Appendix B	Vapour Migration Modelling

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Appendix B
Calculation of Chemical Intake - Methodology

B1.1   General Methodology

The following presents the general methodology adopted for the calculation of chemical intake via inhalation, ingestion and dermal exposure pathways. Most equations are derived from USEPA (1989).

B1.2   Intakes via Inhalation

The assessment of inhalation exposures assumes that exposures associated with the groundwater contamination and HCB car park are associated with volatile chemicals rather than particulates (more likely from combustion sources or dust emissions).On this basis, the following equation is used to calculate intake of volatile chemicals via all inhalation pathways:

$$Daily\ Chemical\ Intake_V = C_a \bullet \frac{InhR \bullet ET \bullet FI \bullet EF \bullet ED}{BW \bullet AT} \quad \text{(mg/kg/day)}$$

where:
C_a = Concentration of chemical in air (as relevant for each pathway assessed) (mg/m^3)
InhR= Inhalation rate (dependant on age and activity) (m^3/hr)
ET   = Exposure time (dependant on activity) (hr/day)
FI   = Fraction inhaled from contaminated source assumed to be 1 or 100% unless noted otherwise (unitless)
EF   = Exposure frequency (days/year)
ED   = Exposure duration (years)
BW = Body weight (dependant on age) (kg)
AT   = Averaging time for threshold and non-threshold exposures (days)

ASTM Model

General

Air concentrations in outdoor air, in excavations and indoors (above impacted soils) have been estimated using the models described by the American Society for Testing and Materials (ASTM 2002), which has been set up in an EXCEL spreadsheet format. These models have been developed by ASTM for use in deriving remediation goals for sites affected by petroleum products and are a collation of the equations used and assumptions made in the Jury, Farmer (US EPA 1980) and Johnson model (Johnson and Ettinger, 1991).

The assessment presented in the main report relates to the assessment of volatile concentrations derived from a groundwater and soil source. Key assumptions and calculations for each scenario assessed in the Main Report are provided within this appendix.

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The ASTM model may be used for estimating the concentration of volatiles being emitted from subsurface sources into outdoor (ambient) air, and the air inside buildings. This is achieved by calculating *volatilisation factors.* These factors, defined below, account for volatilisation from different sources to different endpoints:

VF_{wesp}:   volatilisation factor for vapours from groundwater to enclosed spaces;

VF_{wamb}:   volatilisation factor for vapours from groundwater to ambient (outdoor) air;

VF_{samb}:   volatilisation factor for vapours from soils to ambient air; and

VF_{sesp}:   volatilisation factor for vapours from soils to enclosed spaces.

These factors are used to estimate indoor and outdoor air concentrations of volatiles by using the known chemical concentration in the groundwater and soil:

$$\text{Concentration}_{\text{indoor air}} = VF_{wesp} \times \text{Concentration}_{\text{groundwater}}$$

$$\text{Concentration}_{\text{outdoor air}} = VF_{wamb} \times \text{Concentration}_{\text{groundwater}}$$

$$\text{Concentration}_{\text{indoor air}} = VF_{sesp} \times \text{Concentration}_{\text{soil}}$$

$$\text{Concentration}_{\text{outdoor air}} = VF_{samb} \times \text{Concentration}_{\text{soil}}$$

The ASTM model makes the following assumptions when calculating volatilisation factors:

o The concentration of chemicals in the groundwater and soil remains constant over the exposure duration, i.e. the chemicals do not biodegrade, no transport within water, no absorption or production of the gases.

o The partitioning between the chemicals in the groundwater/soil matrix and vapours is linear.

o Chemical losses by biodegradation do not occur between the groundwater/soil and the surface.

o For outdoor emissions, steady-state atmospheric dispersion of vapours occurs within the breathing zone.

o Steady-state atmospheric dispersion of vapours occurs inside buildings.

o Diffusive transport of volatiles is assumed to be the dominant transport mechanism from the groundwater/soil to the inside of buildings. Convective transport has been accounted for, however it is considered to be only a small factor in the overall estimation of indoor air concentrations.

This assumption is reasonable in cases where there is subsurface generation of gases, such as landfills. In the case of landfills the upward movement (convection sweep) of the landfill gas becomes the controlling factor, greatly accelerating the upward migration and subsequent release into the atmosphere. For convection under normal (non-gas generating situations), the pressure differential between the subsurface and the inside of the building is the result of the air exchange occurring inside, causing the pressure in the subsurface to be very slightly greater than inside. This has more effect in cases where a subsurface basement is present. In cases where no subsurface basement is present, then it can be assumed that such effects are small.
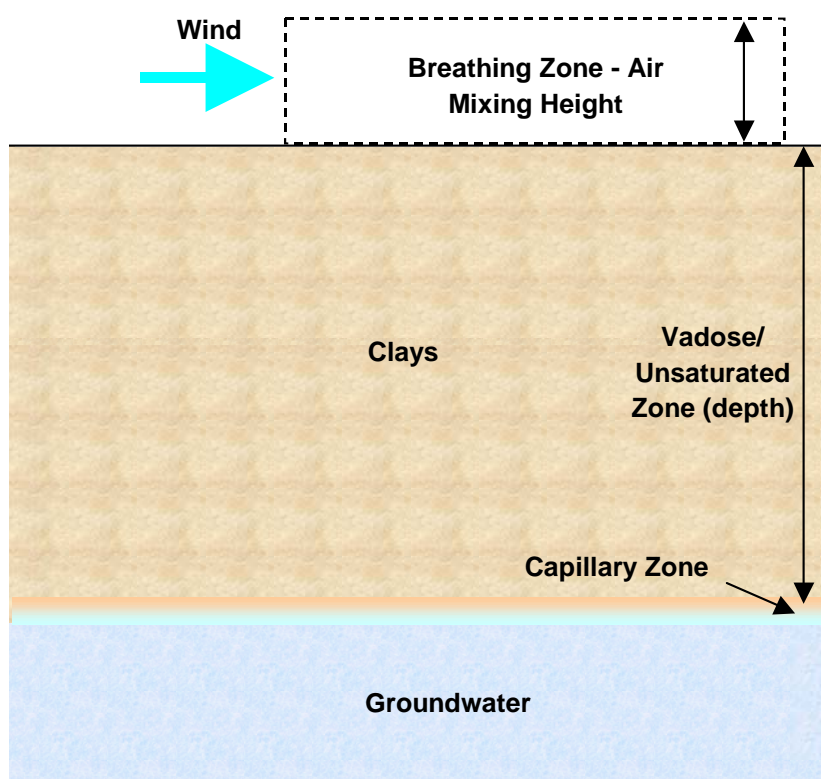
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Estimating The Emission Of Volatiles To Outdoor Air

The calculation of VF_{wamb} and VF_{samb}, and hence the concentration of volatiles outdoors, is based on the movement of volatiles from the soil and groundwater up through the capillary zone, through the unsaturated zone, and emission into the breathing zone in outdoor air.

The figure below illustrates the process under which estimates of outdoor air vapour concentrations have been made.

Conceptual Model of Vapour Migration to Outdoor Air

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Calculation of Chemical Intake - Methodology

Calculating VF$_{wamb}$

The ASTM model uses the following equation to calculate the volatilisation factor from groundwater to ambient air, VF$_{wamb}$:

$$VF_{wamb} = \frac{H}{1 + \left[\dfrac{U_{air} \bullet \delta_{air} \bullet L_{GW}}{W \bullet D_{ws}^{eff}}\right]} \bullet 10^3 \quad (mg/m^3{}_{air})/(mg/L_{groundwater}) \quad ....\textbf{Equation 6}$$

where:

H = Henry's Law constant (cm^3 H$_2$O/cm^3 air)

U_{air} = Wind speed above the ground surface in the ambient mixing zone (cm/s)

δ_{air} = Ambient air mixing zone height (cm)

L_{GW} = Depth to groundwater (= height of capillary zone, h$_{cap}$, + height of unsaturated zone, h$_v$) (cm)

W = Width of source area parallel to wind or groundwater flow direction (cm) (i.e. width and breadth of breathing zone)

$\boxed{}$ = Effective diffusion coefficient between the groundwater and soil surface (cm^2/s)

The diffusion coefficient, $\boxed{}$, is calculated by the following equation:

$$D_{ws}^{eff} = \left(h_{cap} + h_v\right) \bullet \left[\frac{h_{cap}}{D_{cap}^{eff}} + \frac{h_v}{D_s^{eff}}\right]^{-1} \qquad \textbf{....Equation 7}$$

where:

h_{cap} = height of capillary zone (cm)

h_v = height of unsaturated zone (cm)

$\boxed{}$ = effective diffusion coefficient through capillary zone (cm^2/s)

$\boxed{}$ = $D^{air} \bullet \dfrac{\theta_{acap}^{3.33}}{\theta_T^2} + D^{wat} \bullet \dfrac{1}{H} \bullet \dfrac{\theta_{wcap}^{3.33}}{\theta_T^2}$ **....Equation 8**

$\boxed{}$ = effective diffusion coefficient in soil based on vapour-phase concentration (cm^2/s), calculated using Equations 3 and 4

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Calculation of Chemical Intake - Methodology

Estimating VF$_{samb}$

The ASTM model uses the following equation to calculate the volatilisation factor from soil to ambient air, VF$_{samb}$:

$$VF_{samb} = \frac{H \bullet \rho_s}{\left[\theta_{ws} + k_s \bullet \rho_s + H \bullet \theta_{as}\right]\left[1 + \dfrac{U_{air} \bullet \delta_{air} \bullet L_s}{D_s^{eff} \bullet W}\right]} \qquad (mg/m^3{}_{air})/(mg/kg_{soil}) \qquad ....\textbf{Eqtn 9}$$

where:

H = Henry's Law constant (cm^3 H$_2$O/cm^3 air)

ρ_s = Soil bulk density (g soil/cm^3 soil)

θ_{ws} = volumetric water content in unsaturated zone (cm^3 water/cm^3 soil)

θ_{as} = volumetric air content in unsaturated zone (cm^3 air/cm^3 soil)

k_s = Soil-water sorption coefficient (g H$_2$O/g soil)

U_{air} = Wind speed above the ground surface in the ambient mixing zone (cm/s)

δ_{air} = Ambient air mixing zone height (cm)

L_s = Depth to subsurface soil sources (cm)

W = Width of source area parallel to wind or groundwater flow direction (cm) (i.e. width and breadth of breathing zone)

$\boxed{}$ = effective diffusion coefficient in soil based on vapour-phase concentration (cm^2/s) (as calculated for VF$_{wamb}$)
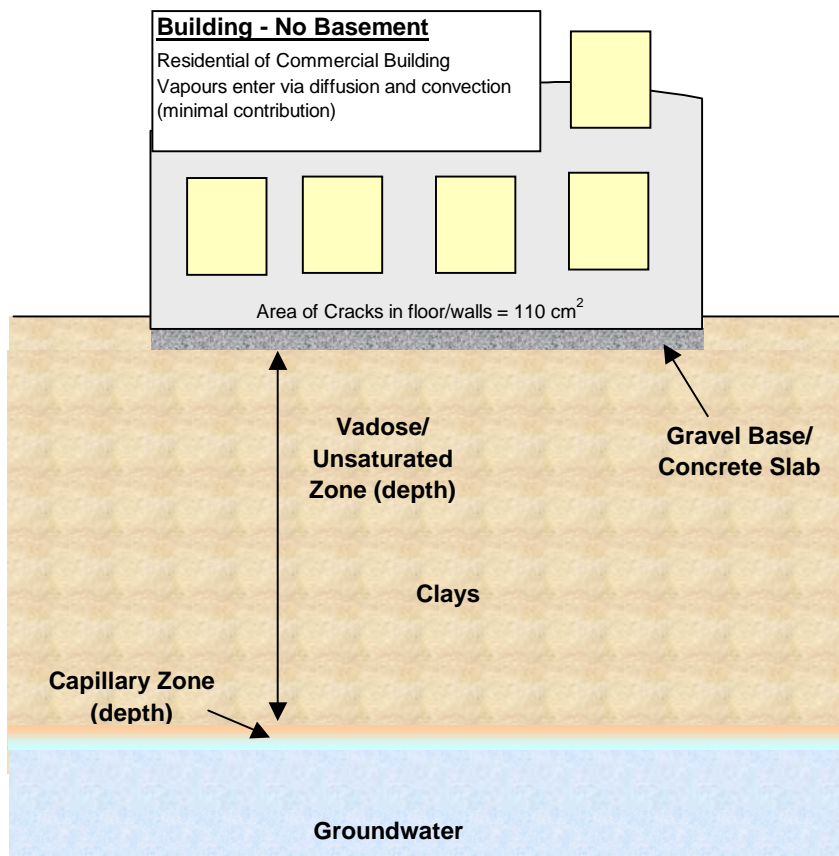
Estimating The Emission Of Volatiles To Indoor Air

The calculation of VF$_{wesp}$ and VF$_{sesp}$, and hence the concentration of volatiles indoors, is based on the movement of volatiles from the soil and groundwater up through the capillary zone, through the unsaturated zone, and emitting into buildings through cracks in the walls and foundations.

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The figure below illustrates the conditions under which estimates of indoor air vapour concentrations have been made.

Building - No Basement
Residential of Commercial Building
Vapours enter via diffusion and convection
(minimal contribution)

Area of Cracks in floor/walls = 110 cm^2

**Vadose/
Unsaturated
Zone (depth)**

**Gravel Base/
Concrete Slab**

Clays

**Capillary Zone
(depth)**

Groundwater

Conceptual Model of Vapour Migration from Soil/Groundwater to Indoor Air

The concentration of volatiles indoors is generally estimated to be greater than the outdoor concentration due to reduced ventilation. Therefore, the exposure pathway of inhalation of vapours indoors is potentially the most significant pathway.

The equations used and assumptions made in calculating VF_{wesp} and VF_{sesp} are presented below.

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Calculating VF_{wesp}

The ASTM model uses the following equation to calculate the volatilisation factor from groundwater into enclosed spaces, VF_{wesp}:

$$VF_{wesp} = \frac{H\left[\dfrac{D_{ws}^{eff}/L_{GW}}{ER \bullet L_B}\right]}{1 + \left[\dfrac{D_{ws}^{eff}/L_{GW}}{ER \bullet L_B}\right] + \left[\dfrac{D_{ws}^{eff}/L_{GW}}{\left(D_{crack}^{eff}/L_{crack}\right) \bullet h}\right]} \bullet 10^3 \quad (mg/m^3_{air})/(mg/L_{groundwater}) \quad ...\textbf{Eqtn 10}$$

where:

H =   Henry's Law constant (cm^3 H$_2$O/cm^3 air)

L_{GW} =   Depth to groundwater (cm)

ER =   Enclosed space air exchange rate (s^{-1})

L_B =   Enclosed space volume/infiltration area ratio (cm)

L_{crack} =   Enclosed space foundation or wall thickness (cm)

$\boxed{}$ =   Effective diffusion coefficient between the groundwater and the soil surface (cm^2/s) (as calculated for VF_{wamb})

$\boxed{}$ =   Effective diffusion coefficient through foundation cracks (cm^2/s)

$$= \quad D^{air} \bullet \frac{\theta_{acrack}^{3.33}}{\theta_T^2} + D^{wat} \bullet \frac{1}{H} \bullet \frac{\theta_{wcrack}^{3.33}}{\theta_T^2} \quad ...\textbf{Equation 11}$$

where: D_{air} =   diffusivity of chemical in air (cm^2/s)

    D_{water} =   diffusivity of chemical in water (cm^2/s)

    θ_T =   total soil porosity (cm^3/cm^3 soil)

    θ_{acrack} =   volumetric air content in foundation/wall cracks (cm^3 air/cm^3 total volume)

    θ_{wcrack} =   volumetric water content in foundation/wall cracks (cm^3 air/cm^3 total volume)

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Calculating VF_sesp

The ASTM model uses the following equation to calculate the volatilisation factor from soil into enclosed spaces, VF_sesp:

$$VF_{sesp} = \frac{[H \bullet \rho_s][D_{ws}^{eff} / L_s]}{[\theta_{ws} + k_s \bullet \rho_s + H \bullet \theta_{as}][ER \bullet L_B]} \bullet 10^3 \over 1 + \left[\dfrac{D_s^{eff} / L_s}{ER \bullet L_B}\right] + \left[\dfrac{D_s^{eff} / L_s}{(D_{crack}^{eff} / L_{crack}) \bullet \eta}\right]} \quad (mg/m^3_{air})/(mg/kg_{soil}) \quad ....\textbf{Eqtn 12}$$

where:

H	=	Henry's Law constant (cm^3 H$_2$O/cm^3 air)
ρ_s	=	Soil bulk density (g soil/cm^3 soil)
η	=	Arial fraction of cracks in foundations/walls (cm^2 cracks/cm^2 total area)
L_s	=	Depth to subsurface soil sources (cm)
L_B	=	Enclosed space volume/infiltration area ratio (cm)
L_{crack}	=	Enclosed space foundation or wall thickness (cm)
θ_{ws}	=	Volumetric water content in unsaturated zone (cm^3 water/cm^3 soil)
θ_{as}	=	Volumetric air content in unsaturated zone (cm^3 air/cm^3 soil)
k_s	=	Soil-water sorption coefficient (g H$_2$O/g soil)
ER	=	Enclosed space air exchange rate (s^{-1})
☐	=	Effective diffusion coefficient between the groundwater and the soil surface (cm^2/s) (as calculated for VF_wamb)
☐	=	Effective diffusion coefficient in soil based on vapour-phase concentration (cm^2/s) (as calculated for VF_wamb)
☐	=	Effective diffusion coefficient through foundation cracks (cm^2/s) (as calculated above for VF_wesp)

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Appendix B
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B1.3 Intakes via Ingestion

B1.3.1 Ingestion of Soils and Sediments

This includes evaluation of the following pathways:

- Ingestion of sediments

- Ingestion of soils (SRA area)

The following equation is used to calculate intake of chemicals via the ingestion of soils and sediment pathways:

$$Daily\ Chemical\ Intake_{Is} = C_s \bullet \frac{IRs \bullet FI \bullet B \bullet CF \bullet EF \bullet ED}{BW \bullet AT} \quad \text{(mg/kg/day)}$$

where:

Cs   = Concentration of chemical in soil or sediment (as relevant for each pathway assessed) (mg/kg)

IRs = Ingestion rate of soil or sediment (dependant on age and activity) (mg/day)

FI   = Fraction of daily ingestion that is derived from contamination source assumed to be 1 or 100% unless noted otherwise (unitless)

B   = Bioavailability or absorption of chemical via ingestion assumed to be 1 or 100% unless noted otherwise (unitless)

CF   = Conversion factor of 1×10^{-6} to convert mg to kg

EF   = Exposure frequency (days/year)

ED   = Exposure duration (years)

BW = Body weight (dependant on age) (kg)

AT   = Averaging time for threshold and non-threshold exposures (days)

B1.4 Intakes via Dermal Exposures

B1.4.1 Mechanisms of Dermal Absorption

Passive diffusion, as governed by Fick's First Law, is considered to be the main process whereby chemicals enter and permeate through the skin. The human skin is the largest organ of the body and it consists of a thin (approximately 100 µm) epidermal layer superimposed on a thick dermal layer (approximately 300-400 µm). The epidermis consists of four layers, the outermost layer being the stratum corneum (SC) (approximately 10-40 µm), which overlays the strata lucidum, granulosum, and germinativum (Figure 1). The SC layer is composed of flat highly keratinised squamous cells that are

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nonviable and are thought to maintain the barrier properties of the skin. If the SC layer is removed by tape stripping, for example, the permeability of the skin to chemicals increases dramatically.

Factors that have an effect on the dermal absorption of chemicals through the skin include:

- Skin hydration with several studies indicating that skin hydration may increase skin permeability;

- Thickness of the SC and anatomic regions with higher absorption expected in areas unprotected by thick SC layers;

- Lipophilicity of chemical. The SC layer tends to be a lipid-rich milieu and hence provides a barrier to hydrophilic compounds but permits the entry of lipophilic compounds;

- Degree of sediment binding;

- The presence of surface slicks typically comprised of fatty substances (e.g., lipids from decomposed organisms and oil from petroleum contamination) which typically cover the surface of all natural bodies of water.

- Environmental factors that include water temperature, pH, turbidity, flow rate (current), and degree of solar illumination.

- Physiologic factors include genetic-related sensitivity (e.g., tendency to sunburn) and individual differences (e.g., age, the presence of skin disease, skin abrasions).

Models that are used to estimate dermal absorption of chemicals present in water and soils/sediment are simplifications of the more complex dermal absorption processes.

B1.4.2 Dermal Contact with Soil

Dermal absorption of chemicals from soil depends on the area of contact, duration of contact, bond between chemical and the soil and the ability of the chemical to penetrate the skin.

USEPA Approach

The USEPA (1989 and 2004) define a simple approach to the evaluation of dermal absorption associated with soil contact. This is presented in the following equation:

$$\textit{Daily Chemical Intake} = C_s \bullet \frac{SAs \bullet AF \bullet ABSd \bullet CF \bullet EF \bullet ED}{BW \bullet AT} \quad \text{(mg/kg/day)}$$

where:
Cs = Concentration in soil (mg/kg)

SAs = Surface area of body exposed to soil (cm^2)

AF = Adherence factor, amount of soil that adheres to the skin per unit area which depends on soil properties and area of body (mg/cm^2 per event)

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ABSd = Dermal absorption fraction (unitless – refer to discussion below)

CF = Conversion factor of 1×10^{-6} to convert mg to kg

EF = Exposure frequency (days/year)

ED = Exposure duration (years)

BW = Body weight (dependant on age) (kg)

AT = Averaging time for threshold and non-threshold exposures (days)

Dermal Absorption Fraction (ABSd)

The approach undertaken by the USEPA utilises a dermal absorption fraction typically derived from experimental studies on different chemicals. On the basis of the studies undertaken and a number of simplifications, ABSd values have been recommended for a range of 10 chemicals and default values for other semi-volatile chemicals. No default is defined (in USEPA 2004) for volatile organic chemicals or inorganic chemicals. It is considered that, with regards to soil exposures, volatile organic chemicals would volatilise from soil on skin and should be accounted for in the assessment of inhalation exposures. For inorganics, the speciation is very important to dermal absorption and hence no generic default values have been determined.

More commonly used values for the assessment of dermal exposure to organics and inorganics utilise defaults for ABSd for organics of 0.01 and inorganics of 0.001 as presented on RAIS (Risk Assessment Information System derived from USEPA 1992), along with the few chemical-specific values available.

The value of ABSd has no consideration of exposure time. Experimental studies used to define ABSd values are associated with dermal application over 24 hours (i.e. the event is considered to be a 24 hour day by default). Due to the lack of information about the rate and relationship of absorption of chemicals through the skin over shorter exposure periods, the USEPA methodology does not recommend adjusting the ABSd to account for exposures over times less than 24 hours, rather it recommended adjusting exposure frequency and exposure duration to reflect site conditions. This approach is utilised to evaluate dermal intake per exposure event (commonly adopted as a day) and is considered to be conservative in the assessment of exposure events that are less than 24 hours in duration or multiple short-term exposure events where absorption would be "double-counted".

Further Review of Dermal Absorption

In reviewing the approach to the assessment of dermal exposure presented in source documents "The Health Risk Assessment and Management of Contaminated Sites" (CSMS, 1991, 1993, 1996, 1998 and enHealth 2002) that are referenced in enHealth (2002) it is noted that the approach suggested by Hawley (1985) has been adopted. The approach is similar to the USEPA approach presented above, with some differences with respect to the evaluation of absorption.

Hawley (1985) provides a review of dermal uptake from soils for organic chemicals based on studies of a number of compounds by humans, rats, rabbits and pigs. The absorption rates obtained for application of a pure compound (or in acetone solvent) were determined to be 11% for an adult over 24 hours. For a 12 hour contact time, the dermal absorption rate was taken to half or 6% (as rounded up from half of 11%) of

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the applied dose. For children a higher rate was assumed to account for more permeable skin of a young child. For children the absorption rate was taken to be twice that of the adult, or 12% of the compound on the skin over 12 hours.

Absorption of contaminants in soils or dust (and sediments) was discussed by Hawley to limited by the physical-chemical binding to the matrix. On this basis Hawley also applied use of a factor to account for the matrix effect of absorption from soils (or relevant matrix) by comparison to the absorption study data that used the pure compound or solvent solution. The value used by Hawley (for TCDD and other organic compounds where no data is available) was 15%.

This approach is also adopted in the assessment of dermal intake of organic chemicals presented in the Dutch sediment exposure model SEDISOIL (1996) and the soil exposure model CSOIL (2001). These models express the dermal absorption of organics presented by Hawley as an absorption rate per hour. Hence for children the absorption rate is 0.01 or 1% per hour and for adults the absorption rate is 0.005 or 0.5% per hour.

This approach was generally utilised by Fitzgerald D.J (CSMS 1991) in the setting of a response level for benzo(a)pyrene where intake via skin absorption for a 2 ½ and 6 year old child utilises the dermal absorption value over 24 hours. For an adult the intake via skin absorption considers exposure to soils over 12 hours and adjusts the intake using a linear relationship for absorption. While many other response levels (in various papers in CSMS) have been established following this approach, they are typically set for a 2 ½ year old child where dermal absorption associated with soils over 24 hours is considered to be relevant. Other references where dermal absorption over shorter exposure periods than 24 hours (using the linear approach) are presented in the following:

- Di Marco P.N. and Buckett K.J in CSMS 1996 in "Derivation of Health Investigation Levels for Beryllium and Beryllium Compounds"

- Di Marco P.N. in CSMS 1993 in "The Assessment and Management of Organochlorine Termiticides" where exposures over 24 hours (children), 8 and 10 hours (adults).

- Di Marco P.N. and Buckett K.J in CSMS 1993 in "Derivation of A Health Investigation Level for PCBs"

It is proposed that the methodology presented by Hawley (1985), SEDISOIL (1996) and CSOIL (2001) be adopted for the assessment of dermal exposures to chemicals identified in sediments. On this basis, dermal intake from exposure to sediment will be determined using the following equation:

$$Daily\ Chemical\ Intake_{Ds} = C_s \bullet \frac{SAs \bullet AF \bullet Abs \bullet ET \bullet ME \bullet CF \bullet EF \bullet ED}{BW \bullet AT} \quad (mg/kg/day)$$

where:

Cs   = Concentration in sediment (mg/kg)

SAs = Surface area of body exposed to sediment (cm^2)

AF   = Adherence factor, amount of sediment that adheres to the skin per unit area which depends on soil/sediment properties and area of body (mg/cm^2 per event)

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Abs = Dermal absorption rate (per hour) – based on chemicals specific information or use of default values of 0.01 per hour for children and 0.005 per hour for adults (as above)

ET = Exposure time to sediments (hours/day)

ME = Matrix effect (unitless) – dependant on the nature of dermal data available, by default 0.15 or 15% assumed (discussed above)

CF = Conversion factor of 1×10^{-6} to convert mg to kg

EF = Exposure frequency (days/year)

ED = Exposure duration (years)

BW = Body weight (dependant on age) (kg)

AT = Averaging time for threshold and non-threshold exposures (days)

For the chemicals expected to be evaluated in the CPWE, there are no chemical-specific dermal absorption parameters available and hence default values as noted above will be used in the assessment.

B1.5   References

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