exchange in a sandy soil is less than 0.1% of the total exchange. For built environments pressure changes across the footprint of a building (upwind to downwind) would be greater than open ground conditions – potentially leading to greater variations in gas profiles in the subsurface (this is discussed further in the modelling Section).

4 The Built Environment

4.1 Construction Types

Built structures and subsurface utilities can in fact change vapour behaviour. The features of built structures that are in contact with the soil and may alter vapour behaviour and ultimately exposure through the indoor air pathway include:

- Slab-on-ground construction
- Crawl space construction
- Structures with basements

Such structures change the exchange processes between the bulk of the soil profile and the near ground surface and atmosphere, and where subsurface utilities are present, may re-direct vapours along preferred (or non-preferred) pathways of gas migration.

Figure 4.1 provides a general schematic of these types of constructions, in relation to a source of vapours near the water table.

For Australian domestic housing conditions, structures with basements would be uncommon compared to slab-on-ground and crawl space constructions. Basements are more common in the USA and Europe. In Australia, commercial premises such as Hotels and Office blocks may commonly have basements.

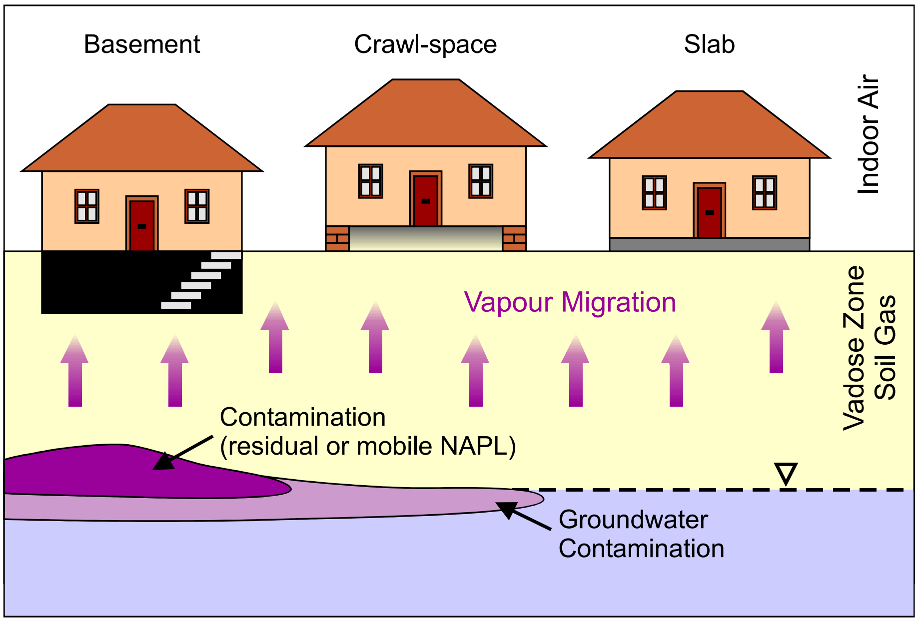


Figure 4.1 Schematic of basement, crawl-space and slab-on-ground constructed buildings overlying NAPL and groundwater sources of vapours.

4.2 Slab-on-ground Construction

Slab-on-ground construction of residential houses is common. Such construction can reduce gas exchange with the atmosphere, i.e., inhibit vapours migrating to the ground surface, but also limit oxygen ingress from the atmosphere.

Figure 4.2 shows gasoline vapour data from a sandy soil profile of the Swan Coastal Plain. Under bare soil conditions (May 2000) vapours penetrated to between 1 and 1.5 m below ground from a source deeper in the soil profile. A month after a cover was laid on the ground (to simulate a house slab) vapour concentrations increased in the soil profile and accumulated under the cover. As such, vapours have the potential to accumulate beneath slab-on-ground structures. The risks they pose to human health through entry from beneath the slab to indoor air will depend on the continuity of pathways for vapour movement either through the slab (i.e., cracks or via diffusion) or through subsurface services (e.g., electricity and telephone conduits, water pipes) that enter a construction.

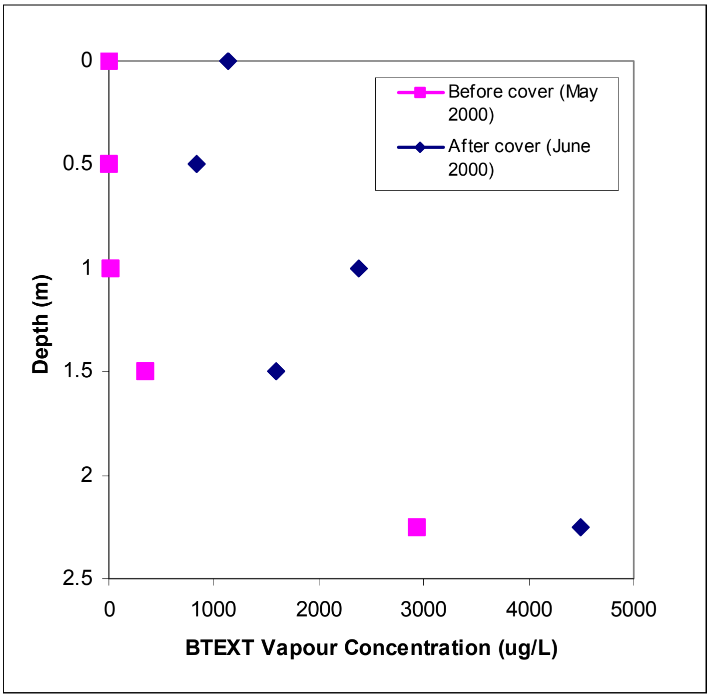


Figure 4.2 Total BTEXT (benzene, toluene, ethylbenzene, the xylene isomers and trimethylebenzenes) vapour concentrations determined from sampling a multi-level sampler in a sandy soil before and after a ground cover was placed on the ground. Under bare ground conditions (May 2000), vapours penetrated to between 1 and 1.5 m below ground from a source deeper in the soil profile. A month after a cover was laid on the ground (to simulate a house slab) vapour concentrations increased all through the soil profile and under the cover.

In addition, oxygen concentrations were non-zero in the profile before the cover was emplaced, and reduced to below detection levels over the entire depth profile by June 2000. The June 2000 depth profiles are like the type C Behaviour in Figure 3.1, however, none of the typical profiles described by Roggemans *et al.* (2002) have vapours accumulating near to the ground surface, even though data trends were determined from situations beneath pavements and basements.

It should be stressed that the example in Figure 4.2 is somewhat artificial, in that as part of this experiment there was no built structure above ground and no ground preparation was carried out as might be done for a building. In this case, a cover was simply placed on the ground surface to simulate the reduction in exchange of vapours and oxygen between the soil and the atmosphere as may be induced by the physical presence of a house slab.

Contrary to the data in Figure 4.2 for the sandy soil profile, Figure 4.3 shows no accumulation of gasoline vapours (VOCs) under an actual house slab. The house is built on a clay soil, with coarse fill material immediately beneath the base of the slab and to a depth of approximately 0.5 m. In this case, it appears that the net flux (migration rate) of vapours from the source zones at depth in the clay material is low compared to the net flux of oxygen from the atmosphere through the coarser fill materials. This difference in net flux apparently allows active biodegradation and removal of the vapours from beneath the house slab. In which case, the contrast in soil properties (coarse fill over clay) limits vapour accumulation under the slab.

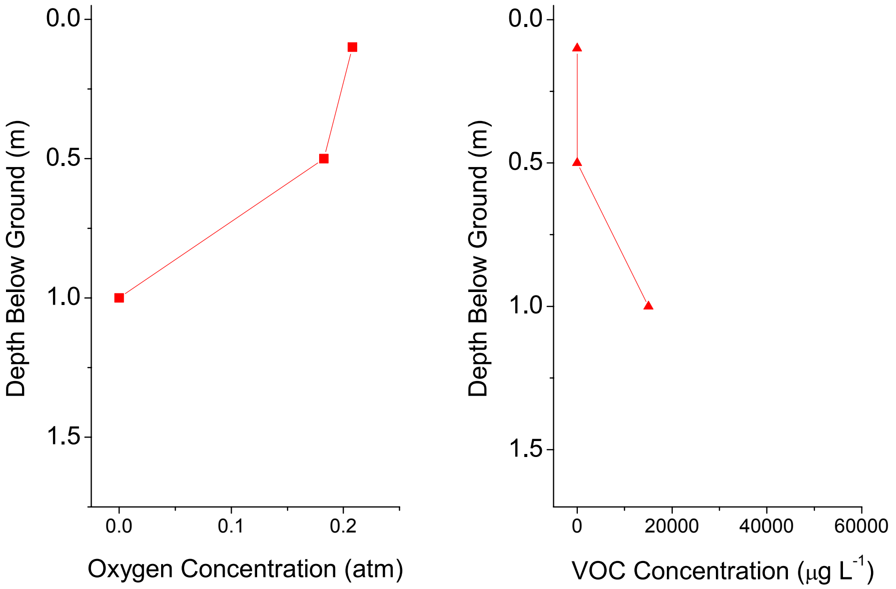


Figure 4.3 Total VOC (volatile organic compound) vapour concentrations and oxygen concentrations as depth profiles in a clay soil beneath a house slab construction. The vapours penetrated to between 1 and 0.5 m below ground from a source deeper in the soil profile, and oxygen concentrations were non-zero to at least 0.5 m below the house slab.

In the sandy soil site in Figure 4.2, there is no significant layering or contrast in soil texture or properties that would lead to differentiated movement of vapours from below or oxygen from above – so in this case vapours were able to accumulate under the base of the cover.

From these examples, apart from the need to define the pathways for vapours to migrate to the interior of built structures, it is clear that the near-slab soil conditions are critical to vapour movement and possibly the risks posed by the vapours, due to accumulation under slab-on-ground constructions. Modelling of such scenarios is currently being undertaken in the US (Abreu and Johnson, 2004) to assess these risks, and some brief discussion is given in Section 6.

4.3 Crawl-space Construction

Crawl-space construction is common for residential houses in parts of Australia. Such construction typically occurred over uneven surface soil conditions or where enhanced ventilation was required (e.g., in northern Queensland). Crawl-space construction consists of an elevated floor (usually of timber construction) above the ground. As the name suggests, the elevation above the ground is usually small, possibly 40-100 cm high. The crawl space is often used to provide access to electrical, telephone and plumbing services and is sometimes used for temporary storage by residents. The air space beneath the elevated floor and above the ground surface is often enclosed to some degree. Vents are commonly installed to allow air circulation. Figure 4.4 shows a schematic of a typical crawl-space construction and issues associated with vapour migration from the subsurface (from Turczynowicz and Robinson, 2001).

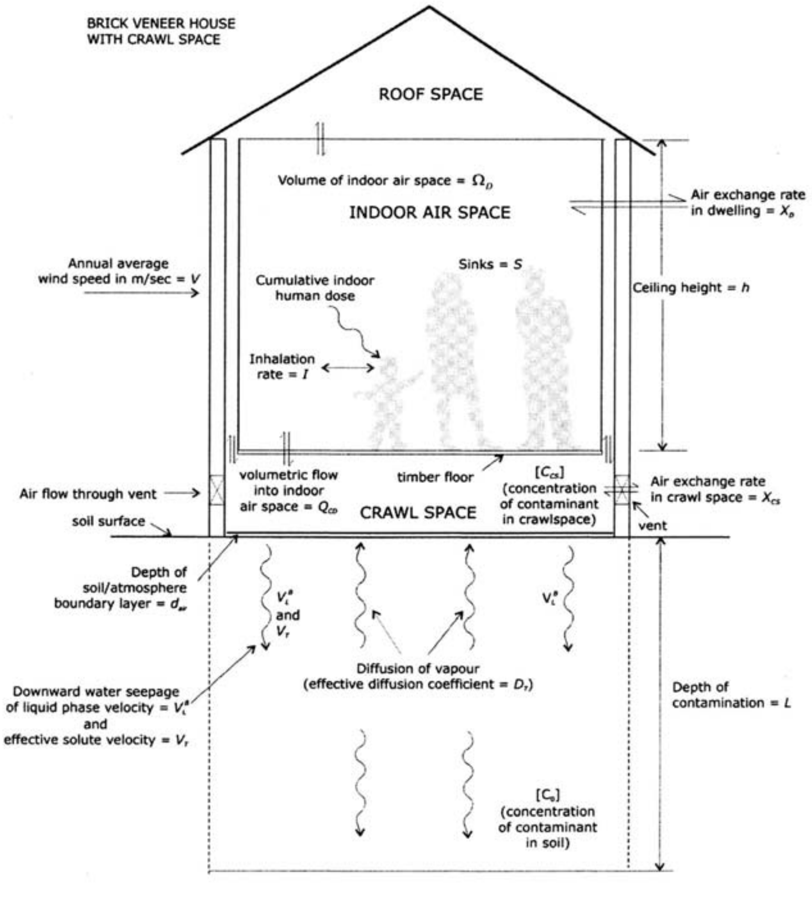


Figure 4.4 Schematic of a typical crawl-space construction and issues associated with vapour migration from the subsurface (from Turczynowicz and Robinson, 2001; Used by permission of copyright holder, Amherst Scientific Publishers).

Turczynowicz and Robinson (2001) developed a volatilisation model of the transport pathways for benzene from the subsurface to crawl-space dwellings. They estimated a cumulative indoor human dose, based on one-dimensional model, a finite source, zero-degradation and a non-homogeneous boundary condition at the ground surface. They found that the dominant influencing parameters were those related to the dwelling, not the soil. In particular, the air exchange within the crawl space governed the extent to which vapours would accumulate within the crawl space. This would also govern the extent to which oxygen might be delivered into the crawl space to stimulate biodegradation, where the vapours of concern were aerobically degradable.

4.4 Structures with basements

Although not common in residential dwellings in Australia, basements are common in commercial buildings and high-rise office and residential buildings. There is extensive literature related to basements – largely due to research carried out on radon gas and landfill gases in the USA and Europe. Johnson and Ettinger (1991) originally developed their model for buildings with basements. Markey and Anderssen (1996) also catalogue early papers in this area - many related to radon.

Of primary concern with basements is the increased surface area for vapour migration to the indoor air space. In addition, often basements are depressurised due to differential indoor-outdoor temperatures, wind loading on buildings or air conditioning – which can induce greater net influx of vapours to the indoor air.

Buildings with basements that pose an additional concern are those built below the water table, and if the groundwater is contaminated with volatile chemicals. In such a case, vapours have a significantly increased potential to migrate to indoor air due to the much reduced travel distance and direct contact of the vapours with the basement structure.

4.5 The Johnson α Ratio

Johnson and Ettinger (1991) introduced 'alpha' (α) as the "vapour attenuation coefficient". Effectively α is the ratio of the concentration of a chemical vapour determined in indoor air relative to that within the source region in the soil gas. The Johnson and Ettinger (1991) model assumed a continuum between these two concentrations accounting for some of the various subsurface processes that control the behaviour of vapours, including source zone partitioning, vadose zone transport, and enclosed-space mixing equations.

Their model indicated that there was a transition zone depending on the permeability of the soil (at 10^{-12} m^2), below which the attenuation coefficient was essentially independent of the soil permeability, and contaminant entry to buildings was essentially diffusion controlled. Above a soil permeability of 10^{-12} m^2, contaminant entry into buildings was found to be pressure (advection) controlled, except where the source was a large distance from the built structure. The 'crack fraction' was important only where diffusion was the dominant transport process. They predicted that the attenuation coefficients would range from 0.001 to 0.01 for soil permeabilities of 10^{-11}-10^{-10} m^2. Diffusion may dominate where the permeability was less than 10^{-12} m^2 or greater than 10^{-10} m^2, or where the source zone was a large distance from the built structure. In this case, the attenuation coefficient was estimated to have a broad range, from 0.00002 to 0.003.

Recently, Johnson *et al*. (2002) reviewed several field data sets related to values of the attenuation coefficient for chlorinated solvents. In this case the values of the attenuation coefficient ranged from 1.3×10^{-5} to 3.4×10^{-4}. The Johnson and Ettinger (1991) model applied to the same data set gave attenuation factors of 4.8×10^{-6} to 2.4×10^{-5}, which are comparable but lower values than those measured.

It should be remembered that prediction of α values is critically dependent on a range of factors associated with the vapour, soil and built environment.

5 Vapour Assessment Techniques and Parameter Estimation

Where vapours may be suspected as posing a risk at a site, it is useful to consider a number of factors prior to carrying out an assessment - many of which are common to any site investigation. These include:

(i) A review of currently available data and site history to determine the most likely chemicals at the site that may give rise to vapours of concern,

(ii) The aim of any vapour assessment,

(iii) The regulatory needs so sampling and monitoring that is undertaken satisfies those needs,

(iv) The type of chemicals and their properties and likely concentrations,

(v) The need for modelling to ensure adequate data are gathered during site assessment.

(vi) Occupational Health, Safety and Environmental issues related to chemicals of interest and the tasks/procedures that might be undertaken to investigate them (Material Safety Data Sheets (MSDS's) may be useful as an initial source of information).

(vii) The techniques that may be used at a site depending on the presence and type of buildings on-site and the soil conditions

In this section we describe some of the soil vapour sampling and monitoring techniques, and provide methodologies for estimating soil and chemical parameters that determine vapour fate and migration. There is a range of vapour assessment techniques – with varying levels of expense and complexity.

5.1 Vapour and Oxygen Sampling and Monitoring Techniques

5.1.1 Flux Chamber Methods

A flux chamber is a device that is placed on the ground surface and vapour concentration build-up within the chamber can be monitored to assess the flux of vapours to the ground surface and into the above-ground atmosphere. The advantage of this technique is that it is somewhat of a direct measure 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 by effectively 'integrating' all subsurface processes (e.g., phase partitioning, bioattenuation, preferential pathways, advective and diffusive transport).

Flux chambers are not suitable for dwellings with basements because of additional potential fluxes from the basement walls to the interior of the dwelling, and flux chambers used on a bare soil surface may not reflect measurements obtained when a structure is in place. In addition, this technique provides little information about the processes that maybe 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 was undertaken. In particular, 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 underestimation of fluxes depending on relative pressure differentials inside and outside a chamber. Two guidance documents were produced under the patronage of the USEPA on the use of particular flux or emission chambers (Kienbusch, 1986; Eklund and Schmidt, 1990).

5.1.2 Passive Sampling Techniques

'Passive' vapour 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 (hrs, 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.

5.1.3 Spear Probing

Spear probing 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 for use at the next location. Spear probing can provide vapour and major gas concentration data at a series of selected depths, but is not a survey technique designed to determine changes over time.

Spear probing generally only provides screening level assessments of the presence of vapours in the subsurface, and can assist with locating "hot spots". 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 1.5-2.0 m or greater below surface, depending on the location of the vapour source and the location of the water table.

Recovery of the samples from the spear probe can be into a glass syringe for vapours (to minimise loss of vapours due to sorption) or to a plastic syringe if collecting a gas sample for analysis of major gases such as oxygen. Analysis of the sample directly from the syringe 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.

5.1.4 Multi-level Samplers

Permanent subsurface soil-gas/soil-vapour monitoring locations can be installed to allow (i) depth profiling of vapour concentrations through the soil profile to the local water table, and (ii) repeat sampling and monitoring over time at fixed locations. Multiple depth (or multi-level) gas sampling installations generally consist of bundles of narrow diameter access tube with ports at various depths below ground surface. Sampling of the multilevel samplers can be carried out as per the procedure for spear probing in Section 5.1.3. In this case, 2-3 times the internal volume of the access tubing for each sampling ports should be extracted and discarded prior to taking the sample for analysis. This parallels the style of purging that would be carried out for sampling of groundwater monitoring wells.

Additionally, during drilling to install the multi-level samplers, a soil core can sometimes be recovered and sub-sampled to determine organic carbon and soil parameters (e.g. bulk density, porosity), at the depths of the sampling ports, or analysis of the soil for the chemicals of concern.

Figure 3.2 shows data from sampling of vapour and major gas concentrations from multi-level samplers, and measurements from soil cores.

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. This is discussed in Section 5.3.

5.1.5 On-line VOC and Oxygen Probes

Near-continuous measurement of total vapour (or volatile organic compounds – VOCs) and oxygen concentrations is possible using on-line VOC and oxygen probes (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 VOC 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 VOC 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), and in sandy and heavier clay soil environments. 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. Data from such probes were shown in Figures 3.3, 3.4, 3.5 and 3.6.

5.2 Soil Physical Properties - Air-filled Porosity

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 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 (10);

$$\theta_a = 1 - [(\frac{\rho_b}{\rho_m}) + \rho_b \frac{\theta_g}{\rho_w}] \tag{10}$$

where θ_a is the effective air-filled porosity ($m^3\ m^{-3}$), ρ_b is the bulk density ($kg\ m^{-3}$), ρ_m is the free solid density (assumed equal to 2650 kg m^{-3}; Rose, 1966), θ_g is the gravimetric moisture content ($kg\ kg^{-1}$) and ρ_w is the density of water ($kg\ m^{-3}$).

The vertical distribution of estimates of air-filled porosity determined in a sandy soil profile at a finer scale is shown in Figure 3.2.

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.

5.3 Zero-order Oxygen Consumption Rates

Oxygen consumption rates can be used to infer the rate of biodegradation of chemical vapours, and in particular petroleum hydrocarbon vapours.

Zero-order oxygen consumption rates can be calculated from vertical distributions of static oxygen concentrations. Modelling of static oxygen concentration depth profiles to estimate oxygen usage rates have previously been carried out for near-linear depth profiles (Ritchie, 1977; Patterson *et al.*, 1999) and non-linear depth profiles (Huesemann and Truex, 1996; Davis *et al.*, 1998, 2000; 2004).

5.3.1 Linear Oxygen Depth Profiles

For linear oxygen concentration depth profiles, the model described by Ritchie (1977) can be used to estimate zero-order (in time) oxygen consumption rates. This model assumes oxygen consumption only occurs at the depth where the oxygen concentration is zero and that this location moves progressively downward through the soil as petroleum hydrocarbon vapours and oxygen are consumed by microbial degradation - assuming the source of hydrocarbon is finite and the source of oxygen (the atmosphere) is infinite.

An oxygen consumption rate coefficient can be estimated by fitting Equation (11), based on Ritchie (1977), to the field data.

$$O_r = \frac{D_{eff}\,C_0}{z^2} \tag{11}$$

where z is the depth below ground surface (m) where the oxygen concentration is zero, C_0 is the oxygen concentration at the ground surface (atm), O_r is the zero-order oxygen consumption rate coefficient (atm day^{-1}), and D_{eff} is the effective diffusion coefficient through the pore space of the soil (m^2 day^{-1}). Equation (11) represents the total oxygen flow rate to the reaction front averaged over the volume of the soil where the oxygen concentration is not zero.

D_{eff} can be estimated via a Millington-Quirk (1961) model (see Equation (6)) using measured data for porosity (n), air-filled fraction (θ_a), and the molecular diffusion coefficient for oxygen in air (D_{mol}). For oxygen in air at 20 ^{o}C, the estimated molecular diffusion coefficient is $D_{mol} = 2.01 \times 10^{-5}$ m^2 s^{-1} (Gliński and Stępniewski, 1985).

5.3.2 Non-Linear Oxygen Depth Profiles

For non-linear oxygen concentration depth profiles, rather than linear (in space), the model described by Davis *et al.* (2000) can be used to estimate zero-order (in time) oxygen consumption rates.

This model assumes a steady state oxygen distribution in the soil profile, that D is constant with depth (which will not necessarily be the case), the ground surface has a constant atmospheric oxygen concentration, and that the oxygen concentration is held at zero at a set depth below ground (based on the profile data). A zero-order oxygen consumption rate coefficient can be estimated by fitting Equation (12), to the field data,

$$C(z) = C_0 - (C_0 + A\,L^2)\,\mathrm{z}/L + A\,z^2 \tag{12}$$

where $C(z)$ is the oxygen concentration or partial pressure of oxygen (atm) at depth z (m), D is the effective diffusion coefficient (m^2 day^{-1}), O_r is the zero-order oxygen consumption rate (atm day^{-1}), and $A = O_r/(2D)$. Note that $C(z) = C_0$ at $z = 0$, and $C(z) = 0$ at $z = L$. There are a number of ways to estimate O_r - one is by curve matching Equation (12) to the entire oxygen profile data, and another is to match at a selected point. If we choose to match Equation (12) to the depth z_0 at which the oxygen concentration drops to half of the atmospheric concentration [$C(z_0) = C_0/2$], then we can write:

$$O_r = \frac{2D\,C_0}{z_0\,L}\,\frac{(0.5 - z_0/L)}{(1 - z_0/L)} \tag{13}$$

Note that this fitting procedure encapsulated in Equation (13) is only accurate where $z_0 < L/2$.

More complex numerical codes and modelling can also be used to fit oxygen and vapour concentration depth profiles, and be used to estimate degradation rates and flux rates (see, e.g., Öhman, 1999).

5.4 Hydrocarbon Degradation Rates

Aerobic degradation rates can be calculated stoichiometrically from the oxidation of a model hydrocarbon (hexane) with oxygen (Hinchee and Ong, 1992) given by Equation (14)

$$D_h = \frac{O_r \theta_a}{RT\,\rho_b} \frac{MW_h\,1000}{9.5} \tag{14}$$

where D_h is the biodegradation rate (mg-hexane kg-soil^{-1} day^{-1}), O_r is the zero-order oxygen consumption rate coefficient (atm day^{-1}), θ_a is the effective air-filled porosity (m^3 m^{-3}), R is the universal gas constant (8.206 x 10^{-5} m^3 atm K^{-1} mol^{-1}), T is temperature (K), ρ_b is the bulk density (kg m^{-3}) and MW_h is the molecular weight of hexane (g mol^{-1}).

Also, a hydrocarbon biodegradation rate in the soil gas (D_g in units mg-hexane L-soil gas^{-1} day^{-1}) can be calculated using Equation (15).

$$D_g = \frac{O_r}{RT} \frac{MW_h}{9.5} \tag{15}$$

5.4.1 Degradation Rate Estimates

Degradation rates have been calculated by a range of authors and for various situations (see Fischer *et al.*, 1996; Davis *et al.* 1998; 2000; 2001; 2004; Franzmann *et al.*, 1999; Hers *et al.*, 2000) – primarily though for aerobic biodegradation of petroleum hydrocarbon vapours.

Zero-order rate estimates were derived from laboratory testing by Franzmann *et al.* (1999), who took four soil samples from 0 to 2.8 m below ground at a sandy site in Perth Western Australia and carried out spiked ^{14}C-benzene mineralisation experiments. They obtained zero-order estimates of 27-83 µmoles kg-soil^{-1} day^{-1}. This rate can also be converted to an oxygen consumption rate of 2-6x10^{-5} % s^{-1}, which was comparable to a consumption rate of 6.1x10^{-5} % s^{-1} determined from oxygen depth profile data at the same site in a dry period. The 6.1x10^{-5} % s^{-1} oxygen consumption rate can be converted to a hydrocarbon degradation rate of 6.6 mg-hexane kg-soil^{-1} day^{-1} or 6.0 mg-hexane L-aqueous phase^{-1} hr^{-1} assuming a soil bulk density of 1.4 kg m^{-3} and a water filled porosity of 0.06 m^3 m^{-3}. Hers *et al.* (2000) estimated BTX zero-order mineralisation rates of 0.6-1.4 mg-BTX L-aqueous phase^{-1}

hr^{-1}. Fischer *et al.* (1996) estimated rates from field data of 0.5-40 mg kg-soil^{-1} day^{-1}, which are comparable to others quoted here.

Franzmann *et al.* (1999) also generated first-order rates from their study. They estimated half-lives of 11-72 days (1-7x10^{-7} s^{-1}), which convert to an oxygen consumption rate of 0.3-2.2x10^{-6} s^{-1} (accounting for stoichiometry). From data in Fischer *et al.* (1996), first order rates of 1.4-3.6x10^{-6} s^{-1} (or for oxygen = 0.45-1.1x10^{-5} s^{-1}) can be estimated. Hers *et al.* (2000) gave BTX first-order rates of 0.5-1.2 hr^{-1} (1.4-3.3x10^{-4} s^{-1}), which convert to an oxygen consumption rate of 0.42-1.1x10^{-3} s^{-1}. Davis *et al.* (2004) used model fits to give first-order oxygen consumption estimates of 0.09-2.6x10^{-4} s^{-1}.

5.5 Vapour and Oxygen Flux Estimates

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

$$q = D_{eff} \frac{\partial C}{\partial z} \tag{16}$$

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

6 Modelling Approaches and RBCA Tools

6.1 Vapour Modelling Studies

The previous sections have discussed common techniques for analysing and predicting soil vapour dynamics in soil profiles (vadose zones). These techniques employ the continuum assumption that soil gas migration is able to be represented by linear flux laws with effective parameters determined from simple averages of soil properties. This assumption allows the simultaneous solution of contaminant transport equations in the soil gas, water and solid (immobile) phase domains. This is done by expressing the mass partitioning and balance between the phase domains in terms of "averaged" volumetric measures for each phase domain, θ_i, where i denotes the gas, water or solid phase. In the simplest picture, the equilibrium partitioning relationships given by Raoult's Law and Henry's Law (see Section 3.2.1) allow direct linear relationships to be deduced between contaminant concentrations in neighbouring phases, i.e., air phase concentrations are equal to the water phase concentration times the air-water partitioning coefficient. These kinds of continuum models are customarily completed by assuming Fickian diffusion as in Equation (5) and specifying how the phase volumetric measures (θ_a, θ_w, θ_{NAPL}) vary in space and/or time. Degradation mechanisms may be included by adding loss terms using zero-order, first-order or non-linear (e.g. Monod) sink terms. Advection may also be easily added to take account of net gas flow situations. The resulting coupled equation systems are well understood mathematically and several numerical codes have been written for their solution.

6.1.1 Continuum Approaches

This continuum modelling framework has been used in a range of hydrocarbon vapour modelling studies (Jury *et al.*, 1983; Baehr, 1987; Falta *et al.*, 1989; Sleep and Sykes, 1989; Jury *et al.*, 1990; Johnson and Ettinger, 1991; Lahvis and Baehr, 1996; Anderssen *et al.*, 1997; Anderssen and Markey, 1997; Bekins *et al.*, 1998; Johnson *et al.*, 1999; Trefry *et al.*, 2000; Trefry *et al.*, 2001; Turczynowicz and Robinson, 2001), some particularly in combination with field studies (Barber and Davis, 1991a, 1991b; Öhman, 1999; Hers *et al.*, 2000, Davis *et al.*, 2004) – but most are primarily for petroleum hydrocarbon vapours. The continuum assumption is by no means the only method of formulating theories of vapour movement, but it does have minimal data requirements. Even so, not all required data are available in every practical situation even for continuum models.

6.1.2 Other Approaches

At the same time, there are competitors to the continuum theories that have been shown, in at least some circumstances, to provide superior predictions. These include macropore/dual-porosity models, e.g. MACRO-DB (Jarvis *et al.*, 1997), based on the soil macropore model MACRO (Jarvis, 1994; Larsbo and Jarvis, 2003), which seek to take explicit account of inhomogeneities in the soil properties and structure (channel flows, solution features etc), and the so-called anomalous diffusion models, which allow the use of non-Fickian diffusion formulae. These anomalous models include "superdiffusive" and "subdiffusive" formulations. Literature on these more sophisticated models is much rarer than the continuum literature, and most of it neglects issues surrounding contaminants in the soil gas phase. Most importantly, the macropore and anomalous diffusion models have higher data requirements than the linear continuum models. Essentially this is because the former models seek to represent more natural variability in the transport process, and this can only be done sensibly by measuring the appropriate field quantities. On the other hand, the continuum models need much less data input to provide sufficient information to guarantee a *mathematical* (as opposed to a realistic and practical) solution to a site-specific gas transport problem. In some cases, simpler continuum models can even outperform the more detailed macropore models (Evans *et al.*, 1999).

Despite all the modelling efforts and related work, there are still only limited field data sets with sufficient detail for evaluating vapour processes in impacted soil profiles, and for model validation. Additional well-documented studies are required (Johnson *et al.*, 1999). Also, changes in soil moisture distribution and soil layering have been reported to impact vapour behaviour and lead to complications when estimating biodegradation rates (Fischer *et al.*, 1996; Davis *et al.*, 2000). Risk-based methodologies can provide assistance in screening contaminated sites where field data is lacking.

6.2 Four RBCA Modelling Tools

All the above issues concerning choice of model formulation for a particular study represent a scientific research question. However, in many situations it is often necessary to choose a simple and well-understood model with which to *estimate* vapour pathways and exposures. For this reason, there is a wide choice of continuum models that can be used in assessing vapour migration and exposure risk in contaminated soil environments. In the following we discuss and compare the capabilities of several major soil vapour modelling codes for assessing the risk of soil vapour entry into buildings. The discussion is brief and focussed more on commonalities and deficiencies rather than on full and detailed review. For fuller compilations and reviews the reader is referred to ASTM (1999), Whittaker *et al.* (2001) and Evans *et al.* (2002), while NZMfE Guidelines (1999) present a New Zealand perspective. The models considered are:

1. The USEPA Johnson & Ettinger Spreadsheet Model (USEPA, 2003)
2. The RISC WorkBench Model (RISC WorkBench, 2004)
3. The GSI RBCA Tool Kit Model (GSI RBCA Tool Kit, 2004)
4. The PHC CWS Spreadsheet Model (PHC CWS, 2003)

Other packaged and widely available models exist, including but not limited to CONSIM (2003), VAPEX (2004), RISC Human Version 3.1 (2004), which implements both the CSOIL and VOLASOIL submodels (Waitz *et al.*, 1996), the PHC CWS Spreadsheet Model (2003) and AERISplus (2004). Of these, the CONSIM model is primarily designed for groundwater simulations within a Monte Carlo framework – its soil vapour model is only rudimentary. At the time of writing this report the authors were unable to obtain detailed information on AERISplus.

6.2.1 USEPA Johnson & Ettinger Spreadsheet Model Version 3

This free 1D model is based on the Johnson and Ettinger (1991) formulation with significant updating of soil and chemical property databases, building properties and toxicity data. There are 8 spreadsheets contained in the package (USEPA, 2003), consisting of separate spreadsheets for soil contamination, groundwater contamination, soil vapour contamination and NAPL contamination, each of these four scenarios have separate "screening" level and "advanced" level implementations. The presentation is functional but not particularly inviting to the user. The model supports both infinite and finite sources, as well as the direct input of observed concentrations and soil properties within the model domain. Explicit account is made for effects of temperature on chemical properties, and a van Genuchten formulation is used to model capillary effects near the water table. A standard Millington-Quirk tortuosity model is used to predict effective vapour diffusion coefficients. The unsaturated zone is idealized as a set of homogeneous horizontal layers over which the vertical net effective diffusion coefficient is calculated by a harmonic layer average. The building inner space is assumed to be perfectly mixed, allowing an α value to be defined. The model uses a single-crack model at the join of the building walls and floor, through which soil vapour may advect into the building space at a rate determined by the specified soil-building pressure gradient. An exposure risk algorithm is supplied, defined in terms of standard exposure quantities (frequency, duration etc).

As noted by the USEPA Guide document in the model release pack, eleven assumptions apply. Chief among these are that:

- no allowance is made for biodegradation processes
- pressure gradients (i.e., from ventilation) are steady

To these we would add that seasonal or other transient effects are also neglected.

Some on-line access to the Johnson and Ettinger model is also available at the USEPA web site: http://www.epa.gov/athens/learn2model/part-two/onsite/JnE_lite.htm

6.2.2 RISC WorkBench Version 4.0

RISC WorkBench (RISC, 2004) is a stand-alone software package based on the BP RISC implementation of the 1D Johnson and Ettinger (1991) vapour model, but with extensive additions in compliance with USEPA's Risk Assessment Guidance for Superfund (USEPA, 1989). RISC WorkBench supports RBCA Tier 1 and Tier 2 assessments, but not Tier 3 or higher. RISC WorkBench is extremely clear and simple to use and contains a comprehensive set of exposure pathway analyses and environmental standards compliance algorithms. It also contains an additional spreadsheet based on RBCA algorithms that can be used in tiered RBCA assessments. RISC WorkBench is an improvement over the USEPA Spreadsheet model in that it supports biodegradation mechanisms and also has a limited capacity to deal with transient issues – it allows seasonal water table elevations to be input. It also has support for Monte Carlo style probabilistic exposure and risk analyses, although the fate and transport model is still entirely deterministic. As for the USEPA spreadsheet model, there is no facility to model soil inhomogeneities other than simple layering and material properties are regarded as constant.

6.2.3 GSI RBCA Tool Kit for Chemical Releases

GSI RBCA Tool Kit (2004) is an Excel-based spreadsheet system that is designed to meet the requirements of the ASTM Standard Guide for Risk-Based Corrective Action (E-2081). It has a more visually busy presentation than the RISC WorkBench Version 4.0. The new release extends the Johnson and Ettinger (1991) model to support transient groundwater modelling, multiple Points of Exposure and metals and chlorinated solvents. GSI RBCA Tool Kit supports the use of redox-limited biodegradation mechanisms, and is suitable for RBCA Tier 1 and Tier 2 assessments, but not Tier 3 or higher. GSI RBCA is closely related to the GSI Atlantic RBCA system used in eastern Canada (GSI RBCA Tool Kit for Atlantic Canada v2.1, 2004)

6.2.4 PHC CWS Spreadsheet Model

The PHC CWS Spreadsheet (PHC CWS 2003) is a Tier 1 and Tier 2 system for the assessment of sites contaminated with petroleum hydrocarbons. The Canada Wide Standards (CWS) process is explicitly based upon both the Canadian Council of the Ministers for the Enviromnent (CCME) Protocol for the Derivation of Environmental and Human Health Soil Quality Guidelines and the ASTM RBCA methodologies. The spreadsheet itself is not intended for stand-alone use – it is to be used in conjunction with supporting guidance documents which are also freely available. The spreadsheet itself is small (300 kB) and is written in Excel format. The spreadsheet is very clear and simple to use and accounts for vapour ingress through cracks in the building envelope, steady pressure differentials, basement or slab-on-ground construction, off-site migration. The source is a finite rectangular zone with infinite duration. Risk calculations are performed for various exposure pathways, including dermal contact, soil ingestion and potable water. Animal exposure is also calculated. However, PHC CWS does not account for intrinsic degradation of vapours within the soil, nor does it account for transient effects to do with seasonal variations or climatic influences other than the ability to enter the number of days per year that the local temperature drops below freezing.

6.3 Summary Comments

Interestingly, despite the common provenance of the transport and transformation submodels used by the packages, i.e., the Johnson and Ettinger (1991) approach is present in all of the packages in various guises, the packages themselves apparently do not give equal solutions to identical test case problems, with differences of an order of magnitude or more measured (Evans *et al.*, 2002; Whittaker *et al.*, 2001). No single model was found to provide a consistently more conservative solution than the others in all test cases. The reason for this lies in the subtly different formulations used for source dissolution and dilution, for crack dynamics and for top surface boundary conditions. Models require increased complexity when associated with built structures. Simplified models and assessments have been proposed (API 1998). However, houses built as slab-on-ground or built elevated with a crawl space beneath, and whether built on sandy or heavier soil, create complexities for describing vapour behaviour that existing codes do not adequately address.

The sensitive and non-linear nature of the vapour transport problem has led to much discussion on the veracity of particular surface boundary conditions (Anderssen and Markey, 1997; Turczynowicz and Robinson, 2001), and crack flow theories (Etheridge, 1998) but much simpler effects can generate significant uncertainty in vapour predictions. For example, Garbesi and Sextro (1989) show that spatially persistent soil layering has the potential to perturb soil gas pressures away from solutions based on homogeneous profiles for distances up to and beyond 10 m around built structures.

Figure 4.2 showed that vapours can accumulate beneath slab-on-ground constructions which restrict oxygen ingress to the shallow soil. Seasonal soil moisture variations have also been shown to control hydrocarbon vapour egress to the soil surface in both sandy environments (Davis *et al.*, 2004) and in heavy soils (see, Figure 3.8 for example). There is also potential for enhanced soil aeration due to wind scouring near built structures. This may conceivably boost the rate of intrinsic biodegradation of aerobically degradable organic vapours in the soil at depths of the order of one metre below the surface. Furthermore, the potential for complex interactions between soil vapours and artificial materials in above-ground structures was highlighted. Indeed building materials and internal furnishings may themselves provide a significant proportion of the indoor vapour load (Bodalal *et al.*, 2000), and none of the assessed models take account of this potential exposure source.

The conclusion is, then, that predictions from the commonly accepted Tier 2 models may not agree with each other to within than an order of magnitude, where the effects due to barometric forcing, building structure and subsurface complexity are neglected or oversimplified.

7 Uncertainties and Gaps in Knowledge

There are a number of uncertainties and gaps in knowledge related to the behaviour of vapours. These include:

(i) Calibration and validation of conceptual and actual models where predictions relate to indoor air exposures,

(ii) Biodegradation processes, which are not well modelled – there is a need to couple the microbial and chemical reactive processes (see e.g. Öhman, 1999) – such as oxygen and petroleum hydrocarbon vapour movement and reaction,

(iii) The intrinsic vapour loads from building materials and furnishings,

(iv) There remain conditions under which only limited data sets are available to assess vapour risks – especially in Australia related to contaminant type, soil type and the variability of built environments.

(v) The behaviour and risks posed by mixtures of petroleum, chlorinated and other chemical (e.g., ketone) vapours in subsurface environments.

As noted in earlier sections, it is not necessarily true that a sophisticated and detailed vapour model will provide accurate predictions of vapour exposures in any particular practical situation. Discrepancies between model and reality may be reduced by calibrating the model against the field setting, i.e. choosing the model input parameters in the light of measured field data. When using vapour models developed overseas it is similarly important to understand that many of the supporting data sets, especially involving soil chemical and microbiological properties, have not been proven to apply to Australian environmental conditions. There is a large spread of reported soil biodegradation rates for petroleum hydrocarbon compounds. It is important to establish the usefulness or otherwise of these data sets in Australian conditions, and to enhance the data sets to provide a more complete summary of soil, climatic and environmental types.

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