Establishing Health-based Investigation Levels for benzene, toluene, ethyl benzene, xylenes, naphthalene, and aromatic and aliphatic ≤EC16 TPH fractions

EPHC

Environment Protection & Heritage Council

This paper was presented at the Fifth National Workshop on the Assessment of Site Contamination

enHEALTH

Proceedings of the Fifth National Workshop on the Assessment of Site Contamination

Editors: Langley A, Gilbey M and Kennedy B

The editors may be contacted through the NEPC Service Corporation for which contact details are provided below.

Further copies of these proceedings can be purchased from:

NEPC Service Corporation
Level 5, 81 Flinders Street
ADELAIDE SA 5000

Phone: (08) 8419 1200
Facsimile: (08) 8224 0912
Email: exec@ephc.gov.au

Printed version ISBN 0-642-32355-0 Electronic (web) ISBN 0-642-32371-2

Establishing Health-based Investigation Levels for benzene, toluene, ethyl benzene, xylenes, naphthalene, and aromatic and aliphatic ≤EC16 TPH fractions

Len Turczynowicz
SA Department of Human Services

ABSTRACT

The establishment of Australian Health-Based Investigation levels (HILs) for volatile hydrocarbons, such as BTEX and certain Total Petroleum Hydrocarbon (TPH) fractions, has been limited due to the lack of a suitable transport model that can be used to predict human exposures. The use of an indoor vapour intrusion model for crawl space homes is presented to estimate cumulative indoor human doses (CIHDs) based on one dimensional movement from a finite sub-surface source through soil. This model represents a non-steady state evaluation of indoor exposures from a finite source over a defined period. The use of Australian experimental field data incorporates consideration of mixing, dilution, ventilation and sink effects and first order degradation of the volatile in air and soil. Indoor human exposures have been compared against overseas ambient air standards and Reference Inhalation Concentrations (*RFC*s) to develop HILs for BTEX, naphthalene, and aromatic and aliphatic TPH fractions ≤ EC16. The HILs developed for the given exposure scenario are 3 mg/kg for benzene; 40 mg/kg for toluene; 530 mg/kg for ethyl benzene; 320 mg/kg for xylenes; 30 mg/kg for naphthalene; 15 mg/kg for aromatic EC>9-16; 310 mg/kg for aliphatic EC>5-8 and 25 mg/kg for aliphatic EC>8-16. The development of the Ambient Air Toxics NEPM which includes benzene, a human carcinogen, will enable a review of the proposed HIL for benzene. Sensitivity analyses have revealed the dominant input parameters that have the greatest effect on the CIHD to be those related to dwelling characteristics. This will allow further model refinement and the establishment of generic criteria for volatiles.

1 INTRODUCTION

The development of health-based soil investigation levels (HILs) for soils contaminated with volatile Total Petroleum Hydrocarbons (TPHs) has been limited due to a lack of a suitable Australian transport model to determine human exposures and the complexities associated with dealing with mixtures. Complex mixtures such as petroleum hydrocarbons incorporate large numbers of different chemicals with diverse toxicological and environmental behaviour properties. This complexity has resulted in difficulties with exposure assessment modelling and the subsequent development of health-based soil criteria for volatile hydrocarbons whose major exposure pathway is by inhalation.

A previous workshop paper (Turczynowicz, 1998) reviewed approaches in assessing soil contaminated with petroleum hydrocarbons including methods proposed by an international group known as the Total Petroleum Hydrocarbon Criteria Working Group (TPHCWG). This international committee has published toxicity and environmental fate and transport data based on equivalent carbon (EC) ranges for both aliphatic and aromatic total petroleum hydrocarbons (Gustafson *et al.*, 1997; Edwards *et al.*, 1997) while

also providing guidance on human health risk evaluation of petroleum-contaminated sites (Vorhees *et al.*, 1999).

Anderssen and Markey (1996, 1998) have reviewed the transport of volatile organic compounds from subsurface sources to air/soil surface boundaries and have extended the Behaviour Assessment Model (BAM) of Jury, Spencer and Farmer (Jury *et al.*, 1983) to one involving flux accumulation at the soil surface. This approach has been further developed by Robinson (2000) to investigate, in detail, soil fluxes and cumulative fluxes for non-zero surface fluxes. This latter model has been applied to the derivation of soil criteria for benzene migrating from soil to the indoor environs of crawl space-based homes (Turczynowicz and Robinson, 2001).

This paper applies the transport model which couples subsurface diffusion and advection with surface flux and above ground ventilation. Flux rates into crawl space and movement into indoor air space are modelled on the basis of diffusion mechanisms and air exchange rates for both crawl space and indoor air environments. Data on ventilation rates have been obtained from experimental data of Australian field experiments. Using TPHCWG and other data on benzene, toluene, ethyl benzene and xylenes (BTEX), naphthalene and volatile aromatic and aliphatic TPH fractions and local data for above surface movement, cumulative indoor human doses (CIHD) meeting specific toxicological endpoints for these substances are determined and from which are calculated Health-based Investigation Levels (HILs). Sensitivity analyses on this transport model provide insights on the impact of the many input variables used.

2 TOXICITY OF BTEX, NAPHTHALENE AND VOLATILE TPH FRACTIONS

2.1 BENZENE, TOLUENE, ETHYL BENZENE AND XYLENES

The lower molecular weight monoaromatic hydrocarbons, benzene, toluene, ethyl benzene and xylenes (BTEX) are widely distributed in the environment and are released from natural and anthropogenic sources (IPCS, 1985, 1993, 1996, 1997). Exposure to BTEX occurs in occupational or environmental settings through inhalation or dermal contact. Combustion engine fuels and their emissions are the major source of exposure.

Benzene partitions mainly to air with inhalation considered the primary route of exposure accounting for more than 99.9% of the total daily intake of benzene (Hattemer-Frey, Travis and Land, 1990). The volatilisation potential and partitioning behaviour of toluene, ethyl benzene and xylenes is comparable to benzene as reflected in the respective Henry's Constants (see Table 5) and inhalation is considered to be the most significant exposure pathway (ATSDR, 1995a, 1997, 1999a, 2000).

The toxicity of BTEX has been extensively reviewed by the Agency for Toxic Substances and Disease Registry (ATSDR, 1995a, 1997, 1999a, 2000) and the WHO International Programme on Chemical Safety (IPCS, 1985, 1993, 1996, 1997) and the reader is referred to those comprehensive reviews for additional information.

Acute toxicity resulting from exposure to benzene has resulted in CNS depression, cardiac arrhythmias and eventually asphyxiation and respiratory failure with elevated exposures (Andrews and Snyder, 1986). Short-term or long-term exposures have identified the most significant health effects from exposure to benzene to be haematotoxicity,

immunotoxicity, neurotoxicity and carcinogenicity (IPCS 1993). Epidemiological and case studies have established benzene as a human leukemogen (IARC 1982, 1987) and exposure has been associated with an excess risk of aplastic anaemia, acute nonlymphocytic leukemia, myelogenous leukemia and acute myeloid leukemia in humans (IPCS, 1993; IARC 1987).

Inhalation exposure to ethyl benzene, toluene and xylenes may result in effects on the central nervous system. Ethyl benzene exhibits low acute and chronic toxicity in both animals and humans compared to toluene and xylenes (IPCS, 1996). Lower level acute exposures to toluene in humans can produce dizziness, exhilaration and confusion while high level exposures may produce incoordination, ataxia, unconsciousness and eventually death (ATSDR, 2000). Reversibility of effects on liver, renal and nervous systems has been observed following exposure to toluene but the central nervous system is considered the most sensitive system (Benignus, 1981). Xylenes exhibit effects consistent with the other monocyclic aromatics with central nervous system depression and symptoms such as lightheadedness, nausea, headache and ataxia at low doses. At high doses confusion, respiratory depression and coma may result (Ellenhorn and Barceloux, 1988).

Both animal and human data suggest that mixed xylenes and the meta, ortho and para isomers all produce similar effects although potency within isomers varies for any given effect. Liver and kidney toxicity is also exhibited in humans although in healthy individuals such effects are unlikely to occur before neurological effects and eye/respiratory tract irritation (ATSDR 1995a).

The carcinogenicity of BETX has been reviewed by US EPA and IARC and is summarised in Table 1.

Table 1: Carcinogenicity of BTEX and naphthalene

Substance	US EPA	IARC	Reference
benzene	Group A proven human carcinogen	Group 1 proven human carcinogen	IRIS, 2002; IARC, 1987
ethyl benzene	Group D not classifiable	Group 2B possibly carcinogenic to humans	IRIS, 2002; IARC, 2000
toluene	Group D not classifiable	Group 3 not classifiable	IRIS, 2002; IARC, 1999a
xylene	Group D not classifiable	Group 3 not classifiable	IRIS, 2002; IARC, 1999b
naphthalene	Group C possible human carcinogen	Not reviewed	IRIS, 2002

2.2 NAPHTHALENE

Naphthalene is a commonly encountered petroleum hydrocarbon mainly used in phthalic anhydride production but also in the production of moth repellents, toilet bowl deodorants, scintillation counting fluid and carbamate insecticides. Naphthalene or its derivatives can be found in wood preservatives, dyes, antiseptics, explosives, lubricants, and tanning agents (ACGIH, 1991). Naphthalene is also commonly encountered as a

minor component of many fuels (Potter and Simmons, 1998) and can subsequently be expected to be found at sites contaminated with total petroleum hydrocarbons.

The relatively volatile nature of naphthalene results in the principal general population exposure being from inhalation with only minor contributions from ingestion of water and food (ATSDR, 1995b). Howard, (1989) has estimated adult inhalation exposures of 19 µg/day based on a respiration rate of 20m^3/day and an average urban/rural air concentration of 0.95 µg/m^3. ATSDR (1995b) in a comprehensive review of the toxicity of naphthalene identified gastrointestinal, haematological, hepatic, ocular and neurological effects following exposure by inhalation. Gastrointestinal effects such as nausea, vomiting and abdominal pain have been observed in adults and children following exposure to naphthalene vapours from mothballs scattered throughout a home (Linick, 1983). Haemolytic anaemia has been reported as the most common outcome of naphthalene exposure and was observed in the Linick (1983) report where indoor air concentrations were determined to be 105 µg/m^3 . This haemolysis is subsequently responsible for jaundice observed in exposed adults and children and also for permanent neurological damage observed in infants induced by the jaundice (ATSDR, 1995b). The carcinogenicity of naphthalene has been reviewed by US EPA but not by IARC (Table 1).

2.3 TPH FRACTIONS

2.3.1 Introduction

The toxicity of the Total Petroleum Hydrocarbons, particular fuel mixtures, and specific petroleum hydrocarbons such as monocyclic aromatics and fuel additives has been reviewed in a previous workshop paper on petroleum hydrocarbons (Turczynowicz, 1998).

It should be noted that the TPH fractions for fate and transport modelling are subsets of the TPH fractions defined for the purposes of toxicity assessment. A total of 13 fractions were established for the purposes of fate and transport modelling based on volatilisation and leaching properties while toxicity criteria were derived for 7 fractions. These fractions are presented in Table 2 in addition to derived toxicity criteria and their basis.

Table 2: TPH fractions and toxicity criteria

Equivalent Carbon number	*RfD* (mg/kg/day)	*RfC* (mg/m^3)	Health effect
Aliphatic fractions			
>5-6 >6-8	5.0	18.4	Hepatotoxicity, nephrotoxicity and neurotoxicity if >53% n-hexane
>8-10 >10-12 >12-16	0.1	1.0	Haematological and hepatic changes
>16-35	2.0	Not available	Hepatic granuloma (foreign body reaction)
Aromatic fractions			
>5-7 (benzene)	Not available	Not available	Human carcinogen
>7-8 (toluene)	0.2	0.4	Hepatotoxicity,

Equivalent Carbon number	*RfD* (mg/kg/day)	*RfC* (mg/m³)	Health effect
			nephrotoxicity
>8-10 >10-12 >12-16	0.04	0.2	Decreased bodyweight
>16-21 >21-35	0.03	Not available	

(Source: Vorhees *et al*, 1999)

2.3.2 Aliphatic TPH fractions in the range EC>5-16

The aliphatic TPH fractions in this range encompass five for fate and transport and two for toxicity, EC>5-8 and EC>8-16.

The EC>5-8 range for which toxicity criteria have been established include some 84 petroleum hydrocarbons identified in the compositional analyses of petroleum streams reviewed by TPHCWG. The EC>5-6 range includes some 19 substances such as n-pentane, n-hexane, methylated butanes, butenes, pentanes, pentenes, cyclopentane, cyclopentene and some alkynes. The EC>6-8 fraction includes approximately 65 substances such as n-heptane, n-octane, methyl and ethyl derivatives of pentanes, hexanes, pentenes and hexenes and cyclohexane and methylated cyclohexanes, cyclopentanes and cyclopentenes (Potter and Simmons, 1998; ATSDR, 1999b).

Toxicity data on substances in the EC>5-8 range are limited to n-hexane, n-heptane, cyclohexane, and methyl cyclohexane with most information on n-hexane. Inhalation exposure to n-hexane over acute, intermediate or chronic periods is associated with peripheral neuropathy in both animals and humans (ATSDR, 1999c). Respiratory and renal effects have also been observed but at levels greater than that inducing peripheral neuropathy (ATSDR, 1999b). Peripheral neuropathy does not appear to be induced by other substances in the EC>5-6 range including n-heptane (Edwards *et al.*, 1997; ATSDR, 1999c). Cyclohexane has been associated with hepatic and renal effects in sub-chronic animal studies while n-heptane and methylcyclohexane have caused CNS depression at high inhalation exposures (Edwards *et al.*, 1997; HSDB, 2002). N-hexane, n-heptane and methylcyclohexane have not been reviewed by IARC but US EPA consider them to be not classifiable as to their human carcinogenicity (Group D) (ATSDR, 1999b).

The EC>8-16 range for which toxicity criteria have been established include some 45 petroleum hydrocarbons identified in the compositional analyses of petroleum streams reviewed by TPHCWG. Constituents of the EC>8-16 range include:

- EC>8-10 encompassing some 33 substances including n-nonane, n-decane, methyl and ethyl brained chain derivatives of pentane, hexane, heptane, octane and cyclohexane and alkenes, nonene and decene,
- EC>10-12 encompassing 6 substances including n-undecane, n-dodecane and pentylcyclopentane,
- EC>12-16 also with 6 substances: n-tridecane, n-tetradecane, n-pentadecane, n-hexadecane, tridecene and hexylcyclohexane. (Potter and Simmons, 1998; ATSDR, 1999b).

Toxicity data on these chemicals are limited and oral and inhalation criteria have been derived on the basis of mixtures such as jet fuels (specifically JP-8) and dearomatised

petroleum streams. ATSDR has published toxicological profiles for JP-5, JP-7, JP-8 and kerosene (ATSDR 1995c, 1995d, 1998) and the major health impacts associated with exposures by inhalation have been neurological effects in humans and hepatic effects in animals. The TPHCWG, in reviewing five inhalation studies of dearomatised petroleum streams, identified reduced weight gain and nephrotoxicity in rats but no developmental or maternal toxicity. Reviews of five oral gavage studies by the TPHCWG identified male rat nephropathy and haematological effects. These studies and health effects were subsequently used in the establishment of the *RfD* and *RfC* for the EC>8-16 TPH fraction (Edwards *et al.,* 1997).

2.3.3 Aromatic TPH fractions in the range EC>5-16

The aromatic TPH fractions in this range encompass five for fate and transport and three for toxicity, EC>5-7, EC>7-8 and EC>8-16 (Edwards *et al.,* 1997). Review of the equivalent carbon numbers (ECs) for ethyl benzene, xylenes and styrene identified a misclassification in the TPHCWG documentation. This results in a requirement to reclassify EC>7-8 to EC>7-9 and EC>8-16 to EC>9-16 for the aromatic TPH fractions. This misclassification has also been reported by Franken *et al.,* (1999) with subsequent alterations being made in the Dutch documentation. These re-classifications are also consistent with those of ATSDR (1999b) and do not change the conclusions that establish the toxicity fraction criteria.

EC>5-7 is unique in that it is represented by an indicator chemical, benzene, a proven human carcinogen. Similarly, EC>7-9 is represented by toluene both in terms of environmental fate and transport properties and in the case of the derivation of the toxicity criteria. The toxicity of both these chemicals has been reviewed in Section 2.1.

The EC>9-16 fractions encompass more than 50 compounds for which EC numbers could be calculated:

- EC>9-10 includes substances such as methyl and ethyl branched chain benzene derivatives, cumene (isopropylbenzene), n-propylbenzene and butylbenzenes,
- EC>10-12 includes trimethyl- and diethylbenzene derivatives, indan and tetralin methylated derivatives and naphthalene,
- EC>12-16 includes triethyl benzenes, n-hexylbenzene and n-heptylbenzene, phenylcyclohexane, biphenyl, methyl- and dimethylnaphthalenes, acenaphthylene and acenaphthene (Potter and Simmons, 1998; ATSDR, 1999b).

ATSDR (1999b) report that inhalation exposure to isopropylbenzene (cumene) and trimethylbenzene has been associated with respiratory and neurological effects although these effects were considered as possibly not the most sensitive effects of inhalation exposure to this fraction. Data on C9 aromatic mixtures composing mainly trimethylbenzene and methylethylbenzene isomers have been used by the TPHCWG for the *RfC* determination with renal and hepatic effects being the critical health effects (Edwards *et al.,* 1997).

Limited data on other components such as 1-methyl naphthalene, acenaphthene, and biphenyl suggest respiratory and haematological effects, hepatic effects, and renal and haematological effects respectively (ATSDR 1999b).

IARC has not reviewed the carcinogenicity of these compounds.

3 THE VOLATILISATION MODEL AND MODEL PARAMETERS

The volatilisation model is designed to estimate cumulative indoor human doses (CIHD) based on the movement of a volatile sub-surface soil contaminant via the crawl space into a brick veneer dwelling. This volatile migrates through soil to a stagnant surface boundary layer where it is mixed and diluted according to crawl space ventilation rates with subsequent flow into the indoor air space through floor, wall and roof space. Volatile sinks and sources within the indoor air space, ventilation of the indoor space and degradation of the volatile in air and soil are considered.

The mathematical constructs, solution methods and assumptions for the transport model have been presented in detail in the papers by Robinson (2000) and Turczynowicz and Robinson (2001) and the reader is referred to the relevant papers. The following is a summary of the key mass balance equations and the relevant parameters involved. Detail on the transport model is presented at this workshop by Robinson, (2002).

The five principal model equations are:

(a) The soil transportation equation:

$$\frac{\partial C_T}{\partial t} + \mu_T C_T = \frac{\partial J_T}{\partial z} = \frac{\partial}{\partial z}\left[D_T \frac{\partial C_T}{\partial z} - V_T C_T \right] \quad , \quad C_T = C_T\left(z,\ t\right) \tag{1}$$

(b) The soil flux equation:

$$J_T\left(0,\ t\right) \ = \ D_T \frac{\partial C_T\left(0,\ t\right)}{\partial z} - V_T C_T\left(0,\ t\right) \ = \ H_a\left(\frac{C_T\left(0,\ t\right)}{R_G} - C_{CS}\left(t\right) \right) \ , \quad t \geq 0 \tag{2}$$

(c) The crawl space transportation equation:

$$\Omega_{CS}\left[\frac{\partial C_{CS}}{\partial t} + \mu_a C_{CS} \right] + \Omega_{CS} X_{CS} C_{CS} = A_F J_T\left(0,\ t\right) \tag{3}$$

(d) The dwelling transportation equation:

$$\Omega_D\left[\frac{\partial C_D}{\partial t} + \mu_a C_D \right] + \Omega_D X_D C_D + S\ C_D = Q_{CD} C_{CS} \tag{4}$$

(e) The cumulative indoor human dose:

$$\text{Dose}\left(t\right) = I \int_0^t C_D\left(\tau\right) d\tau \tag{5}$$

where

z is the arbitrary depth below the soil surface,

t is the time from the beginning of occupation of the house,

$J_T = J_T\left(z,t\right)$ is flux towards the surface,

μ_T is a linear soil degradation rate constant,

D_T is a constant coefficient for diffusion and V_T a velocity, positive downwards,

R_G is the gaseous phase equilibrium partition coefficient connecting the soil gas-phase concentration $C_G\left(z,\ t\right)$, to the total concentration by $C_T\left(z,\ t\right) = R_G C_G\left(z,\ t\right)$,

H_a, is a diffusion coefficient defined by $H_a = D_G^{air} / d_{air}$,

$C_{CS}(0) = C_{amb}$ = 0, is the crawl space concentration at t = 0, assumed to reflect ambient levels,
Ω_{CS} is crawl-space volume with plan area, A_F,
X_{CS} is crawl space air exchange rate,
μ_a is the volatile degradation rate in air,
$C_D(0) = C_{amb} = 0$, is the indoor dwelling air concentration at t = 0, assumed to reflect ambient levels,
Ω_D and X_D are volume and air exchange rate, respectively, for the dwelling interior,
I, is the inhalation for a human receptor, (in this case a child of 2.5 years of age) and is also a component of the sink summation, *S*,
S, is the total inhalation by indoor occupants consisting of the inhalation for a child and two adults without any other indoor sinks (or sources),
Q_{CD} is the volumetric flow rate from crawl space to dwelling via floor but also through wall and ceiling cavities**.**
In addition, a subgroup of parameters are required to define D_T, the volatile effective diffusivity, V_T, the effective velocity and R_G, the gaseous phase equilibrium partition coefficient and the surface transfer coefficient, H_a. The respective relationships are presented in the Behaviour Assessment Model (Jury *et al.*, 1983) and discussed by Robinson, (2000).

The additional parameters include:
R_L, the liquid phase equilibrium partition coefficient,
θ_L, the volumetric water content,
θ_G, the volumetric air content,
ϕ, the soil porosity,
ρ_B, the soil bulk density,
K_H, the Henry's constant for the volatile,
K_D, the distribution constant,
f_{oc}, the organic carbon fraction of the soil,
K_{oc}, the organic carbon partition coefficient of the volatile,
D_G^{air}, the volatile diffusivity of the chemical in air,
D_L^{water}, the volatile diffusivity of the chemical in water,
V_L^B, the downward bulk liquid phase velocity,
V_G^B, the upward bulk gaseous phase velocity, with $V_G^B = 0$.
d_{air}, the thickness of the boundary layer.

The model product, the Cumulative Indoor Human Dose (CIHD), is a mass intake value over a certain period of volatile emission. For the purposes of the modelling in this paper, the period for exposure is set at 99% of the emissions for a 70 year (lifetime) period due to the asymptotic nature of the emission profile. The model parameters are set at particular values consistent with a particular soil profile (McLaughlin, personal communication) and the chemical concentration is set at 1 mg/kg (wet weight). Proportionality between soil mass and CIHD allows appropriate scaling when calculating HILs from a health guideline

value for atmospheric exposure. Sensitivity analyses allow evaluation of the input variables used in the modelling and these are discussed in Section 4 of this paper.

The exposure scenario for the modelling is as detailed in Figure 1 with parameter values presented in Tables 3, 4, 5 and 6.

Figure 1: Modelling scenario for volatile hydrocarbons from TPH contaminated soil

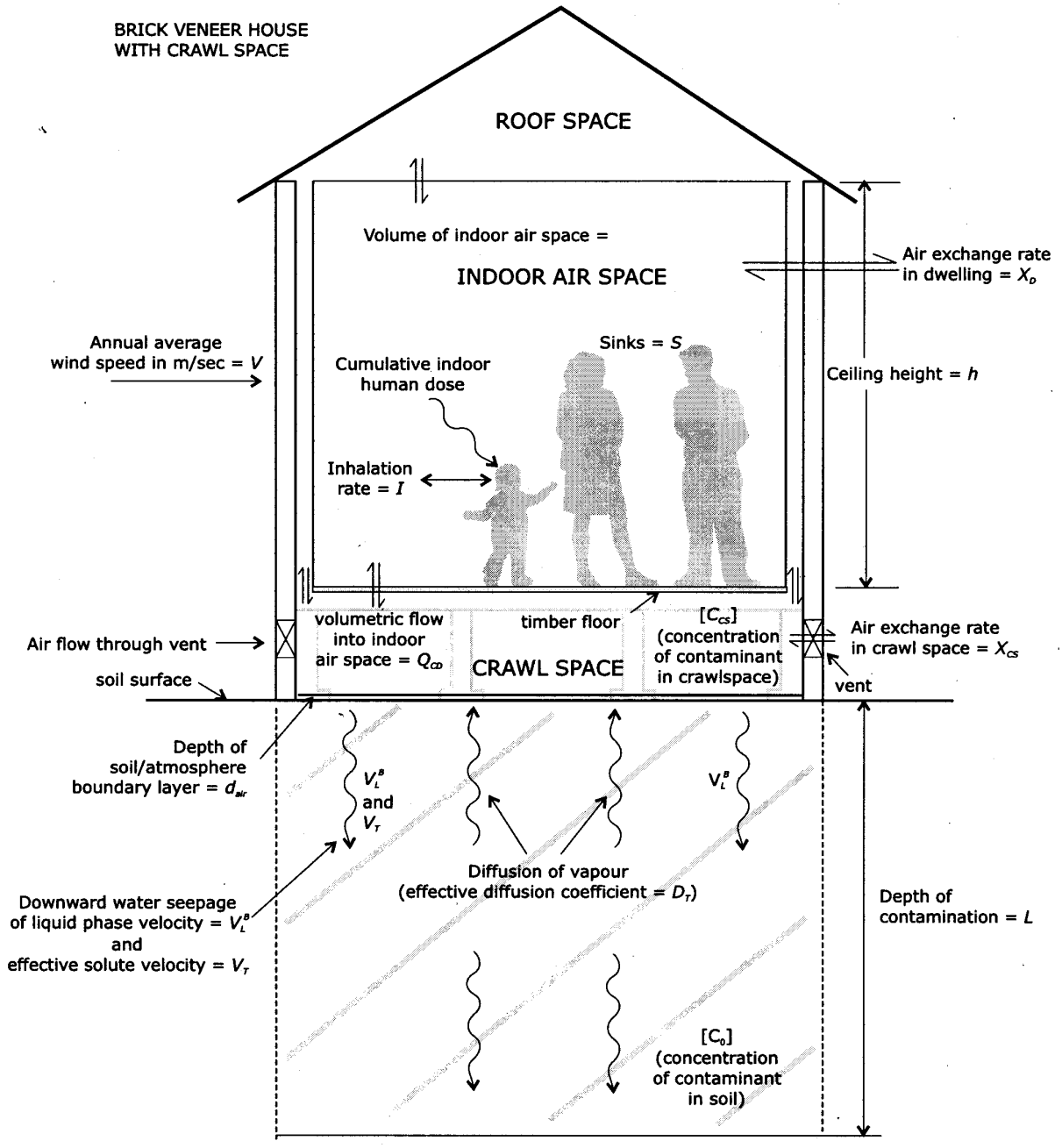


Table 3: Soil parameters

Parameter	Value	Units	Reference/Comment
ϕ_T , total soil porosity	0.45	$m^3\ m^{-3}$	Little *et al*., 1992; Gustafson *et al*., 1997; Marshall *et al*., 1996
θ_L , water-filled porosity	0.05 (v/v)	$m^3\ m^{-3}$	assumed, (see Olweny *et al*., 1998)
ρ_B , dry bulk density	1.4575×10^6	$g\ m^{-3}$	Little *et al*., 1992
f_{oc} , organic carbon fraction	0.005	unitless	Northcote *et al*., 1975
V_L^B , volumetric soil water flux	1.0×10^{-3}	$m\ day^{-1}$	assumed, (see Jury *et al*., 1983)
d_{air} , depth of the soil/atmosphere boundary layer	0.005	m	Jury *et al*., 1983

Table 4: Dwelling parameters

Parameter	Value	Units	Reference/Comment
A_F , area of the floor of the house	127	m^2	Olweny *et al*., 1998; Delsante *et al*., 1998a,b
Ω_{CS} , volume of the crawl space	63.8	m^3	Olweny *et al*., 1998; Delsante *et al*., 1998a,b
Ω_D , volume of interior of house, (Ω_D = A_F x height = $127 m^2$ x 2.7m)	342.9	m^3	Olweny *et al*., 1998; Delsante *et al*., 1998a,b
X_{CS} , ventilation rate of crawl space	411.36	day^{-1}	Olweny *et al*., 1998; Delsante *et al*., 1998a,b
X_D , ventilation rate of indoor air	11.28	day^{-1}	Biggs *et al*., 1987
Q_{CD} , volumetric flow rate (crawl space to indoor air)	966.98	$m^3\ day^{-1}$	Olweny *et al*., 1998
S, inhalation by indoor occupants (without other sinks or sources)	35.1	$m^3\ day^{-1}$	US EPA 1997

Table 5: Physico-chemical parameters

Substance	K_{oc} **($m^3\ g^{-1}$)**	K_H **($cm^3 cm^{-3}$)**	D_G^{air} **($m^2\ day^{-1}$)**	D_L^{water} **($m^2\ day^{-1}$)**	μ_T **(day^{-1})**	μ_a **(day^{-1})**	C_0 **($mg\ m^{-3}$)**	L **(m)**
benzene	8.12E-5	0.225	0.76032	8.4672E-5	0.00167	0.05172	1507.5	3
toluene	2.34E-4	0.274	0.7516	7.4304E-5	0.0033	0.1599	1507.5	3
ethyl benzene	5.37E-4	0.358	0.6480	6.7392E-5	0.0030	0.1943	1507.5	3
xylenes	5.863E-4	0.252	0.67824	1.5379E-4	0.001925	0.3780	1507.5	3
naphthalene	8.44E-4	0.0174	0.50976	6.480E-5	0.00269	0.5634	1507.5	3
Aromatic								
EC 5-6	fraction properties as for benzene							
EC >7-8	fraction properties as for toluene							
EC>8-10	1.585E-3	0.480	0.864	8.64E-5	0.00193	0.37869	1507.5	3
EC>10-12	2.511E-3	0.140	0.864	8.64E-5	0.00268	0.56341	1507.5	3
EC>12-16	5.012E-3	0.053	0.864	8.64E-5	0.00170	1.87297	1507.5	3

Substance	K_{oc} ($m^3\ g^{-1}$)	K_H ($cm^3 cm^{-3}$)	D_G^{air} ($m^2\ day^{-1}$)	D_L^{water} ($m^2\ day^{-1}$)	μ_T (day^{-1})	μ_a (day^{-1})	C_0 ($mg\ m^{-3}$)	L (m)
Aliphatic								
EC 5-6	0.794E-3	33.0	0.864	8.64E-5	0.000693	0.23897	1507.5	3
EC>6-8	3.981E-3	50.0	0.864	8.64E-5	0.00103	0.19117	1507.5	3
EC>8-10	3.162E-2	80.0	0.864	8.64E-5	0.00139	0.693	1507.5	3
EC>10-12	2.51E-1	120.0	0.864	8.64E-5	0.00173	0.693	1507.5	3
EC>12-16	5.012	520.0	0.864	8.64E-5	0.00231	0.693	1507.5	3

Footnotes: 1. K_{oc}, K_H, D_G^{air} and D_L^{water} values were obtained from Gustafson *et al*., (1997).

2. μ_T and μ_a were obtained from Howard *et al*., (1991): Mackay *et al*., (1992a, 1992b, 1993). There were limited data on aliphatic degradation rates. μ_T was estimated for all aliphatic fractions except EC>6-8 and μ_a was estimated for all aliphatic fractions except EC 5-6 and EC>6-8 based on existing knowledge of environmental behaviour.
3. C_0, the initial soil concentration was set at 1mg/kg wet weight; L is an assumed finite depth of the soil contaminant concentration which is considered to be homogeneous in its distribution.

Table 6: Other parameters

Parameter	Value	Units	Reference/Comment
θ_G, air-filled porosity	0.40	$m^3\ m^{-3}$	Anderssen and Markey, 1996
ρ_P, particle density	2650 x10^3	$g\ m^{-3}$	Little *et al*., 1992; Marshall *et al*., 1996
K_D, distribution coefficient ($f_{oc} . K_{oc}$)	0.406 x10^{-6}	$m^3\ g^{-1}$	Gustafson *et al*., 1997
D_T, effective diffusion coefficient	Calculated for each volatile within model	$m^2\ day^{-1}$	Anderssen and Markey, 1996
V_T, effective solute velocity	Calculated for each volatile within model	$m\ day^{-1}$	Anderssen and Markey, 1996
R_G, partition coefficient for the vapour	Calculated for each volatile within model	unitless	Anderssen and Markey, 1996
I, inhalation rate, 2.5 year old child	8.64	$m^3\ day^{-1}$	Langley, 1991
Time for exposure	70	years	Lifetime, US EPA 1997
Cumulative indoor human dose (CIHD)	model output	mg	-

4 SENSITIVITY ANALYSES

4.1 PARAMETER GROUPINGS

In order to determine the impact of the respective variables on the product output, the CIHD, sensitivity analyses were undertaken for the modelling of BTEX, naphthalene and the aromatic and aliphatic TPH fractions. The substance of this type of analysis and its application to the modelling of benzene has been presented previously (Turczynowicz and Robinson, 2001) and is not reproduced here.

In summary, a total of 21 parameters of the 22 parameters can be placed in three groups relating to soil, volatile or house as follows:

Soil : $\left[\phi, \theta_L, \rho_B, f_{oc}, V_L^B, d_{air}\right]$

Volatile : $\left[K_{oc}, K_H, D_G^{air}, D_L^{water}, C_0, L, \mu_T, \mu_a\right]$

House : $\left[A_F, \Omega_{CS}, \Omega_D, X_{CS}, X_D, Q_{CD}, S\right]$

The 22nd parameter, *I*, is the inhalation for a human receptor, (in this case a child of 2.5 years of age) and is also a component of the sink summation, *S*, and is subsequently excluded from the grouping. It should be noted that *S* consists of the inhalation for a child and two adults without any other indoor sinks (or sources).

Each of these groups can then be varied with the others held constant to assess the impact of each group on the CIHD. An arbitrary variance value of +/-30% was applied across each of these groupings in the analysis.

4.2 RESULTS

Plots of the sensitivity analyses are presented in Appendix 1, Figures 1-5. These identify that the initial observations with benzene (Turczynowicz and Robinson, 2001) (Figure 1) are consistent with those for toluene, ethyl benzene, xylenes and aliphatic and aromatic TPH fractions (Figures 2, 3). The decreasing magnitude in each chemical or group is also consistent with the profiles for variance in physico-chemical parameters for aromatic TPH fractions (Figure 4) and aliphatic TPH fractions (Figure 5) confirming that this model correctly represents volatilisation characteristics of the substances of interest.

Soil parameters $\left[\phi, \theta_L, \rho_B, f_{oc}, V_L^B, d_{air}\right]$ and physico-chemical parameters $\left[K_{oc}, K_H, D_G^{air}, D_L^{water}, C_0, L, \mu_T, \mu_a\right]$, when examined by group exert only marginal effects, however, dwelling characteristics $\left[A_F, \Omega_{CS}, \Omega_D, X_{CS}, X_D, Q_{CD}, S\right]$ are a dominant influence on the CIHD. The effects of the dwelling parameters are not surprising as alteration in dwelling dimensions and ventilation have a direct effect on indoor benzene concentrations and the CIHD. Detailed comment on the influences of individual parameters and quantitative comparisons for effects on soil benzene concentrations is presented in Turczynowicz and Robinson (2001).

The conclusion is that for the crawl space model for indoor vapour intrusion, the dwelling characteristics are the main contributors to the large changes in the theoretical dose that are observed when variations in all of the input parameters are considered. Furthermore, as soil properties do not significantly influence this model, there is the potential to establish a generic soil criterion for volatiles provided that variance in real dwelling input parameters can be taken into account.

Further exploration of the real variance in soil properties and dwelling dimensions for Australian conditions is recommended in order to ascertain the impacts of real life settings.

5 DERIVATION OF HILS FOR HOMES WITH CRAWL SPACES

5.1 HEALTH ENDPOINTS

The establishment of Health-based Investigation Levels for contaminated sites where the contaminants are volatiles and the major exposure route is by inhalation requires some air standard that is considered to represent a safe level of exposure. In Australia, a regulatory air standard for ambient or indoor BTEX, naphthalene or volatile TPH fractions has not been established although some preliminary work on benzene has been undertaken (Wadge and Salisbury, 1997).

In indoor air exposure modelling of emissions of sub-surface benzene, Ferguson, Krylov and McGrath (1995) used the Air Quality Standard of 5 ppb (16.01 µg m^{-3}) set by the UK Expert Panel on Air Quality Standards (UK Department of Environment, 1994). The UK-recommended Air Quality Standard is based on human epidemiological data and includes estimations of background exposures within the exposure framework. The use of such a guideline value therefore does not require examination of the background exposure contribution to the acceptable target indoor air concentration.

In order to compare the use of the UK Expert Panel on Air Quality Standards value it was considered appropriate to also use the US Environmental Protection Agency's quantitative estimate of cancer risk from benzene inhalation. The US risk estimate for benzene inhalation is 1 in 100,000 at an air concentration of 1.3-4.5 µg/m^3 (IRIS, 2002). These data refer to chronic exposures to carcinogens with lifetime (70 year) exposure periods.

In Australia a Benchmark Dose methodology (BMD) has been developed in order to establish acceptable levels of exposure for soil carcinogens (NHMRC, 1999). The application of this methodology is still in process and it is anticipated that the recommended HIL for benzene presented in this paper will be reviewed with further BMD evaluation.

In the case of non-carcinogens such as toluene, ethyl benzene and xylenes the use of ambient air guidelines that incorporate background exposures is recommended and the WHO guideline values (WHO, 2000) were used in the HIL assessment. Ambient air guideline values for naphthalene were limited but in the USA a number of States have established acceptable ambient air concentrations for naphthalene. The lowest of these was used, based on an annual average value established by the State of Massachusetts (ATSDR, 1995b). It is acknowledged that regional factors may influence such values for an Australian setting and it is anticipated any HILs proposed in this paper will be reviewed on the establishment of Australian ambient or indoor air quality values.

There are no ambient air guideline values for volatile aromatic and aliphatic TPH fractions and subsequently Reference Concentrations for chronic inhalation exposure (*RfCs*) developed by the TPHCWG are used (Vorhees *at al.*, 1999). An *RfC* value represents "an estimate (with uncertainty spanning perhaps an order of magnitude) of continuous inhalation exposure to the human population, including sensitive sub-groups, that is likely to be without an appreciable risk of deleterious effects during a lifetime" (IRIS, 2002). In this instance the contribution of background exposures are required to be estimated and an allowable contribution from the sub-surface contaminant source to the

acceptable daily intake determined. Table 7 summarises the air guideline values employed to derive HILs.

Table 7: Air guideline values used in HIL derivation

Substance	Air parameter	Value (μg/m³)	Reference
benzene[1]	ambient air quality standard Air risk estimate	16 (annual average) 10^{-5} at 1.3-4.5	UK Department of Environment (1994) IRIS (2002) based on US EPA (2000) review
toluene	ambient air guidance value	260 (1 week average)	WHO, 2000
ethyl benzene	ambient air guidance value	22000 (annual average) 2200 (odour threshold)	WHO, 2000; IPCS, 1996
xylenes	ambient air guidance value	870 (annual average)	WHO, 2000
naphthalene	acceptable ambient air concentration	14.3	ATSDR, 1995b
aromatic EC>5-7[2]	NA	NA	Vorhees *et al.*, (1999)
aromatic EC>7-9	*RfC*	400	Vorhees *et al.*, (1999)
aromatic EC>9-16	*RfC*	200	Vorhees *et al.*, (1999)
aliphatic EC>5-8	*RfC*	18400	Vorhees *et al.*, (1999)
aliphatic EC>8-16	*RfC*	1000	Vorhees *et al.*, (1999)

[1] The use of an air guideline for benzene, a human carcinogen, will be subject to review on the development of an Australian guideline value.

[2] TPH fraction represented by benzene.

5.2 EXPOSURE ASSESSMENT AND BACKGROUND EXPOSURES

The exposure pathways from TPH-contaminated sites have been previously identified (ASTM, 1995) and encompass ingestion of contaminated soil or groundwater, inhalation of vapours both from outdoor and indoor environs arising from contaminated soil or groundwater, and dermal contact with contaminated soil or groundwater. The TPHCWG have determined risk-based screening levels (RBSLs) using the ASTM Risk Based Corrective Action (RBCA) exposure equations for 11 pathways for fresh JP-4. These calculations demonstrate that apart from direct ingestion of contaminated groundwater, the most sensitive pathway for volatiles is inhalation from 'soil vapour intrusion into indoor air' arising from contaminated soil or groundwater. This pathway is therefore frequently associated with the lowest RBSLs (Vorhees *et al.*,1999). On the basis of these data and conclusions, the present paper therefore focuses on this pathway as being the dominant pathway for which HILs are established. The application of models recently developed incorporating the influence of TPH-contaminated groundwater on indoor vapour intrusion (Robinson, 2002) will allow a refinement of the crawl space model presented in this paper.

The question of what constitutes a volatile substance or fraction requires some resolution. Vapour pressure is a measure of chemical volatility and is important in determining a chemical's potential for inhalation exposure but is affected by temperature, wind speed, soil conditions on a site and soil adsorption and water solubility characteristics (ATSDR, 1993). The use of Henry's Constant (H), a ratio of vapour pressure and aqueous solubility, has been suggested and volatility estimates determined (ATSDR, 1993) but they do not

readily apply to the TPH fractions. ATSDR (1993) specify that a 'moderately' volatile substance has an H of 4.1E-4 and a 'highly' volatile substance, an H of greater than 0.041. In the case of the aromatic fractions H decreases with increasing molecular weight; H is 0.053 for EC>12-16 and 0.013 for EC>16-21. In the case of aliphatic fractions where H increases with increasing molecular weight (and clearly petroleum-derived greases are not volatile) such guidelines cannot be used and some professional judgement is required. Bossert and Botha (1986) suggest that n-alkanes greater than C18 are not substantially volatilised at ambient temperatures but lighter fractions (<C18) are subject to volatilisation. On the basis of these data, volatiles modelling was undertaken for TPH fractions up to and including EC16.

The assessment of background contributions when using an ambient air guideline or standard is not required as it is assessed and accounted for as part of the guideline or standard development process. If an *RfC* is used, however, estimates of background are required to allow an appropriate apportionment of the daily acceptable intake. Background exposures to TPHs have been reviewed in a previous workshop (Turczynowicz, 1998) and some estimates of TPH exposures from petrol were made. The ubiquitous nature of exposure to volatile petroleum hydrocarbons (encompassing all fuel mixtures and individual chemicals that constitute these fractions) makes the quantification of population exposures to TPHs extremely difficult. At the present time there are no data to determine such exposures, though one study reports estimates from non-methane hydrocarbons based on ambient air data from the mid 1970s and mid 1980s in Holland (Franken *et al.*, 1999). A 20% proportion of the *RfC* from volatile soil contaminants for the respective TPH fractions is suggested until further data become available.

5.3 CALCULATION OF HILS

The method of HIL calculation involved basically the following process. The crawl space model was set to baseline conditions as defined in Tables 3, 4, 5 and 6 with the contaminant set at 1mg/kg wet weight. The model was run for each chemical or TPH fraction and the period for 99% emission during the lifetime (70 years) Cumulative Indoor Human Dose (CIHD) determined. This period was used as the period of exposure (by inhalation) for a 2.5 year old child with a daily inhalation rate of 8.64m^3 (exposure 24 hours per day indoors) and an acceptable CIHD determined from an air guideline or standard or from 20% of the *RfC* for the TPH fraction. Appropriate re-scaling of the observed emissions to achieve acceptable emissions against the baseline wet weight soil concentration then provided the respective HIL. Emission profiles for BTEX, naphthalene, aromatic and aliphatic TPH fractions are presented in Appendix 2, Figs 1-3 and the HILs and calculations presented in Table 8.

Table 8: Health-based Investigation Levels and calculations

Substance	Exposure from ~99% CIHD from model (mg)	Emission period for ~99% CIHD (days)	Air standard (µg/m³)	CIHD[1] (mg) (for air standard)	HIL[2] (mg/kg)
benzene	35.26	750 (2.0 yrs)	UK 16.01 US 1.3-4.5 Risk = 1E-5	103.7 8.4- 9.2	2.9 (3)[3] 0.24-0.83 (0.2-0.8)
toluene	27.63	539 (1.5 yrs)	260	1211	43.8 (40)
ethyl benzene	23.94	674 (1.9 yrs)	22000 2200 (odour)	128114 12811	5351 (5350) 535 (530)
xylenes	23.87	1034 (2.8 yrs)	870	7772	326 (320)
naphthalene	4.726	1157 (3.2 yrs)	14.3	143.0	30.3 (30)
Aromatic					
EC>5-7	as for benzene				
EC>7-9	as for toluene				
EC>9-16	EC>9-10 = 23.45 (23.66@1907days) EC>10-12 = 10.74 (10.84@1907days) EC>12-16 = 5.334 **Total = 39.834** **(@1907 days)**	1056 (2.9 yrs) 1079 (3.0 yrs) 1907 (5.2 yrs)	200	3295 x 0.20[4] = 659.1	16.6 (15)
Aliphatic					
EC>5-8	EC>5-6 = 42.48 EC>6-8 = 41.06 (41.13@811 days) **Total = 83.61** **(@ 811 days)**	811 (2.2 yrs) 739 (2.0 yrs)	18400	128930 x 0.20 = 25786	308 (310)
EC>8-16	EC>8-10 = 35.10 (35.28@1132 days) EC>10-12 = 26.44 (26.50@1132 days) EC>12-16 = 15.04 **Total = 76.82** **(@1132 days)**	839 (2.3 yrs) 1041 (2.9 yrs) 1132 (3.1 yrs)	1000	9780.5 x 0.20 = 1956	25.5 (25)

[1] Calculated from - Air standard (µg/m³) x 8.64m³ x emission period (days)

[2] Calculated from $\frac{\text{CIHD (air standard)}}{\text{CIHD (~99\% CIHD from model)}}$ x 1.0 (mg/kg)

[3] Approximation

[4] A 20% contribution to the *RfC* from a soil source is proposed

5.4 INTERACTIONS AND MIXTURES

The understanding of the influence of interactions between chemicals within a mixture to which a human receptor may be exposed is still an area of development. Interactions were briefly discussed in a previous workshop paper on TPHs (Turczynowicz, 1998) including the limitations of the TPH fraction methodology as recognised by the TPHCWG. These included that, (i) the toxicity of fractions as tested does not change significantly with weathering; (ii) the composition of the fractions does not vary significantly from the surrogate tested; and (iii) the toxicological interactions of various fractions are assumed to be additive (Edwards *et al.,* 1997).

A hazard index of dose additivity was proposed by the US EPA, based on the assumption that components have the same mode of action (US EPA, 1986), and it appears that there has been little variance on those recommendations although there has been progressive investigation of this area, including at least one extensive symposium on chemical mixtures and quantitative risk assessment in the US (Simmons, 1994).

ATSDR (1999b) report that competitive or non-competitive inhibitory interactions with active sites of enzymes such as cytochrome P-450 isoenzymes or epoxide hydrolases can influence hydrocarbon metabolism leading to antagonism of toxic effects mediated by metabolic intermediates or to synergism or potentiation of toxic effects due to parent hydrocarbon compounds. It was furthermore inferred from studies with BTEX, naphthalene, methylnaphthalene and hexane that alterations in enzyme activities such as induction or enhancement can also alter catabolic rate or capacity leading potentially to non-additive effects. The compositional complexity of TPH mixtures and the uncertainties associated with exposures, however, has still led to the use of additivity with mixtures as being the preferred option (ATSDR, 1999b: Franken *et al.,* 1999).

ATSDR (1999b) use an Index Of Concern, measured as the sum of the ratios of the monitored level of exposure to the accepted level of exposure, while the Dutch use a site-specific contamination index measured as the sum of the ratio of soil contaminant concentration to human-toxicological serious soil contaminant concentrations (Franken *et al.,* 1999).

It is recommended that for Australian conditions the HILs for TPH fractions be treated in a consistent approach to TPHCWG, ATSDR and the National Institute of Public Health and Environment (Netherlands) until more appropriate techniques are developed. The procedure for sites contaminated with TPHs should initially involve an assessment of indicator chemicals (Turczynowicz, 1998), followed by individual TPH fractions. Should soil concentrations for individual TPH fractions be below their HILs, a TPH Health Investigation Level Index for the site should be determined by:

$$\text{TPH HIL Index} = \sum \frac{\text{measured soil TPH fraction concentrations}}{\text{individual TPH fraction HILs}} < 1.$$

6 DISCUSSION

6.1 SUMMARY OF HILS FOR VOLATILE HYDROCARBONS

A summary of proposed HILs representing concentrations in soil for benzene, toluene, ethyl benzene, xylenes, naphthalene and all Total Petroleum Hydrocarbon fractions is

presented in Table 9. In the case of the volatile hydrocarbons for which indoor vapour intrusion is the dominant exposure pathway, the HILs are based on the exposure scenario as depicted in Figure 1 with variable parameters as described in Tables 3, 4, 5 and 6.

Table 9: Proposed Health-based Investigation Levels for volatile hydrocarbons in soil, based on indoor vapour intrusion for a crawl space home

Substance	HIL (mg/kg)
benzene	3
toluene	40
ethyl benzene	5350 530 (odour)
xylenes	320
naphthalene	30
Aromatic	
EC>5-7	3
EC>7-9	40
EC>9-16	15
EC>16-35[1]	90
Aliphatic	
EC>5-8	310
EC>8-16	25
EC>16-35[1]	5600
EC>35[1]	56000

[1] from Turczynowicz, (1998), based on ingestion, dermal uptake and particle inhalation

It is emphasised that the numbers generated from the volatiles modelling are only preliminary. As the period of emission from a finite source occurs over a relatively short period (1.5-5.2 years), there are difficulties in the application of standards based on long-term or cumulative lifetime exposure. Further investigation as to whether a lifetime cumulative dose over 70 years should be considered when emissions predominantly cease after a few years is required. The exposure for that emission period should not be averaged over 70 years of lifetime exposure to derive (higher) soil criteria unless there are toxicological data available that will validate such an approach.

In addition, the values have been derived for a particular exposure scenario and dwelling characteristics. Dwelling characteristics such as dwelling dimensions and experimental ventilation data were drawn from the same field study. As sensitivity analyses have identified dwelling characteristics as being the dominant influencing group of variables affecting the CIHD and subsequently the HIL, additional data on dwelling characteristics for crawl space housing stocks in Australia should be obtained to evaluate their variance. Consequently it should be noted that the HILs developed in this paper are specific to the exposure scenario as represented and are tentative until endorsed by an appropriate national body.

6.2 ISSUES FOR FURTHER CONSIDERATION

The volatiles modelling presented in this paper has used child exposures arising from indoor vapour intrusion from subsurface environs in the development of HILs for BTEX, naphthalene, and aromatic and aliphatic TPH fractions ≤ EC16. This modelling has used

Australian experimental data to refine the modelling process and the modelling is considered more appropriate for Australian conditions than overseas models. The HILs developed in this paper have not been endorsed by any official body.

Sensitivity analyses have revealed that although some input variables exert a significant influence on the CIHD when considered individually, these influences change when input variables are grouped into soil, physico-chemical and house parameters with house parameters having the greatest effect on proposed health-based soil investigation levels in soil.

Advantages of the approach used in this paper employing the crawl space vapour intrusion model have been previously reviewed by Turczynowicz and Robinson and include:

- "a scenario that is representative of dwellings with crawl spaces (not assuming basements as with key US models). Dwellings with crawl spaces are common in Australia;
- the model is not based on steady-state conditions above ground but acknowledges variations in above ground conditions from, e.g. meteorological conditions;
- Australian experimental ventilation data have been used and these have been coupled to measured wind velocities;
- the effects of mixing and sinks have been included;
- degradation of the contaminant in soil and air has been included;"
  (p407, Turczynowicz and Robinson, 2001)
- that the use of sensitivity analysis has identified the key parameters to be related to housing parameters rather than soil or physico-chemical parameters. This will simplify site-specific appraisals and assist in developing generic soil criteria.

Issues for further consideration include:

- establishment of Australian air standards for benzene, toluene, ethyl benzene, xylenes and naphthalene and also for other volatile organic compounds (VOCs)
- the resolution of the use of standards based on lifetime exposures against less-than-lifetime exposures for volatile contaminants as the modelling predicts that nearly all the exposure will occur within a few years
- further investigation of the application of quantitative risk assessment to mixtures
- the acquisition of data on dwelling characteristics for crawl space Australian homes to ensure HILs are protective of all real life settings
- application of the model representing the influence of groundwater contaminated with light non-aqueous phase liquids should be undertaken as this may represent another sensitive indoor vapour intrusion and exposure pathway
- field validation to establish how accurately the model represents reality; part of this validation work is presently in progress.

ACKNOWLEDGEMENTS

The author acknowledges Drs Mike McLaughlin and Angelo Delsante of the CSIRO for advice on soil properties and information on dwelling characteristics respectively; Dr Neville Robinson, CSIRO Mathematical and Information Sciences for the sensitivity plots and comments on the draft manuscript; Ms Sandra Sowerby, Department of Human Services for her graphics work; and Dr Jim Fitzgerald, Department of Human Services and Dr Andrew Langley, Sunshine Coast Public Health Unit for comments on the draft

manuscript. The services of librarians Tricia Brooks and Robyn Davis and other DHS library staff are also gratefully acknowledged.

DISCLAIMER

This document has been prepared in good faith exercising due care and attention. However, no representation or warranty, expressed or implied, is made as to the relevance, accuracy, completeness or fitness for the purpose of this document in respect of any particular user's circumstances. Users of this document should satisfy themselves concerning its application to, and where necessary seek expert advice about, their situation. The Department of Human Services shall not be liable to the reader or any other person or entity with respect to any liability, loss or damage caused or alleged to have been caused directly or indirectly by this publication.

This paper does not necessarily represent the views of the Department of Human Services and will not necessarily be incorporated into future policy.

REFERENCES

ACGIH (1991) *Documentation of the Tthreshold Limit Values and Biological Exposure Indices*. Sixth edition. Cincinnati, Ohio, American Conference of Governmental Industrial Hygienists, Inc: p1063.

Anderssen RS and Markey BR (1996) Volatilisation from Soil and Exposure

Assessment. In: Langley A, Markey B and Hill H. (eds). *The Health Risk Assessment and Management of Contaminated Sites. Proceedings of the Third National Workshop on the Health Risk Assessment and Management of Contaminated Sites.* Contaminated Sites Monograph Series No.5. Adelaide, South Australian Health Commission: pp 441-468.

Anderssen RS and Markey BR (1998) Exposure to Volatiles from Below-Ground Sources. In: Langley A., Imray P., Lock W. and Hill H. (eds). *The Health Risk Assessment and Management of Contaminated Sites. Proceedings of the Fourth National Workshop on the Health Risk Assessment and Management of Contaminated Sites.* Contaminated Sites Monograph Series No.7. Adelaide, South Australian Health Commission: pp 93-105.

Andrews LS and Snyder R (1986) Toxic effects of solvents and vapours. In: Casarett LJ & Doull J (eds). *Toxicology: The Basic Science of Poisons, 3rd Ed*. New York, McMillan Publishing Co: p641.

ASTM (1995) *Standard Guide for Risk-Based Corrective Action Applied at Petroleum Release Sites.* American Society for Testing and Materials. E1739-95. West Conshohocken, PA.

ATSDR (1993) *Public Health Assessment Guidance Manual.* Atlanta, Georgia, Agency for Toxic Substances and Disease Registry, US Department of Health and Human Services.

ATSDR (1995a) *Toxicological Profile for Xylenes (Update).* Atlanta, Georgia, Agency for Toxic Substances and Disease Registry, US Department of Health and Human Services.

ATSDR (1995b) *Toxicological Profile for Naphthalene. (Update).* Atlanta, Georgia, Agency for Toxic Substances and Disease Registry, US Department of Health and Human Services.

ATSDR (1995c) *Toxicological Profile for Jet Fuels (JP-4 and JP-7).* Atlanta, Georgia, Agency for Toxic Substances and Disease Registry, US Department of Health and Human Services.

ATSDR (1995d) *Toxicological Profile for Fuel oils.* Atlanta, Georgia, Agency for Toxic Substances and Disease Registry, US Department of Health and Human Services.

ATSDR (1997) *Toxicological Profile for Benzene. (Update).* Atlanta, Georgia, Agency for Toxic Substances and Disease Registry, US Department of Health and Human Services.

ATSDR (1998) *Toxicological Profile for Jet Fuels (JP-5 and JP-8).* Atlanta, Georgia, Agency for Toxic Substances and Disease Registry, US Department of Health and Human Services.

ATSDR (1999a) *Toxicological Profile for Ethyl Benzene.* Atlanta, Georgia, Agency for Toxic Substances and Disease Registry, US Department of Health and Human Services.

ATSDR (1999b) *Toxicological Profile for Total Petroleum Hydrocarbons (TPH).* Atlanta, Georgia, Agency for Toxic Substances and Disease Registry, US Department of Health and Human Services.

ATSDR (1999c) *Toxicological Profile for Hexane.* Atlanta, Georgia, Agency for Toxic Substances and Disease Registry, US Department of Health and Human Services.

ATSDR (2000) *Toxicological Profile for Toluene.* Atlanta, Georgia, Agency for Toxic Substances and Disease Registry, US Department of Health and Human Services.

Benignus VA (1981) Neurobehavioural effects of toluene: a review. *Neurobehav Toxicol Teratol* **3** (4): 407-415.

Biggs KL, Bennie ID and Michell D (1987) Air infiltration rates in some Australian houses. *Aust Inst Build Pap* 2: 49-61.

Bossert ID and Bartha R (1986) Structure-biodegradability relationships of polycyclic aromatic hydrocarbons in soil. *Bull Environ Contam Toxicol* 37: 490-495.

Delsante A, Chan C, Threlfall G, Williamson, TJ and Olweny M (1998a) A progress report on the measurement of ventilation rates in sub-floor spaces of houses with suspended timber floors. In: *Environmentally Responsible Housing for Australia. Proceedings of a Research Seminar, School of Architecture, University of Adelaide, March 1998*, Adelaide, South Australia: pp 41-51.

Delsante A, Chan C, Threlfall G, Williamson TJ and Olweny M (1998b) Further measurements of ventilation rates in the sub-floor spaces of houses with suspended timber floors. In: *Environmentally Responsible Housing for Australia, Proceedings of a Research Seminar/Workshop, Forest and Wood Products Research and Development Corporation. Timber Development Association 31 July 1998*, Melbourne, Victoria: pp 35-42.

Edwards DA, Andriot MD, Amoruso MA, Tummey AC, Tveit A, Bevan CJ, Hayes LA, Youngren SH and Nakles DV (1997) *Development of Fraction Specific Reference Doses (RfDs) for Total Petroleum Hydrocarbon (TPH).* Volume 4. Total Petroleum Hydrocarbon Criteria Working Group Series. Massachusetts, Amherst Scientific Publishers.

Ellenhorn MJ and Barceloux DG (1988) *Medical Toxicology - Diagnosis and Treatment of Human Poisoning.* New York, Elsevier Science Publishing Co Inc: p962.

Ferguson CC, Krylov VV and McGrath PT (1995) Contamination of indoor air by toxic soil vapours: a screening risk assessment model. *Building and Environment* 30 (3): 375-383.

Franken ROG, Baars AJ, Crommentuijn GH and Otte P (1999) *A proposal for revised Intervention Values for petroleum hydrocarbons ("minerale olie") on base of fractions of petroleum hydrocarbons.* Bilthoven, National Institute of Public Health and the Environment. RIVM report 711701015.

Gustafson JB, Tell JG and Orem D (1997) *Selection of Representative TPH*

Fractions Based on Fate and Transport Considerations. Total Petroleum Hydocarbon Criteria Working Group Series. Volume 3. Massachusetts, Amherst Scientific Publishers.

Hattemer-Frey HA, Travis CC and Land ML (1990) Benzene: Environmental partitioning and human exposure. *Environ Res* 53: 221-232 .

Howard PH (1989) *Handbook of Environmental Fate and Exposure Data for Organic Chemicals.* Vol 1. Chelsea, Michigan, Lewis Publishers: pp 408-421.

Howard PH, Boethling RS, Jarvis WF, Meylan WM and Michalenko EM (1991) *Handbook of Environmental Degradation Rates.* Chelsea, Michigan, Lewis Publishers.

HSDB (2002) *Hazardous Substances Data Bank.* Specialised Information Services, TOXNET (Toxicology Data Network). US National Library of Medicine.

IARC (1982) Benzene. In: *Some Industrial Chemicals and Dyestuffs.* IARC Monographs on the Evaluation of Carcinogenic Risks to Humans. Volume 29. International Agency for Research on Cancer. Lyon, France, IARC/WHO: pp 93-148.

IARC (1987) Benzene. In: *Overall Evaluations of Carcinogenicity: an updating of selected IARC Monographs from Volumes 1 to 42.* IARC Monographs on the Evaluation of Carcinogenic Risks to Humans. Supplement 7. International Agency for Research on Cancer. Lyon, France, IARC/WHO: pp 120-122.

IARC (1999a) Toluene. In: *Re-evaluation of Some Organic Chemicals, Hydrazine and Hydrogen Peroxide (Part Two*). IARC Monographs on the Evaluation of Carcinogenic Risks to Humans. Volume 71. International Agency for Research on Cancer. Lyon, France, IARC/WHO: pp 829-864.

IARC (1999b) Xylenes. In: *Re-evaluation of Some Organic Chemicals, Hydrazine and Hydrogen Peroxide (Part Three*). IARC Monographs on the Evaluation of Carcinogenic Risks to Humans. Volume 71. International Agency for Research on Cancer. Lyon, France, IARC/WHO: pp 1189-1208.

IARC (2000) Ethyl benzene. In: *Some Industrial Chemicals*. IARC Monographs on the Evaluation of Carcinogenic Risks to Humans. Volume 77. International Agency for Research on Cancer. Lyon, France, IARC/WHO: pp 227-257.

IPCS (1985) *Toluene*. Environmental Health Criteria 52. International Programme on Chemical Safety. Geneva, World Health Organization.

IPCS (1993) *Benzene.* Environmental Health Criteria 150. International Programme on Chemical Safety. Geneva, World Health Organization.

IPCS (1996) *Ethyl benzene.* Environmental Health Criteria 186. International Programme on Chemical Safety. Geneva, World Health Organization.

IPCS (1997) *Xylenes.* Environmental Health Criteria 190. International Programme on Chemical Safety. Geneva, World Health Organization.

IRIS (2002) *Integrated Risk Information System.* Specialised Information Services, TOXNET (Toxicology Data Network). US National Library of Medicine.

Jury WA, Spencer WF and Farmer WJ (1983) Behaviour Assessment Model for trace organics in soil: I. Model description. *J Environ Qual* 12 (4): 558-564.

Langley AJ (1991) Setting Investigation Levels for Cadmium. In: El Saadi O and Langley (eds). *The Health Risk Assessment and Management of Contaminated Sites. Proceedings of a National Workshop on the Health Risk Assessment of Contaminated Sites*, Adelaide, South Australian Health Commission: pp 37-52.

Linick M (1983) Illness associated with exposure to naphthalene in mothballs - Indiana. *MMWR* 32: 34-35.

Little JC, Daisy JM and Nazaroff WW (1992) Transport of subsurface contaminants into buildings. *Environ Sci Technol* 26 (11): 2058-2066.

Mackay D, Shiu WY and Ma Kuo Ching (1992a) *Illustrated Handbook of Physical-chemical Properties and Environmental Fate for Organic Chemicals. Volume I. Monoaromatic Hydrocarbons, Chlorobenzenes and PCBs.* Boca Raton, Florida, Lewis Publishers.

Mackay D, Shiu WY and Ma Kuo Ching (1992b) *Illustrated Handbook of Physical-chemical Properties and Environmental Fate for Organic Chemicals. Volume II. Polynuclear Aromatic Hydrocarbons, Polychlorinated Dioxins and Dibenzofurans.* Boca Raton, Florida, Lewis Publishers.

Mackay D, Shiu WY and Ma Kuo Ching (1993) *Illustrated Handbook of Physical-chemical Properties and Environmental Fate for Organic Chemicals. Volume III. Volatile Organic Chemicals.* Boca Raton, Florida, Lewis Publishers.

Marshall TJ, Holmes JW and Rose CW (1996) *Soil Physics*. Cambridge, England, Cambridge University Press.

NHMRC (1999) *Toxicity Assessment for Carcinogenic Soil Contaminants.* Canberra, ACT, National Health and Medical Research Council.

Northcote KH, Hubble GD, Isbell RF and Thompson CH (1975) *A Description of Australian Soils.* Melbourne, CSIRO.

Olweny MRO, Williamson TJ, Delsante A, Chan C and Threlfall G (1998) An investigation of the thermal performance of suspended timber floors. In: *Proceedings of the 32nd Annual Australia and New Zealand Architectural Science Association Conference, 15-17 July 1998*, Wellington, New Zealand: pp 219-226.

Potter TL and Simmons KE (1998) *Composition of Petroleum Mixtures.* Volume 2, Total Petroleum Hydrocarbon Criteria Working Group Series. Massachusetts, Amherst Scientific Publishers.

Robinson NI (2000) Cumulative losses of buried volatile organic compounds. *Water Resour Res* 36 (3): 801-806.

Robinson NI (2002) Modelling the migration of VOCs from soil to dwelling interiors. NEPC Contaminated Sites Technical Workshop, 13th-15th May 2002. Draft.

Simmons JE (ed) (1994) Chemical mixtures and quantitative risk assessment. Proceedings of a symposium sponsored by the Health Effects Research Laboratory of the US Environmental Protection Agency, November 7-10, 1994. *Toxicology* 105: 109-441

Turczynowicz L (1998) The development of health-based soil criteria for total petroleum hydrocarbons. In: Langley A., Imray P., Lock W. and Hill H., (eds). *The Health Risk Assessment and Management of Contaminated Sites. Proceedings of the Fourth National Workshop on the Health Risk Assessment and Management of Contaminated Sites.* Contaminated Sites Monograph Series No.7. Adelaide, South Australian Health Commission: pp 107-150.

Turczynowicz L and Robinson NI (2001) A model to derive soil criteria for benzene migrating from soil to dwelling interior in homes with crawl spaces. *Human and Ecological Risk Assessment* 7 (2): 387-415.

UK Department of Environment (1994) *Benzene*. Expert Panel on Air Quality Standards. London, HMSO.

US EPA (1986) *Guidelines for the Health Risk Assessment of Chemical Mixtures*. United States Environmental Protection Agency. Washington DC, Risk Assessment Forum. EPA/630/R-98/002.

US EPA (1997) *Exposure Factors Handbook Volume I. General Factors.* United States Environmental Protection Agency. Washington DC, Office of Research and Development. EPA/600/P-95/002Fa.

Vorhees DJ, Weisman WH and Gustafson JB (1999) *Human health-risk based evaluation of petroleum release sites: Implementing the working group approach*. Total Petroleum Hydrocarbon Criteria Working Group. Volume 5. Amherst, Massachusetts, Amherst Scientific Publishers.

Wadge A and Salisbury J (1997) *Benzene.* National Environmental Health Forum Monographs. Air Series No.2. Adelaide, South Australian Health Commission.

WHO (2000) *Guidelines for Air Quality*. Geneva, World Health Organization.

List of Abbreviations and acronyms

ACGIH	American Conference of Governmental Industrial Hygienists
ASTM	American Society for Testing and Materials
ATSDR	Agency for Toxic Substances and Disease Registry
BAM	Behaviour Assessment Model
BMD	Benchmark Dose (methodology)
BTEX	Benzene, Toluene, Ethyl benzene, Xylene
CIHD	Cumulative Indoor Human Dose
CNS	Central Nervous System
CSIRO	Commonwealth Scientific and Industrial Research Organisation
C9	Substance with nine carbons in chemical structure
C18	Substance with eighteen carbons in chemical structure
DHS	SA Department of Human Services
EC	Equivalent Carbon (number)
HIL	Health-based Investigation Level
HSDB	Hazardous Substances Data Bank
IARC	International Agency for Research on Cancer
IPCS	International Program on Chemical Safety
IRIS	Integrated Risk Information System
NHMRC	National Health and Medical Research Council
NEPC	National Environment Protection Council
NEPM	National Environment Protection Measure
RBCA	Risk-based Corrective Action
RBSL	Risk-based Screening levels
RfC	Reference Concentration for chronic inhalation exposure
RfD	Reference Dose for chronic oral exposure
TPH	Total Petroleum Hydrocarbon
TPHCWG	Total Petroleum Hydrocarbon Working Group
US EPA	United States Environmental Protection Agency
VOCs	Volatile Organic Compounds

Appendix 1

Figure 1. Benzene. Dose Ranges for Variations of Group Parameters

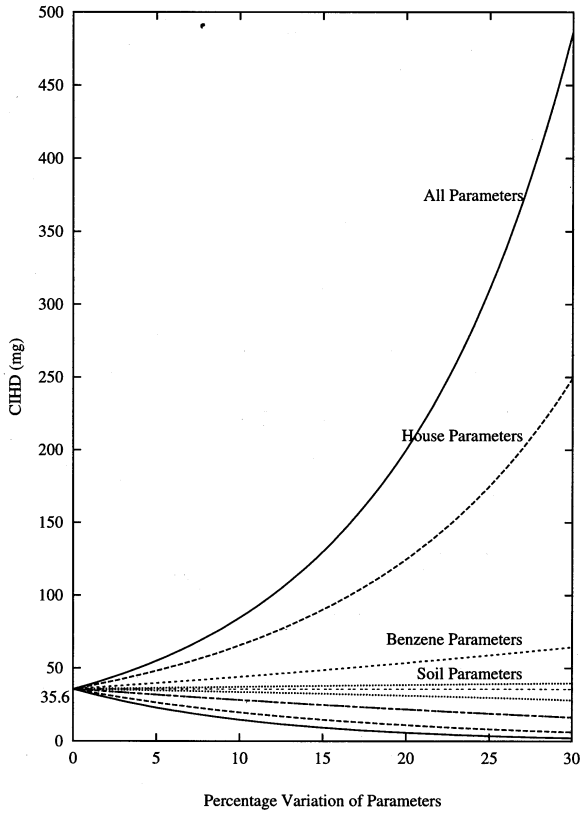


Figure 2. Doses for Variations of All Model Parameters for Aromatics

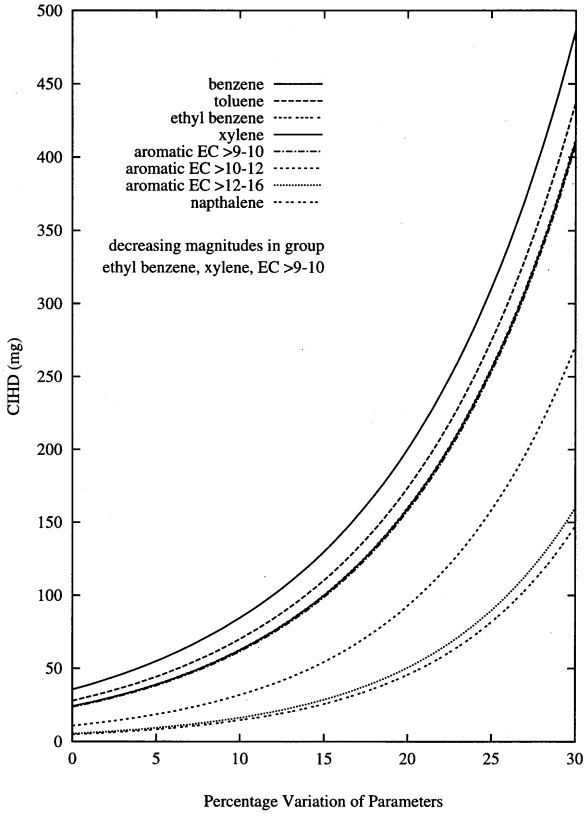


Figure 3. Doses for Variations of All Model Parameters for Aliphatics

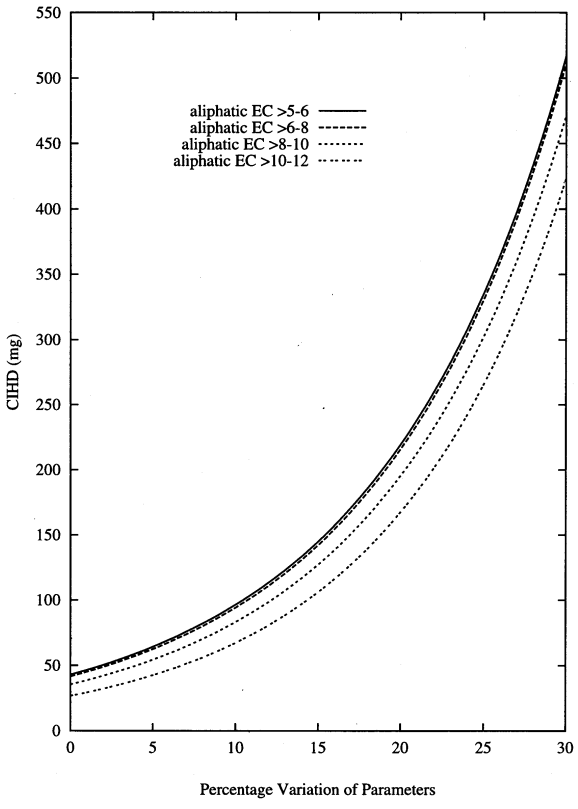


Figure 4. Doses for Variations of All VOC Parameters for Aromatics

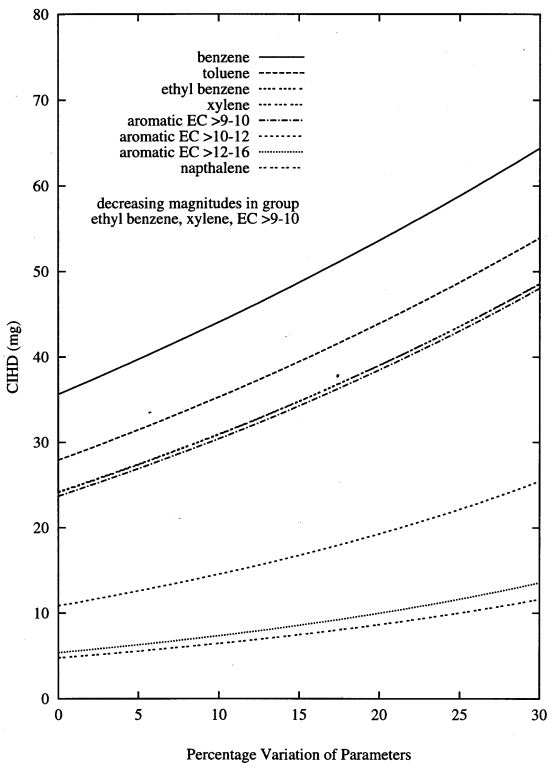
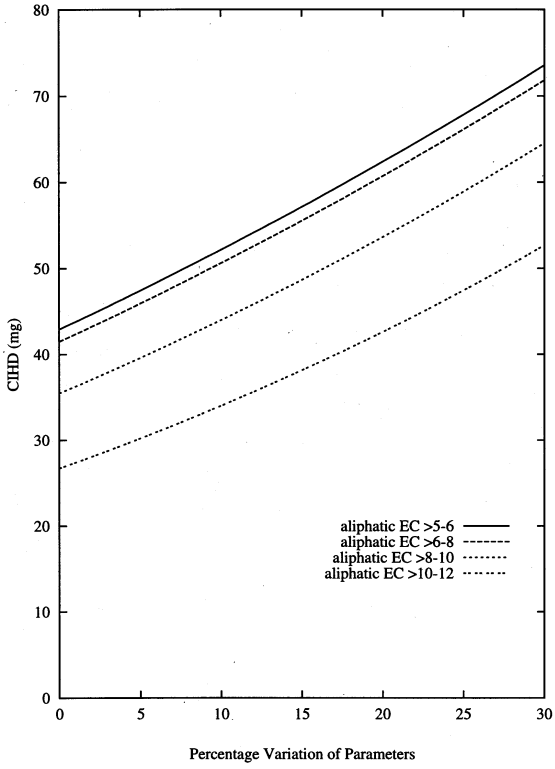


Figure 5. Doses for Variations of All VOC Parameters for Aliphatics



Appendix 2

Figure 1: Emission profiles for BTEX and naphthalene, representing 99% CIHD over 2.0, 1.5, 1.9, 2.8 and 3.2 years respectively

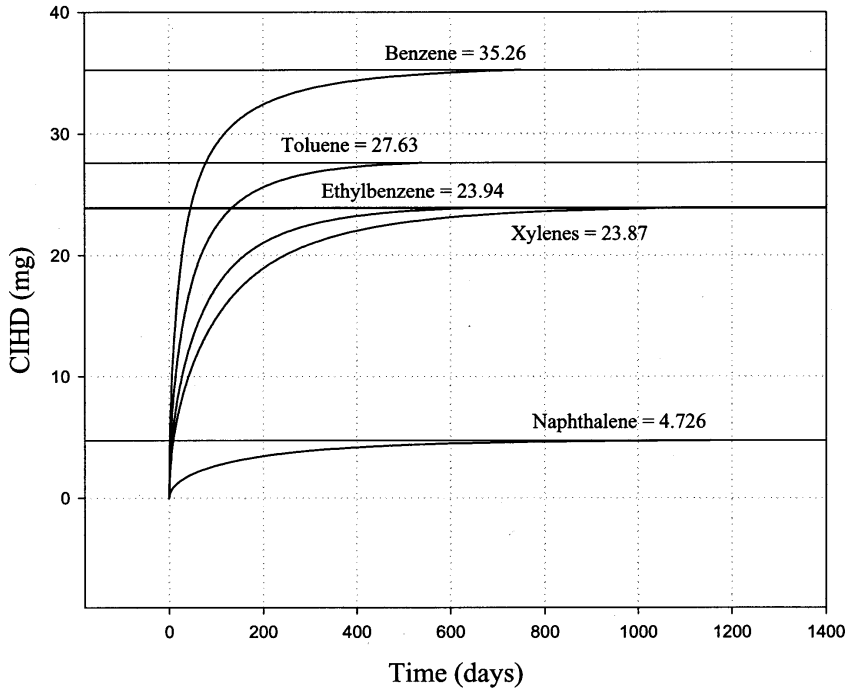


Figure 2: Aromatic EC>9-16, emission profile representing ~99% CIHD over 5.2 years

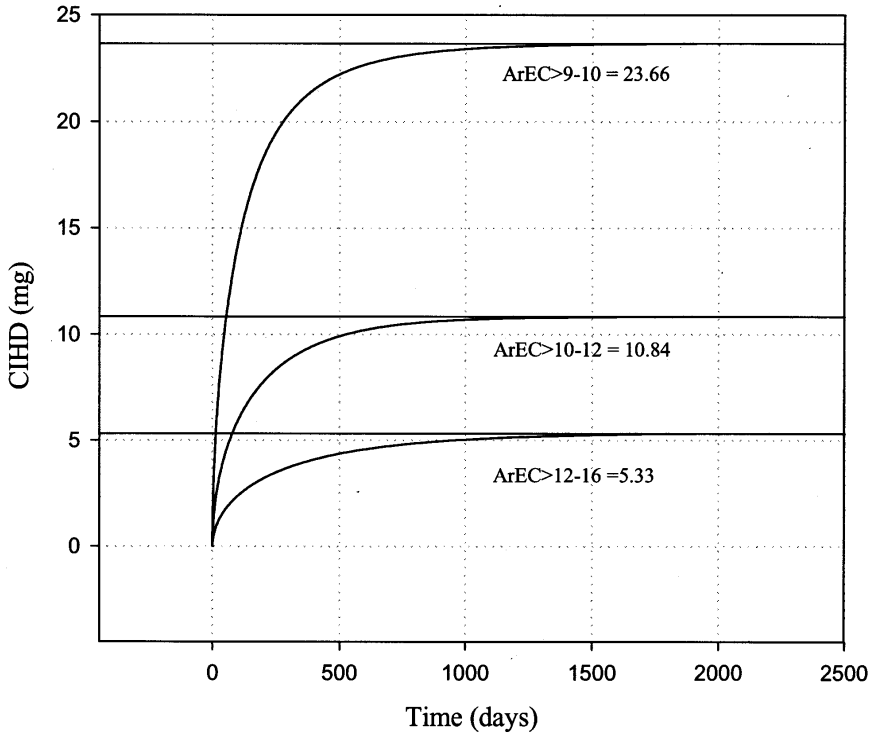


Figure 3: Aliphatic EC>5-8 and EC>8-16 emission profiles, representing 99% CIHD over 2.2 and 3.1 years respectively