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The VOLASOIL risk assessment model based on CSOIL for soils contaminated with volatile compounds

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PREFACE

This research of the Soil and Groundwater Laboratory (LBG) at the National Institute of Public Health and the Environment (RIVM) has been carried out by Ministry of Housing, Spatial Planning and the Environment (VROM) on commission of the Directorate General of Environment (DGM), Department of Soil Protection.

During the preliminary research phase, modelling possibilities were discussed in an internal scientific advisory board comprising Dr ir. S.M. Hassanizadeh (RIVM/LBG), Ir. J.J. Kliest (RIVM/Environmental Incidents, IEM) and Ing. R. Koops (RIVM/LBG).

The results have been extensively discussed in an external advisory board composed of a number of scientific experts from several institutes, universities and private companies, and representatives of different levels of government. Members of this external advisory board were:

Dr ir. A.E. Boekhold	Ministry of Housing, Spatial Planning and the Environment (VROM/DGM)
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A user-friendly Windows-application has been developed for using the VOLASOIL model in practice. This computer program can be obtained at the RIVM. Although both the document and the model code have been produced with care, these products cannot be claimed to be free of errors. Use of the results obtained by means of these materials is for the full responsibility of the user. Use of the model is encouraged and feedback is welcomed. However, other than by means of this document, no technical support is being offered.

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SUMMARY

The CSOIL exposure model was developed for derivation of Intervention Values for soil and groundwater clean-up. These Intervention Values are based on potential risks to humans exposed to soil contaminants. The CSOIL's volatilization module estimates the indoor-air concentration in a building. Consequently, CSOIL has been used for actual risk assessment in case of volatile compounds. Because of CSOIL's limitations it was also recommended to perform measurements in contact media. Theoretical evaluation of the CSOIL's volatilization module has shown it to be not suitable for actual risk assessment. For this reason, the VOLASOIL model has been developed for actual risk assessment in case of volatile soil contaminants. This model can be seen as an optimum between scientifically sound and applicable in practice.

The VOLASOIL model calculates the indoor air concentration for the Dutch situation in buildings situated on soils contaminated with volatile compounds. The model is suitable for site-specific risk assessment because of the possibility of flexible combination of modelling and measurements. The VOLASOIL model can be used for several specific contamination cases, for instance floating contaminant layers, contaminant sources beneath the groundwater table, pure contaminant in the open capillary zone, contaminated groundwater in crawl spaces, et cetera.

With respect to the CSOIL model, several new features are incorporated in the VOLASOIL model. Most important features are pressure-driven vapour flow in soils and buildings, building construction characteristics and the capillary transition boundary above the groundwater table between the full and the open capillary zone (depending on soil characteristics).

The VOLASOIL model could be used as a decision-support tool within the framework of soil clean-up priority (Soil Protection Act), construction permit issues (Housing Act), and soil quality management (spatial planning). Finally, incorporation of VOLASOIL in CSOIL is possible, this may result in amendments to the Intervention Values (Soil Protection Guide) for soil and groundwater clean-up for volatile compounds during a future evaluation of Intervention Values.

SUMMARY (Dutch)

Het blootstellingsmodel CSOIL is ontwikkeld voor de afleiding van de Interventiewaarden voor bodem- en grondwatersanering. Deze Interventiewaarden zijn gebaseerd op het potentiële risico voor de mens bij blootstelling aan bodemverontreiniging. Met de vervluchtigingsmodule uit het CSOIL-model kan de binnenluchtconcentratie in een gebouw worden geschat. Het model werd daarom ook, in het geval van vluchtige verbindingen, gebruikt voor actuele risico-analyse. Als gevolg van beperkingen van het CSOIL-model werd aangeraden metingen te doen in contact-media. Theoretische evaluatie van de vervluchtigingsmodule uit het CSOIL-model heeft aangetoond dat de module niet geschikt is voor actuele risico-analyse. Daarom is het VOLASOIL-model ontwikkeld voor de actuele risico-analyse in het geval van bodemverontreiniging met vluchtige verbindingen. Het model kan beschouwd worden als een optimum tussen degelijke theoretische onderbouwing en toepasbaarheid in de praktijk van het bodemonderzoek.

Het VOLASOIL-model berekent voor de Nederlandse situatie, de binnenluchtconcentratie in een huis dat gebouwd is op een bodem die verontreinigd is met vluchtige verbindingen. Doordat een flexibele combinatie mogelijk is tussen meten en rekenen en omdat het model berekeningen kan uitvoeren voor verschillende verontreinigingssituaties (drijflaag, bron onder de grondwaterspiegel, puur produkt in de onverzadigde zone, gecontamineerd grondwater in de kruipruimte, etc.), kan het model gebruikt worden voor locatie-specifieke risico-analyse.

Ten opzichte van het CSOIL-model zijn er verschillende nieuwe aspecten beschouwd in het VOLASOIL-model. De belangrijkste hiervan zijn de stroming van gecontamineerde lucht door de bodem en in het huis ten gevolge van luchtdrukverschillen, bouwtechnische karakteristieken van het huis en de capillaire overgangsgrens boven de grondwaterspiegel tussen de onverzadigde en verzadigde zone (afhankelijkheid van bodemeigenschappen).

Het VOLASOIL-model zou gebruikt kunnen gaan worden als een beslissingsondersteunend instrument in het kader van de saneringsurgentiesystematiek (Wet Bodembescherming), de systematiek voor de beoordeling van de bodemkwaliteit bij bouwvergunningsaanvragen (Woningwet) en Actief Bodembeheer (Ruimtelijke Ordening). Tenslotte kan VOLASOIL ook als module in CSOIL geplaatst worden. Dit zou in de toekomst, tijdens een evaluatie van de Interventiewaarden voor bodem- en grondwatersanering, kunnen leiden tot aanpassing van Interventiewaarden voor vluchtige verbindingen.

1 INTRODUCTION

The CSOIL exposure model was developed for the derivation of Intervention Values for soil and groundwater clean-up. These Intervention Values are based on potential risks resulting in adverse health effects on humans exposed to soil contaminants [Van den Berg, 1995]. Physicochemical properties of the contaminant, together with soil properties, plant uptake characteristics, human physical characteristics, human behaviour, climatological/meteorological standards and other assumptions lead to quantification of the potential exposure.

Exposure is compared with the human toxicologically based Maximum Permissible Risk (MPR). The MPR is defined as the Tolerable Daily Intake (TDI) or Acceptable Daily Intake (ADI) of compounds using the estimated daily intake level that can be ingested by humans during an entire lifetime without resultant adverse health effects (threshold approach). This applies to genotoxic carcinogens (non-threshold approach) as the exposure level with an exess lifetime cancer risk of 10^{-4} [Janssen *et al.*, 1995]. Matching the MPR with the soil concentration gives the human toxicologically based Intervention Value (former C-value) for soil and groundwater for a standardized situation [DGM, 1994a,b]. Exceedance of the human toxicologically based Intervention Values means "serious soil contamination", an unacceptably increased risk to humans, taking into account all possible exposure pathways [Van den Berg *et al.*, 1993].

The CSOIL model is also used for actual risk assessment. Because of CSOIL's limitations it was also recommended to perform measurements in contact media. Actual risk analysis with CSOIL can be used for determining the priority for soil clean-up. Assessing the exposure with CSOIL in a case of soil contamination involves estimation of relevant exposure routes. These are valid for a specific situation, with a certain soil use and in a particular soil contamination situation. Besides comparison of the total exposure with MPR, calculated indoor-air concentrations of volatile compounds are also compared with the human toxicologically based Tolerable Concentration in Air (TCA). Exceedance of the TCA means an unacceptably increased risk to humans.

Site-specific risk assessment with the CSOIL exposure model for volatile compounds is at the moment unsatisfactory. Measured indoor concentrations can differ largely from calculated concentrations. Uncertain model calculations could be due to an incomplete modelling in the CSOIL volatilization module [TCB, 1994]. Note that it is impossible to precisely predict the indoor air concentration with an indicative compartment model on the basis of equilibrium partitioning and stationary transport equations. Therefore measurements in contact media should be combined with model calculations.

1.1 Project objectives

This report focuses on assessing the risk of resulting adverse health effects to humans exposed to volatile compounds in the case of site-specific actual soil contaminations for the Dutch situation (a crawl space beneath the building, shallow groundwater table, no rocky soils). The most important element is the prediction of the indoor air concentration in buildings situated on a soil contaminated with volatile compounds. Important project objectives are:

1) description and theoretical evaluation of the current CSOIL volatilization module;
2) development of a new volatilization model: VOLASOIL;
3) comparison of model calculations with measurements of indoor air concentrations.

The proposed new VOLASOIL model should correspond to the general outline and boundary conditions as the CSOIL exposure model. Incorporation of the VOLASOIL model into the current CSOIL exposure model will then be possible in future. Recommended properties of the model:

1) the model has to be scientifically based;
2) the model has to be applicable in practice;
3) the model should use parameters which can be obtained by standardized soil investigation;
4) incorporation of measurements must be possible.

The VOLASOIL volatilization model could be used for site-specific risk assessment and can be a decision-support tool within the framework of the priority for soil clean-up (Soil Protection Act), construction permit issues (Housing Act) and soil quality management (spatial planning). In the longer term, incorporation of VOLASOIL in CSOIL may be possible, perhaps resulting in amendments to the assessment of Intervention Values for soil and groundwater clean-up for volatile compounds during a future evaluation of Intervention Values.

1.2 Reader's guide

General information and project objectives are given in Chapter **1**, the introduction to the reported project. Chapter **2** gives a complete description of the CSOIL volatilization module. In Chapter **3** the CSOIL volatilization module is extensively evaluated.

The scientific basis for the proposed new volatilization model, VOLASOIL, is presented in Chapter **4** (floating and sinking layers inclusive). Note that new equations have equation numbers in bold. Application of the VOLASOIL volatilization model and recommended default and input values are shown in Chapter **5**. Model sensitivity and uncertainty analyses are given in Chapter **6**.

Measurements are compared with model calculations in Chapter **7**. Conclusions and recommendations are given in Chapter **8**.

We have endeavoured to write the chapters so as to be read independently of each other; repetition is therefore inevitable. Background information, data and mathematical derivations are given in Appendixes 1 to 8.

2 DESCRIPTION OF CSOIL VOLATILIZATION MODULE

Since 1991 the CSOIL exposure model has been used for the derivation of Intervention Values for soil and groundwater clean-up. These Intervention Values are based on potential risks resulting in adverse health effects on humans exposed to soil contaminants [Van den Berg, 1995]. The exposure is compared with the human toxicologically based Maximum Permissible Risk (MPR). Matching the MPR with the soil concentration gives the human toxicologically based Intervention Value (former C-value) for soil and groundwater for a standardized situation [DGM, 1994a,b]. Exceedance of the human toxicologically based Intervention Values means "serious soil contamination", an unacceptably increased risk to humans, taking into account all possible exposure pathways [Van den Berg *et al.*, 1993].

The CSOIL model is also used for actual risk assessment. Because of CSOIL's limitations it was also recommended to perform measurements in contact media. In the year 1994 it is decided that CSOIL can be used for assessing the actual risk for determination of the priority for soil clean-up. In case of volatile compounds, besides comparison of the total exposure with MPR, calculated and measured indoor-air concentrations of volatile compounds are also compared with the human toxicologically based Tolerable Concentration in Air (TCA). Exceedance of the TCA means an unacceptably increased risk to humans. It was recognized that great uncertainties exist upon the accuracy of calculated and measured indoor-air concentrations. This Chapter describes the current CSOIL volatilization module as it is used within the framework of the priority for soil clean-up.

The CSOIL model, an indicative compartment model based on equilibrium partitioning and stationary transport equations, is limited in the following aspects:
1) lack of (biological) degradation;
2) a contaminant source at a certain depth in the soil is inexhaustible;
3) a soil is homogeneous;
4) equilibrium exists at a certain depth in the soil, but not above this depth;
5) lack of lateral transport or leaching.

Assessing the exposure with CSOIL involves quantification of relevant exposure routes. The set of formulas is described in Van den Berg [1995]. Figure 1 depicts a schematic view of the exposure model CSOIL. The exposure route in the shaded box is relevant for the volatilization module.
In order to give a description of the CSOIL volatilization module, it is necessary to describe, apart from the concentration in the gas phase, also the concentrations in the water and the solid phases.

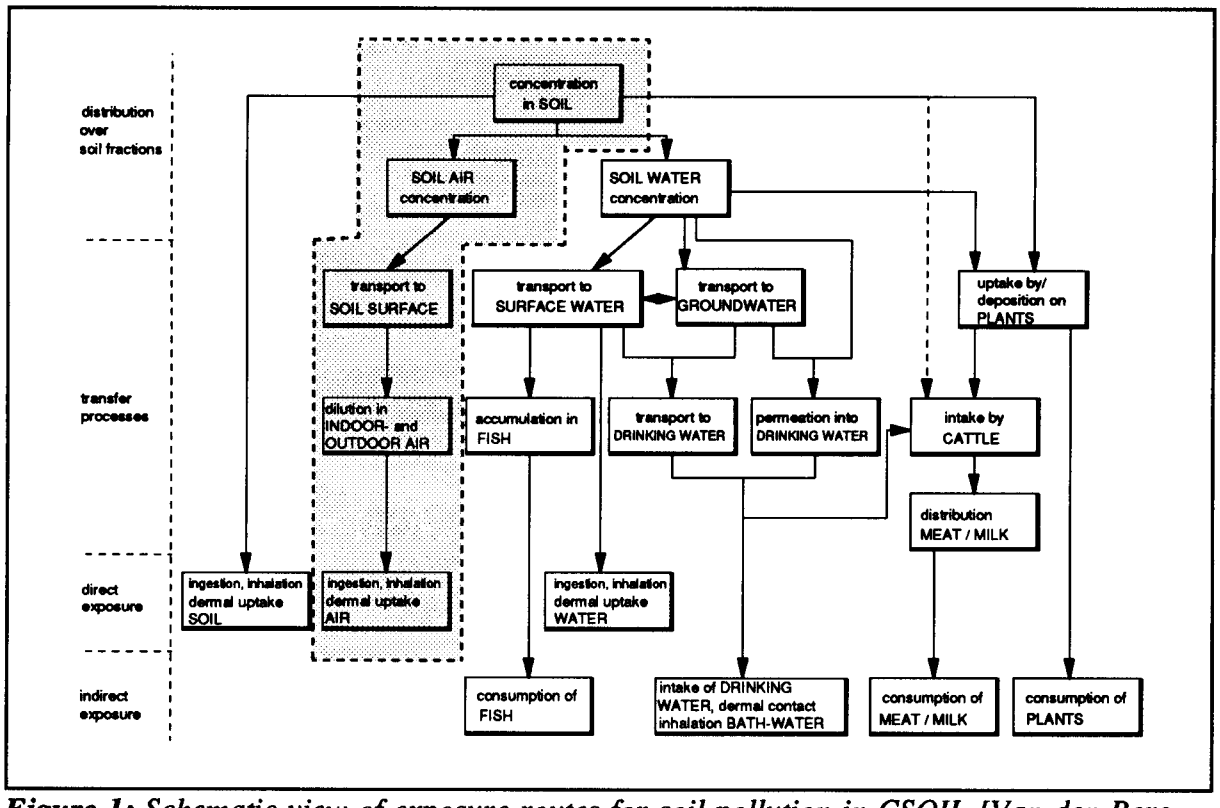


Figure 1: *Schematic view of exposure routes for soil pollution in CSOIL [Van den Berg, 1995]. The exposure route in the shaded box is relevant for the volatilization module.*

Equilibrium concentrations in soil air, soil water and the solid phase are calculated on the basis of partitioning coefficients of soil—water (Kd), air—water (Henry coefficient), and several soil parameters.

The exposure pathways in CSOIL are based on a virtual homogeneous soil (clay content = 25%) with default parameter values for potential risk analyses (Table 1). This default soil is used for calculation of Intervention Values. Parameter values can be changed for site-specific risk assessment.

In CSOIL [Van den Berg, 1995] the migration process by which contaminants may leave the soil and infiltrate the indoor or outdoor air is described as the resultant of a number of stationary equilibrium processes.

It is assumed that at a depth of 1.25 m, the contaminant is distributed over the solid, liquid, and gas phases by equilibrium partitioning. This is followed by, vertical transport through the soil, resulting in emission from the soil system. During emission to the outdoor air, and to a lesser extent, to the indoor air, a certain degree of dilution will occur. Indoor air concentrations are due to transport of volatile compounds from the soil, via the crawl space, into the indoor space.

***Table 1:** Default soil properties in CSOIL*

Parameter	Notation	Value
volume fraction air	V_a	0.2
volume fraction water	V_w	0.2
volume fraction solids	V_s	0.6
organic matter fraction	f_{om}	0.1
bulk density	SD	1.5 [kg.dm^{-3}]
soil temperature	T	283 [K]
acidity	pH	6

The crawl space is situated below the house, which, in the Dutch situation as a rule, is not screened off from the soil. Here, dilution takes place by means of ventilation with the outdoor air through ventilation holes. Concentrations of volatile compounds, of which the intake takes place via inhalation of air, depending on time spent indoors and outdoors, are calculated in both indoor and outdoor air. Finally, average lifelong exposure is assessed (see Figure 2).

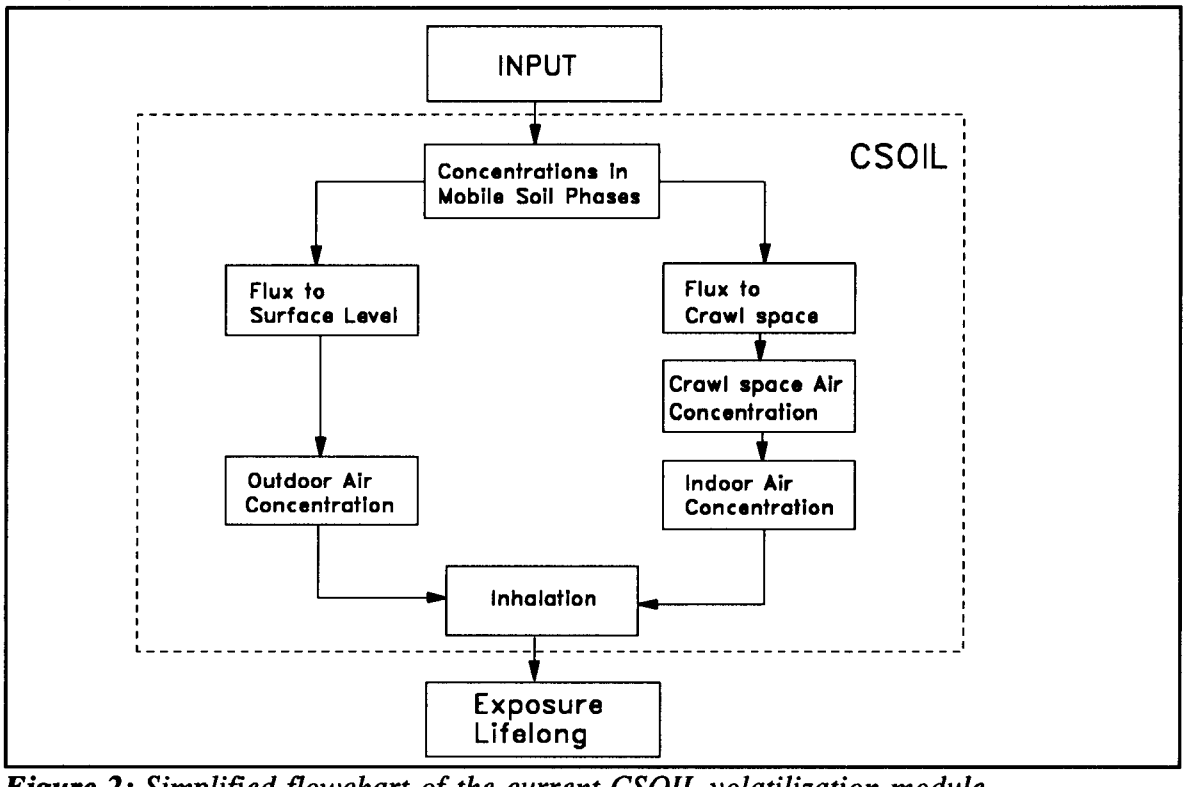


***Figure 2:** Simplified flowchart of the current CSOIL volatilization module.*

2.1 Distribution over soil phases

Equilibrium concentrations in the soil-air phase and the soil-water phase are calculated on the basis of total concentration in the soil (see Figure 1). It is assumed that equilibrium exists between the three phases. The calculation of the distribution over the three soil phases is based on the fugacity theory of Mackay *et al.* [1985]. The organic compounds are divided in dissociating and non-dissociating organics.

2.1.1 Distribution coefficients

Solid—liquid partitioning

Sorption of contaminants on the soil matrix is often described with the Freundlich isotherm: $C_s = K_f * C_l^{1/n}$, where C_s is the equilibrium concentration of the solid phase ($mg.kg^{-1}$), C_l the equilibrium concentration of the liquid phase ($mg.L^{-1}$), and K_f and *n* empirical coefficients dependent on the soil and the contaminant [Harter, 1991]. The parameter *n* is very important because it is directly related to the shape of the sorption isotherm. It is indicative for the degree of linearity between the concentration in the liquid phase and the sorption on the solid phase. The sorption isotherm becomes linear when *n* approaches 1. The parameter K_f is a measure of the sorption strength. The sorption isotherm exhibits linearity in relatively low concentration intervals, then the coefficient *n* equals 1. In that case K_f is comparable to the distribution coefficient (K_d, in $dm^3.kg^{-1}$) of a linear sorption isotherm [Fetter, 1993]: $C_s = K_d * C_l$. The K_d relates the concentration in solution directly to the fraction in the solid phase.

Due to the large role ascribed to organic matter with regard to sorption of organic contaminants in soils, the K_d in CSOIL is related to organic matter.

$$K_d = K_{oc} f_{oc} \tag{1}$$

$$f_{oc} = 0.58 f_{om} \tag{2}$$

where: K_d = partitioning coefficient soil—water [$(mol.kg^{-1})/(mol.dm^{-3})$]
K_{oc} = partitioning coefficient soil—water, corrected for organic carbon [$(mol.kg^{-1})/(mol.dm^{-3})$]
f_{oc} = fraction organic carbon [$kg_{org\ C}.kg^{-1}$ dry soil]
f_{om} = fraction organic matter [0.1]

It is very difficult to obtain the correct K_d value. The K_{oc} is related to the K_{ow} via the empirical formula (3) of Karickhoff [1981]. The K_{ow} is expressing the distribution of a compound between octanol (hydrophobe phase) and water. It is known for a lot of compounds, and it is relatively easy to determine.

$$K_{oc} = 0.411\ K_{ow} \tag{3}$$

where: K_{oc} = partitioning coefficient soil-water, corrected for organic carbon [(mol.kg^{-1})/(mol.dm^{-3})]
K_{ow} = octanol—water partitioning coefficient [(mol.dm^{-3})/(mol.dm^{-3})]

For dissociating organics, a correction is used for the K_d, based on Slooff *et al.* [1990] and research of Schellenberg *et al.* [1984] on sorption of chlorinated phenols by natural sediments and aquifer materials:

$$K_{d,c} = K_d\, f_{nd} \tag{4}$$

$$f_{nd} = \frac{1}{1 + 10^{(pH - pKa)}} \tag{5}$$

where: $K_{d,c}$ = partitioning coefficient soil—water, corrected for dissociation [(mol.kg^{-1})/(mol.dm^{-3})]
K_d = partitioning coefficient soil—water [(mol.kg^{-1})/(mol.dm^{-3})]
f_{nd} = fraction non-dissociated compound [-]
pH = acidity of soil [-]
pKa = acid dissociation constant [-]

Default pH value in CSOIL is 6. The fraction non-dissociated compound (f_{nd}) equals approximately 1, when a compound has a high acid dissociation constant (weak acid => high pKa). The fraction non-dissociated compound will be smaller than 1 at low acid dissociation constants (strong acid => low pKa). This moves the partitioning of the (polar) compound between the water phase and the solid phase, towards the water phase, resulting in a lower K_d.

Liquid—gas partitioning

Henry's Law states there is a linear relationship between the vapour pressure of a solute above its aqueous solution and the concentration in solution [Fetter, 1993]. Partitioning between air and water is accomplished by means of the dimensionless Henry constant (K_{lw}):

$$K_{lw} = \frac{Vp}{S\ R\ T} \tag{6}$$

or:

$$K_{lw} = \frac{H}{R\ T} \tag{7}$$

where: Klw = air—water partitioning constant or dimensionless Henry constant [(mol.m^{-3} air)/(mol.m^{-3} water)][-]
H = Henry's constant [Pa.m^3.mol^{-1}]
Vp = vapour pressure [Pa]
S = solubility [mol.m^{-3}]
R = gas constant [8.3144 Pa.m^3.mol^{-1}.K^{-1}]
T = temperature [K]

2.1.2 Fugacities

Soil contaminants will be distributed over soil-air, soil-water and the solid-soil phases. At equilibrium, concentrations in each soil compartment will be different. Mackay *et al.* [1985] have developed a fugacity theory. Equilibrium concentrations in the soil compartments are calculated, on the basis of the mass balance, and the volumes and fugacity capacities of the soil phases. The partitioning of contaminants over soil phases from the total soil concentration is calculated by using fugacities.

Fugacity can be regarded as the "escaping tendency" of a compound from a certain soil phase. By definition, mass will always be transferred from high to low fugacity [Mackay *et al.*, 1985]. The fugacity capacity is the maximum possible concentration of a compound in a soil phase at a given temperature and pressure. In CSOIL this capacity is called the fugacity constant.

Fugacity constants of the soil-air phase, soil-water phase, and the solid-soil phase are calculated by using the following equations [Van den Berg, 1995].

$$Z_a = \frac{1}{R\,T} \tag{8}$$

$$Z_w = \frac{S}{Vp} \tag{9}$$

$$Z_s = \frac{K_d\,SD\,Z_w}{V_s} \tag{10}$$

where:
- Z_a = fugacity constant air [$mol.m^{-3}.Pa^{-1}$]
- Z_w = fugacity constant water [$mol.m^{-3}.Pa^{-1}$]
- Z_s = fugacity constant solids [$mol.m^{-3}.Pa^{-1}$]
- R = gas constant [8.3144 $Pa.m^3.mol^{-1}.K^{-1}$]
- T = temperature [K]
- S = solubility [$mol.m^{-3}$]
- Vp = vapour pressure [Pa]
- K_d = partitioning coefficient soil—water [$(mol.kg^{-1})/(mol.dm^{-3})$]
- SD = bulk density of soil [kg dry soil/dm^3 moist soil]
- V_s = volume fraction solid phase [-]

The volume fraction of the solid-soil phase is the total volume minus the soil porosity ($V_a + V_w$):

$$V_s = 1 - (\,V_a + V_w\,) \tag{11}$$

where:
- V_s = volume fraction solid-soil phase [-]
- V_a = volume fraction soil air [-]
- V_w = volume fraction soil water [-]

2.1.3 Concentrations

Mass fractions are calculated for the different soil phases, using volumes and fugacity constants [Mackay *et al.*, 1985; Van den Berg, 1995].

$$P_a = \frac{Z_a V_a}{Z_a V_a + Z_w V_w + Z_s V_s} \tag{12}$$

$$P_w = \frac{Z_w V_w}{Z_a V_a + Z_w V_w + Z_s V_s} \tag{13}$$

$$P_s = \frac{Z_s V_s}{Z_a V_a + Z_w V_w + Z_s V_s} \tag{14}$$

where: P_a = mass fraction in soil air [-]
P_w = mass fraction in soil water [-]
P_s = mass fraction in solid-soil phase [-]
V_a = volume fraction soil air [-]
V_w = volume fraction soil water [-]
V_s = volume fraction solid-soil phase [-]

Starting from the total soil concentration (initial soil concentration), concentrations in soil air and soil water are estimated by:

$$C_{sa} = \frac{C_t \, SD \, P_a}{V_a} \tag{15}$$

$$C_{sw} = \frac{C_t \, SD \, P_w}{V_w} \tag{16}$$

where: C_t = total soil content [mol.kg^{-1} dry soil or mg.kg^{-1} dry soil]
C_{sa} = concentration in soil air [mol.dm^{-3} or g.m^{-3}]
C_{sw} = concentration in soil water [mol.dm^{-3} or g.m^{-3}]
SD = bulk density of dry soil [kg dry soil/dm^3 moist soil]
P_a = mass fraction soil air [-]
P_w = mass fraction soil water [-]
V_a = volume fraction soil air [-]
V_w = volume fraction of soil water [-]

A boundary condition is that pore-water concentration may not exceed the water solubility. Then, Equations (15) and (16) will be replaced by:

$$C_{sa} = \frac{S\ V_w\ P_a}{P_w\ V_a} \tag{17}$$

$$C_{pw} = S \tag{18}$$

where:
- C_{sa} = concentration in soil air [mol.dm^{-3} or g.m^{-3}]
- C_{sw} = concentration in soil water [mol.dm^{-3} or g.m^{-3}]
- S = solubility [mol.m^{-3}]
- P_a = mass fraction soil air [-]
- P_w = mass fraction soil water [-]
- V_a = volume fraction soil air [-]
- V_w = volume fraction of soil water [-]

2.2 Fluxes

Upward transport of soil contaminants takes place via the soil-air phase and the soil-water phase (see Figure 1). Bioturbation is not considered. In CSOIL, diffusion in soil air and soil water, and convective transport in pore-water, are considered (Figure 3). For the calculation model use has been made of the general concepts of stationary transport processes in soil [Jury *et al.*,1983; 1984]. Important limitations for application compared with the Jury model are:

1) no exhaustion takes place;
2) the concentration gradient in the soil is calculated from the concentration at the soil surface, which is assumed to equal zero, and the concentration at a known depth in the soil;
3) no (bacterial) degradation takes place.

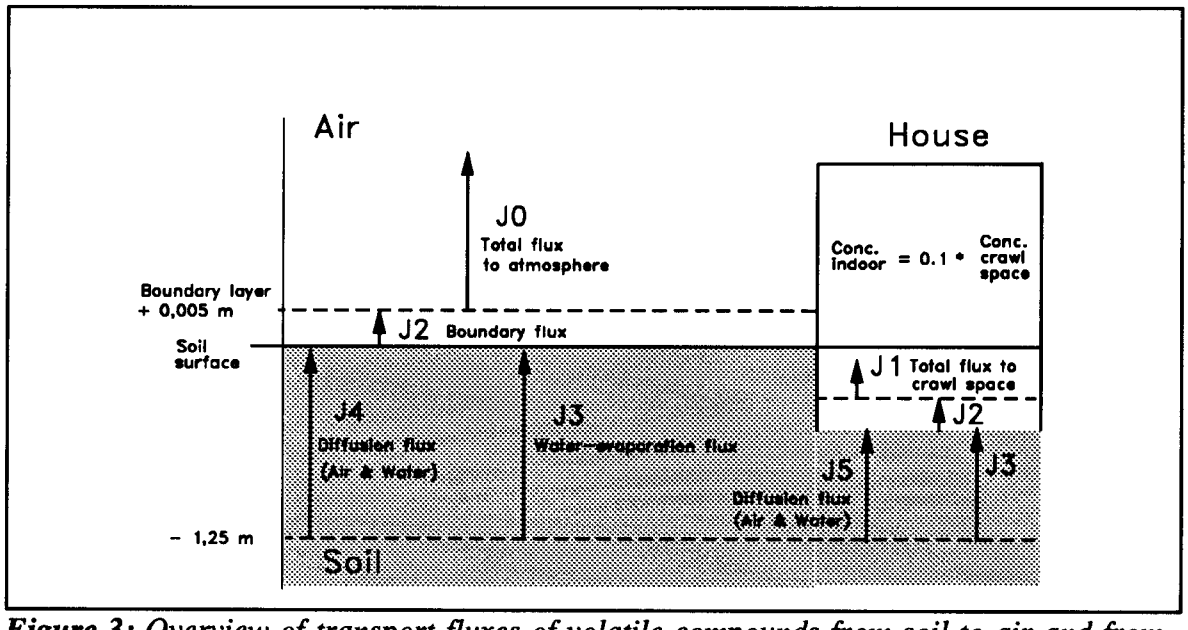


***Figure 3:** Overview of transport fluxes of volatile compounds from soil to air and from soil to indoor space of a house.*

The following contaminant fluxes are calculated:

J0: total soil flux to atmosphere;
J1: total soil flux to crawl space;
J2: flux through the boundary layer, which limits the fluxes from the soil to (indoor) air;
J3: water evaporation flux from soil to surface (of the soil or crawl space);
J4: diffusion flux from soil to soil surface (in soil air and soil water);
J5: diffusion flux from soil to crawl space (in soil air and soil water).

The water evaporation flux (J3) is an empirically lumped flux in which transport of compounds by capillary rise of water from the groundwater table is combined with evaporation together with water at the surface. The water evaporation flux is equal in both cases (flux to the soil surface and flux to the crawl space).

The diffusion of contaminants in soil water and soil air, from soil to soil surface or to crawl space, is the total diffusion flux. Two total diffusion fluxes are distinguished: the total diffusion flux from soil to soil surface (J4) and the total diffusion flux from soil to crawl space (J5). Transport of contaminants from soil to atmosphere may be limited by the presence of a stagnant layer of air at the atmosphere—soil interface (boundary layer). Transport within this thin, laminar layer is effected by diffusion, and not by turbulent transport processes.

The sum of the diffusion flux from soil to soil surface (J4) and water evaporation flux (J3) is the total flux from soil to air (J0). If this exceeds the theoretical maximum boundary flux (J2), then the total flux from soil to air is equal to this boundary flux.

The sum of the diffusion flux from soil to crawl space (J5) and water evaporation flux (J3) is the total flux from soil to crawl space (J1). If this exceeds the theoretical maximum boundary flux (J2), then the total flux from soil to crawl space is equal to this boundary flux.

2.2.1 Diffusion fluxes

The total diffusion flux of volatile compounds from soil to air consists of diffusion in soil air and soil water, neglecting the very slow diffusion in the solid phase. The diffusion flux is dependent on the concentration gradient in the soil, assuming a linear concentration decrease from a maximum concentration at 1.25 m beneath soil surface to zero concentration at the soil surface [Van den Berg, 1995]. An additional assumption is that no equilibrium exists between soil phases above 1.25 m beneath soil surface. Two important diffusion pathways are distinguished: the diffusion flux from soil to air and from soil to crawl space.

Diffusion coefficients of compounds in free air (D_a) and in free water (D_w), are calculated according to Grahams Law [Sawyer & McCarty, 1989], using following equations. These simple equations only depend on molecular weight [Van den Berg, 1995].

$$D_a = 0.036 \sqrt{\frac{76}{M}} \tag{19}$$

$$D_w = 3.6*10^{-6} \sqrt{\frac{76}{M}} \tag{20}$$

where: D_a = diffusion coefficient in free air [$m^2.h^{-1}$]
D_w = diffusion coefficient in free water [$m^2.h^{-1}$]
M = molecular weight [$g.mol^{-1}$]

Effective diffusion coefficients, calculated with the Millington-Quirk equation [Jury *et al.*, 1983], depend on the volume fraction of soil air (V_a) or soil water (V_w), the porosity ($1-V_s$), and corrections for tortuosity. Using diffusion coefficients in free air and water, effective diffusion coefficients in the soil-air phase and soil-water phase are derived by:

$$D_{sa} = V_a^{10/3} \frac{D_a}{(1 - V_s)^2} \tag{21}$$

$$D_{sw} = V_w^{10/3} \frac{D_w}{(1 - V_s)^2} \tag{22}$$

where: D_{sa} = diffusion coefficient in soil air [$m^2.h^{-1}$]
D_{sw} = diffusion coefficient in soil water [$m^2.h^{-1}$]
D_a = diffusion coefficient in free air [$m^2.h^{-1}$]
D_w = diffusion coefficient in free water [$m^2.h^{-1}$]
V_a = volume fraction soil-air phase [-]
V_w = volume fraction soil-water phase [-]
V_s = volume fraction solid-soil phase [-]

The diffusion coefficients in soil air and soil water are used for assessing the resulting soil diffusion flux. Based on the relative importance of the two diffusion routes (soil air, soil water), a weighted average soil diffusion coefficient is calculated:

$$D_u = \frac{P_a D_{sa}}{V_a} + \frac{P_w D_{sw}}{V_w} \tag{23}$$

where: D_u = soil diffusion coefficient [$m^2.h^{-1}$]
D_{sa} = diffusion coefficient in soil air [$m^2.h^{-1}$]
D_{sw} = diffusion coefficient in soil water [$m^2.h^{-1}$]
P_a = mass fraction in soil air [-]
P_w = mass fraction in soil water [-]
V_a = volume fraction soil-air phase [-]
V_w = volume fraction soil water phase [-]

Diffusion flux from soil to soil surface

Fick's first law of diffusion is applicable, assuming no exhaustion takes place; the concentration gradient in the soil is calculated from the concentration at the soil surface (which approximates zero) and the concentration at a known depth in the soil, and no (bacterial) degradation takes place. The diffusion flux from soil to soil surface (J4) is calculated by using the average soil diffusion coefficient (D_u), the total soil content (C_t), and the bulk density. Setting the highest soil concentration at 1.25 m beneath soil surface and a zero concentration at the soil surface, a linear concentration gradient is accomplished.

$$J4 = D_u \frac{C_t\, SD}{dp} \tag{24}$$

where: J4 = total diffusion flux from soil to soil surface [$g.m^2.h^{-1}$]
D_u = total diffusion coefficient in soil [$m^2.h^{-1}$]
C_t = total soil content [$mol.kg^{-1}$ dry soil or $mg.kg^{-1}$]
SD = bulk density [kg dry soil/dm^3 moist soil]
dp = average depth of contaminant [m]

A boundary condition is that soil-water concentration may not exceed water solubility. Total diffusion flux J4 will then be replaced by:

$$\text{IF: } C_{sw} > S \text{ THEN: } J4 = D_u \frac{S\ V_w}{dp\ P_w} \tag{25}$$

where: C_{sw} = concentration in soil water [mol.dm^{-3} or g.m^{-3}]
S = solubility [mol.m^{-3}]
J4 = total diffusion flux from soil to soil surface [g.m^2.h^{-1}]
D_u = total diffusion coefficient in soil [m^2.h^{-1}]
V_w = volume fraction soil water [-]
dp = average depth of contaminant [m]
P_w = mass fraction soil water [-]

Diffusion flux from soil to crawl space

Relevant for the human exposure to volatile soil contaminants is the diffusion flux from soil to crawl space. Equation (24) is replaced by Equation (26). Default values for crawl space characteristics are: the floor of crawl space is 0.5 m below soil surface, and depth of the crawl space is 0.5 m. In order to calculate the diffusion flux from soil to crawl space, the concentration in the crawl space is assumed to be negligibly low relative to the soil concentration [Van den Berg, 1995]. This is due to the high air-exchange rate in the crawl space. As a result, in case of diffusion from soil to crawl space, a greater concentration gradient is used, compared to diffusion from soil to soil surface due to a shorter diffusion length.

$$J5 = D_u \frac{C_t\ SD}{dp - dc} \tag{26}$$

where J5 = diffusion flux from soil to crawl space [g.m^2.h^{-1}]
D_u = total diffusion coefficient in soil [m^2.h^{-1}]
C_t = total soil content [mol.kg^{-1} dry soil or mg.kg^{-1}]
SD = bulk density [kg dry soil/dm^3 moist soil]
dp = average depth of contaminant [m]
dc = depth of crawl space beneath soil surface [0.5 m]

Again, a boundary condition is that soil-water concentration may not exceed water solubility. Total diffusion flux J5 will then be replaced by:

$$\text{IF: } C_{sw} > S \text{ THEN: } J5 = D_u \frac{S\ V_w}{(dp - dc)\ P_w} \tag{27}$$

where:
- C_{sw} = concentration in soil water [mol.dm^{-3} or g.m^{-3}]
- S = solubility [mol.m^{-3}]
- J5 = diffusion flux from soil to crawl space [g.m^2.h^{-1}]
- D_u = total diffusion coefficient in soil [m^2.h^{-1}]
- V_w = volume fraction soil-water phase [-]
- dp = average depth of contaminant [m]
- dc = depth of crawl space beneath soil surface [0.5 m]
- P_w = mass fraction soil water [-]

2.2.2 Water evaporation flux

The water evaporation flux in the CSOIL model is an empirically lumped flux in which transport of compounds by capillary rise of water from the groundwater table is combined with evaporation together with water at the surface. Upward convective transport of contaminants in the soil-water phase is possible when evaporation of soil water at the soil surface occurs [Fast *et al.*,1987]. Evaporation causes capillary rise of soil water. In this way, compounds in the water may be transported upwards, and released at the soil surface. No shifting groundwater level, induced by convective water transport, is considered.

The contaminant flux is dependent on the magnitude of the water flux. If a contaminant has a lower enthalpy of vaporization than water, then the possible contaminant flux of evaporation is greater than the contaminant flux with capillary rise of water. The contaminant flux with capillar rising water limits the contaminant flux of evaporation. If a contaminant has a higher enthalpy of vaporization than water, then the possible contaminant flux of evaporation is smaller than the contaminant flux with capillary rise of water. In this case, the contaminant flux with capillary rise of water also limits the contaminant flux of evaporation. The ratio of vaporizing water molecules and compound molecules has to be equal to the ratio of transported water molecules and compound molecules [Kliest, 1991; Fast *et al.*,1987].

Upward convective transport of contaminants via the water evaporation flux is modelled according to the Dutch situation. Kliest [1991] proposed a water evaporation flux from soil to crawl space of 0.0001 $m^3.m^{-2}.d^{-1}$ (0.1 $mm.day^{-1}$). It is based on extensive research of Fast *et al.* [1987] on measurements of temperature and air humidity of more than a hundred crawl spaces at different locations in the Netherlands. The water evaporation flux from soil to the surface of the soil, or crawl space, is (factor 24 is used for conversion days into hours):

$$J3 = C_{sw} \frac{Ev}{24} \tag{28}$$

where: J3 = water evaporation flux [$g.m^{-2}.h^{-1}$]
Csw = soil pore-water concentration [$mol.dm^{-3}$ or $g.m^{-3}$]
Ev = flux of evaporating water [Fast *et al.*, 1987: 0.0001 $m^3.m^{-2}.d^{-1}$]

The amount of evaporated organic compounds from soil water is dependent on factors which influence the water evaporation (groundwater level, soil characteristics and meteorological factors) and physicochemical compound properties [Fast *et al.*, 1987]. Evaporation of soil water is hampered when temperature and air humidity of the atmosphere are higher than soil air. No evaporation of water occurs when the groundwater table is very low; this makes capillary rise of water up to the soil surface impossible. Compoundspecific properties like Henry's constant (H) or the partitioning soil—water coefficient, corrected for organic carbon (K_{oc}), control the partitioning over the different soil phases. Combination of a high Henry's constant and a low K_{oc} gives a relatively high evaporation flux.

2.2.3 Boundary flux

Transport from soil to the atmosphere may be limited by the presence of a stagnant layer of air of a certain thickness at the atmosphere—soil interface. Transport within this thin, laminar layer is described by Fick's first law of diffusion [Glotfelty & Schomburg, 1991]. It is assumed that the compound concentration in the atmosphere above the laminar layer is equal to zero by approximation because of the rapid removal of the volatilized vapour. The thickness of the boundary layer is a function of the concentration gradient, the resulting flux and the diffusion coefficient of the diffusing compound [Spencer *et al.*, 1988]. In CSOIL this is not taken into account. According to Jury *et al.* [1984], the boundary layer thickness is taken at 0.005 m.

The boundary flux J2 in CSOIL is written as:

$$J2 = D_a \frac{C_{sa}}{d} \tag{29}$$

where: J2 = boundary flux [$g.m^{-2}.h^{-1}$]
D_a = diffusion coefficient in free air [$m^2.h^{-1}$]
C_{sa} = concentration in soil air [$mol.dm^{-3}$ or $g.m^{-3}$]
d = boundary layer thickness [0.005 m]

The sum of the diffusion flux from soil to soil surface (J4) or crawl space (J5) and the water evaporation flux (J3) may not exceed the theoretical maximum boundary flux (J2). Therefore, in the case of a contaminant flux from soil to soil surface, the following restrictive pair of equations are valid:

$$\text{IF: } J3 + J4 < J2 \quad \text{THEN: } J0 = J4 + J3 \tag{30}$$

$$\text{IF: } J3 + J4 \geq J2 \quad \text{THEN: } J0 = J2 \tag{31}$$

where: J0 = total soil flux to atmosphere [$g.m^{-2}.h^{-1}$]
J2 = boundary flux [$g.m^{-2}.h^{-1}$]
J3 = water evaporation flux [$g.m^{-2}.h^{-1}$]
J4 = total diffusion flux from soil to soil surface [$g.m^2.h^{-1}$]

In the case of a contaminant flux from soil to crawl space, the following restrictive pair of equations are valid:

$$\text{IF: } J3 + J5 < J2 \quad \text{THEN: } J1 = J3 + J5 \tag{32}$$

$$\text{IF: } J3 + J5 \geq J2 \quad \text{THEN: } J1 = J2 \tag{33}$$

where: J1 = total soil flux to crawl space [$g.m^2.h^{-1}$]
J2 = boundary flux [$g.m^{-2}.h^{-1}$]
J3 = water evaporation flux [$g.m^{-2}.h^{-1}$]
J5 = total diffusion flux from soil to crawl space [$g.m^2.h^{-1}$]

2.3 Concentration in air

Differences between indoor-air and outdoor-air concentrations, combined with different indoor and outdoor exposure times (see Figure 2) makes separate calculation of indoor- and outdoor-air concentrations necessary. The set of formulas for calculation of the outdoor-air concentration is largely based on the SOILRISK model [Ten Berge, 1990]. The dilution in air is calculated due to horizontal and vertical mixing for an inexhaustible source. The dilution rate is based on wind velocity and mixing height, which are dependent on dispersion in air and atmospheric stability. In the CSOIL model Dutch weather conditions are used. The set of formulas for calculation of the indoor-air concentration is based on research of Fast *et al.* [1987] and according to Kliest [1991]. Indoor-air concentration is directly correlated with the concentration in the crawl space air.

2.3.1 Outdoor-air concentration

The Pasquill weather stability class D is chosen as a default weather type. The atmosphere shows neutral conditions, temperature rises equally with height in atmosphere [Pasquill & Smith, 1983]. In this situation turbulent convective air movements are the result of friction to the earth's surface. The length of roughness (Zo), i.e. the height above the earth's surface where the extrapolated wind velocity is zero, is a measure for the earth's surface roughness. This height is influenced by the volume, distribution, and geometry of the obstacles on the earth's surface [Strom, 1976]. In CSOIL the length of roughness is taken as 1.0 m, equal to the roughness of an urban area [Van Leeuwen & Van Buytenen, 1992]. Longer lengths of roughness cause greater convective turbulent air movements, resulting in a higher Pasquill dispersion coefficient. Therefore the Pasquill dispersion coefficient (Sz) is corrected for the length of roughness (the diameter of the contaminated area is taken as 100 m):

$$Sz = 0.20\ Co\ Lp^{0.76} \tag{34}$$

$$Co = (10 * Zo)^{(0.53\ Lp^{-0.22})} \tag{35}$$

where:
- Sz = Pasquill dispersion coefficient for vertical movements, related to Pasquill weather stability class D [m]
- Co = correction factor for length of roughness [-]
- Lp = diameter of contaminated area [100 m]
- Zo = length of roughness [1.0 m]

The wind velocity in a neutral atmosphere (above a uniform surface) in the surface layer of the troposphere, increases logarithmically with altitude. However, no change in wind direction occurs in this layer, which implies that friction in the surface layer does not change with altitude. Eddies (= turbulent air movements), and therefore the turbulent air exchange, increase with higher altitudes, because friction with the uneven earth's surface decreases [Van Boxtel, 1988]. This friction is expressed as the friction velocity (V'). The friction velocity is a scaling variable for the velocity which is related to turbulent air exchange, altitude and the Von Karman constant, given by:

$$V' = k \frac{V_{10}}{\ln (Z_{10} / Zo)} \tag{36}$$

where: V' = friction velocity [$m.h^{-1}$]
k = von Karman constant [0.4]
V_{10} = wind velocity at 10 m altitude [18000 $m.h^{-1}$]
Z_{10} = altitude [10 m]
Zo = length of roughness [1.0 m]

The average Dutch wind velocity at 10 m above soil surface is 18 000 $m.h^{-1}$ [Ten Berge, 1990]. Using the friction velocity, wind velocity at breathing height of an adult and a child (1.5 m; 1.0 m) can be calculated:

$$V_x = \ln(\frac{Z}{Zo}) \frac{V'}{k} \tag{37}$$

where: V_x = wind velocity at x m altitude [$m.h^{-1}$]
Z = breathing height [adult: 1.5 m; child: 1.0 m]
Zo = length of roughness [1.0 m]
V' = friction velocity [$m.h^{-1}$]
k = von Karman constant [0.4]

The mean wind velocity (Vg) is calculated as the arithmetic mean of the wind velocity at breathing height (V_x) and the friction velocity (V') by:

$$Vg = \frac{V' + V_x}{2} \tag{38}$$

where: Vg = mean wind velocity [$m.h^{-1}$]
V' = friction velocity [$m.h^{-1}$]
V_x = wind velocity at x m altitude [$m.h^{-1}$]

Mean wind velocity (Vg), Pasquill dispersion coefficient (Sz), and diameter of contaminated area (Lp) filled in Equation (39), gives the dilution velocity of the soil contaminant flux for an adult (Vf_a) or a child (Vf_c):

$$Vf = Sz \frac{Vg}{Lp} \tag{39}$$

where: Vf = dilution velocity [$m.h^{-1}$]
Vg = mean wind velocity [$m.h^{-1}$]
Sz = Pasquill dispersion coefficient for vertical movements, related to Pasquill weather stability class D [m]
Lp = diameter of contaminated area [100 m]

Finally, the air concentration at breathing height (adult or child) is determined by the quotient of the total soil contaminant flux and the dilution velocity:

$$Coa_a = \frac{J0}{Vf_a} \tag{40}$$

$$Coa_c = \frac{J0}{Vf_c} \tag{41}$$

where: Coa_a = concentration outdoor air, at adult breathing height [$g.m^{-3}$]
Coa_c = concentration outdoor air, at child breathing height [$g.m^{-3}$]
Vf_a = dilution velocity, adult at 1.5 m [$m.h^{-1}$]
Vf_c = dilution velocity, child at 1.0 m [$m.h^{-1}$]
J0 = total soil flux to atmosphere [$g.m^{-2}.h^{-1}$]

2.3.2 Indoor-air concentration

Calculation of the indoor-air concentration is based on Fast *et al.* [1987] and according to Kliest [1991]. Empirical research showed that indoor-air concentrations are correlated directly with the concentrations in the crawl space air.

The concentration of volatile compounds in the crawl space results from transport of the contaminants and dilution by ventilation. Ventilation depends on building construction characteristics. Volume and surface area of the crawl space has a default of 25 m^3 and 50 m^2; air-exchange rate of crawl space is set at 1.25 h^{-1}.

These default values are based on extensive research of Fast *et al.* [1987] on measurements of air-exchange rates of more than a hundred crawl spaces in the Netherlands at different locations. Crawl space air-exchange rates (vv_c) ranges from 0.03 to 7.4 (mean = 1.25 h^{-1}). Concentration in crawl space is:

$$Cca = \frac{J1\ A_c}{V_c\ vv_c} \tag{42}$$

where: Cca = concentration in crawl space air [$g.m^{-3}$]
J1 = total soil flux from soil to crawl space [$g.m^{-2}.h^{-1}$]
A_c = surface area of crawl space [50 m^2; Fast *et al.*, 1987]
V_c = volume of crawl space [25 m^3; Fast *et al.*, 1987]
vv_c = air-exchange rate of crawl space [1.25 h^{-1}; Fast *et al.*, 1987]

The indoor-air concentration is assumed to be an empirical mean fraction of the concentration of the crawl space. This contribution of the crawl space to the indoor air as a fraction (fbi) varies between 0 and 0.68 (mean = 0.11) [Fast *et al.*, 1987]. The indoor air is considered as a well-mixed container, and concentration does not change with height. Therefore breathing height is not important, and difference between a child and an adult is negligible. Concentration in indoor air is calculated by:

$$Cia = fbi * Cca \tag{43}$$

where: Cia = concentration indoor air [$g.m^{-3}$]
Cca = concentration in crawl space air [$g.m^{-3}$]
fbi = contribution of the crawl space to the indoor air as fraction [0.1; Fast *et al.*, 1987]

A boundary condition is that the outdoor-air concentration may not exceed the indoor-air concentration. When this is the case, indoor-air concentration will be equal to outdoor-air concentration at breathing height of a child (worse case). Equation (43) will then be replaced by:

$$\text{IF: } Cia < Coa_c \text{ THEN: } Cia = Coa_c \tag{44}$$

where: Cia = concentration indoor air [$g.m^{-3}$]
Coa_c = concentration in outdoor air, for a child at breathing height [$g.m^{-3}$]

2.4 Inhalation

Primarily, exposure to volatile soil contaminants takes place via inhalation of air (see Figure 1). A distinction has been made between inhalation of indoor air and outdoor air because of differences in concentration. In CSOIL no distinction has been made between active and passive breathing periods. Children and adults are assumed to be present at a location, 24 hours a day.

Intake of volatile compounds depends on the concentration in indoor and outdoor air, time spent indoors and outdoors, breathing volume, absorption of contaminants in lungs and body weight. Values of the above-mentioned parameters, different for children and adults (see Table 2), are in accordance with Linders [1990]. Intake of volatile soil contaminants by adults or children is calculated by:

$$IV_a = \frac{(Cia\ tf_{i,a}\ t_{i,a} + Coa_a\ tf_{o,a}\ t_{o,a})\ AV_a\ fa\ 1000}{W_a} \tag{45}$$

$$IV_c = \frac{(Cia\ tf_{i,c}\ t_{i,c} + Coa_c\ tf_{o,c}\ t_{o,c})\ AV_c\ fa\ 1000}{W_c} \tag{46}$$

where:
- IV_a = intake of contaminants through inhalation of air, adult [$mg.kg^{-1}.d^{-1}$]
- IV_c = intake of contaminants through inhalation of air, child [$mg.kg^{-1}.d^{-1}$]
- Cia = concentration indoor air [$g.m^{-3}$]
- Coa_a = concentration outdoor air, for an adult at breathing height [$g.m^{-3}$]
- Coa_c = concentration outdoor air, for a child at breathing height [$g.m^{-3}$]
- $t_{i,a}$ = daily indoor exposure duration, adult [$h.d^{-1}$]
- $t_{i,c}$ = daily indoor exposure duration, child [$h.d^{-1}$]
- $t_{o,a}$ = daily outdoor exposure duration, adult [$h.d^{-1}$]
- $t_{o,c}$ = daily outdoor exposure duration, child [h^{-1}]
- $tf_{i,a}$ = time fraction for time spent indoors, correction from daily to yearly average exposure, adult [-]
- $tf_{i,c}$ = time fraction for time spent indoors, correction from daily to yearly average exposure, child [-]
- $tf_{o,a}$ = time fraction for time spent outdoors, correction from daily to yearly average exposure, adult [-]
- $tf_{o,c}$ = time fraction for time spent outdoors, correction from daily to yearly average exposure, child [-]
- AV_a = breathing volume, adult [$m^3.d^{-1}$]
- AV_c = breathing volume, child [$m^3.d^{-1}$]
- fa = relative absorption factor of contaminants in lungs [-; default set at 1]
- W_a = body weight, adult [kg]
- W_c = body weight, child [kg]

***Table 2:** Default parameters for calculation intake of volatile contaminants by adults and children [Van den Berg, 1995; Linders,1990]*

Parameters		Adult	Child
breathing volume	AV	20 $m^3.d^{-1}$ = 0.83 $m^3.h^{-1}$	7.6 $m^3.d^{-1}$ = 0.32 $m^3.h^{-1}$
daily indoor exposure duration	t_i	8 $h.d^{-1}$	16 $h.d^{-1}$
daily outdoor exposure duration	t_o	8 $h.d^{-1}$	8 $h.d^{-1}$
time fraction for time spent indoors, correction from daily to yearly average exposure	tf_i	2.856	1.322
time fraction for time spent outdoors, correction from daily to yearly average exposure	tf_o	0.143	0.357
body weight	W	70 kg	15 kg
breathing height	Z*	1.5 m	1.0 m

* : see outdoor-air concentration

Daily exposure durations are multiplied by time fractions, giving yearly averaged daily exposure times. Combination of daily exposure durations and time fractions are used for exposure time correction, due to an irregular exposure time distribution over the year. This makes a daily exposure duration and a time fraction a unique combination. Lifelong average daily exposure to volatile soil contaminants is calculated by using Equation (47). The exposure is the weighted average of the intake of contaminants through inhalation of air for an adult and a child. The human lifetime is 6 years for a child and 64 years for an adult.

$$DOSE_{IV} = \frac{6\ IV_c + 64\ IV_a}{70} \tag{47}$$

where: $DOSE_{iv}$ = lifelong average daily exposure to volatile contaminants [$mg.kg^{-1}.d^{-1}$]
IV_a = intake of contaminants through inhalation of air, adult [$mg.kg^{-1}.d^{-1}$]
IV_c = intake of contaminants through inhalation of air, child [$mg.kg^{-1}.d^{-1}$]

3 EVALUATION OF THE CSOIL VOLATILIZATION MODULE

This Chapter discusses the volatilization module of the CSOIL model [Van den Berg, 1995], following roughly the same sequence used in the preceding Chapter. Moreover, the theoretical uncertainties in parameters and (choice of) processes are considered. Also, conclusions are drawn with respect to the new VOLASOIL volatilization model.

3.1 Distribution over soil phases

Equilibrium between the three phases and the mass balance is taken into consideration for calculating the distribution of the contaminant over the soil phases (solid phase, soil moisture and soil air). A key-factor of the volatilization module is the potential quantity of volatile compounds in the soil air. Equilibrium partitioning coefficients (K_{oc}-distribution coefficient), the solubility and vapour pressure are closely related to this.

The equilibrium principle used [Mackay *et al.*, 1985] is primarily based on laboratory observations, where equilibrium between soil and soil moisture is established very quickly, for instance, within 24-28 hours. In a realistic soil environment equilibrium conditions do not always prevail. Brusseau & Rao [1991] present processes held responsible for non-equilibrium sorption of organic compounds by natural sorbents. They divide soil into sorption domains, where instantaneous sorption and rate-limited sorption occurs, and suggest an inverse relationship between values for first-order desorption rate constants (k_2) and equilibrium sorption constants (K_p). Research by Imhoff & Jaffe [1994] on unsaturated sand indicates that the gas—water-phase mass transfer speed was sufficient for equilibrium between gas and water phases to be achieved in a soil column experiment at all sampling locations.

Because non-equilibrium sorption processes are still difficult to quantify, and because of the overall simplicity of the CSOIL set of formulas, it is not possible to implement non-equilibrium conditions into the VOLASOIL volatilization model. The assumption of equilibrium conditions between the three soil phases will result for aged contaminations in an overestimation of the volatilization flux compared to non-equilibrium conditions.

3.1.1 K_{oc}-distribution coefficient

The Karickhoff [1981] linear relation for neutral hydrophobic solutes (generally water solubilities < 10^{-3} mol.L^{-1}) was used for the relation between the groundwater distribution coefficient corrected for organic carbon (K_{oc}) and the octanol—water distribution coefficient (K_{ow}). On the Kd or K_{oc} calculations, Karickhoff concluded the correspondence between measured and computed K_{oc} values for substances with a log K_{ow} between 1 and 4.5 to be generally good, with deviations up to a factor 3, with a few exceptions. For the 49 substances considered in the article the difference between log-measured K_{oc} and log-estimated K_{oc} was 0.20 ± 0.46.

In Appendix 3, two methods are described for obtaining K_{oc}, where K_{ow} values are missing. Karickhoff [1981] presents an equation for calculating K_{oc} based on solubility corrected for crystal energy, and Sabljić [1987] introduces a molecular connectivity model, which is a accurate predictive tool for the soil sorption coefficients of a wide range of organic chemicals (see Appendix 3).

Calculated K_{oc} values can be significant different from measured values. Besides, there is a considerable spatial variation at a site, caused by soil heterogenity. But measured K_{oc} values can also show large variations due to specific soil/compound characteristics. If measured K_{oc} values are available to a sufficient extent, measurements are preferable (Bockting *et al.*, 1993). It is not necessary to change the current CSOIL set of formulas due to above uncertainties.

3.1.2 Solubility and vapour pressure

The physicochemical properties of solubility and vapour pressure are used as input for the CSOIL model. Solubility and vapour pressure are measured under standard conditions at 20 °C. Mean soil temperature in the Netherlands is about 10 °C [Feddes & Huinink, 1990]. Both solubility and vapour pressure are strongly temperature-dependent and show, in general, lower values at lower temperatures. Therefore temperature corrections for solubility and vapour pressure could be necessary.

3.2 Fluxes

CSOIL is an indicative compartment model based on equilibrium partitioning and stationary transport equations. Large differences are possible in comparing with reality due to spatial and temporal varieties of soils.

3.2.1 Diffusion fluxes

The total diffusion flux in soil is calculated by using Fick's first law of diffusion. The diffusion coefficient is comprised from the diffusion coefficients in soil air and soil moisture, the former being most important in case of volatile compounds. Gas-phase diffusion coefficients are approximately 10^4 times greater than liquid-phase diffusion coefficients [Glotfely & Schomburg, 1991].

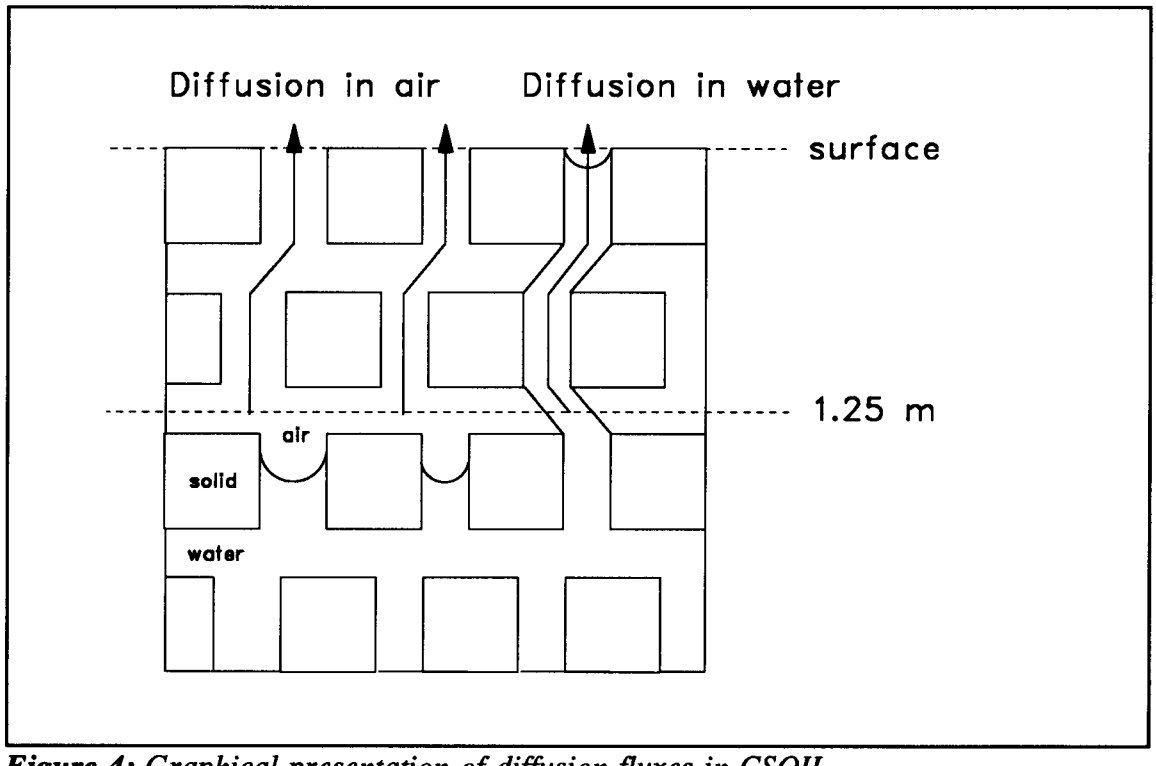


Figure 4: *Graphical presentation of diffusion fluxes in CSOIL.*

The diffusion rate through soil air is less than that through free air because of:

1) the reduced cross-sectional area normal to the direction of the flux available for diffusion;
2) the increased path length brought about by the tortuosity of the channels;
3) the water blocking of connections between pores [Koorevaar *et al.*,1991].

Effective diffusion coefficients in soil air and soil water are calculated by using the Millington-Quirk equation: Equations (21) and (22). Sallam *et al.* [1984] compared measured gas diffusion at low air porosity levels (using an inert gas), with data predictions from various models. They concluded that the Millington-Quirk model to be superior to the other proposed models. It slightly underestimated the measured gas diffusion coefficients. It has to be noted that this empirical model does not take soil properties in account, other than porosity and volumetric air content. Under very dry conditions in the soil (relatively high air-filled porosities), the model might not predict realistic diffusion coefficients.

Freijer [1994a,b] carried out combined measurements of water retention curves, air-filled porosities and relative diffusion coefficients to evaluate the effects of water distribution in the soil pores on the relative diffusion coefficient. After soil samples were saturated with water the residual air-filled porosity ranged from 0.051 m^3 m^{-3} to 0.167 m^3 m^{-3} and the relative diffusion coefficient practically zero, which is due to blockage of gas-filled pores by soil water. It is concluded that the air entry value in the water retention curve can be an important parameter that can be used to indicate the water content at which pore-blocking becomes relevant. Thus, in the case of nearly saturated soils, gas diffusion coefficients will be overestimated using the Millington-Quirk equations.

In CSOIL, the total volumetric air content is available for diffusion in soil air, and the total volumetric water content is available for diffusion in soil water (Figure 4).

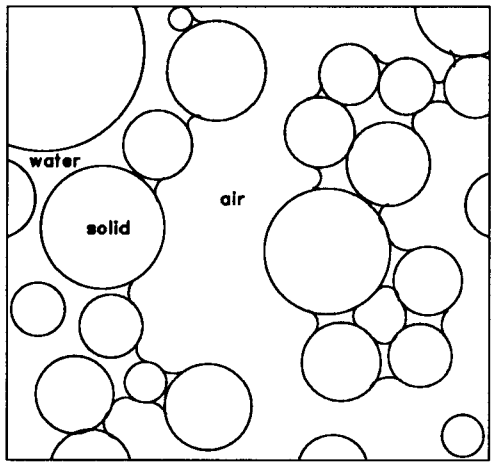


Figure 5: *Cross-section of soil. Soil particles forming soil pores, partly filled with liquid and gas.*

In the field soil air and soil water are not distributed in parallel tubes, and do not form continuous routes up to the surface (Figure 5). Soils are very complex in their composition and variable in their occurrence and properties. Their complex nature, dynamic behaviour and variable spatial distribution are the result of non-homogeneous mixing and interaction of all their components. Soil particles (solids) range widely in size. The larger particles form the framework of the soil, while the smaller ones fill the space around the contact points. The space between the solids are the soil pores; their shape and size is determined by the shape, size and arrangement of the solid particles. Within the pores, the liquid and gas phases reside and move [Koorevaar *et al.*, 1991].

Water, blocking connections between pores, influences the magnitude of total diffusion. Under very wet conditions the CSOIL model might overestimate diffusion coefficients.

Because diffusion in soil air is the most important diffusion process in the open capillary zone in case of volatile compounds, diffusion in soil water will not be considered in VOLASOIL.

3.2.2 Water evaporation flux

The water evaporation flux in the CSOIL model is an empirically lumped flux in which transport of compounds by capillary rise of water from the groundwater table is combined with evaporation together with water at the surface. Theoretically, water evaporation involves four elements [Kutílek & Nielsen, 1994]:

1) the transport of water to an evaporating surface located either within the soil profile or on the geographical soil surface;
2) a phase change from liquid water to vapour water;
3) the transfer of water vapour from the soil surface to higher elevations within the atmosphere;
4) in general, the process also includes the simultaneous transport of matter and heat according to conservative concepts of mass and energy.

Jury *et al.* [1984] compared predicted volatilization fluxes with measured fluxes and introduced the water evaporation flux into their behaviour assessment model. This volatilization flux is valid when soil is exposed to the atmosphere. Under these circumstances evaporating water will be diluted and mixed in the atmosphere, and a constant pressure-head gradient will be established, inducing transport of water from soil to atmosphere. In the case of evaporation of water from the soil to the crawl space of houses, this concentration gradient will not establish, because water contents in crawl space air are near saturation [Fast *et al.*, 1987].

Using the water evaporation flux implicates constant capillary rise of water from the groundwater table to the surface (no leaching). This will be the case when there is a very shallow groundwater table. In reality, water will rise approximately up to the capillary transition boundary. In this section flowing water will take compounds in upward direction. Water will evaporate from the capillary transition boundary into gaseous water molecules and be transported to the surface predominately by diffusion, which is a much slower process than liquid flow. Since in CSOIL, this top layer functions as a strong hydraulic resistance, the actual evaporation is much less than the potential evaporation [Kutílek & Nielsen, 1994]. In this last section transport of chemical compounds sorbed onto gaseous water molecules is of very minor importance; it is probably possible for very hydrophobic compounds, but not for volatile compounds.

The CSOIL water evaporation flux (in the open capillary zone) is a static flux, weakly scientifically based, and not important in the case of volatile compounds. Therefore, the water evaporation flux will not be considered in the VOLASOIL model.

3.3 Groundwater table

The ratio between diffusion in soil water and in soil air is closely related to the spatial distribution of soil particles, soil water and soil air. An important governing factor is the boundary between the full capillary zone and the open capillary zone (Capillary Transition Boundary). In the full capillary zone diffusion in water is the dominant diffusion flux, whereas in the open capillary zone, diffusion in air is the most important diffusion flux. When the groundwater table is high, almost all of the soil pores are filled with water; in this case diffusion in air is almost zero.

The depth of groundwater table is not incorporated in CSOIL. The diffusion flux is determined by the concentration gradient in the soil, while assuming that there is a linear concentration gradient with a maximal content in the soil at a depth of 1.25 m and a concentration equal to zero at the surface.

The depth of the groundwater table will be incorporated in the VOLASOIL volatilization model because it has a large impact on volatilization fluxes. Because the model is based on stationary transport, seasonal fluctuations of the groundwater table are not considered.

3.4 Concentration in air

Measured indoor concentrations can differ largely from concentrations calculated with CSOIL. Crawl space air-exchange rates (vv_c) range from 0.03 to 7.4 (mean = 1.25 h^{-1}) and contribution of the crawl space to the indoor air as a fraction (fbi) varies between 0 and 0.68 (mean = 0.11) [Fast *et al.*, 1987]. Large temporal differences which may be caused by convective flow of air are observed, which is not incorporated in the CSOIL model.

Johnson & Ettinger [1991] state that field data will only be correlated by models that incorporate both convective and diffusive transport mechanisms. Detailed research of Nazaroff *et al.* [1985] showed that pressure-driven flow was even more important than diffusion as a mechanism for radon entry in a house. Dynamic pressure of wind and pressure differences resulting from indoor/outdoor temperature differences cause the infiltration of outdoor air through cracks and a variety of unintentional openings in the building envelop [Godish, 1989].

The wind is the major driving force for infiltration of air into the building. As wind approaches a building, it decelerates, producing a positive pressure on the windward side. As wind is deflected by the windward face of the building, the flow separates at building edges formed by corners and the roof or building top. This flow results in internal negative pressures building up which, although small in respect to atmospheric pressure, are sufficient to induce flows of large volumes of air. Negative pressures also occur on the leeside of the building in the wake area. The effect of these pressure differences is to induce an inflow of air on the windward side, where air pressure is positive and an outflow on the leeward side where air pressure is negative. The exact pressure distribution on a building will depend on a variety of factors. These include wind speed, geometrical construction and size, incident angle of the wind and the presence of barriers to air movement, such as other buildings, trees and shrubbery [Godish, 1989].

Pressure differences may also be caused by differences between indoor and outdoor temperatures [Godish, 1989]. Under cool to cold outdoor temperature (heating season) conditions, warm air rises and flows out of the building near the top. This exfiltrated air is replaced by cooler air that flows in by infiltration near the bottom of the building. For the Netherlands the indoor temperature is on average higher than the outdoor temperature. The effect of these indoor/outdoor temperature differences on pressure distribution on a building during the heating season is illustrated in Figure 6.

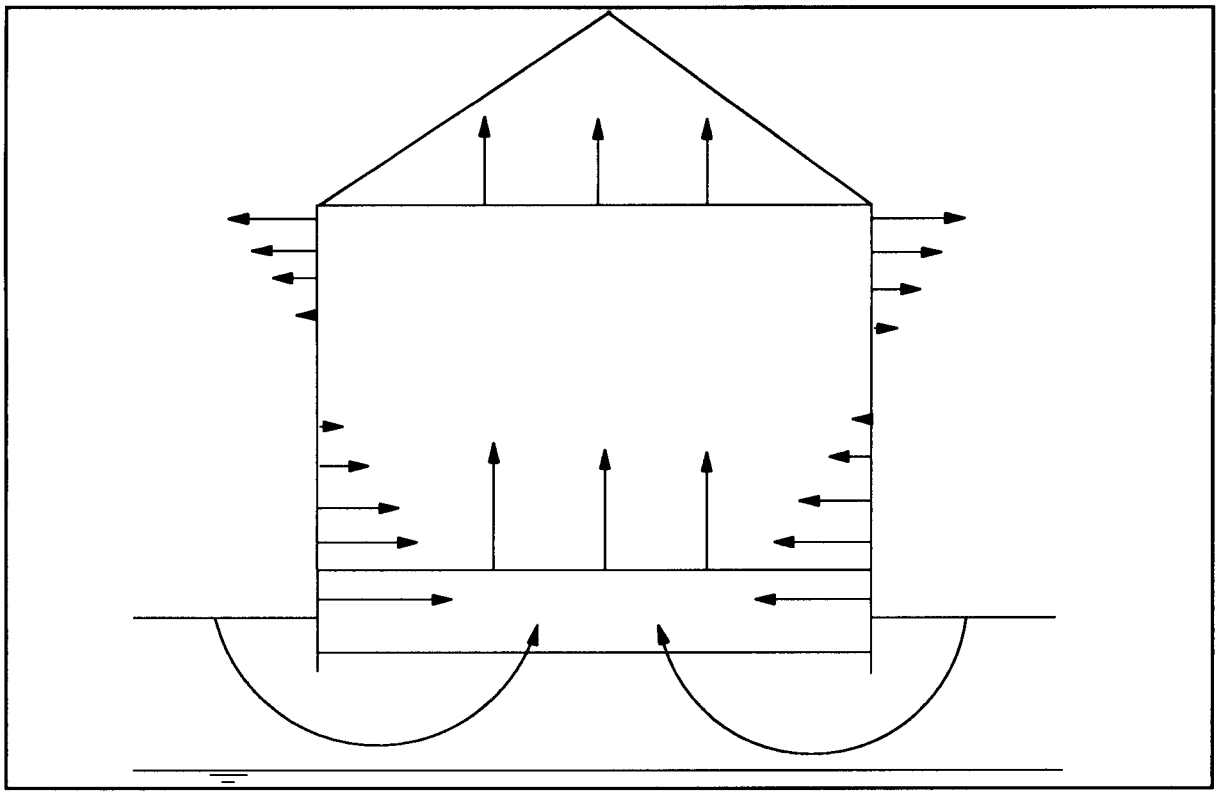


Figure 6: *Convective air transport caused by air pressure differences in a house, associated with indoor temperature higher than outdoor temperature (→ = convective transport of air from high to low air pressure) [adopted from Godish, 1989].*

In addition, Massmann & Farrier [1992] suggest that temporal variations in barometric pressure due to weather patterns may induce air intrusion into the subsurface. This air intrusion can affect monitoring activities aimed at characterizing the composition and movement of gases in the open capillary zone. Also horizontal pressure gradients can develop at sites with near-surface heterogenities. Massmann & Farrier [1992] developed a transport model. Diffusive vapour flow and pressure-driven vapour flow are combined in their model.

Convection of volatile compounds by soil air can be comparable in magnitude to diffusion of volatile compounds in soil air. The transport process of volatile compounds from soil to surface is a combination of diffusion and convection. Convection of air is the major transport process within a building. It is evident that pressure-driven vapour flow will be introduced in the volatilization model.

3.5 Exposure due to inhalation

Exposure due to inhalation of volatile compounds depends on the indoor/outdoor concentration of air, daily duration of indoor/outdoor exposure, annual average time fractions for residential time indoors/outdoors, relative absorption factor and human physiological characteristics, such as breathing volume and body weight.

3.5.1 Exposure times

Daily duration of exposure indoor/outdoor (t) is closely correlated with the annual average time fractions (tf) for staying indoors/outdoors. They cannot be separated and they are also difficult to understand. It is better to use the multiplication of the two, being the averaged annual daily indoor/outdoor exposure time (T). This parameter is much better to understand, although in reality significant deviations are possible. This concept is described in Appendix 8.

3.5.2 Absorption coefficients

Absorption refers to the amount of a chemical or substance that is able to cross biological membranes and, once in the body, be taken up by the blood for subsequent distribution to target tissues. The term "absorption coefficient" is a numerical descriptor characterizing the fractional uptake by the blood and represents an approximation of the biological dose ultimately responsible for toxicity or other effects following exposure or chemical administration. But, absorption coefficients do not exist for many chemicals due to lack of appropriate toxicological data.

Table 3: *Absorption coefficients for chemicals via inhalation route of exposure [adapted from Owen, 1990]*

acrylonitrile	0.98 (0.80-1.00)
benzene	0.47 (0.28-0.60)
chloroform	0.63 (0.49-0.77)
1,1 -dichloroethylene	0.98
ethylbenzene	0.64 (0.44-0.64)
ethylene oxide	1.00
methylene chloride	0.50 (0.50-0.75)
toluene	0.50 (0.37-0.70)
vinyl chloride	0.64 (0.54-0.68)
xylene	0.64 (0.54-0.68)

Because of lack of knowledge, the relative absorption factor (fa) of volatile compounds in the lungs is set at 1 in CSOIL, which in some cases overestimates the real exposure. Owen [1990] presented absorption coefficients of chemicals via inhalation route of exposure (Table 3). They are intended to reflect absorption by the average adult. Unfortunately, no standard calculations are known for the derivation of these absorption coefficients; they are all empirically based.

The CSOIL model could be changed for the exposure times. Because of lack of empirical data, default CSOIL absorption coefficients will not change. However, in future a more realistic absorption factor might be incorporated.

3.6 Summary

The CSOIL exposure model was developed for derivation of Intervention Values for soil and groundwater clean-up. These Intervention Values are based on potential risks to humans exposed to soil contaminants. The CSOIL's volatilization module estimates the indoor-air concentration in a building. Consequently, CSOIL has been used for actual risk assessment in case of volatile compounds. Because of CSOIL's limitations it was also recommended to perform measurements in contact media. Theoretical evaluation of the CSOIL's volatilization module has shown it to be not suitable for actual risk assessment. For this reason, the VOLASOIL model has been developed for actual risk assessment in case of volatile soil contaminants. The following conclusions can be drawn for the new volatilization model VOLASOIL:

1) Pressure-driven vapour flow will be incorporated (3.4);
2) The water evaporation flux is not considered (3.2.2);
3) The groundwater table will be incorporated (3.3);
4) Diffusion in soil water is not considered, only diffusion in soil air (3.2.1);
5) The transport process of volatile compounds from soil to surface is a combination of diffusion and convection (3.4).

Besides, temperature corrections for solubility and vapour pressure are proposed (3.1.2).

If the VOLASOIL model is combined with CSOIL exposure calculations, then the following conclusions can be drawn:

1) Implementation of non-equilibrium conditions into the CSOIL model cannot take place (3.1);
2) Calculation of K_{oc} values do not have to change in the CSOIL model (3.1.1);
3) The exposure time calculations could be simplified (3.5.1).

4 VOLASOIL MODEL DESCRIPTION

The volatilization model VOLASOIL has been developed as discussed in the foregoing chapter. This chapter presents the scientific basis for the proposed VOLASOIL model (version 1.9). Note that new equations have equation numbers in bold.

The VOLASOIL model is based on stationary transport. Important limitations and assumptions are:

1) no (biological) degradation;
2) an inexhaustible contaminant source at a certain depth in the soil;
3) a homogeneous soil;
4) no (non-equilibrium) sorption of volatile compounds in the open capillary zone;
5) no lateral transport or leaching.

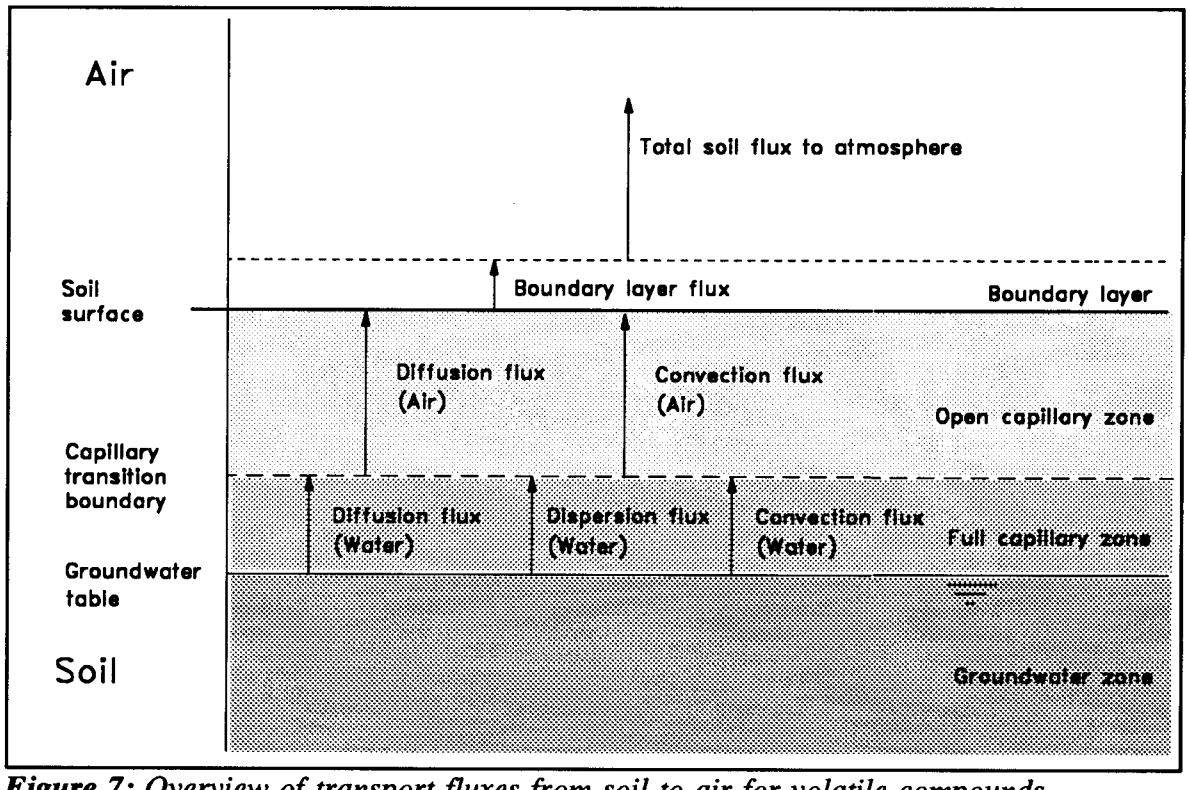


Figure 7: *Overview of transport fluxes from soil to air for volatile compounds.*

The groundwater table and the height above the groundwater table of the boundary between the open and the full capillary zone (Capillary Transition Boundary) are incorporated in the model. In the open capillary zone, diffusion in soil air and pressure-driven vapour flow will be quantified. Diffusion in soil water, water evaporation flux and contribution of the crawl space to the indoor air as a fraction, as used in CSOIL,

are not considered in the VOLASOIL model. Relevant for the indoor-air concentration is the height of the capillary transition boundary above the groundwater table (Figure 7).

The capillary transition boundary is the boundary between the full and the open capillary zones. Beneath this boundary (in the full capillary zone), the relevant transport mechanisms are diffusion and dispersion in soil water, and convective transport by flowing soil water. Above this boundary (in the open capillary zone) the most important transport mechanisms are diffusive and convective transport in soil air, especially for houses situated on the soil surface. Volatile soil contaminants can enter a house by convective and diffusive transport mechanisms [Ferguson *et al.*, 1995]. It is assumed that in this open capillary zone no sorption of volatile compounds takes place. Convective transport of volatile compounds in soil water is of minor importance in this zone [Glotfelty & Schomburg, 1991].

Under steady-state conditions, fluxes in the full capillary zone must be equal to fluxes in the open capillary zone. Description of fluxes in the full capillary zone is not necessary when assuming that an open capillary zone always exists. In this case, description of fluxes in the open capillary zone is adequate.

The VOLASOIL model quantifies the indoor-air concentration for a house situated on a homogeneous soil contaminated with volatile compounds for the Dutch situation. Calculations with VOLASOIL can be made for different specific cases. Specific cases are combinations of the location and the physical appearance of the contaminant in the soil, that lead to different transport processes. For every application one should assess which specific case is valid. The VOLASOIL model presented in Sections 4.1 to 4.5 can be considered as specific case A: a groundwater contamination, assuming the groundwater to be a well-mixed container.

Section 4.6 describes specific cases where distictive conditions are valid (e.g. floating contaminant layer, groundwater in a crawl space, contaminant source beneath the groundwater table, et cetera). These specific cases are linked with VOLASOIL on different places of the model. The general VOLASOIL model structure is shown in Figure 8. The following specific cases are considered:

	Case
- Groundwater contamination; well-mixed container	**A**
- Contaminated groundwater in crawl space	**B**
- Floating soil-contaminant layer	**C**
- Groundwater in crawl space and a floating soil-contaminant layer	**D**
- Pure contaminant in open capillary zone	**E**
- Very low groundwater table	**F**
- Sinking soil-contaminant layer; well-mixed container	**G**
- Contaminant source beneath the groundwater table; a not well-mixed container	**H**

It does not make sense to sum calculated indoor-air concentrations of different cases (e.g. groundwater contamination and pure contaminant in the open capillary zone). Independent calculations should be made in order to assess the highest potential risk.

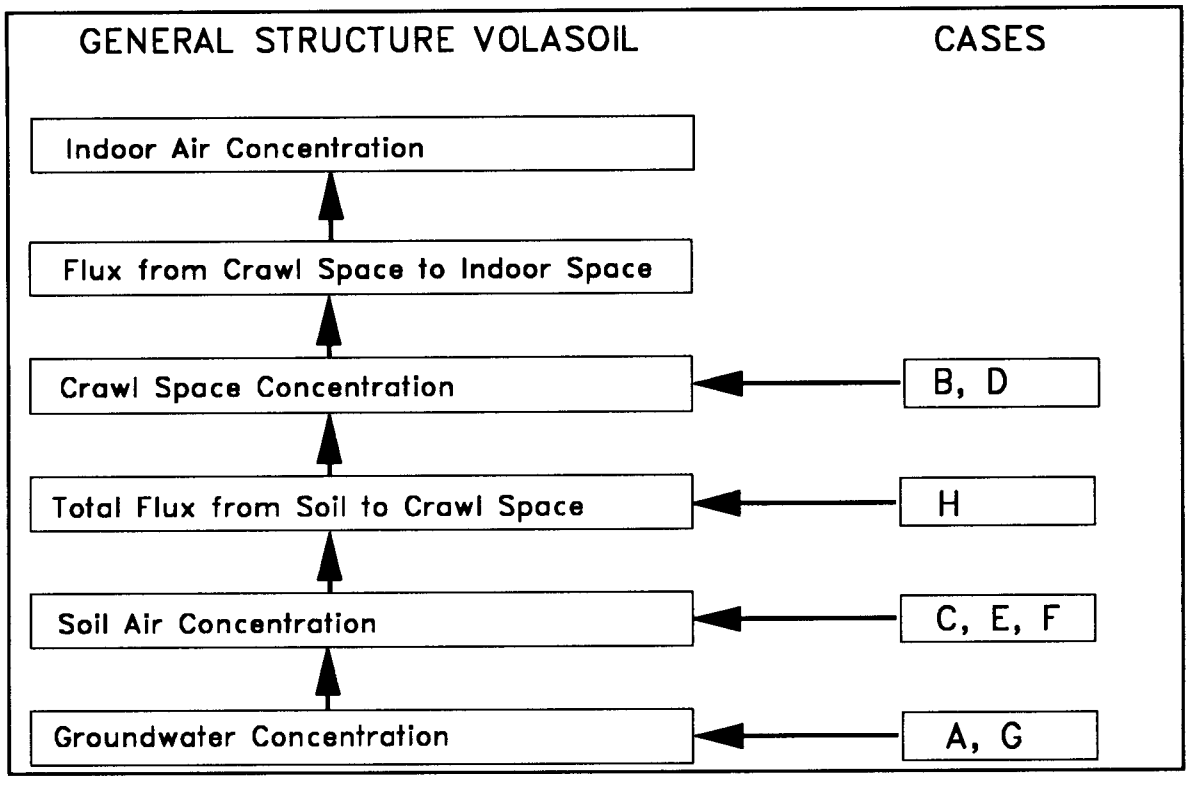


Figure 8: *General structure of VOLASOIL. Letters in boxes indicate input positions for different specific cases:*
A *= groundwater contamination (well-mixed container);*
B *= contaminated groundwater in crawl space;*
C *= floating soil-contaminant layer;*
D *= groundwater in crawl space and a floating soil-contaminant layer;*
E *= pure contaminant in open capillary zone;*
F *= very low groundwater table;*
G *= sinking soil-contaminant layer (well-mixed container);*
H *= contaminant source beneath the groundwater table (a not well-mixed container).*

4.1 Groundwater table

The depth of the groundwater table can be easily measured in the field or taken from groundwater maps. The height of the capillary transition boundary above the groundwater table is dependent on soil properties. This height can be calculated using the water retention curve of the soil together with an average capillary rise of water, and the pressure-head corresponding to the air-entry value (also know as the bubbling point).

The air-entry value is an important parameter to indicate the water content at which blocking of water-filled pores becomes relevant [Freijer, 1994a,b]. At higher water contents there will be air pockets which are not in contact with each other. Diffusion in soil air is then practically zero [Troeh *et al.*, 1982], which is due to pore-blocking by soil water. At lower water contents (higher air-filled porosity) air pockets will be in contact with each other. Continuous air-filled pores will develop and diffusion in soil air can occur.

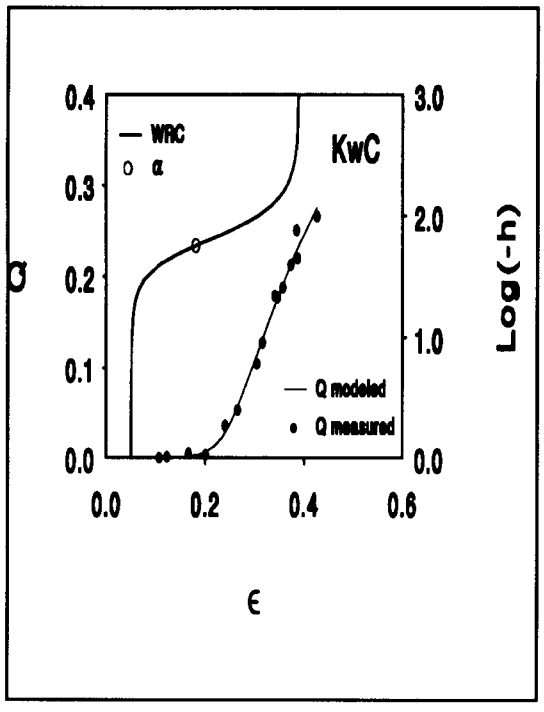
The air-entry value can be defined as the pressure-head, h = -1/α. The parameter α is taken from the Van Genuchten equation [Van Genuchten, 1980] for the water retention curve:

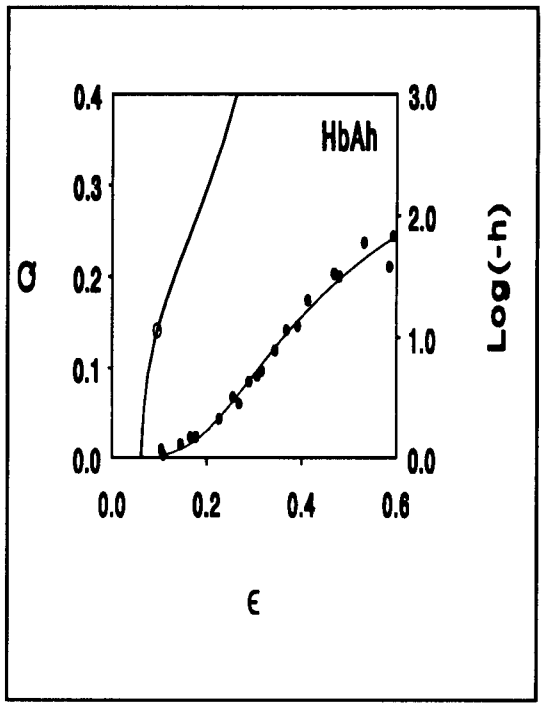
$$\theta = \theta_r + \frac{\theta_s - \theta_r}{(1+|\alpha.h|^n)^{1-\frac{1}{n}}} \qquad \textbf{(48)}^*$$

where θ ($cm^3.cm^{-3}$) is the volumetric water content at pressure-head h (cm), θ_r the residuarly water content (in practice θ_r is the water content at very large negative values of the pressure-head, h = $-1*10^6$ cm), θ_s the water content at saturation, and n a dimensionless parameter correlated with the angle of the S-shaped water retention curve [Wösten *et al.*, 1994]. The parameter α (cm^{-1}) is the point of inflection in the water retention curve (pF curve), where $d\theta/dh$ is maximal [Van Genuchten, 1980]. This inflection point is correlated with the soil texture. The Staring series [Wösten *et al.*, 1994] is coupled with the soil map of the Netherlands [Bakker & Schelling, 1989], and provides the α's for the 18 most frequently occurring soils in the Netherlands. The pressure-head (h) at the air-entry value equals -1/α.

From column experiments with different soils, Freijer [1994a,b] concluded that the air-filled porosity at the inflection point (α) of the water retention curve (pF curve), is well correlated with the lowest air-filled porosity where gas diffusion becomes relevant. In Figures 9 & 10 this is demonstrated for a sandy (KwC) and a clayey soil (HbAh); water retention curves are also shown, together with diffusibility curves.

* New equations have equation numbers in bold





Figures 9 & 10: *Measured and modelled soil diffusibilities: Q (left y-axis) as a function of air-filled porosity (ε). Water retention curves (WRC) according to Van Genuchten [1980] are displayed as well (right y-axis). The open circle refers to h = -1/α in the water retention curve. The left figure is for a sandy soil (KwC) and the right for a clayey soil (HbAh) [Freijer, 1994a,b].*

The height of the capillary transition boundary above the groundwater table at a certain steady upward flow depends on soil characteristics. It can be calculated from pressure profiles, which are unique for each soil [De Laat, 1980]. These pressure profiles give the relation between the height above the groundwater table (z) and the pressure-head (h) for different values of steady upward flow (Figure 12). In the Staring series [Wösten *et al.*, 1994] these curves are given for most soils occurring in the Netherlands. Finally this will give the height of the capillary transition boundary above the groundwater table.

According to the method described, and the following illustrative example, heights above the groundwater table of the capillary transition boundary can be assessed for 18 different soil types (Table 4).

Example

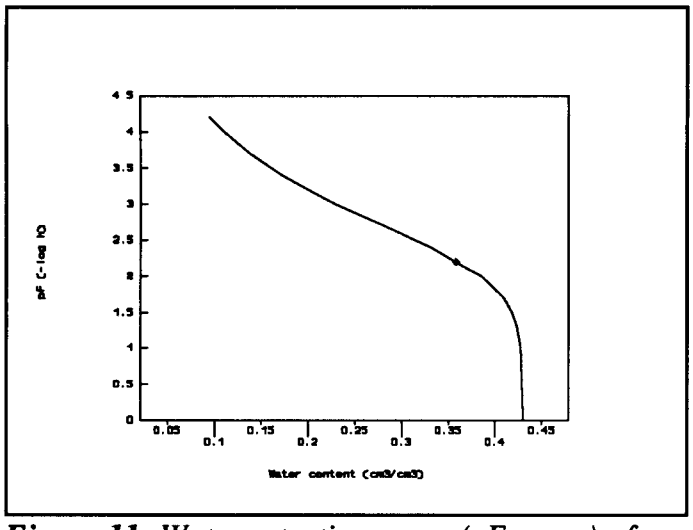


Figure 11: *Water retention curve (pF-curve) of clayey loam (Soil B9 from the Staring series). The open circle refers to the inflection point [adapted from Wösten et al., 1994].*

The standard soil in CSOIL is composed virtually of 10% organic matter and 25% clay. This is compared to a clayey loam (Soil B9) from the Staring series, Figure 11 shows the water retention curve. The parameter α = 0.0065 cm^{-1} for this soil (Table 4).

The pressure-head (h) can be calculated using α:
$h = -1/\alpha = -1/0.0065 = -153.8$ cm
(pF = 2.2).

The height above the groundwater table, corresponding to pF 2.2, equals 90 cm (Figure 12), according to the average Dutch capillary upward flow of 0.1 $cm.dag^{-1}$, for agricultural soils [Wösten, 1994]. Finally the capillary transition boundary is 90 cm above the groundwater table.

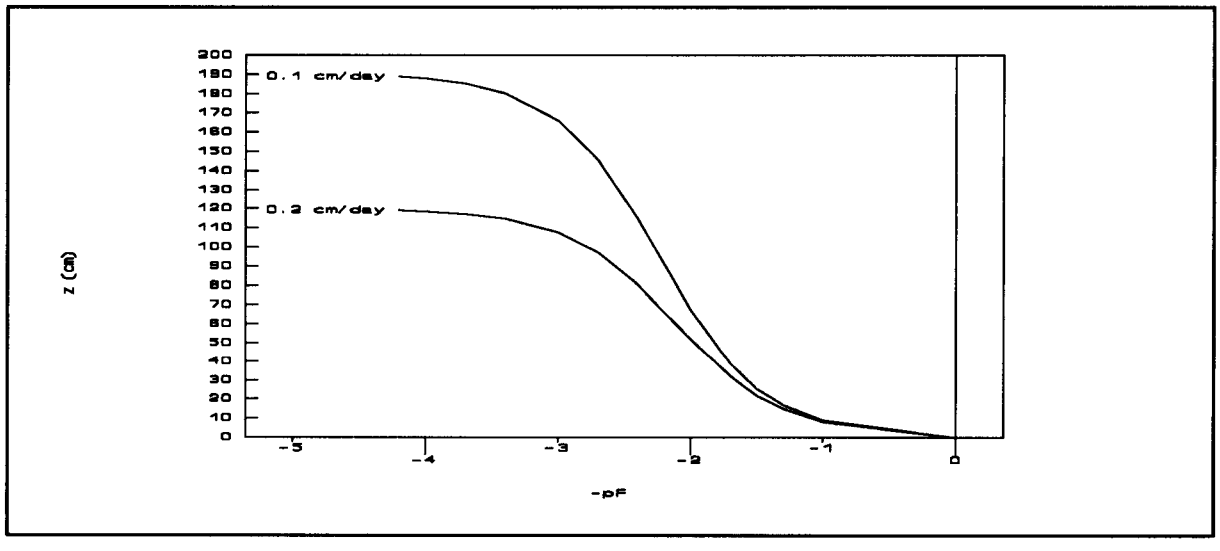


Figure 12: *Pressure profiles of clayey loam (Soil B9 from the Staring series), giving the relation between the height above the groundwater table (z) and the pressure-head, -pF (log h), for two different steady upward flows: 0.1 $cm.day^{-1}$ and 0.2 $cm.day^{-1}$ [adapted from Wösten et al., 1994].*

Table 4: *Height of the capillary transition boundary (z) above groundwater table , at head pressure (h = -1/α) corresponding with the air-entry value (α) for a steady upward water flow of 0.1 cm.day^{-1} for different soils from the Staring series [Wösten et al., 1994], according to the Dutch soil texture terminology [Bakker & Schelling, 1986]*

	SOIL	LOAM (%)	CLAY (%)	ORG. MATTER (%)	M50 (µm)	α (cm^{-1})	h (cm)	z (cm)
B1	very fine and medium fine sand, little loam	0-10		0-15	105-210	0.0249	-40.2	38.0
B2	very fine and medium fine sand, medium loamy	10-18		0-15	105-210	0.0227	-44.5	41.3
B3	very fine and medium fine sand, very loamy	18-33		0-15	105-210	0.0152	-65.8	60.9
B4	very fine and medium fine sand, extremely loamy	33-50		0-15	105-210	0.0163	-61.3	60.0
B7	light loam		8-12	0-15		0.0194	-51.5	44.5
B8	medium loam		12-18	0-15		0.0096	-104.2	64.6
B9	clayey loam		18-25	0-15		0.0065	-153.8	84.3
B10	light clay		25-35	0-15		0.0118	-84.7	35.3
B11	medium clay		35-50	0-15		0.0243	-41.2	20.3
B12	heavy clay		50-100	0-15		0.0532	-18.8	12.2
B14	silt loam	85-100		0-15		0.0051	-196.1	71.0
B16	sandy peat and peat		0-8	23-100		0.0134	-74.6	64.6
B17	peaty clay		8-100	16-45		0.0180	-55.6	27.3
B18	clayey peat		8-100	25-70		0.0197	-50.8	31.7

Texture in % of mineral parts, organic matter content in % of total soil, and the median of the sand fraction (M50) in µm.

The subdivision of Table 4 into different soil classes could be too differentiated, and does not correspond to the standard soil survey as described in NVN 5740 [NNI, 1991]. Because silt analyses are not part of standard soil survey, the following simplification is proposed: the groundwater table is assumed to be location specific, and the height above the groundwater table of the capillary transition boundary (z) is the arithmetic mean of soils within a class (Table 5). However, for more detailed soil research Table 4 can be applied.

Table 5: *Proposed (rounded off downward) height (z) of the capillary transition boundary above the groundwater table for a steady upward water flow of 0.1 cm.day^{-1} for different soil classes*

Soil	Arithmetic mean of: (see Table 4)	Clay (%)	Organic matter (%)	z (cm)
sand	B1,B2,B3,B4	< 8	0-15	50
loam	B7,B8,B9	8-25	0-15	60
clay	B10,B11,B12	25-100	0-15	20
peat	B16,B17,B18	0-100	16-100	40

Texture in % of mineral parts and organic matter content in % of total soil.

4.2 Concentration in soil air

The equilibrium concentration in the soil-air phase is calculated based on the concentration in the soil-water phase. It is assumed that equilibrium exists between the two phases. It is assumed that concentration in soil water at the capillary transition boundary is equal to the concentration in groundwater; the full capillary zone is thus considered as a well-mixed container.

Henry's Law states there is a linear relationship between the vapour pressure of a solute above its aqueous solution and the concentration in solution [Fetter, 1993]. Partitioning between air and water is accomplished by means of the Henry constant (H):

$$H = \frac{Vp}{S} \tag{49}$$

where: H = Henry's constant [$Pa.m^3.mol^{-1}$]
Vp = vapour pressure [Pa]
S = solubility [$mol.m^{-3}$]

Both, vapour pressure and solubility are highly temperature dependent. The vapour pressure and solubility used in the CSOIL set of formulas [Van den Berg, 1995] are empirically derived at 20°C (293 K), whereas in the Netherlands the average standard soil temperature is 10° C (283 K). Therefore these values can be corrected for temperature. Derivation of the temperature corrections are given in Appendix 2.

The dimensionless Henry's constant (K_{lw}) is:

$$K_{lw} = \frac{H}{R\,T} \tag{50}$$

where K_{lw} = air—water partitioning constant or dimensionless Henry constant [($mol.m^{-3}$ air)/($mol.m^{-3}$ water)][-]
H = Henry's constant [$Pa.m^3.mol^{-1}$]
R = gas constant [8.3144 $Pa.m^3.mol^{-1}.K^{-1}$]
T = temperature [K]

Karimi *et al.* [1987] have reported that where substances may move in soils by molecular diffusion, both in the vapour phase and in the solution phase, the relative importance of each mechanism is determined by the relative magnitude of the concentration in air and the concentration in the solution phase. Compounds with dimensionless Henry's constant (K_{lw}) >> 10^{-4} will diffuse mainly in the vapour phase, and those with K_{lw}'s << 10^{-4} will diffuse primarily in the solution phase.

At the capillary transition boundary the concentration in soil air (C_{sa}) can be derived from the concentration in soil water (C_{sw}) by using this dimensionless Henry's constant K_{lw}:

$$C_{sa} = K_{lw} * C_{sw} \tag{51}$$

where C_{sa} = concentration in soil air [$g.m^{-3}$]
C_{sw} = concentration in soil water [$g.m^{-3}$]
K_{lw} = air—water partitioning constant or dimensionless Henry constant [($mol.m^{-3}$ air)/($mol.m^{-3}$ water)][-]

In addition, Section 4.6.8 describes a situation where the full capillary zone cannot be considered as a well-mixed container.

4.3 Diffusion in soil air

Calculation of diffusion fluxes in soil air are modified due to the introduction of the groundwater table and the capillary transition boundary. Revised equations for diffusion of volatile compounds from soil to surface and from soil to the crawl space of a house are presented.

The diffusion coefficient in free air (D_a), based on Grahams Law [Sawyer & McCarty, 1989], can be calculated based on molecular mass [Van den Berg, 1995]:

$$D_a = 0.036 \sqrt{\frac{76}{M}} \tag{52}$$

where: D_a = diffusion coefficient in free air [$m^2.h^{-1}$]
M = molecular mass [$g.mol^{-1}$]

The effective diffusion coefficient in soil air (D_{sa}) depending on the volume fraction of soil air (V_a), the porosity ($1-V_s$) and correction for tortuosity, is calculated by using the Millington-Quirk equation [Jury *et al.*, 1983]:

$$D_{sa} = V_a^{10/3} \frac{D_a}{(1-V_s)^2} \tag{53}$$

where: D_{sa} = diffusion coefficient in soil air [$m^2.h^{-1}$]
D_a = diffusion coefficient in free air [$m^2.h^{-1}$]
V_a = volume fraction soil air [-]
V_s = volume fraction solid phase [-]

For calculation of the diffusion flux the following conditions are assumed: maximum concentration of the contaminant in the soil is assumed at the capillary transition boundary; as upper boundary condition, that concentration in the crawl space and at soil surface is negligibly low (zero) in comparison to the concentration in soil air; concentrations do not change with time, and finally, the concentration decreases from the capillary transition boundary to the crawl space. Under these conditions Fick's first law of diffusion is applicable.

When convective air fluxes are not considered, the diffusion flux of volatile compounds from soil to soil surface is [Van den Berg, 1995]:

$$Jd_{ss} = D_{sa} \frac{C_{sa}}{dp} \tag{54}$$

where: Jd_{ss} = diffusion flux from soil to soil surface [$g.m^2.h^{-1}$]
D_{sa} = diffusion coefficient in soil air [$m^2.h^{-1}$]
C_{sa} = concentration in soil air at depth dp [$g.m^{-3}$]
dp = average depth of contaminant [m]

Average depth of the contaminant is assumed to be at the capillary transition boundary.

$$dp = dg - z \tag{55}$$

where: dp = average depth of contaminant [m]
dg = depth of groundwater table [m]
z = height of capillary transition boundary above groundwater table [m]

For calculation of the diffusion flux of volatile compounds from soil to crawl space, when convective air fluxes are not considered, Equation (54) is changed into Equation (56):

$$Jd_{sc} = D_{sa} \frac{C_{sa}}{L_s} \tag{56}$$

where: Jd_{sc} = diffusion flux from soil to crawl space [$g.m^2.h^{-1}$]
D_{sa} = diffusion coefficient in soil air [$m^2.h^{-1}$]
C_{sa} = concentration in soil air at depth dp [$g.m^{-3}$]
L_s = length of soil column [m]

The length of the soil column L_s is:

$$L_s = dp - dc \tag{57}$$

where: L_s = length of soil column [m]
dp = average depth of contaminant [m]
dc = depth of crawl space beneath soil surface [m]

When convective air fluxes are considered, equations for diffusion and convection have to be combined and integrated, giving a total transport (Equation (74); Section 4.5.1).

4.4 Pressure-driven vapour flow

Volatile soil contaminants can enter a house by convective and diffusive transport mechanisms [Ferguson *et al.*, 1995]. In the open capillary zone diffusion will take place predominantly in soil air, diffusion in soil water is of minor importance [Glotfelty & Schomburg, 1991]. Diffusion in soil air has been described in Section 4.3. In a house convective transport dominates over diffusive transport [Nazaroff *et al.*, 1985]. Outdoor (background concentrations) and indoor sources (smoking, paints, domestic chemicals, et cetera) of contaminants, and temporal pressure differences due to wind, are not considered.

4.4.1 Flow of air

Figure 13 depicts a schematic diagram of a Dutch house, situated on a soil which is contaminated with volatile compounds. The house is considered as one large cube. A floor divides the house into the indoor space and a crawl space. The crawl space, partly above soil surface, is ventilated by several ventilation openings above the soil surface and is in contact with the outdoor air.

A mean negative indoor-air pressure relative to the soil air (soil-air pressure > indoor-air pressure) induces a pressure-driven vapour flow from soil air to indoor space. The pressure gradient induces contaminant fluxes from soil to indoor air via connected pore spaces, gaps and cracks. Pressure-driven vapour flow is most important during the winter months [Ferguson *et al.*, 1995] because pressure differences are relatively large due to great temperature differences between soil air and indoor space. Mean air pressure differences between the indoor space and the crawl space can be approximately 2 Pa, and mean air pressure differences between the crawl space and soil air can also be approximately 2 Pa [Nazaroff *et al.*, 1985; Put & Meijer, 1989], although large differences can be possible. Maximum air pressure difference between the indoor space and the crawl space is approximately 15 Pa, maximum air pressure difference between the crawl space and outdoor air is approximately 20 Pa [Put & Meijer, 1989].

Analogous to several studies [Gunst, 1981; Nazaroff *et al.*, 1985; Put & Meijer, 1989; Vaas *et al.*, 1991; Johnson & Ettinger, 1991; Ferguson *et al.*, 1995] the following air fluxes are considered. The suffixes **s**, **c**, **i** and **o** are used for **s**oil air, **c**rawl space, **i**ndoor space and **o**utdoor air respectively (Figure 13). Diffusion through the floor is not considered because convection transport through floor holes dominates [Ferguson *et al.*, 1995] and crawl spaces are not screened off from the soil.

With respect to the indoor space, ingoing air fluxes are those from the outdoor air to the indoor space (**Foi**) and from crawl space through the floor into the indoor space (**Fci**); the outgoing air flux is from the indoor space to the outdoor air (**Fio**).

With respect to the crawl space, ingoing air fluxes are those from soil air to crawl space (**Fsc**) and from the outdoor air to the crawl space (**Foc**); the outgoing air fluxes are those from crawl space to outdoor air (**Fco**) and from crawl space through the floor into the indoor space (**Fci**).

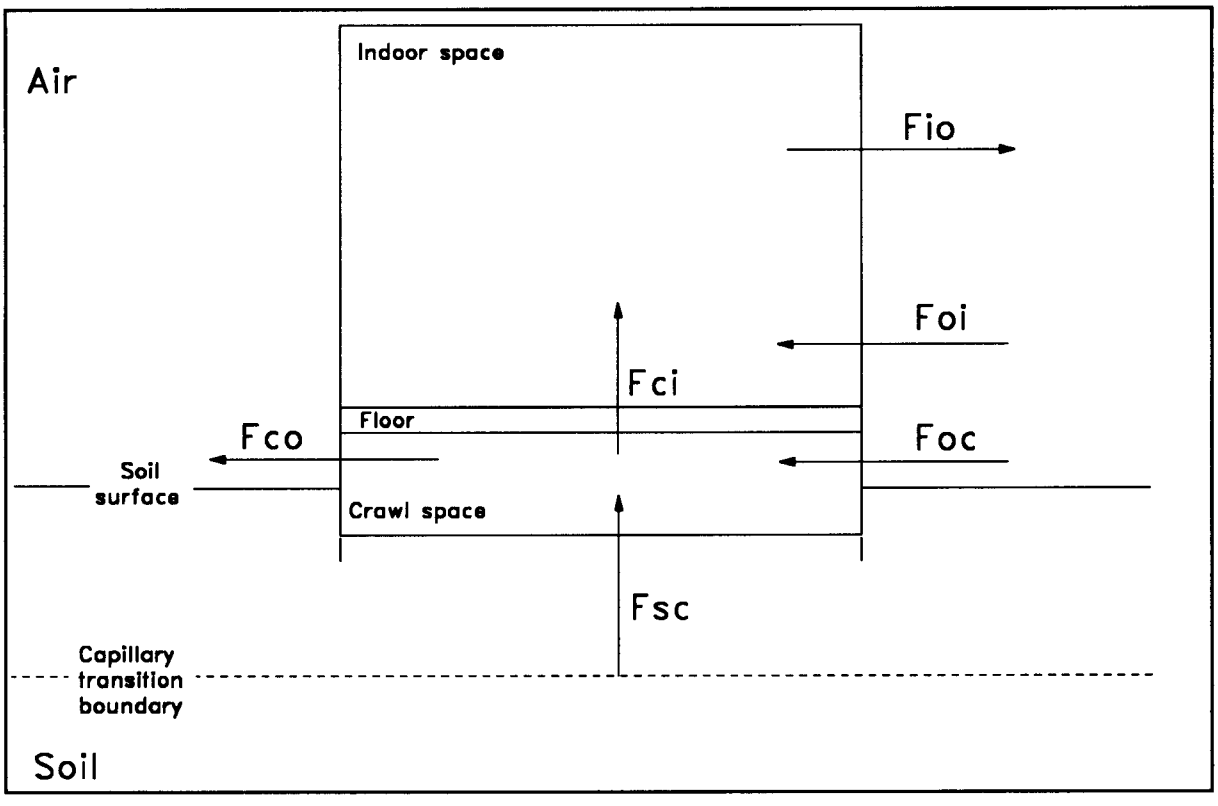


Figure 13: *Schematic diagram of a Dutch house. Arrows indicate relevant convective fluxes of air: Fsc = from soil to crawl space; Foc = from outdoor air to crawl space; Fco = from crawl space to outdoor air; Fci = from crawl space to indoor space through the floor; Foi = from outdoor air to indoor space; Fio = from indoor space to outdoor air.*

In the case of lower air pressures in indoor space than soil air and considering stationary transport of air, the following assumptions can be made:

1) On opposite sides of the house pressure differences can be important. These pressure differences cause horizontal air movements in the crawl space from ventilation openings to oppositely positioned ventilation openings. This can be seen as a basic crawl space ventilation, caused by dynamic pressure of wind.
2) The indoor air originates from the outdoor air and crawl space.
3) The air in the crawl space comes from the outdoor air and the soil air (see also Figure 13).

Thus, equilibrium exists between ingoing and outgoing fluxes of crawl space and indoor space.

$$\text{Crawl space:} \quad Foc + Fsc = Fci + Fco \tag{58}$$

$$\text{Indoor space:} \quad Foi + Fci = Fio \tag{59}$$

Sample calculations in Appendix 1 show that the air flux from the outdoor air through the ventilation openings to the crawl space (Foc) is much greater (factor 2000) than the air flux from soil to the crawl space (Fsc): Foc >> Fsc. Taking only air fluxes, not the contaminant fluxes, Equation (58) can be reduced to

$$Fci = Foc - Fco \tag{60}$$

However, note that air flux Fsc is very important in relation to the convective contaminant flux from soil to crawl space! It is assumed that the contaminant concentration in the outdoor air is negligible compared to the crawl space concentration. This is due to rapid dilution in the outdoor air by turbulent air movements. The air flow resistance from the floor is assumed to be higher than that from the walls (with ventilation openings) of the crawl space. As a consequence, flow of air from crawl space to indoor space is influenced by the construction characteristics of the house and the floor.

4.4.2 Convective flux from soil air to crawl space

In general, the flow of gas under a pressure gradient through a one-dimensional system can be described by Darcy's law [Koorevaar *et al.*, 1991]:

$$f_a = -K_a \frac{dp}{ds} \tag{61}$$

where f_a is the air flux in $m^3.m^{-2}.s^{-1}$, or $m.s^{-1}$, dp/ds the air pressure gradient in $Pa.m^{-1}$ and K_a the air conductivity in $m^2.Pa^{-1}.s^{-1}$. The air flux from soil to crawl space due to air pressure differences between soil air and crawl space can be calculated by using Darcy's law [Koorevaar *et al.*, 1991] (upward direction is positive):

$$Fsc = K_s \frac{\Delta p_{cs}}{L_s} \tag{62}$$

where: Fsc = air flux from soil to crawl space [$m^3.m^{-2}.h^{-1}$]
K_s = air conductivity of soil [$m^2.Pa^{-1}.h^{-1}$]
Δp_{cs} = air pressure difference between crawl space and soil [Pa]
L_s = length of soil column [m]

Air conductivity of soil (K_s) depends on the air permeability (κ) and the dynamic viscosity of air (η). Air permeabilities of different soils (Table 6) can be found in various references [Johnson & Ettinger, 1991; Ferguson *et al.*, 1995; Nazaroff *et al.*, 1988; Sextro *et al.*, 1986; Put & Meijer, 1989].

$$K_s = \frac{\kappa}{\eta} \tag{63}$$

where: K_s = air conductivity of soil [$m^2.Pa^{-1}.h^{-1}$]
κ = air permeability of soil [m^2]
η = dynamic viscosity of air [$6.0*10^{-9}$ Pa.h]

The length of the soil column L_s is analogue to diffusion from soil to crawl space:

$$L_s = dp - dc \tag{64}$$

where: L_s = length of soil column [m]
dp = average depth of contaminant [m]
dc = depth of crawl space beneath soil surface [m]

The corresponding convective contaminant flux through the soil, driven by a pressure gradient is closely related to the diffusion flux of volatile compounds from soil to crawl space. Therefore the equations for diffusion and convection have to be combined and integrated, giving a total transport equation (see Section 4.5.1).

***Table 6:** Permeability of soils at field capacity moisture content*

Soil type	Permeability κ (m^2)	Reference
coarse sand	10^{-10}	c;d;e
medium sand	$10^{-10.5}$	a;b
fine sand	$10^{-11.5}$	a;b
silty sand	$10^{-12.5}$	a;b
silt	$10^{-13.5}$	a;b
clay	10^{-16}	c;d;e

a: Johnson & Ettinger, 1991; **b**: Ferguson *et al.*, 1995; **c**: Nazaroff *et al.*, 1988; **d**: Sextro *et al.*, 1986; **e**: Put & Meijer, 1989.

4.4.3 Convective flux from crawl space to indoor space

The air flux from crawl space through the floor into the indoor space, due to air pressure differences between crawl space and indoor space, can be calculated by using Darcy's law. If floor thickness is equal to L_f then Equation (61) may be written as:

$$Fci = K_f \frac{\Delta p_{ic}}{L_f} \tag{65}$$

where: Fci = air flux from crawl space through the floor into indoor space [$m^3.m^{-2}.h^{-1}$]
Δp_{ic} = air pressure difference between indoor space and crawl space [Pa]
K_f = air conductivity of floor [$m^2.Pa^{-1}.h^{-1}$]
L_f = floor thickness [m]

Convection of air from crawl space to indoor air occurs through gaps, cracks and holes in the floor. Convection of air through the floor is simplified to flow of air through tubes of uniform radius. Combining Poiseulle's law for laminar flow in cylindrical tubes (micro scale) and Darcy's law (macro scale) [Koorevaar *et al.*, 1991] yields the air conductivity of the floor K_f (for derivation, see Appendix 1):

$$K_f = \frac{\varepsilon}{\tau^2} \frac{r^2}{8\eta} \tag{66}$$

where: K_f = air conductivity of floor [$m^2.Pa^{-1}.h^{-1}$]
ε = air-filled porosity of floor [$m^3.m^{-3}$]
τ = tortuosity [$m.m^{-1}$]
r = average radius of tube [m]
η = dynamic viscosity of air [Pa.h]

It can be assumed that tortuosity equals 1 for a floor, Equation (66) is then reduced to:

$$K_f = \frac{\varepsilon r^2}{8\eta} \tag{67}$$

The air-filled porosity of floor (ε) can be expressed as fraction of floor occupied by openings (f_{of}).

$$\varepsilon = f_{of} = \frac{A_{of}}{A_f} \tag{68}$$

where: ε = air-filled porosity of floor [$m^3.m^{-3}$]
f_{of} = fraction of openings in floor [$m^2.m^{-2}$]
A_{of} = total area of openings in floor [m^2]
A_f = area of floor [m^2]

The average radius (r) of the openings is:

$$r = \sqrt{\frac{f_{of}}{n\pi}} \tag{69}$$

where: r = average radius of openings in floor [m]
f_{of} = fraction of openings in floor [$m^2.m^{-2}$]
n = number of openings per floor area [m^{-2}]

The number of openings per floor area (n) can be calculated by:

$$n = \frac{N}{A_f} \tag{70}$$

where: n = number of openings per floor area [m^{-2}]
N = total number of openings in floor [-]
A_f = area of floor [m^2]

Combining Equations (65),(67),(68) and (69) gives the final expression for Fci, the air flux from crawl space through the floor into indoor space:

$$Fci = \frac{f_{of}^{\,2}}{n\pi * 8\eta} \frac{\Delta p_{ic}}{L_f} \tag{71}$$

where: Fci = air flux from crawl space through the floor into indoor space [$m^3.m^{-2}.h^{-1}$]
f_{of} = fraction of openings in floor [$m^2.m^{-2}$]
η = dynamic viscosity of air [Pa.h]
n = number of openings per floor area [m^{-2}]
Δp_{ic} = air pressure difference between indoor space and crawl space [Pa]
L_f = floor thickness [m]

The corresponding contaminant flux from crawl space to indoor space is:

$$Jc_{ci} = Fci * C_{ca} \tag{72}$$

where: Jc_{ci} = convective contaminant flux from crawl space to indoor space [$g.m^{-2}.h^{-1}$]
Fci = air flux from crawl space through the floor into indoor space [$m^3.m^{-2}.h^{-1}$]
C_{ca} = concentration in crawl space air [$g.m^{-3}$]

4.5 Concentration in air

Concentration in the air of crawl space and indoor space can be calculated by using the total contaminant flux from soil to crawl space, air-exchange rates of the spaces, and dimensions of the crawl and the indoor space.

4.5.1 Crawl space air concentration

The concentration in the crawl space air depends on the total contaminant flux from soil to crawl space and the air-exchange rate of the crawl space. Basic horizontal crawl space ventilation due to dynamic pressure of wind, and vertical air movements from crawl space to indoor space due to temperature caused air pressure differences largely contribute to the total air-exchange rate of the crawl space (see Figure 13).

The total contaminant flux from soil to crawl space is a combination of the convective flux and the diffusive flux. The convective and diffusive contaminant fluxes are closely related and influence each other [Massmann & Farrier, 1992]. Diffusion and convection of volatile compounds in soils cannot be considered as two parallel transport routes. Therefore the equations for diffusion and convection have been combined and integrated, assuming stationary transport (for derivation, see Appendix 4), giving a total transport equation of volatile contaminants from soil to crawl space (J1):

$$J1 = \frac{-Fsc\ (C_{sa} - C_0 * \exp\ (\frac{-Fsc}{D_{sa}} L_s\ )}{\exp\ (\frac{-Fsc}{D_{sa}} L_s\ ) - 1} \qquad (73)$$

where:
- J1 = total contaminant flux from soil to crawl space [$g.m^{-2}.h^{-1}$]
- Fsc = air flux from soil to crawl space [$m^3.m^{-2}.h^{-1}$]
- C_{sa} = concentration in soil air at depth dp [$g.m^{-3}$]
- C_0 = concentration in air at surface [$g.m^{-3}$]
- L_s = length of soil column [m]
- D_{sa} = diffusion coefficient in soil air [$m^2.h^{-1}$]

The negligibly low (zero) concentration at the surface (C_0) in comparison to the concentration in soil air is stated as upper boundary condition. Equation (73) can then be reduced to:

$$J1 = \frac{-Fsc * C_{sa}}{\exp\left(\frac{-Fsc}{D_{sa}} L_s\right) - 1} \tag{74}$$

where: J1 = total contaminant flux from soil to crawl space [$g.m^{-2}.h^{-1}$]
Fsc = air flux from soil to crawl space [$m^3.m^{-2}.h^{-1}$]
C_{sa} = concentration in soil air at depth dp [$g.m^{-3}$]
L_s = length of soil column [m]
D_{sa} = diffusion coefficient in soil air [$m^2.h^{-1}$]

When the convective flux of soil air does not occur, diffusion is the only driving force for transport of volatile compounds from soil to crawl space. In this case the air flux from soil to crawl space (Fsc) is negligibly low. If Fsc approaches zero (for example taken as Fsc = $1.0*10^{-9}$ $m^3.m^{-2}.h^{-1}$), Equation (74) becomes similar to the diffusion flux from soil to crawl space (Figure 14) and will show a linear soil-air concentration profile.

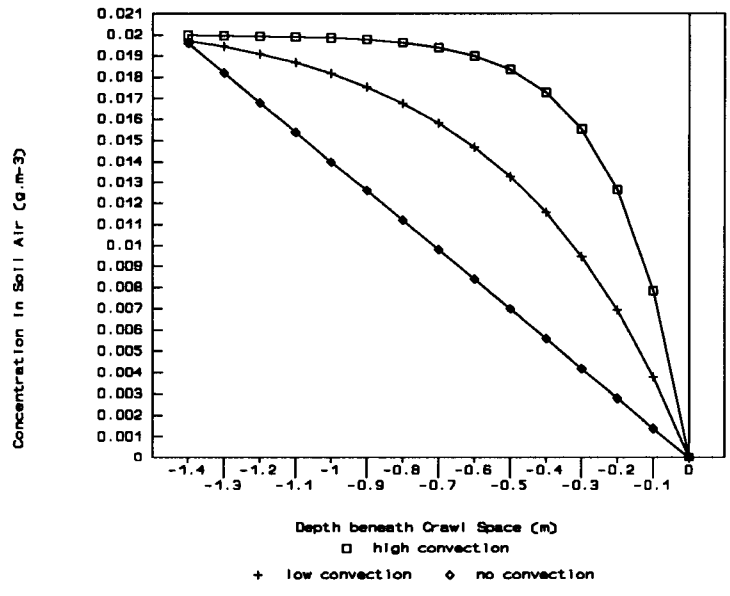


Figure 14: *Concentration profile in soil air beneath a crawl space for three different situations: High convection (Fsc = 0.05 $m^3.m^{-2}.h^{-1}$, D_{sa} = 0.01 $m^2.h^{-1}$, J1 = 0.001 $g.m^{-2}.h^{-1}$); Low convection (Fsc = 0.02 $m^3.m^{-2}.h^{-1}$, D_{sa} = 0.01 $m^2.h^{-1}$, J1 = 0.00042 $g.m^{-2}.h^{-1}$); No convection (Fsc = $1*10^{-9}$ $m^3.m^{-2}.h^{-1}$, D_{sa} = 0.01 $m^2.h^{-1}$, J1 = 0.00014 $g.m^{-2}.h^{-1}$).*

Rearangment of Equation (74) and substituting "optional depth beneath the crawl space in open capillary zone" (do) for "length of soil column" (L_s) gives:

$$C_{sa,do} = \frac{J1 * \exp\left(\frac{-Fsc}{D_{sa}}\, do\right) - J1}{-Fsc} \qquad (75)$$

where: $C_{sa,do}$ = concentration in soil air at optional depth do [$g.m^{-3}$]
J1 = total contaminant flux from soil to crawl space [$g.m^{-2}.h^{-1}$]
Fsc = air flux from soil to crawl space (positive upwards) [$m^3.m^{-2}.h^{-1}$]
do = optional depth beneath crawl space in open capillary zone (positive downwards) [m]
D_{sa} = diffusion coefficient in soil air [$m^2.h^{-1}$]

Using above described equation it is possible to calculate the soil air concentration at a certain depth beneath the crawl space in the open capillary zone.

The concentration in the crawl space can be calculated on the basis of total contaminant flux from soil to crawl space, the air-exchange rate and dimensions of the crawl space. The air-exchange rate of the crawl space depends on the (vertical) air flux from crawl space to indoor space, the basic (horizontal) crawl space ventilation due to dynamic pressure of wind and the dimensions of the crawl space.

$$vv_c = \frac{vr_{c,b} + Fci\ A_f}{V_c} \qquad (76)$$

where: vv_c = air-exchange rate of crawl space [h^{-1}]
$vr_{c,b}$ = basic ventilation rate of crawl space [$m^3.h^{-1}$]
V_c = volume of crawl space [m^3]
Fci = air flux from crawl space through the floor into indoor space [$m^3.m^{-2}.h^{-1}$]
A_f = surface area of floor [m^2]

Fast *et al.* [1987] did extensive research on measurements of air-exchange rates of more than a hundred crawl spaces in the Netherlands at different locations. The geometrically weighted mean air-exchange rate is 1.05 as can be distilled from Fast *et al.* [1987].

Using Equations (74) and (76) and assuming the surface area of the floor to equal that of the crawl space, the concentration in crawl space can be calculated:

$$C_{ca} = J1\ \frac{A_f}{V_c\ vv_c} \qquad (77)$$

where: C_{ca} = concentration in crawl space air [$g.m^{-3}$]
J1 = total contaminant flux from soil to crawl space [$g.m^{-2}.h^{-1}$]
A_f = surface area of floor [m^2]
V_c = volume of crawl space [m^3]
vv_c = air-exchange rate of crawl space [h^{-1}]

4.5.2 Indoor-air concentration

Precise calculation of the indoor-air concentration is very difficult. Ventilation is critically important in determining vapour concentrations in indoor living spaces [Ferguson *et al.*, 1995; Salthammer *et al.*, 1995]. Building construction of houses have a large impact on ventilation properties (e.g. characteristics of floor). Relative temperature and air pressure differences, open doors and windows cause large temporal differences in ventilation of indoor spaces. Therefore ventilation is expressed as an average air-exchange rate. Indoor-air concentration can then be calculated analogue to Equation (77) of Section 4.5.1:

$$C_{ia} = Jc_{ci} \frac{A_f}{V_i \, vv_i} \tag{78}$$

where: C_{ia} = indoor-air concentration [$g.m^{-3}$]
Jc_{ci} = total contaminant flux from crawl space to indoor space [$g.m^{-2}.h^{-1}$]
A_f = surface area of floor [m^2]
V_i = volume of indoor space [m^3]
vv_i = air-exchange rate of indoor space [h^{-1}]

Average air-exchange rates can be deduced from the required ventilation properties for houses. These are laid down in the Dutch Building Regulations [Bercken, 1992]. The advisory report of the Health Council [Biersteker *et al.*,1984], and the NEN 1087 norm [NNI, 1991] require a minimal ventilation rate (vr_i) of 75 $m^3.h^{-1}$ for the indoor living space. The air-exchange rate (vv_i) of indoor space is related to above-mentioned ventilation rate and the total air flux (Fci) from crawl space through the floor into the indoor space:

$$vv_i = \frac{vr_i + Fci \, A_f}{V_i} \tag{79}$$

where: vv_i = air-exchange rate of indoor space [h^{-1}]
vr_i = ventilation rate of indoor space [$m^3.h^{-1}$]
V_i = volume of indoor space [m^3]
Fci = air flux from crawl space through the floor into indoor space [$m^3.m^{-2}.h^{-1}$]
A_f = surface area of floor [m^2]

4.6 Specific cases

The VOLASOIL model quantifies the indoor-air concentration for a house situated on homogeneous soil with groundwater contaminated with volatile compounds for the Dutch situation. The model can be used for different specific cases.

Apart from building construction characteristics and conditions relating to the house, other conditions which influence the indoor-air concentration are the location and the physical appearance of the contaminant. Higher groundwater tables are related to higher concentrations in the crawl space (and the indoor space). This is because the distance between the soil vaporization level and the crawl space decreases. Contaminants which appear as pure chemicals (also floating layers) cause high concentrations in soil air of the open capillary zone. This is due to the fact that a more-or-less saturated contaminant vapour is found on top of pure chemicals. Also, the capillary transition boundary above the groundwater table between the full (saturated) and open (unsaturated) capillary zones plays an important role.

The specific cases described are combinations of the location and the physical appearance of the contaminant in the soil that lead to different transport processes. These specific cases are linked with VOLASOIL on different places of the model. The general VOLASOIL model structure is shown in Figure 8. For every application one should assess which specific case is valid. It does not make sense to sum calculated indoor-air concentrations of different cases (e.g. groundwater contamination and pure contaminant in the open capillary zone). Independent calculations should be made in order to assess the highest potential risk. The application of the volatilization model is described in the following specific cases:

- Groundwater contamination; well-mixed container (4.6.1)
- Contaminated groundwater in crawl space (4.6.2)
- Floating soil-contaminant layer (4.6.3)
- Groundwater in crawl space and a floating soil-contaminant layer (4.6.4)
- Pure contaminant in open capillary zone (4.6.5)
- Very low groundwater table (4.6.6)
- Sinking soil-contaminant layer; well-mixed container (4.6.7)
- Contaminant source beneath the groundwater table; not a well-mixed container (4.6.8)

4.6.1 Groundwater contamination; well-mixed container

It is assumed that the contaminant is dissolved in groundwater and the groundwater is considered as a well-mixed container (see Figure 15), it can be considered as a homogeneous groundwater contamination.

Concentrations in groundwater samples are assumed to represent the concentration in this well-mixed container. This specific case is extensively presented in Sections 4.1 to 4.5.

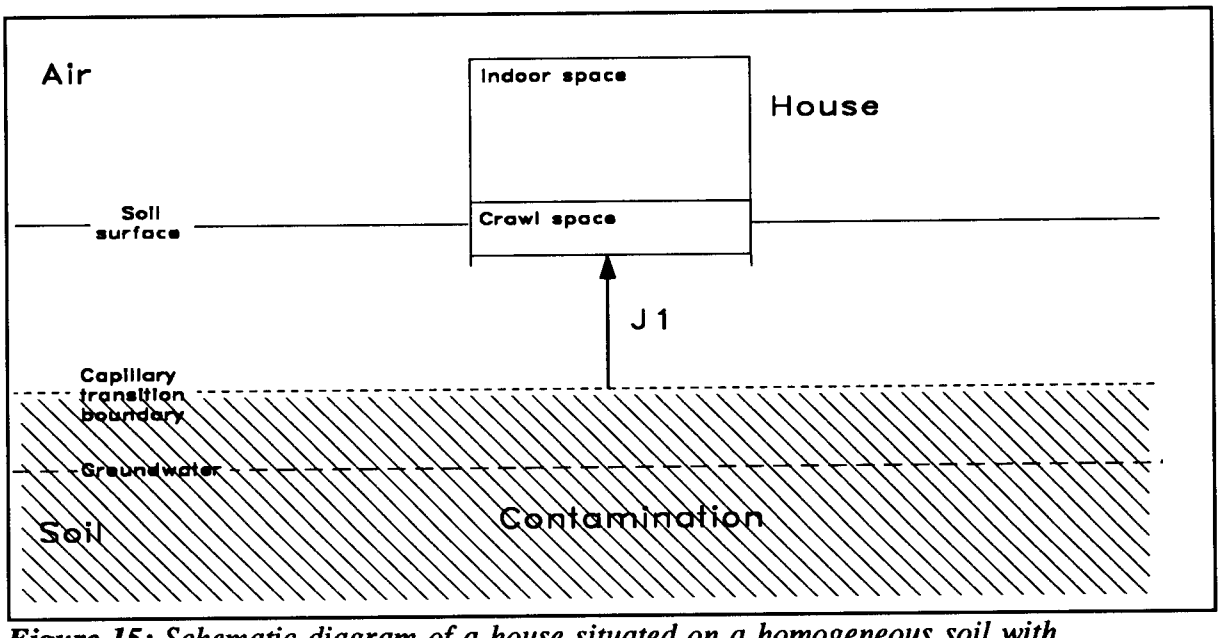


Figure 15: Schematic diagram of a house situated on a homogeneous soil with contaminated groundwater, assuming a well-mixed container (J1 = total contaminant flux from soil to crawl space).

4.6.2 Contaminated groundwater in crawl space

When a very high groundwater table exists, contaminated groundwater can rise by capillary flow up into the crawl space (Figure 16). The theoretical depth of the capillary transition boundary is than equal to (or higher than) the depth beneath soil surface of the crawl space. Concentration in crawl space (C_{ca}) is then calculated by using the dimensionless Henry coefficient K_{lw}:

$$C_{ca} = K_{lw} * C_{sw} \tag{80}$$

where: C_{ca} = concentration in crawl space air [g.m^{-3}]
Klw = air—water partitioning constant or dimensionless Henry constant [-]
C_{sw} = concentration in soil water [g.m^{-3}]

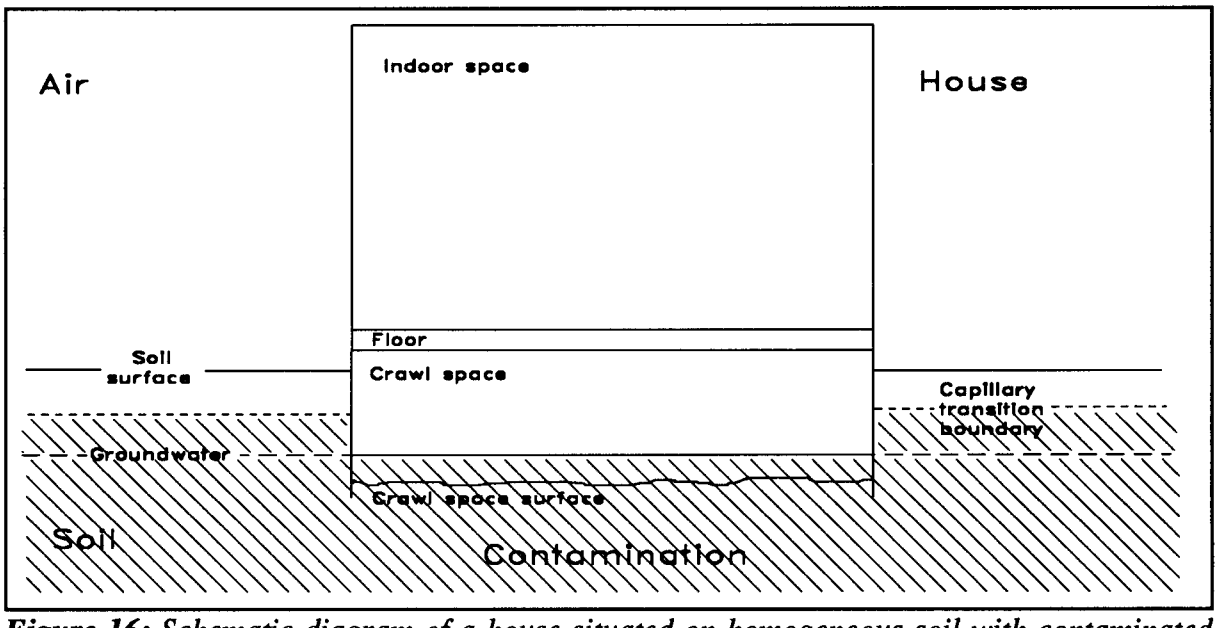


Figure 16: *Schematic diagram of a house situated on homogeneous soil with contaminated groundwater in the crawl space.*

4.6.3 Floating soil-contaminant layer

When a floating soil-contaminant layer occurs, pure contaminant liquid floats on the groundwater (Figure 17). It is assumed that the floating layer is situated at the capillary transition boundary (= dp, average depth of contaminant). At depth of the capillary transition boundary, the soil air is saturated with the contaminant, meaning that the soil-air concentration will be calculated on the basis of the maximum contaminant vapour density (Vd) at 283 Kelvin [Fetter, 1993]:

$$Vd = \frac{Vp\ M}{R\ T} \tag{81}$$

where: Vd = vapour density [$g.m^{-3}$]
Vp = vapour pressure [Pa]
M = molecular weight [$g.mol^{-1}$]
R = gas constant [8.3144 $Pa.m^3.mol^{-1}.K^{-1}$]
T = temperature [K]

In this case, the concentration in soil air is considered equal to the vapour density:

$$C_{sa} = Vd \tag{82}$$

where: C_{sa} = concentration in soil air [$g.m^{-3}$]
Vd = vapour density [$g.m^{-3}$]

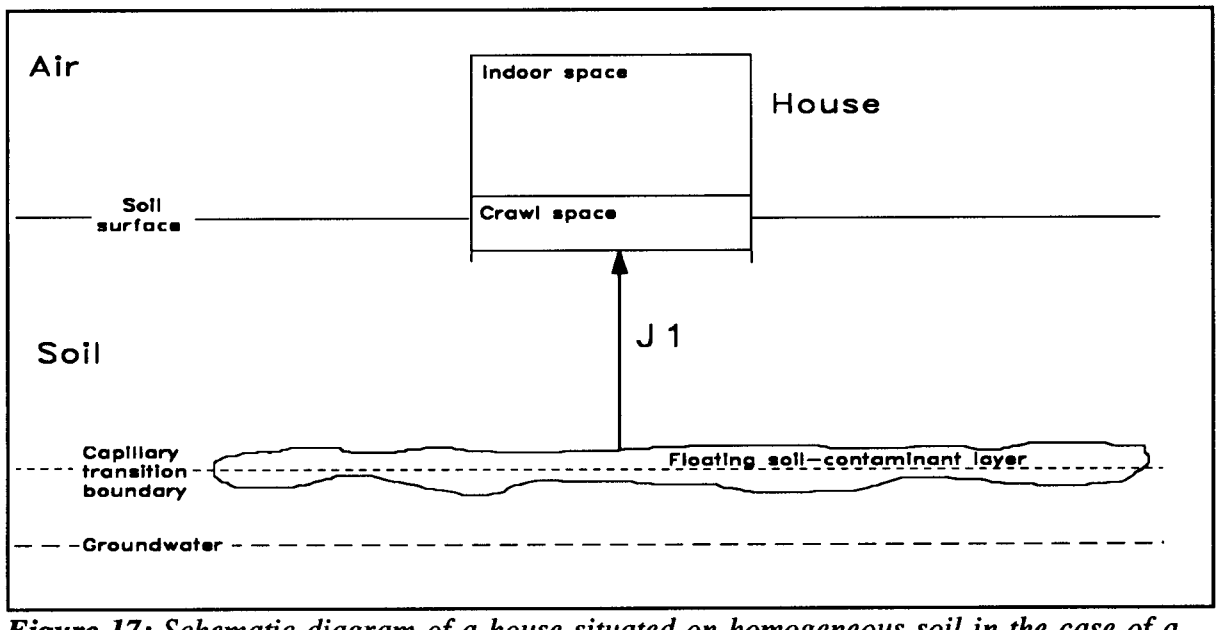


Figure 17: Schematic diagram of a house situated on homogeneous soil in the case of a floating soil-contaminant layer (J1 = total contaminant-flux form soil to crawl space).

4.6.4 Groundwater in crawl space and a floating soil-contaminant layer

A floating soil-contaminant layer can exist in combination with a theoretical depth of the capillary transition boundary equal to (or higher than) depth beneath soil surface of the crawl space (Figure 18). The concentration in the crawl space is calculated by using Equation (83). The concentration in the crawl space is then equal to the vapour density:

$$C_{ca} = Vd \tag{83}$$

where C_{ca} = Concentration in crawl space air [$g.m^{-3}$]
Vd = vapour density [$g.m^{-3}$]

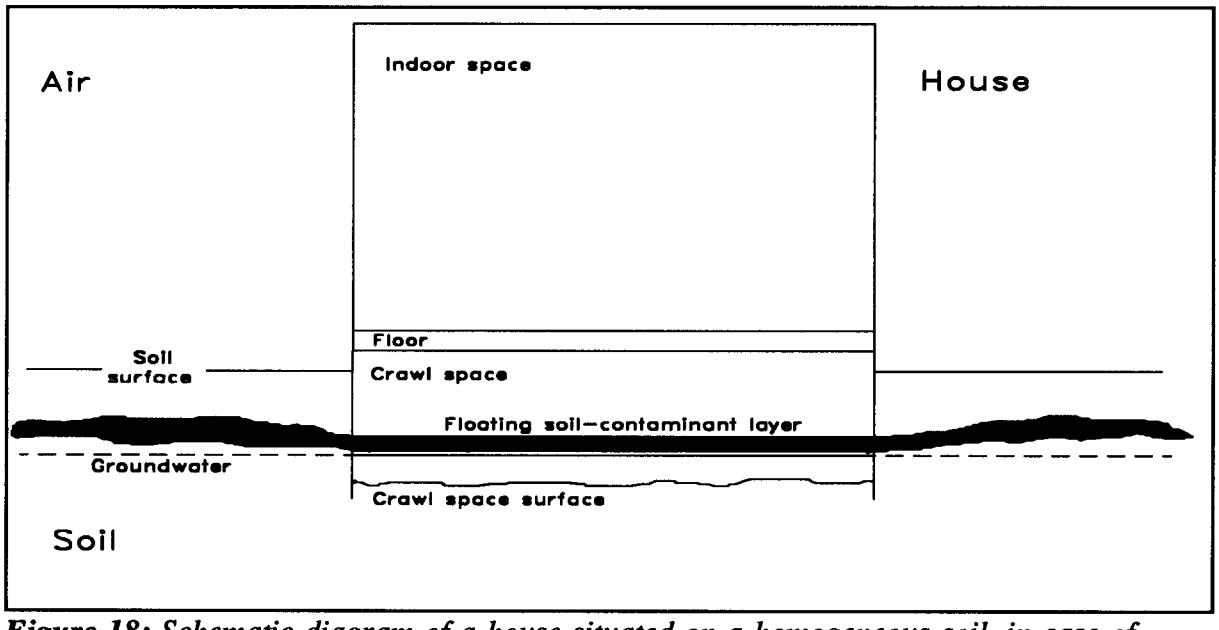


Figure 18: Schematic diagram of a house situated on a homogeneous soil, in case of groundwater and a floating soil-contaminant layer in the crawl space.

Waitz, *et al.* [1996]: The VOLASOIL risk assessment model based on CSOIL for soils contaminated with volatile compounds.

4.6.5 Pure contaminant in open capillary zone

Liquid soil contaminants heavier than water (e.g. tetrachloroethene) can be transported as pure product from soil surface to the groundwater. In the open capillary zone (unsaturated zone), vertical flow of liquid contaminants can be hampered by relatively impermeable layers of clay, peat and loam (aquitardes or aquicludes) [Appelo & Postma, 1993]. In that case a pure contaminant layer exists in the open capillary zone (Figure 19). The soil air above this layer is assumed to be saturated with the contaminant. Therefore, the soil-air concentration at the depth of this layer (= dp, average depth of contaminant) is calculated on the basis of the maximal contaminant vapour density (Vd) at 283 Kelvin [Fetter, 1993]:

$$Vd = \frac{Vp\ M}{R\ T} \tag{84}$$

where: Vd = vapour density [$g.m^{-3}$]
Vp = vapour pressure [Pa]
M = molecular weight [$g.mol^{-1}$]
R = gas constant [8.3144 $Pa.m^3.mol^{-1}.K^{-1}$]
T = temperature [K]

The concentration in soil air is considered equal to the vapour density:

$$C_{sa} = Vd \tag{85}$$

where: C_{sa} = concentration in soil air [$g.m^{-3}$]
Vd = vapour density [$g.m^{-3}$]

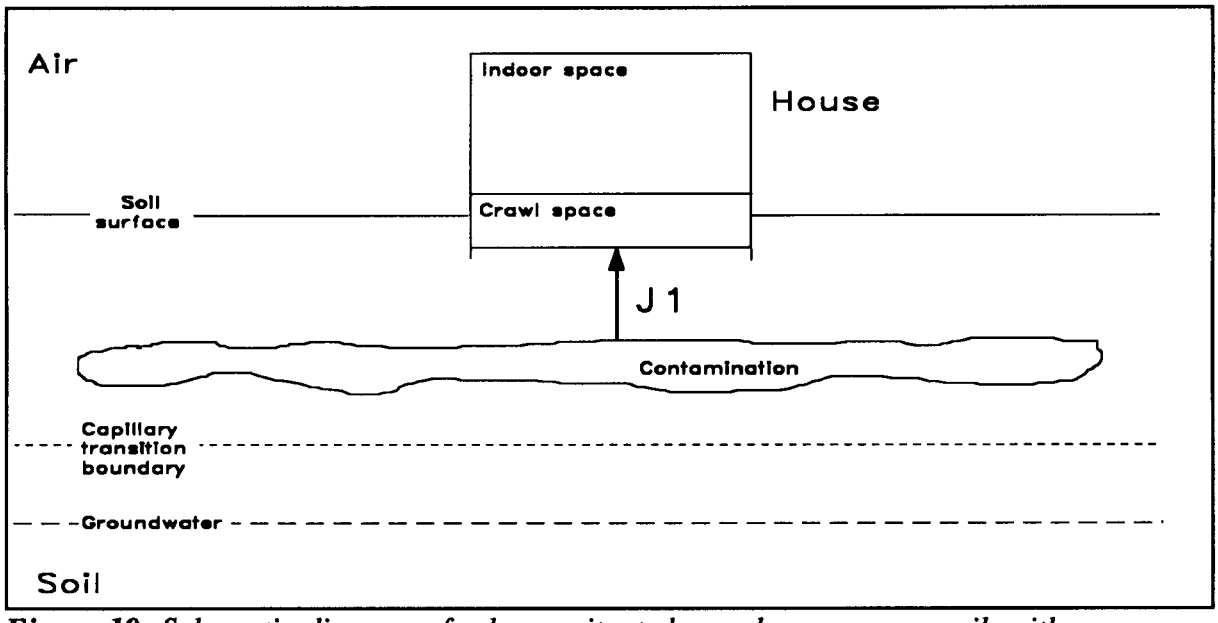


Figure 19: *Schematic diagram of a house situated on a homogeneous soil, with pure contaminant in the open capillary zone (J1 = total contaminant-flux from soil to crawl space).*

Waitz, *et al.* [1996]: The VOLASOIL risk assessment model based on CSOIL for soils contaminated with volatile compounds.

4.6.6 Very low groundwater table

When a very low groundwater table exists, groundwater concentrations could be difficult to achieve, against high expenses. In this case the concentration in soil air at a certain depth (dp = average depth of contaminant) above the groundwater table can be used as VOLASOIL input (Figure 20).

The concentration in soil air can be achieved in two ways:
1) soil-air measurements;
2) calculation from the total soil content (C_t) by using fugacity calculations. Note that, this method might not give accurate predictions.

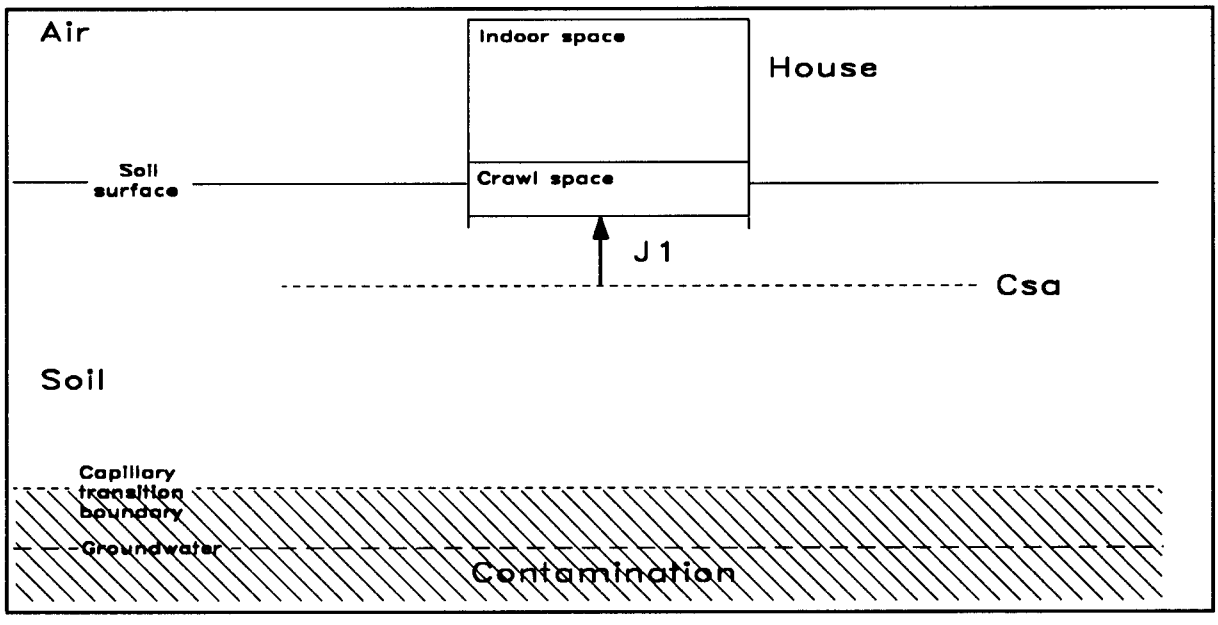


Figure 20: *Schematic diagram of a house situated on a homogeneous soil in the case of very deep contaminated groundwater (J1 = total contaminant flux from soil to crawl space; C_{sa} = concentration in soil air at a certain depth).*

4.6.7 Sinking soil-contaminant layer (well-mixed container)

When a sinking soil-contaminant layer occurs (Figure 21), pure liquid contaminant may exist beneath the upper groundwater zone above an aquitarde or aquiclude. Layers of clay, peat and loam (which are considered impermeable) are termed aquicludes or, when almost impermeable, aquitards [Appelo & Postma, 1993].

Under steady-state conditions, the concentration in groundwater is in equilibrium with the sinking contaminant layer, which consits of pure product. It is assumed that the concentration in soil water at the capillary transition boundary is equal to the concentration in groundwater (well-mixed container), but lower than the concentration in the sinking soil-contaminant layer. Therefore measured groundwater concentrations can be used for application of VOLASOIL. In order to calculate the contaminant fluxes, the average depth of the contaminant (dp) must be equal to the depth of the capillary transition boundary.

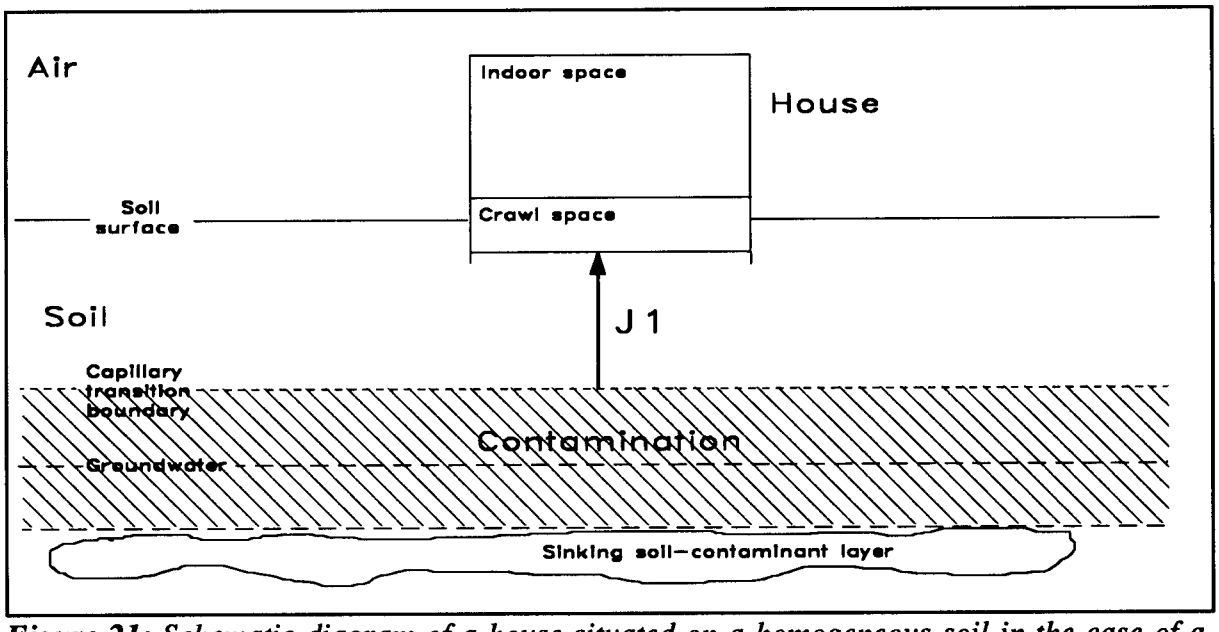


Figure 21: Schematic diagram of a house situated on a homogeneous soil in the case of a sinking soil-contaminant layer, assuming a well-mixed container (J1 = total contaminant flux from soil to crawl space).

4.6.8 Contaminant source beneath the groundwater table (a not well-mixed container)

If a distinct contaminant source exists beneath the groundwater table, transport fluxes in the open capillary zone will be limited by the contaminant supplying flux in the saturated zone. The total contaminant flux from a contaminant source beneath the groundwater table to the crawl space can be seen as a flow transport problem through two media placed in series with different resistances. The full capillary zone can in this case not be considered as a well-mixed container. It is assumed that flow of water does not occur (no water evaporation flux); only diffusion of contaminants in groundwater and full capillary zone is relevant (Figure 22).

Diffusion coefficients of compounds in free water (D_w), are calculated on the basis of Graham's Law [Sawyer & McCarty, 1989] using the following equation. This simple equation is only dependent on molecular weight [Van den Berg, 1995].

$$D_w = 3.6*10^{-6} \sqrt{\frac{76}{M}} \tag{86}$$

where: D_w = diffusion coefficient in free water [$m^2.h^{-1}$]
M = molecular weight [$g.mol^{-1}$]

The effective diffusion coefficient depends on the volume fraction of soil water (V_w), the porosity ($1-V_s$), and a correction for tortuosity by using the Millington-Quirk equation [Jury *et al.*, 1983]. Using the diffusion coefficient in free water, and assuming that total porosity is occupied by water, effective diffusion coefficients in the soil-water phase is derived by:

$$D_{sw} = V_w^{10/3} \frac{D_w}{(1 - V_s)^2} \tag{87}$$

where: D_{sw} = diffusion coefficient in soil water [$m^2.h^{-1}$]
D_w = diffusion coefficient in free water [$m^2.h^{-1}$]
V_w = volume fraction soil-water phase [0.4]
V_s = volume fraction solid-soil phase [0.6]

The diffusion flux of volatile compounds in groundwater from a source under the groundwater table to the capillary transition boundary is:

$$Jd_{gw} = D_{sw} \frac{C_{sw,gw} - C_{sw,ctb}}{L_{gw}} \quad (88)$$

where: Jd_{gw} = diffusion flux in groundwater from a source beneath groundwater table to the capillary transition boundary [$g.m^2.h^{-1}$]
D_{sw} = diffusion coefficient in soil water [$m^2.h^{-1}$]
$C_{sw,gw}$ = concentration in soil water at source depth in groundwater [$g.m^{-3}$]
$C_{sw,ctb}$ = concentration in soil water at capillary transition boundary [$g.m^{-3}$]
L_{gw} = diffusion length of groundwater column [m]

It is assumed that at the capillary transition boundary, concentration in soil air (C_{sa}) is in equilibrium with concentration in soil water ($C_{sw,ctb}$). In the open capillary zone, transport of volatile compounds from soil to crawl space is a combination of the convective and the diffusive fluxes.

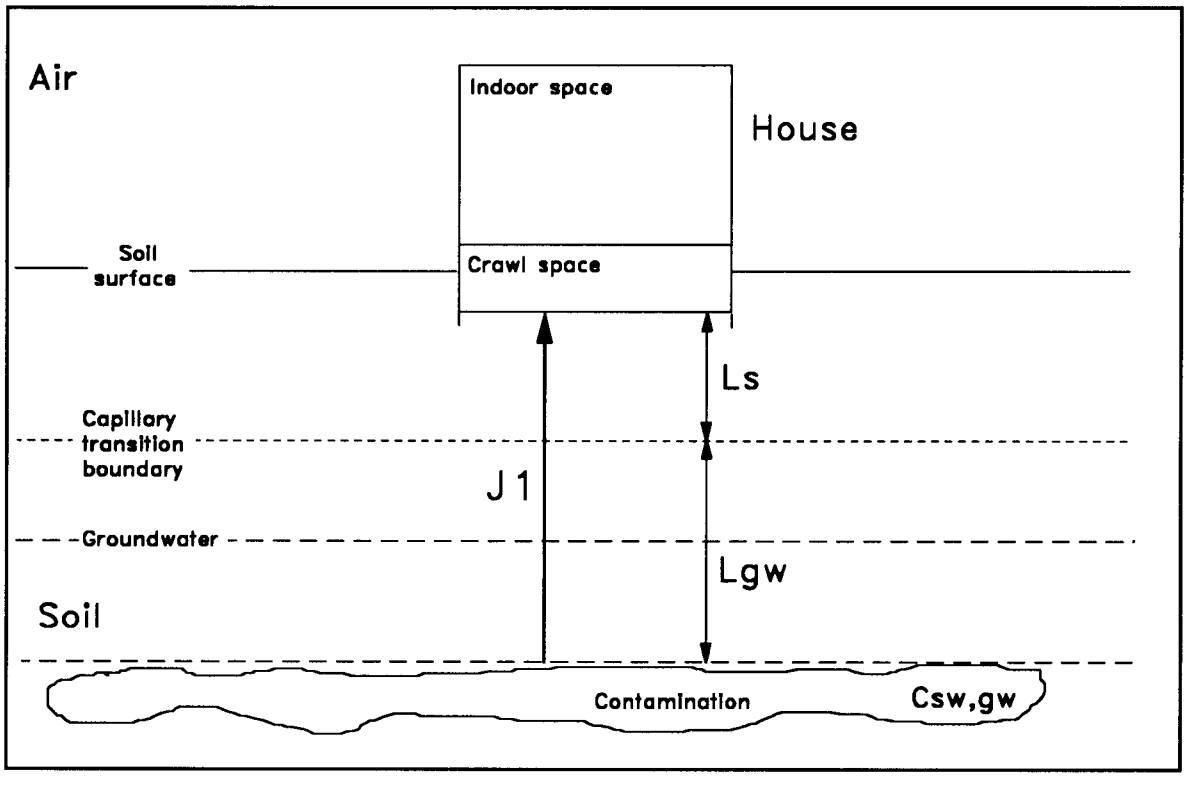


Figure 22: Schematic diagram of a house situated on a homogeneous soil in the case of a contaminant source beneath the groundwater table; a not well-mixed container (J1 = total contaminant flux from soil to crawl space; L_s = length of soil column; L_{gw} = diffusion length of groundwater column; $C_{sw,gw}$ = concentration in soil water at source depth in groundwater).

The total contaminant flux from a contaminant source beneath the groundwater table to the crawl space can be seen as a flow transport problem through two media placed in series with different resistances (Figure 22). Equations (88), (74), and (51) can be combined and assuming stationary transport gives the total contaminant flux from a contaminant source beneath the groundwater table to the crawl space (for derivation, see Appendix 4):

$$J1 = \frac{-Fsc\ K_{lw}\ C_{sw,gw}}{\exp\left(-Fsc\ \frac{L_s}{D_{sa}}\right) - 1 - Fsc\ K_{lw}\ \frac{L_{gw}}{D_{sw}}} \qquad (89)$$

where:
- J1 = total contaminant flux from soil to crawl space [$g.m^{-2}.h^{-1}$]
- Fsc = air flux from soil to crawl space [$m^3.m^{-2}.h^{-1}$]
- $C_{sw,gw}$ = concentration in soil water at source depth in groundwater [$g.m^{-3}$]
- K_{lw} = air—water partitioning constant or dimensionless Henry constant [(mol.m^{-3} air)/(mol.m^{-3} water)][-]
- L_s = length of soil column [m]
- L_{gw} = diffusion length of groundwater column [m]
- D_{sa} = diffusion coefficient in soil air [$m^2.h^{-1}$]
- D_{sw} = diffusion coefficient in soil water [$m^2.h^{-1}$]

The diffusion length of groundwater column L_{gw} is calculated by:

$$L_{gw} = ds_{gw} + z \qquad (90)$$

where:
- L_{gw} = diffusion length of groundwater column [m]
- ds_{gw} = depth of contaminant source beneath groundwater table [m]
- z = height of capillary transition boundary above groundwater table [m]

When the convective flux of soil air does not occur, diffusion is the only driving force for transport of volatile compounds from soil to crawl space. In this case the air flux from soil to crawl space (Fsc) is negligibly low. If Fsc approaches zero (for example set at $1.0*10^{-9}$ $m^3.m^{-2}.h^{-1}$), Equation (89) becomes only dependent on diffusion fluxes in groundwater and soil air.

Note, that if the contaminant source is located between the groundwater table and the capillary transition boundary, ds_{gw} will have a negative value, which is physically possible.

5 APPLICATION OF VOLASOIL

The proposed VOLASOIL volatilization model (Chapter 4) seems to be complicated, but VOLASOIL is in practice straightforward in its application.

The VOLASOIL model can be used for site-specific risk assessment because flexible combination of modeling and measurements is possible and calculations can be made for several specific contamination cases. The model could also be a decision-support tool within the framework of the priority for soil clean-up (Soil Protection Act), construction permit issues (Housing Act), and soil quality management (spatial planning).

In a case study, the proposed volatilization model VOLASOIL is applied for an hypothetical soil, contaminated with a volatile compound. Since parameter values are chosen conforming to CSOIL application for derivation of Intervention Values, these can be seen as default parameter values. The case study is followed by a list of recommended default and input parameter values.

5.1 Case study

Molecular weight	78 $g.mol^{-1}$
Solubility	22.788 $mol.m^{-3}$
Vapor pressure	10133 Pa

Physicochemical proporties of benzene

Conditions

Consider a house situated on a sandy soil with a groundwater table at 2.00 m depth. The groundwater is contaminated with benzene (see box for physicochemical properties). The concentration in groundwater is 15 $mg.L^{-1}$ (C_{sw} = 15.0 $g.m^{-3}$). A schematic view of the house is given in Figure 23. It has been estimated that ten gaps per floor area occupy 0.0005 m^2 of total floor area.

What is the estimated indoor-air concentration?

The following items have to be calculated for estimating the risk due to volatile soil contaminants:

1) concentration in soil air
2) diffusion in soil air
3) convective air flux from soil to crawl space
4) crawl space air concentration
5) convective flux from crawl space to indoor space
6) concentration in indoor space
7) comparing with TCA

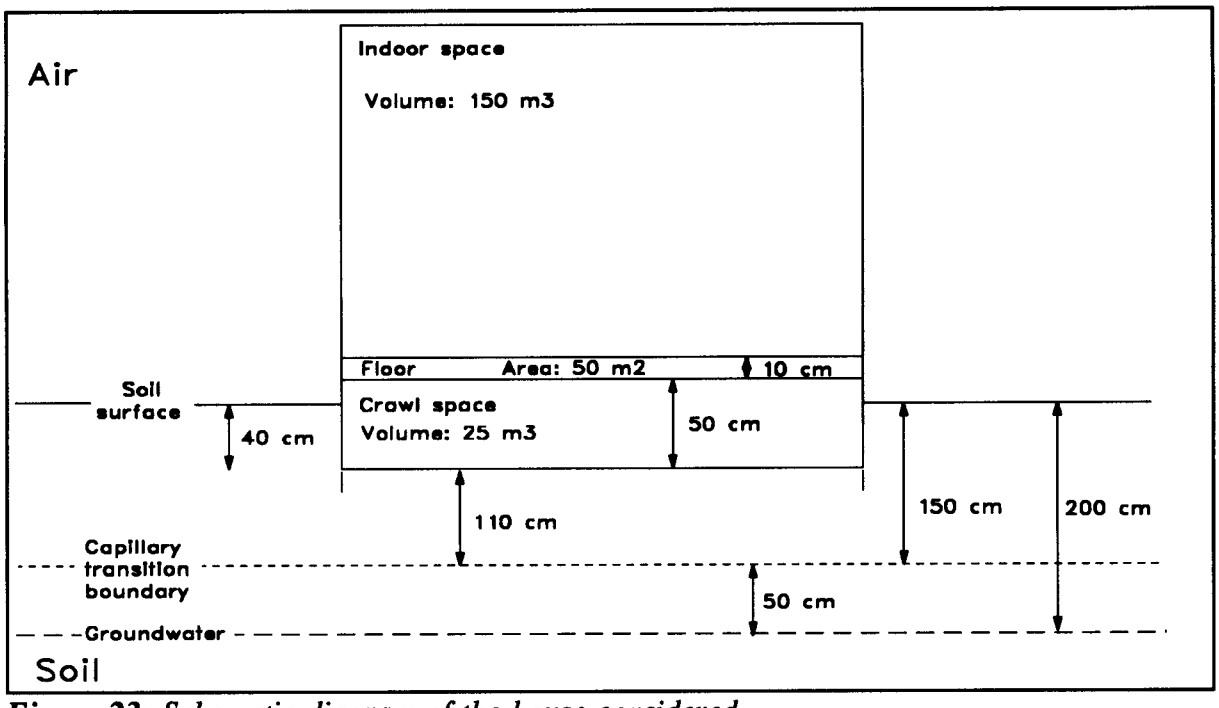


Figure 23: Schematic diagram of the house considered.

For sandy soils the capillary transition boundary is (according to Table 5) 50 cm above the groundwater table (z = 0.5 m). The groundwater table is at 2.00 m depth (dg = 2 m), Therefore average depth of contaminant is considered at 1.50 m (dp = 1.5 m) beneath soil surface (Figure 23):

$$dp = dg - z = 2.00 - 0.50 = 1.50\ m \tag{91}$$

The average depth of benzene beneath soil surface (dp = 1.50 m) and the depth of crawl space beneath the soil surface (dc = 0.4 m) are used for calculation of the length of the soil column (L_s):

$$L_s = dp - dc = 1.50 - 0.40 = 1.10\ m \tag{92}$$

Values for solubility and vapour pressure are given at 20°C. Because default CSOIL soil temperature is 10°C, solubility and vapour pressure are corrected according to the temperature correction by using method A (see Appendix 2). The corrected solubility is 17.242 mol.m^{-3}, and the corrected vapour pressure is 6031 Pa.

Concentration in soil air

Henry's constant is:

$$H = \frac{Vp}{S} = \frac{6031}{17.242} = 349.8\ Pa\ m^3\ mol^{-1} \tag{93}$$

Using the gas constant (R = 8.3144 $Pa.m^3.mol^{-1}.K^{-1}$), and temperature (283 K), the dimensionless Henry's constant (K_{lw}) is:

$$K_{lw} = \frac{H}{R\ T} = \frac{349.8}{8.3144 * 283} = 0.149 \tag{94}$$

Concentration in soil water at the capillary transition boundary is assumed to be equal to the concentration in groundwater; the full capillary zone is thus considered as a well-mixed container. The concentration in soil air (C_{sa}) at the capillary transition boundary, is derived from the concentration in soil water by using the dimensionless Henry's constant K_{lw}:

$$C_{sa} = K_{lw} * C_{sw} = 0.149 * 15.0 = 2.24\ g\ m^{-3} \tag{95}$$

Diffusion in soil air

The diffusion coefficient of benzene in free air (D_a) is:

$$D_a = 0.036 \sqrt{\frac{76}{M}} = 0.036 \sqrt{\frac{76}{78}} = 0.036\ m^2\ h^{-1} \tag{96}$$

Using the standard CSOIL equations with default soil parameters (Table 1), the effective diffusion coefficient in soil air (D_{sa}) is:

$$D_{sa} = V_a^{10/3} \frac{D_a}{(1 - V_s)^2} = 0.2^{10/3} \frac{0.036}{(1 - 0.6)^2} = 0.0010\ m^2\ h^{-1} \tag{97}$$

Convective air flux from soil to crawl space

The air permeability κ of a medium sandy soil is $10^{-10.5}$ m^2 (Table 6) and dynamic viscosity of air η is $6.0*10^{-9}$ Pa.h; air conductivity of soil (K_s) is:

$$K_s = \frac{\kappa}{\eta} = \frac{1*10^{-10.5}}{6.0*10^{-9}} = 5.3*10^{-3}\ m^2\ Pa^{-1}\ h^{-1} \qquad (98)$$

Assuming an air pressure difference between the crawl space and the soil air of 2 Pa, the air flux from soil to crawl space (Fsc) is:

$$Fsc = K_s \frac{\Delta p_{cs}}{L_s} = 5.3*10^{-3} \frac{2}{1.10} = 9.6*10^{-3}\ m^3\ m^{-2}\ h^{-1} \qquad (99)$$

Crawl space air concentration

The total benzene flux (J1) from soil to crawl space is calculated by the combined diffusion/convection equation. In this equation the following values are used: the air flux from soil to crawl space (Fsc = $9.6*10^{-3}$ $m^3.m^{-2}.h^{-1}$), concentration in soil air at the capillary transition boundary (C_{sa} = 2.24 $g.m^{-3}$), effective diffusion coefficient in soil air (D_{sa} = 0.001 $m^2.h^{-1}$) and the length of soil column (L_s = 1.10 m: the depth of crawl space beneath the soil surface is 0.4 m and average depth of benzene, calculated at 1.50 m beneath soil surface).

$$J1 = \frac{-Fsc*C_{sa}}{\exp(\frac{-Fsc}{D_{sa}}L_s)-1} = \frac{-9.6*10^{-3}*2.24}{\exp(\frac{-9.6*10^{-3}}{0.0010}1.1)\ -1} = 21.4*10^{-3} g m^{-2} h^{-1} \qquad (100)$$

The air-exchange rate of the crawl space (vv_c) is calculated by using the air flux from crawl space through the floor into indoor space (Fci = 0.066 $m^3.m^{-2}.h^{-1}$, calculated under following header), the basic ventilation rate of crawl space ($vr_{c,b}$ = 20 $m^3.h^{-1}$) and default floor (floor area = 50 m^2) and crawl space (volume crawl space = 25 m^3) characteristics:

$$vv_c = \frac{vr_{c,b} + Fci * A_f}{V_c} = \frac{20 + 0.066 * 50}{25} = 0.93\ h^{-1} \qquad (101)$$

Fast *et al.* [1987] did extensive research on measurements of air-exchange rates of more than a hundred crawl spaces in the Netherlands at different locations. The above calculated air-exchange rate of the crawl space (vv_c) is comparable with the geometrically weighted mean air-exchange rate (1.05) as can be distilled from Fast *et al.* [1987].

The benzene concentration in the crawl space (C_{ca}) is calculated by:

$$C_{ca} = J1 \frac{A_f}{V_c * vv_c} = 21.4*10^{-3} \frac{50}{25 * 0.93} = 0.046\ g\ m^{-3} \qquad (102)$$

Convective flux from crawl space to indoor space

In total, ten gaps (N = 10) occupy 0.0005 m^2 (A_{of} = 0.0005 m^2) of the total floor area (A_f = 50 m^2). The number of openings in floor per floor area (n) is:

$$n = \frac{N}{A_f} = \frac{10}{50} = 0.2\ m^{-2} \qquad (103)$$

The fraction of openings in the floor (f_{of}) is calculated by:

$$f_{of} = \frac{A_{of}}{A_f} = \frac{0.0005}{50} = 0.00001 \qquad (104)$$

The air pressure difference between the crawl space and indoor space (Δp_{cs}) is assumed to be 2 Pa, dynamic air viscosity $6.0*10^{-9}$ Pa.h and floor thickness 10 cm. The air flux (Fci) from crawl space through the floor into indoor space is:

$$Fci = \frac{f_{of}^2}{n\pi * 8\eta} \frac{\Delta p_{ic}}{L_f} = \frac{0.00001^2}{0.2\pi * 8 * 6.0*10^{-9}} \frac{2}{0.1} = 0.066\ m^3\ m^{-2}\ h^{-1} \qquad (105)$$

Note that in realistic cases the fraction of openings in floor (f_{of}) also influences the pressure difference between the crawl space and indoor space (Δp_{cs}). If f_{of} becomes very large, then Δp_{cs} will become smaller.

The corresponding benzene flux from crawl space to indoor space (Jc_{ci}) is:

$$Jc_{ci} = Fci * C_{ca} = 0.066 * 0.046 = 3.0*10^{-3}\ g\ m^{-2}\ h^{-1} \qquad (106)$$

Concentration in indoor space

Using a minimal (normal) indoor ventilation rate of 75 $m^3.h^{-1}$, an indoor space volume of 150 m^3, an air flux (Fci) from crawl space through the floor into indoor space of 0.066 $m^3.m^{-2}.h^{-1}$ and a floor area (A_f) of 50 m^2, the indoor air-exchange rate (vv_i) is calculated by:

$$vv_i = \frac{vr_i + Fci\ A_f}{V_i} = \frac{75 + 0.066 * 50}{150} = 0.52\ h^{-1} \qquad (107)$$

Harrje [1991] describes extensively the research of Grot & Clark, who did research on air-exchange rates of 266 houses in 14 different American cities; the data follows a log normal distribution. The above calculated indoor air-exchange rate can be considered as a realistic worse case, compared with the data of Grot & Clark [1981].

Finally, indoor-air concentration (C_{ia}) of benzene is:

$$C_{ia} = Jc_{ci} \frac{A_f}{V_i * vv_i} = 3.0*10^{-3} \frac{50}{150 * 0.52} = 1.9*10^{-3}\ g\ m^{-3} \qquad (108)$$

Comparing with TCA

The Tolerable Concentration in Air (TCA) is $0.03*10^{-3}$ $g.m^{-3}$ [Koolenbrander, 1995].
The indoor-air concentration thus exceeds the TCA by a factor of 63:

$$C_{ia} = 1.9*10^{-3}\ g\ m^{-3} > TCA = 0.03*10^{-3}\ g\ m^{-3} \qquad (109)$$

Exceedance of the TCA means an unacceptably increased risk to humans.

5.2 Default and input values

The VOLASOIL model is rather flexible in its application. Recommended default and input parameter values are assessed on the basis of the literature, expert-guess/judgement and other models (see foregoing Chapters). In practice however, in many cases it should be necessary to measure or to determine the location-specific parameters. The necessary input values are correlated with physicochemical and toxicological properties of the contaminant, soil type, groundwater characteristics and building construction characteristics.

Default values

A_f	= area of floor	[50 m^2]
dc	= depth of crawl space beneath soil surface	[0.4 m]
L_f	= floor thickness	[0.1 m]
N	= total number of openings in floor	[10]
R	= gas constant	[8.3144 $Pa.m^3.mol^{-1}.K^{-1}$]
T	= temperature	[283 K]
V_a	= volume fraction soil air	[0.2]
V_c	= volume of crawl space	[25 m^3]
V_i	= volume of indoor space	[150 m^3]
$vr_{c,b}$	= basic ventilation rate of crawl space	[20 $m^3.h^{-1}$]
V_s	= volume fraction solid phase	[0.6]
V_w	= volume fraction soil-water phase	[0.2]
Δp_{cs}	= air pressure difference between crawl space and soil	[2 Pa]
Δp_{ic}	= air pressure difference between indoor space and crawl space	[2 Pa]
η	= dynamic viscosity of air	[$6.0*10^{-9}$ Pa.h]

Input values

A_{of} = total area of openings in floor [0.005 m^2]

Quality of floor	A_{of} [m^2]	Fraction of openings in floor (f_{of}) [$m^2.m^{-2}$]
bad	0.005	0.0001
normal	0.0005	0.00001
good	0.00005	0.000001

C_{sw}	= concentration in soil water	[mol.dm^{-3} or g.m^{-3}]
dg	= depth of groundwater table	[m]
M	= molecular weight	[g.mol^{-1}]
S	= solubility	[mol.m^{-3}]
TCA	= Tolerable Concentration in Air	[g.m^{-3}]

vr_i = ventilation rate of indoor space [m^3.h^{-1}]

Ventilation characteristics	Ventilation rate of indoor space (vr_i) [m^3.h^{-1}]
very bad	25
bad	50
normal	75
good	100
very good	150

Vp = vapour pressure [Pa]

z = height of capillary transition boundary above groundwater table (see also Tables 4 and 5) [m]

Soil	Clay [%]	Organic matter [%]	z [m]
sand	< 8	0-15	0.50
loam	8-25	0-15	0.60
clay	25-100	0-15	0.20
peat	0-100	16-100	0.40

κ = air permeability of soil (see also Table 6) [m^2]

Soil	Permeability κ [m^2]
coarse sand	10^{-10}
medium sand	$10^{-10.5}$
fine sand	$10^{-11.5}$
silty sand	$10^{-12.5}$
silt	$10^{-13.5}$
clay	10^{-16}

6 VOLASOIL SENSITIVITY AND UNCERTAINTY ANALYSES

VOLASOIL, a model which is based on literature studies, expert- guess/judgement and several models, can be a useful tool in the study of contamination problems. In order to allow VOLASOIL to be reliably used, it is imperative to perform a sensitivity and uncertainty analyses:

1) to clarify the crucial aspects of the model;
2) to get insight into uncertainties in the model output;
3) to know which of the model inputs needs to be quantified with a high level of accuracy.

This insight may be gained by performing sensitivity and uncertainty analyses based on a Monte Carlo-oriented approach, using the **UNCSAM** software package.

The **sensitivity analysis** is the study of the influence of variations in model parameters, boundary and initial conditions (model inputs) on selected model outputs; it gives insight into the behaviour of the model itself. The **uncertainty analysis** deals with the influence of real distributions of all these model inputs on selected model outputs; it provides insight into the combined effect of real distributions and model behaviour and in the uncertainties in the model outputs. **Implication** for individual model inputs can be achieved by combining sensitivity and uncertainty results.

6.1 UNCSAM analyses

Sensitivity and uncertainty analyses are carried out using the UNCSAM software package [Janssen *et al.*, 1992]. This package provides a standardized method for performing model analyses on a large variety of mathematical models on the basis of a Monte Carlo-oriented approach, using Latin Hypercube Sampling technique. Monte Carlo-based methods for sensitivity and uncertainty analysis rely on the fact that variations in model inputs can be described by specifying probability distributions, which reflect the variation of model input around a 'nominal' value. Sampling is performed from these distributions, resulting in a set of values for the various model inputs. The sampled model inputs are used to simulate model outputs. The further analyses consists of computing basic statistical information (means, percentiles and variances) and performing regression and correlation analyses to obtain insight into the contribution of the various model inputs to sensitivity and uncertainty of the model output. It should be stressed that the uncertainty in the model description is not considered.

The VOLASOIL model is programmed in a LOTUS-123 (version 2.3) spreadsheet. The sensitivity and uncertainty analyses have been carried out for an hypothetical situation. It is assumed that a house is situated on a homogeneous soil where groundwater is contaminated with benzene. Calculations with VOLASOIL are performed by using specific case A (groundwater contamination, well-mixed layer). Spatial variations are not considered. For example the probability distribution of concentration in soil water is only due to measurement uncertainty.

With respect to the sensitivity and uncertainty analysis, the relevant VOLASOIL model output is the calculated indoor-air concentration. Six model input parameters used in this study are assumed not to be relevant in respect to uncertainty and have been considered as fixed values (Table 7). The other model input parameters have been considered as relevant uncertain parameters, of which probability distributions are specified (Table 8).

For each VOLASOIL run, sampling by UNCSAM was performed from these distributions, resulting in a set of values for the various model inputs (Appendix 7: file 951116-a.bam). In total 200 VOLASOIL runs were performed with the sampled model inputs.

Note that UNCSAM analyses were carried out with VOLASOIL version 1.5, whereas due to the iterative process of modelling a revised version is presented in the report (Chapter 4). Differences are relatively minor. What is important is that the model input "number of openings per floor area" (n) is replaced by "total number of openings in floor" (N). Analyses results for N would be comparable to n.

Table 7: *Fixed values of VOLASOIL model inputs used for sensitivity and uncertainty analyses as performed with the UNCSAM software package on the basis of a Monte Carlo-oriented approach (model input description in Section 5.2)*

Model inputs	Unit	Value
R	$Pa.m^3.mol^{-1}.K^{-1}$	8.3144
T	K	283
V_a	-	0.2
V_s	-	0.6
V_w	-	0.2
η	Pa.h	6.0E-9

***Table 8:** Probability distributions of VOLASOIL model inputs used for sensitivity and uncertainty analyses as carried out with the UNCSAM software package (model input description in Section 5.2)*

Model inputs	Unit	Distribution type	Distribution parameters
A_f	m^2	uniform	min = 25; max = 150
dc	m	normal	10th %tile = 0.30 90th %tile = 0.50
L_f	m	normal	5th %tile = 0.08 95th %tile = 0.12
n	m^{-2}	normal	10th %tile = 8 90th %tile = 12
V_c	m^3	normal	10th %tile = 20 90th %tile = 30
V_i	m^3	normal	10th %tile = 140 90th %tile = 160
$vr_{c,b}$	$m^3.h^{-1}$	logistic	median = 20; min = 1; max = 60 [a]
vr_i	$m^3.h^{-1}$	logistic	median = 75; min = 25; max = 150 [a]
Δp_{cs}	Pa	logistic	median = 2; min = 1E-09; max = 10 [a]
Δp_{ic}	Pa	logistic	median = 2; min = 1E-9; max = 15 [a]
A_{of}	m^2	uniform	min = 0.005; max = 0.050
C_{sw}	$g.m^{-3}$	normal	2.5th %tile = 27.00 97.5th %tile = 33.00
dg	m	normal	5th %tile = 1.40 95th %tile = 1.60
M	$g.mol^{-1}$	normal	mean = 78.11 variance = 5.00E-5
S	$mol.m^{-3}$	logistic	mean = 22.95226 variance = 0.01345 [a]
Vp	Pa	logistic	mean = 6294.7 variance = 14.71 [a]
z	m	uniform	min = 0.38; max = 0.60
κ	m^2	normal	1th %tile = 1.00E-13 99th %tile = 1.00E-11

[a]: based on non-transformed logistic values

6.2 Results

The results of sensitivity and uncertainty analyses, are strongly dependent on choice of specific case considered and the assumed probability distributions of the model inputs. Results of sensitivity and uncertainty analyses are focused on three model outputs:

1) concentration in soil air,
2) concentration in crawl space air,
3) concentration in indoor air.

The results of the sensitivity analysis are described only for the most important model output, the indoor-air concentration. The results of the uncertainty analysis are described for the three above-mentioned model outputs, but with emphasis on the modelled concentration in indoor air. Extended UNCSAM results of sensitivity and uncertainty analyses are given in Appendix 7.

6.2.1 Sensitivity analysis

The Normalized Regression Coefficient (NRC) is a suitable measure for expressing the relative sensitivity contribution in sensitivity analysis: it expresses the effect of relative changes with respect to average values, and is independent of the scale or dimension of the model inputs. The NRC is an expression of the fractional (i.e. relative) change of the model output due to a fractional change of a model input [Janssen *et al.*, 1992]. A NRC of for example 2, means that a relative 1% increase of a model input results in a 2% increase of the model output.

Table 9 presents the NRC of the model inputs in decreasing order. The table shows that physicochemical compound properties like molecular weight (M), vapour pressure (Vp) and solubility (S) are the most sensitive model inputs, followed by depth of groundwater table (dg) and the concentration in soil water (C_{sw}). The extremely large NRC of molecular weight is unrealistically high, this could be because of arithmetic rounding-off differences between the LOTUS-123 and UNCSAM software.

The least sensitive model inputs are in descending order: the number of openings in the floor (n), basic ventilation rate of crawl space ($vr_{c,b}$), air pressure difference between indoor space and crawl space (Δp_{ic}), floor thickness (L_f) and the total area of openings in floor (A_{of}).

Waitz, *et al.* [1996]: The VOLASOIL risk assessment model based on CSOIL for soils contaminated with volatile compounds.

Table 9: Ranked results of VOLASOIL sensitivity analysis

Model input		NRC	Rank
M	molecular weight	285	1
V_p	vapour pressure	-68.6	2
S	solubility	14.8	3
dg	depth of groundwater table	-1.77	4
C_{aw}	concentration in soil water	1.14	5
vr_i	ventilation rate of indoor space	-0.83	6
Δp_{cs}	air pressure difference between crawl space and soil	0.67	7
V_i	volume of indoor space	0.55	8
A_f	area of floor	0.54	9
κ	air permeability of soil	0.39	10
z	height of capillary transition boundary above groundwater table	0.35	11
dc	depth of crawl space beneath soil surface	0.31	12
V_c	volume of crawl space	-0.18	13
A_{of}	total area of openings in floor	0.15	14
L_f	floor thickness	0.10	15
Δp_{ic}	air pressure difference between indoor space and crawl space	0.06	16
$vr_{c,b}$	basic ventilation rate of crawl space	-0.05	17
n	number of openings per floor area	0.01	18

NRC = fractional change of calculated model output (indoor-air concentration) due to a fractional change of a model input

6.2.2 Uncertainty analysis

Results of the uncertainty analysis will be described with emphasis on the model inputs, followed by resulting distribution uncertainties of model outputs.

Model inputs

The Standardized Regression Coefficient (SRC) is a measure of the fraction of the uncertainty in the model output, which is contributed by a model input [Janssen *et al.*, 1992]. In Table 10 the SRC's of the model inputs are presented in decreasing order. The SRC can be used for calculation of the CTU. The CTU is the percentile contribution of a model input to the uncertainty of the model output [Janssen, 1995], and can be calculated by using:

$$CTU = SRC^2 * 100 \qquad (110)$$

Table 10 shows that the air pressure difference between crawl space and soil (Δp_{cs}), ventilation rate of indoor space (vr_i), and air permeability of soil (κ) make a large contribution to uncertainty of the model output, with respectively 60%, 10% and 2% contribution to uncertainty. As a result, attention should be focused on detailed identification of these parameters for improving the calculation of the indoor air.

Other model inputs contribute less than 1% to the uncertainty of the model output. These uncertainty contributions are so small, that the ranking order is of minor importance.

***Table 10:** Ranked results of uncertainty analysis of VOLASOIL*

Model	input	CTU (%)	SRC	Rank
Δp_{cs}	air pressure difference between crawl space and soil	60	0.772	1
vr_i	ventilation rate of indoor space	10	-0.318	2
κ	air permeability of soil	1.7	0.129	3
S	solubility	0.34	0.058	4
dg	depth of groundwater table	0.31	-0.056	5
A_{of}	total area of openings in floor	0.30	0.055	6
A_f	area of floor	0.27	0.052	7
Δp_{ic}	air pressure difference between indoor space and crawl space	0.23	0.048	8
dc	depth of crawl space beneath soil surface	0.21	0.046	9
C_{sw}	concentration in soil water	0.20	0.045	10
z	height of capillary transition boundary above groundwater table	0.13	0.036	11
$vr_{c,b}$	basic ventilation rate of crawl space	0.11	-0.033	12
V_p	vapour pressure	0.11	-0.033	13
V_i	volume of indoor space	0.05	0.023	14
V_c	volume of crawl space	0.05	-0.022	15
M	molecular weight	0.04	0.020	16
L_f	floor thickness	0.01	0.009	17
n	number of openings per floor area	0.0004	0.002	18

SRC = fraction of the uncertainty in the model output (calculated indoor-air concentration) contributed by a model input; CTU = percentile contribution of a model input to uncertainty of the model output

Model outputs

The distribution of the model outputs are illustrated in Figures 24, 25 and 26. The distribution of concentration in soil air (Figure 24) resembles a normal distribution. Distributions of concentrations of crawl space air (Figure 25) and indoor air (Figure 26) show a skew distribution.

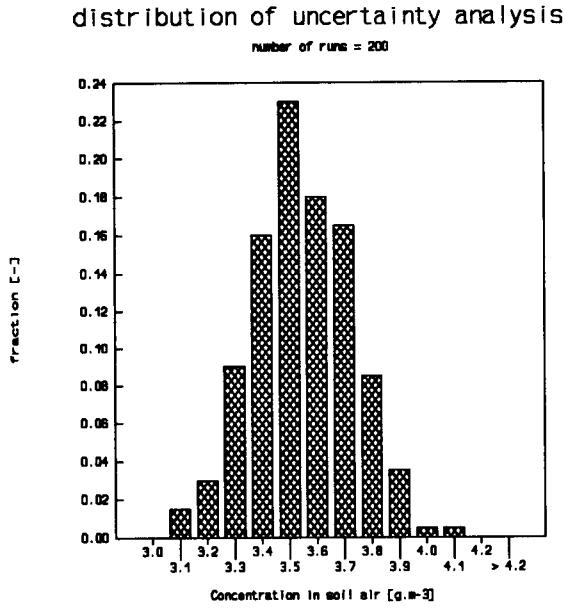


Figure 24: Distribution of modelled benzene concentration in soil air, resulting from uncertainty analysis by Monte-Carlo simulations.

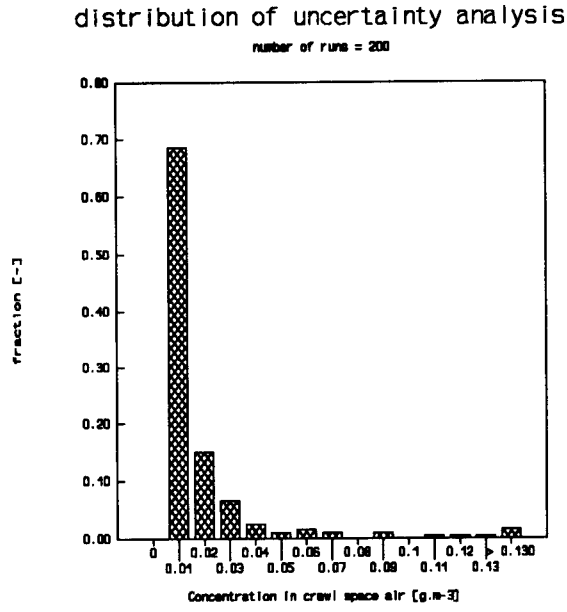


Figure 25: Distribution of modelled benzene concentration in crawl space air, resulting from uncertainty analysis by Monte-Carlo simulations.

The most important model output is the indoor-air concentration. The skew distribution (Appendix 7) might be caused by assumed logistic probability distributions of the VOLASOIL model inputs: air pressure differences and ventilation rates.

Mean indoor-air concentration is 0.0135 $g.m^{-3}$ ($\bar{y}$) using mean model inputs like UNCSAM did. As can be derived from Figure 26, 80% of modelled indoor-air concentrations are between $0 < \bar{y} < 0.02$ $g.m^{-3}$ and 1% is higher than $10 * \bar{y}$ (in this particular case). Moreover, due to variation in model inputs, 85% of modelled indoor-air concentration is found within a factor of 5 lower or higher than mean indoor-air concentration ($\bar{y}$). More detailed information is given in Table 11.

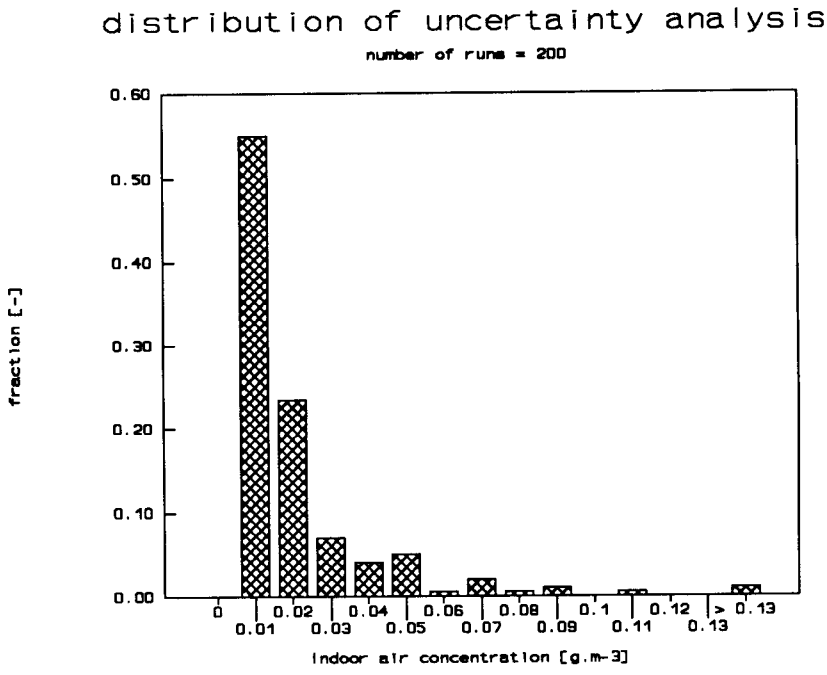


Figure 26: *Distribution of modelled benzene concentration in indoor air resulting from uncertainty analysis by Monte-Carlo simulations.*

One should keep in mind that, in general, neglecting model input uncertainty distributions will result in lower model output values. Therefore, it is important to pay attention to model inputs which have a large contribution to uncertainty of the model output.

Table 11: *Percentile values of modelled benzene concentrations in indoor air resulting from uncertainty analysis by Monte-Carlo simulations*

Percentile	Indoor-air concentration, C_{ia} ($g.m^{-3}$)
97.5	0.08
95	0.06
90	0.04
80	0.02
50	0.01

6.3 Implication of uncertainty results for the use of VOLASOIL

UNCSAM results of sensitivity and uncertainty analyses are only valid for the specific case considered and the assumed specifications of the various model inputs. Model inputs which are highly uncertain could, under different modelling conditions, result in a much lower uncertainty ranking. Because sensitivity analysis is partly incorporated in uncertainty analysis, the main focus will be on implications of uncertainty analysis results. Note that cross-correlations are not considered. Three uncertainty divisions are made arbitrarily (see also Table 10) on the basis of the CTU contribution to uncertainty:

1) high uncertainty ascribed to rank 1-3, CTU is higher than 1%
2) moderate uncertainty ascribed to rank 4-13, CTU is between 0.1% and 1.0%
3) low uncertainty ascribed to rank 14-19, CTU is lower than 0.1%

Results are illustrated in Table 12.

***Table 12:** Uncertainty divisions based on results of VOLASOIL uncertainty analysis*

Uncertainty divisions	Model	input
HIGH	Δp_{cs}	air pressure difference between crawl space and soil
	vr_i	ventilation rate of indoor space
	κ	air permeability of soil
MODERATE	S	solubility
	dg	depth of groundwater table
	A_{of}	total area of openings in floor
	A_f	area of floor
	Δp_{ic}	air pressure difference between indoor space and crawl space
	dc	depth of crawl space beneath soil surface
	C_{sw}	concentration in soil water
	z	height of capillary transition boundary above groundwater table
	$vr_{c,b}$	basic ventilation rate of crawl space
	V_p	vapour pressure
LOW	V_i	volume of indoor space
	V_c	volume of crawl space
	M	molecular weight
	L_f	floor thickness
	n	number of openings per floor area

Waitz, *et al.* [1996]: The VOLASOIL risk assessment model based on CSOIL for soils contaminated with volatile compounds.

It must be stressed that the position of model inputs within the uncertainty divisions must be treated with great caution. The "number of openings per floor area" is assigned a low contribution to uncertainty of the VOLASOIL model output. But under different circumstances (different floor), it is likely that the number of openings per floor area will be in the moderate uncertainty division.

High uncertainty

Model inputs in this division should be known very accurate; measurements or quantitative determinations are preferable.

Depending on site-specific conditions, model inputs can be measured accurately (Δp_{cs}, vr_i), and assessed with quantitative determination techniques or taken as default tabled values (κ, vr_i).

Moderate uncertainty

Model inputs in this box should be known fairly accurate; attention has to be paid on assessing proper quantitative values. Measurements and quantitative determinations could be useful.

Depending on site-specific conditions, model inputs can be measured accurately (Δp_{ic}, C_{sw}), assessed with qualitative determination techniques (dc, A_{of}, A_f, dg) and taken as default tabled values (z). The least that can be done is to pay much to assessing proper quantitative values (S, Vp). For example, solubility and vapour pressure could, in some cases, be corrected for temperature (from 20°C to 10°C) as described in Appendix 2.

Low uncertainty

Model inputs in this box can be taken as default values (M,n,$vr_{c,b}$) or assessed with qualitative determination techniques (V_c,V_i, L_f).

7 COMPARING VOLASOIL AND CSOIL CALCULATIONS

The CSOIL exposure model was developed for derivation of Intervention Values for soil and groundwater clean-up. These Intervention Values are based on potential risks to humans exposed to soil contaminants. The CSOIL's volatilization module estimates the indoor-air concentration in a building. Consequently, CSOIL has been used for actual risk assessment in case of volatile compounds. Because of CSOIL's limitations it was also recommended to perform measurements in contact media. Theoretical evaluation of the CSOIL's volatilization module has shown it to be not suitable for actual risk assessment. For this reason, the VOLASOIL model has been developed for actual risk assessment in case of volatile soil contaminants.

In this Chapter an attempt has been made to compare VOLASOIL calculations of indoor air concentrations with CSOIL calculations. Firstly, it is tried to make a comparison based on measurement data from investigation reports. Secondly, direct comparison is made based on hypothetical contamination situations. Finally, conclusions are drawn.

7.1 Comparison based on measurements

An attempt has been made to compare VOLASOIL and CSOIL model calculations with measurements. In order to make a comparison possible, measurement data should be collected. Therefore an inventory has been made of 16 site investigation reports, which also contained measurement data of indoor and crawl space air. These inventories took place for several municipalities and provinces. The data in the reports are shown in Appendix 6. It was attempted to distil the best available data from each data set by using criteria based on an 'ideal data set' for comparison of the models (Table 13):

***Table 13:** Ideal data set for comparing VOLASOIL and CSOIL with measurements*

- concentration in groundwater
- concentration in soil
- concentration in crawl space air
- concentration in indoor air
- concentration in outdoor air[1]
- depth of groundwater table
- soil profile (below crawl space)
- conditions of the house (quality of floor, ventilation characteristics, pressure differences, volume crawl space, volume indoor space, et cetera)
- meteorologic data (for interpretation of data)
- measurements which are causal related in time and place

[1] concentration in outdoor air is necessary for comparison with indoor air/crawl space air.

The concentration in groundwater is an important VOLASOIL input value. Whereas the CSOIL model calculates with the total soil concentration. Groundwater concentrations needed to be converted in total soil concentrations. Therefore it is assumed that the concentration in groundwater is related to the total soil concentration by means of partitioning. Although this calculation is not very accurate, this total soil concentration is used as input for the CSOIL model. Calculation results are shown in Appendix 6.

In total, 16 reports were collected on site investigations in the Netherlands. It appeared very difficult to obtain representative ideal data sets from these reports. Some of the problems appearing will be discussed. Note that interpretation of measurement data of indoor air concentrations is very difficult due to temporal and spatial variations.

1) In some investigations the compounds that were analyzed in the different media were not comparable (e.g. concentration of total aromatic compounds in groundwater was reported, but in crawl space air only benzene was measured). These data have no well-defined relation and can therefore not be used as model input.

2) In some cases, the indoor-air concentration was higher than the concentration in crawl space air of the same house. Therefore there is probably no relation between the concentration in the soil and groundwater and the concentration in the indoor air. Possibly the indoor-air concentration is being influenced by other sources (inside or outside the house). However theoretically, there might still be relation between the groundwater concentration and indoor-air concentration.

3) In other cases, the indoor-air concentration was lower or equal to the outdoor-air concentration (at a low concentration level). Only when the indoor concentration is (significantly) higher, might there be a relation between soil concentration and indoor-air concentration. The concentration in the crawl space might be a helpful tool in making a decision. When this concentration is low, no relation between polluted soil and indoor space is to be expected.

4) In many reports, only outdoor, crawl space and indoor-air measurements were performed. From these investigations, no relation with soil and groundwater can be found.

5) A crucial problem is the fact that different measurements were hardly ever taken at the same place and/or time. In the best-case situation, the groundwater and soil samples should be taken at the same location, directly below the crawl space. In any other case, the relation between measurements is rather uncertain. In order to make calculations, a causal relation within a certain range (of about 10 m) is assumed. It was not possible to take into account the (direction of) horizontal movement of the contaminant with time, which may lead to large discrepancies between measurements and calculations.

6) In all cases, information on construction of the houses was insufficient or absent. Therefore it was necessary to use default VOLASOIL parameters in describing the condition of the house (see Chapter 5: Application of VOLASOIL). In case of a site-specific risk assessment these default values might not lead to realistic output values.

7) Weather conditions at the location are necessary for interpretation of the air measurements. These weather conditions on the location were not always available, which makes interpretation of the air measurements (which are influenced by several factors) impossible. Air measurement should not be taken during extreme weather conditions, such as extreme storm, temperatures and rainfall.

8) The soil profiles described are mostly located next to the house instead of below the crawl space of the house.

As a result of all these problems, none of the data sets were sufficient for comparing VOLASOIL and CSOIL with measurements. From all the sets of data, only a few were chosen for comparing model calculations with measurements.

From comparison of the measured and calculated values of indoor air and crawl space air it can be concluded that more-or-less large discrepancies exist between measured and calculated values. This is because of:
1) incomplete data sets,
2) lack of reliable measurements,
3) lack of parameterized models,
4) temporal and spatial variations.

The differences between measured and calculated values may be caused by the total influence of all the problems described above. Because of all the uncertainties, no pronouncement can be made about the quality of the different models in relation to the measurement data.

The differences between the CSOIL calculations and the VOLASOIL calculations may be caused by the fact that in both models different processes and parameters are used. It should also be noted that for the same parameters, different values are chosen as default. The CSOIL and VOLASOIL calculations could lead to underestimation as well as overestimation of the measurement data. Important VOLASOIL parameters were not determined in the different investigations. In fact there was not one good data set. Therefore no conclusions can be drawn on basis of model calculations and measurements. A comparison should be made on the basis of a theoretical evaluation.

7.2 Direct comparison

Direct comparison between VOLASOIL and CSOIL is made on the basis of hypothetical contamination situations. Results are shown in Table 14.

In general, calculations with CSOIL result in higher indoor-air concentrations compared to calculations with VOLASOIL (factor 1.5 - factor 340 higher). But note that CSOIL calculations always give the same indoor-air concentration when using different soils and different floor qualities, whereas VOLASOIL shows a clear differentiation in calculated indoor-air concentrations. VOLASOIL calculates a higher indoor-air concentration than CSOIL in case of very bad ventilation of indoor space.

Furthermore, VOLASOIL is able to cope with specific cases, such as floating contaminant layers, contaminant sources beneath the groundwater table and pure contaminant in the open capillary zone, whereas with CSOIL it is not possible to make any calculations.

***Table 14:** Direct comparison between VOLASOIL and CSOIL, based on hypothetical benzene contamination situations*

Hypothetical contamination situation	VOLASOIL Indoor-air concentration	CSOIL Indoor-air concentration
groundwater contamination soil: sand depth groundwater: 3 m conc.: 0.16 $g.m^{-3}$ (water); 5.4 $mg.kg^{-1}ds$ (soil) floor: normal; ventilation: normal	11 $\mu g.m^{-3}$	21 $\mu g.m^{-3}$
groundwater contamination soil: clay depth groundwater: 3 m conc.: 0.16 $g.m^{-3}$ (water); 5.4 $mg.kg^{-1}ds$ (soil) floor: normal; ventilation: normal	0.94 $\mu g.m^{-3}$	21 $\mu g.m^{-3}$
groundwater contamination soil: sand depth groundwater: 15 m conc.: 0.16 $g.m^{-3}$ (water); 5.4 $mg.kg^{-1}ds$ (soil) floor: normal; ventilation: normal	1.60 $\mu g.m^{-3}$	4.5 $\mu g.m^{-3}$
floating soil contaminant layer soil: sand depth groundwater: 15 m floor: normal; ventilation: normal	14 000 $\mu g.m^{-3}$	not possible
groundwater contamination soil: sand depth groundwater: 3 m conc.: 0.16 $g.m^{-3}$ (water); 5.4 $mg.kg^{-1}ds$ (soil) floor: good; ventilation: normal	0.13 $\mu g.m^{-3}$	21 $\mu g.m^{-3}$
groundwater contamination soil: sand depth groundwater: 3 m conc.: 0.16 $g.m^{-3}$ (water); 5.4 $mg.kg^{-1}ds$ (soil) floor: bad; ventilation: normal	14 $\mu g.m^{-3}$	21 $\mu g.m^{-3}$
groundwater contamination soil: sand depth groundwater: 3 m conc.: 0.16 $g.m^{-3}$ (water); 5.4 $mg.kg^{-1}ds$ (soil) floor: normal; ventilation: very bad	30 $\mu g.m^{-3}$	21 $\mu g.m^{-3}$
contaminant sourche 0.5 m below groundwater level soil: sand depth groundwater: 3 m conc.: 0.16 $g.m^{-3}$ (water); 5.4 $mg.kg^{-1}ds$ (soil) floor: normal; ventilation: normal	0.02 $\mu g.m^{-3}$	not possible
pure contaminant in open capillary zone soil: sand depth of contaminant: 5 m floor: normal; ventilation: normal	42 000 $\mu g.m^{-3}$	not possible
groundwater in crawl space soil: sand conc.: 0.16 $g.m^{-3}$ (water); 5.4 $mg.kg^{-1}ds$ (soil) floor: normal; ventilation: normal	1000 $\mu g.m^{-3}$	340 000 $\mu g.m^{-3}$

7.3 Conclusions

It is obvious that from a conceptual point of view VOLASOIL gives a more realistic description of the processes involved in comparison with the CSOIL volatilization module. However, on the basis of incomplete data sets it is not possible to draw any conclusion based on quantitive comparison between the two models.

Depending on site-specific soil or building characteristics, VOLASOIL shows more diferentiation in calculated indoor-air concentrations than CSOIL. VOLASOIL is also able to cope with specific cases, such as floating contaminant layers, contaminant sources beneath the groundwater table, pure contaminant in the open capillary zone, water in crawl spaces, et cetera. This is not possible for CSOIL.

In order to compare VOLASOIL and CSOIL with measurements, site-specific research should be done. Measurements at soil contamination sites will have to be done, especially for the purpose of comparing VOLASOIL with CSOIL.

Research is needed to provide data to calibrate and, if possible, validate VOLASOIL. Site-specific spatially and temporally correlated measurements should be part of such research. Measurements should be performed in different seasons, at different locations with different buildings and considering different soils. This means that the 'ideal' data set will have to be created.

8 CONCLUSIONS AND RECOMMENDATIONS

This Chapter describes general, theoretical and practical conclusions, and recommendations.

8.1 General conclusions

The CSOIL exposure model was developed for derivation of Intervention Values for soil and groundwater clean-up. These Intervention Values are based on potential risks to humans exposed to soil contaminants. The CSOIL's volatilization module estimates the indoor-air concentration in a building. Consequently, CSOIL has been used for actual risk assessment in case of volatile compounds. Because of CSOIL's limitations it was also recommended to perform measurements in contact media. Theoretical evaluation of the CSOIL's volatilization module has shown it to be not suitable for actual risk assessment. For this reason, the VOLASOIL model has been developed for actual risk assessment in case of volatile soil contaminants. This model gives an indication of the indoor-air concentration (model output) in buildings situated on soils contaminated with volatile compounds for the Dutch situation. The VOLASOIL model can be seen as an optimum between scientifically sound and applicable in practice. The following conclusions refer to the VOLASOIL volatilization model.

8.2 Theoretical conclusions

In the VOLASOIL volatilization model the following new features are incorporated:
1) pressure-driven vapour flow in soils and buildings;
2) groundwater table;
3) the capillary transition boundary between the full and open capillary zone above the groundwater table;
4) flexibility of soil characteristics (soil-air permeability);
5) flexibility of floor characteristics;
6) flexibility of ventilation characteristics of indoor space.

VOLASOIL can be used for several groundwater contamination cases:
1) groundwater contamination, well-mixed container;
2) contaminated groundwater in crawl space;
3) floating soil-contaminant layer;
4) groundwater in crawl space and a floating soil-contaminant layer;
5) pure contaminant in open capillary zone;
6) very low groundwater table;
7) sinking soil-contaminant layer, well-mixed container;
8) contaminant source beneath the groundwater table, a not well-mixed container.

In general, ignoring model input uncertainty distributions will result in lower model output values. Therefore it is important to focus on model inputs which make a large contribution to the uncertainty of the model output. VOLASOIL sensitivity and uncertainty analyses indicate that:

1) The largest contributions to the uncertainty of model output can be attributed to the following model inputs:
   - air pressure differences between crawl space and soil,
   - ventilation rate of indoor space,
   - air permeability of soil.

   For improving the calculation of the indoor-air concentration, attention should be focused on detailed determination of these model inputs.

2) Due to variation in model inputs, 85% of modelled indoor-air concentration is found within a factor of 5 lower or higher than mean indoor-air concentration (not considering spatial and temporal variations in groundwater concentrations).

Due to a lack of suitable data sets it was not possible to calibrate or validate VOLASOIL and CSOIL.

8.3 Practical conclusions

From a conceptual point of view, the VOLASOIL volatilization model gives a more realistic description of processes involved compared to the CSOIL volatilization module.

A combination of modelling and measurements is possible. The following parameter catagories can be measured and used in combination with VOLASOIL:

1) model inputs,
2) intermediate model outputs (e.g. air-exchange rates, fraction of openings in floor),
3) concentrations in contact media (e.g. concentration in soil air or crawl-space air).

Incorporation of these measurements will diminish the current uncertainty of the calculated indoor-air concentration.

The VOLASOIL model is based on the CSOIL exposure model. Incorporation of VOLASOIL into the current CSOIL exposure model will be possible in future.

8.4 Recommendations

The VOLASOIL volatilization model can be used for site-specific risk assessment because a flexible combination of modelling and measurements is possible and calculations can be made for several specific contamination cases.

VOLASOIL could become a decision-support tool within the framework of the priority for soil clean-up (Soil Protection Act), construction permit issues (Housing Act) and soil quality management (spatial planning).

Incorporation of VOLASOIL in CSOIL is possible. In future, this might result in:
1) amendments to Intervention Values for volatile compounds during an evaluation of Intervention Values for soil and groundwater clean-up;
2) amendments to the system of priority for soil clean-up (Soil Protection Act).

Research is needed to provide data to calibrate and, if possible, validate VOLASOIL. Site-specific spatially and temporally correlated measurements should be part of such research. Measurements should be performed in different seasons, at different locations with different buildings and considering different soils.

Comparison with dynamic models is necessary to evaluate the limitations of the stationary transport assumed in VOLASOIL.

Possibilities and limitations when using VOLASOIL need to be identified. For example, VOLASOIL is not applicable in cases with rocky soils and landfills; in such cases measurements of the indoor-air concentration are preferred to calculations. In other cases calculations in combination with measurements are preferred, but note that measurements could exhibit large differences due to temporal variations.

CSOIL exposure time calculations should be simplified according to Appendix 8 because of overall complexity of CSOIL calculations.

Both vapour pressure and solubility are highly temperature dependent. The values used are empirically derived at 20°C, whereas the average standard soil temperature in the Netherlands is 10°C. For the use in CSOIL and VOLASOIL, it is therefore important to correct vapour pressure and solubility for temperature according to Appendix 2.

Research is needed for assessing realistic inhalative absorption factors of volatile compounds.

NOTATION

CHAPTER 2: CSOIL VOLATILIZATION MODULE

A_c = surface area of crawl space [50 m^2]
AV_a = breathing volume, adult [$m^3.d^{-1}$]
AV_c = breathing volume, child [$m^3.d^{-1}$]
Co = correction factor for length of roughness [-]
Cca = concentration in crawl space air [$g.m^{-3}$]
Cia = concentration indoor air [$g.m^{-3}$]
Coa_a = concentration outdoor air, for an adult at breathing height [$g.m^{-3}$]
Coa_c = concentration outdoor air, for a child at breathing height [$g.m^{-3}$]
C_{sa} = concentration in soil air [$mol.dm^{-3}$ or $g.m^{-3}$]
C_{sw} = concentration in soil water [$mol.dm^{-3}$ or $g.m^{-3}$]
C_t = total soil content [$mol.kg^{-1}$ dry soil or $mg.kg^{-1}$ dry soil]
d = boundary layer thickness [0.005 m]
D_a = diffusion coefficient in free air [$m^2.h^{-1}$]
dc = depth of crawl space beneath soil surface [0.5 m]
$DOSE_{iv}$ = lifelong average daily exposure to volatile contaminants [$mg.kg^{-1}.d^{-1}$]
dp = average depth of contaminant [m]
D_{sa} = diffusion coefficient in soil air [$m^2.h^{-1}$]
D_{sw} = diffusion coefficient in soil water [$m^2.h^{-1}$]
D_u = soil diffusion coefficient [$m^2.h^{-1}$]
D_w = diffusion coefficient in free water [$m^2.h^{-1}$]
Ev = flux of evaporating water [0.0001 $m^3.m^{-2}.d^{-1}$]
fa = relative absorption factor of contaminants in lungs [-; default set at 1]
fbi = contribution of the crawl space to the indoor air as fraction [0.1]
f_{nd} = fraction non-dissociated compound [-]
f_{oc} = fraction organic carbon [$kg_{org\ C}.kg^{-1}$ dry soil]
f_{om} = fraction organic matter [0.1]
H = Henry's constant [$Pa.m^3.mol^{-1}$]
IV_a = intake of contaminants through inhalation of air, adult [$mg.kg^{-1}.d^{-1}$]
IV_c = intake of contaminants through inhalation of air, child [$mg.kg^{-1}.d^{-1}$]
J0 = total soil flux to atmosphere [$g.m^{-2}.h^{-1}$]
J1 = total soil flux to crawl space [$g.m^2.h^{-1}$]
J2 = boundary flux [$g.m^{-2}.h^{-1}$]
J3 = water evaporation flux [$g.m^{-2}.h^{-1}$]
J4 = total diffusion flux from soil to soil surface [$g.m^2.h^{-1}$]
J5 = total diffusion flux from soil to crawl space [$g.m^2.h^{-1}$]

k	= von Karman constant [0.4]
K_d	= partitioning coefficient soil—water [(mol.kg^{-1})/(mol.dm^{-3})]
$K_{d,c}$	= partitioning coefficient soil water, corrected for dissociation [(mol.kg^{-1})/(mol.dm^{-3})]
Klw	= air—water partitioning constant or dimensionless Henry constant [(mol.m^{-3} air)/(mol.m^{-3} water)][-]
K_{oc}	= partitioning coefficient soil—water, corrected for organic carbon [(mol.kg^{-1})/(mol.dm^{-3})]
K_{ow}	= octanol—water partitioning coefficient [(mol.dm^{-3})/(mol.dm^{-3})]
Lp	= diameter of contaminated area [100 m]
M	= molecular weight [g.mol^{-1}]
P_a	= mass fraction in soil air [-]
pH	= acidity of soil [-]
pKa	= acid dissociation constant [-]
P_s	= mass fraction in solid-soil phase [-]
P_w	= mass fraction in soil water [-]
S	= solubility [mol.m^{-3}]
SD	= bulk density of soil [kg dry soil/dm^3 moist soil]
Sz	= Pasquill dispersion coefficient for vertical movements, related to Pasquill weather stability class D [m]
R	= gas constant [8.3144 Pa.m^3.mol^{-1}.K^{-1}]
T	= temperature [K]
$tf_{i,a}$	= time fraction for time spent indoors, correction from daily to yearly average exposure, adult [-]
$tf_{i,c}$	= time fraction for time spent indoors, correction from daily to yearly average exposure, child [-]
$tf_{o,a}$	= time fraction for time spent outdoors, correction from daily to yearly average exposure, adult [-]
$tf_{o,c}$	= time fraction for time spent outdoors, correction from daily to yearly average exposure, child [-]
$t_{i,a}$	= daily indoor exposure duration, adult [h.d^{-1}]
$t_{i,c}$	= daily indoor exposure duration, child [h.d^{-1}]
$t_{o,a}$	= daily outdoor exposure duration, adult [h.d^{-1}]
$t_{o,c}$	= daily outdoor exposure duration, child [h.d^{-1}]
V'	= friction velocity [m.h^{-1}]
V_{10}	= wind velocity at 10 m altitude [18000 m.h^{-1}]
V_a	= volume fraction soil air [-]
V_c	= volume of crawl space [25 m^3]
Vf	= dilution velocity [m.h^{-1}]
Vf_a	= dilution velocity, adult at 1.5 m [m.h^{-1}]
Vf_c	= dilution velocity, child at 1.0 m [m.h^{-1}]

Vg	= mean wind velocity [$m.h^{-1}$]
Vp	= vapour pressure [Pa]
V_s	= volume fraction solid phase [-]
vv_c	= air-exchange rate of crawl space [1.25 h^{-1}]
V_w	= volume fraction soil water [-]
V_x	= wind velocity at x m altitude [$m.h^{-1}$]
W_a	= body weight, adult [kg]
W_c	= body weight, child [kg]
Z	= breathing height [adult: 1.5 m; child: 1.0 m]
Zo	= length of roughness [1.0 m]
Z_{10}	= altitude [10 m]
Z_a	= fugacity constant air [$mol.m^{-3}.Pa^{-1}$]
Z_s	= fugacity constant solids [$mol.m^{-3}.Pa^{-1}$]
Z_w	= fugacity constant water [$mol.m^{-3}.Pa^{-1}$]

CHAPTER 4: VOLASOIL VOLATILIZATION MODEL

A_f = area of floor [m^2]
A_{of} = total area of openings in floor [m^2]
C_{ca} = concentration in crawl space air [$g.m^{-3}$]
C_{ia} = indoor-air concentration [$g.m^{-3}$]
C_{sa} = concentration in soil air at depth dp [$g.m^{-3}$]
$C_{sa,do}$ = concentration in soil air at optional depth do [$g.m^{-3}$]
C_{sw} = concentration in soil water [$g.m^{-3}$]
$C_{sw,ctb}$ = concentration in soil water at capillary transition boundary [$g.m^{-3}$]
$C_{sw,gw}$ = concentration in soil water at source depth in groundwater [$g.m^{-3}$]
D_a = diffusion coefficient in free air [$m^2.h^{-1}$]
dc = depth of crawl space beneath soil surface [0.4 m]
dg = depth of groundwater table [m]
do = optional depth beneath the crawl space in open capillary zone [m]
dp = average depth of contaminant [m]
D_{sa} = diffusion coefficient in soil air [$m^2.h^{-1}$]
ds_{gw} = depth of contaminant source beneath groundwater table [m]
D_{sw} = diffusion coefficient in soil water [$m^2.h^{-1}$]
D_w = diffusion coefficient in free water [$m^2.h^{-1}$]
Fci = air flux from crawl space through the floor into indoor space [$m^3.m^{-2}.h^{-1}$]
f_{of} = fraction of openings in floor (gap fraction) [$m^2.m^{-2}$]
Fsc = air flux from soil to crawl space [$m^3.m^{-2}.h^{-1}$]
h = pressure-head [cm]
H = Henry's constant [$Pa.m^3.mol^{-1}$]
H_{vap} = enthalpy of vaporization at 298 K [$J.mol^{-1}$]
J1 = total contaminant flux from soil to crawl space [$g.m^{-2}.h^{-1}$]
Jc_{ci} = convective contaminant flux from crawl space to indoor space [$g.m^{-2}.h^{-1}$]
Jd_{gw} = diffusion flux in groundwater from a source beneath groundwater table to the capillary transition boundary [$g.m^2.h^{-1}$]
Jd_{sc} = diffusion flux from soil to crawl space [$g.m^2.h^{-1}$]
Jd_{ss} = diffusion flux from soil to soil surface [$g.m^2.h^{-1}$]
K_f = air conductivity of floor [$m^2.Pa^{-1}.h^{-1}$]
K_{lw} = air—water partitioning constant or dimensionless Henry constant [(mol.m^{-3} air)/(mol.m^{-3} water)][-]
K_s = air conductivity of soil [$m^2.Pa^{-1}.h^{-1}$]
L_f = floor thickness [m]
L_{gw} = diffusion length of groundwater column [m]
L_s = length of soil column [m]
M = molecular mass [$g.mol^{-1}$]

n	= number of openings per floor area [m^{-2}]
n	= parameter water retention curve (pF curve) [-]
N	= total number of openings in floor [-]
pF	= log(-h) [-]
R	= gas constant [8.3144 $Pa.m^3.mol^{-1}.K^{-1}$]
r	= average radius of tube [m]
S	= solubility [$mol.m^{-3}$]
T	= temperature [K]
TCA	= Tolerable Concentration in Air [$g.m^{-3}$]
V_a	= volume fraction soil air [-]
V_c	= volume of crawl space [m^3]
Vd	= vapour density [$g.m^{-3}$]
V_i	= volume of indoor space [m^3]
Vp	= vapour pressure [Pa]
$vr_{c,b}$	= basic ventilation rate of crawl space [$m^3.h^{-1}$]
vr_i	= ventilation rate of indoor space [$m^3.h^{-1}$]
V_s	= volume fraction solid phase [-]
vv_c	= air-exchange rate of crawl space [h^{-1}]
vv_i	= air-exchange rate of indoor space [h^{-1}]
V_w	= volume fraction soil-water phase [0.4]
z	= height of capillary transition boundary above groundwater table [m]

α	= point of inflection in the water retention curve (pF curve) [cm^{-1}]
Δp_{cs}	= air pressure difference between crawl space and soil [Pa]
Δp_{ic}	= air pressure difference between indoor space and crawl space [Pa]
ε	= air-filled porosity of floor [$m^3.m^{-3}$]
ε	= air-filled porosity of soil [-]
η	= dynamic viscosity of air [$6.0*10^{-9}$ Pa.h]
θ	= volumetric soil-water content at pressure-head *h* [$cm^3.cm^{-3}$]
θ_r	= residuary soil-water content [$cm^3.cm^{-3}$]
θ_s	= soil-water content at saturation [$cm^3.cm^{-3}$]
κ	= air permeability of soil [m^2]
τ	= tortuosity [$m.m^{-1}$]

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APPENDIX 1: Tube models for air conductivity in porous systems

J.I. Freijer and M.F.W. Waitz

Tortuous tubes of uniform radius

The system considered is a column consisting of porous material, with length L, and unit area. Air-filled pores are represented as n tortuous tubes with uniform radius r, and length l. The length of the pores, l, is larger than, or equal to, the length of the column, L. The total cross-sectional area of the tubes is smaller than the cross-sectional area of the column.

Poiseulle's law for one tube is [Koorevaar *et al.*, 1991]

$$Q = -\frac{\pi r^4}{8\eta}\frac{\partial p}{\partial s} \tag{1}$$

Ignoring gravitational potential, Darcy's law reads

$$f_R = -K\frac{\partial p}{\partial s} \tag{2}$$

If a number of tubes are considered per unit area column (1) becomes

$$nQ = -\frac{n\pi r^4}{8\eta}\frac{\partial p}{\partial s} \tag{3}$$

where n is the number of tubes per unit area (m^{-2}). The left hand side of (3) is equal to f_R. If the porelength is equal to l then (3) may be written as

$$f_R = -\frac{n\pi r^4}{8\eta}\frac{\Delta p}{l} \tag{4}$$

Equation (2) written for column length L is

$$f_R = -K\frac{\Delta p}{L} \tag{5}$$

Combination of (5) and (4) yields

$$K = \frac{n\pi r^4}{8\eta}\frac{L}{l} \tag{6}$$

Air-filled porosity of the column is given by

$$\varepsilon = n\pi r^2\tau \tag{7}$$

where tortuosity, τ, is defined as

$$\tau = \frac{l}{L} \tag{8}$$

Upon usage of (7) and (8), (6) reduces to

$$K = \frac{\varepsilon}{\tau^2}\frac{r^2}{8\eta} \tag{9}$$

Air permeability, κ , is defined as [Corey, 1986]

$$\kappa = K\,\eta \tag{10}$$

Tortuous tubes of non-uniform radius

The system considered is a column with length L, and radius R. Air-filled pores are represented as N classes of tortuous tubes with radius r_i and length l for each pore class i. Again, the length of the pores, l, is larger than, or equal to, the length of the column, L. The total cross-sectional area of the tubes is smaller than the cross-sectional area of the column.

For the above system, Poiseulle's law for column area becomes

$$f_R = -\frac{1}{8\eta}\frac{\Delta p}{l}\sum_{i=1}^{N} n_i\pi r_i^4 \tag{11}$$

Combination of (5) and (11) yields

$$K = \frac{1}{8\eta}\frac{L}{l}\sum_{i=1}^{N} n_i\pi r_i^4 \tag{12}$$

Use the definition of tortuosity in (8) and define air-filled porosity of pore i as:

$$\varepsilon_i = n_i\pi r_i^2\tau \tag{13}$$

Then (12) becomes

$$K = \frac{1}{8\eta\tau^2}\sum_{i=1}^{n} \varepsilon_i r_i^2 \tag{14}$$

Tortuous jointed tubes of non-uniform radius

The system considered is a column with length L, and radius R. Air-filled pores are represented as N classes of tortuous tubes, each divided in w segments, occupying length L_j in the column. A pore segment ij has a radius r_{ij} and length l_{ij}. The lengths of one pore i Σl_{ij}, is larger than, or equal to, the length of the column, L. For each segment j the total cross-sectional area of the tube segments is smaller than the cross-sectional area of the column.

Applying theory of serial conductances [Ball, 1981; Freijer, 1994; Steele and Neeber, 1994] we obtain:

$$K = \frac{1}{8\eta} \sum_{i=1}^{N} \left(\sum_{j=1}^{w} \tau_{ij}^2 / (\varepsilon_{ij} r_{ij}^2) \right)^{-1} \tag{15}$$

with

$$\tau_{ij} = \frac{l_{ij}}{L_j} \tag{16}$$

$$\varepsilon_{ij} = n_i \pi r_{ij}^2 \tau_{ij} \tag{17}$$

Examples of tortuous tubes of uniform radius

Example 1: Crawl Space

Consider a crawl space with 0.1 m thick walls and 1.6 % wall area occupied by openings to the ambient air (outdoor air). Total area of crawl space walls is 15 m^2. The opening density is 0.53 m^{-2}. In the wall tortuosity τ=1.0 m m^{-1} and air-filled porosity ε=0.016 m^3 m^{-3}. The dynamic viscosity of air is η= 20.0 µPa s. The average radius of the openings is calculated from

$$r = \sqrt{0.016/(0.53 \times \pi)} = 0.098 \text{ m} \tag{18}$$

Using (9), air conductivity is calculated

$$K = \frac{0.016}{1} \frac{0.098^2}{8 \times 20 \times 10^{-6}} = 0.960 \text{ m}^2 \text{ Pa}^{-1}\text{s}^{-1} \tag{19}$$

Air permeability is

$$\kappa = 0.960 \times 20 \times 10^{-6} = 19.2 \times 10^{-6} \text{ m}^2 \tag{20}$$

Assuming a pressure difference between the groundwork compartment and the ambient air of 2 Pa, air-flux density is computed from Darcy's law

$$f_R = 0.960 \frac{2}{0.1} = 19.2 \text{ m}^3 \text{ m}^{-2} \text{ s}^{-1} \tag{21}$$

Example 2: Soil column

Consider a soil column of 1.25 m length, tortuosity τ=1.3 m m^{-1} [Freijer, 1994], and an air-filled porosity of ε=0.2 m^3 m^{-3}. The dynamic viscosity of air is η= 20.0 µPa s. The radius of the air-filled pores is taken 0.005 m. Using (9), air conductivity is calculated

$$K = \frac{0.2}{1} \frac{0.005^2}{8 \times 20 \times 10^{-6}} = 3.125 \times 10^{-4} \text{ m}^2 \text{ Pa}^{-1}\text{s}^{-1} \tag{22}$$

Air permeability is

$$\kappa = 3.125 \times 10^{-4} \times 20 \times 10^{-6} = 6.25 \times 10^{-9} \text{ m}^2 \tag{23}$$

Assuming a pressure gradient of 2 Pa / 1.25 m, air-flux density is computed from Darcy's law

$$f_R = 3.125 \times 10^{-4} \frac{2}{1.25} = 5.0 \times 10^{-4} \text{ m}^3 \text{ m}^{-2} \text{ s}^{-1} \tag{24}$$

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Notation

L	column length (m)
L_j	length of column segment j containing tube segment j (m)
K	air conductivity (m^2 pa^{-1} s^{-1})
Q	air flow through one tube (m^3 s^{-1})
f_R	air-flux density through unit porous medium (m^3 m^{-2} s^{-1})
l	length of tortuous tube (m)
l_{ij}	length of tube segment j in jointed tortuous tube i (m)
n	number of tubes per unit area (m^{-2})
n_i	number of tubes in class i per unit area (m^{-2})
N	number of pore classes
p	air pressure (Pa)
r	radius of tube (m)
r_i	radius of tube i (m)
r_{ij}	radius of tube i, segment j (m)
s	space coordinate (m)
w	number of tube segments
τ	tortuosity (m m^{-1})
τ_{ij}	tortuosity of tube i in column segment j (m m^{-1})
ε	air-filled porosity (m^3 m^{-3})
ε_{ij}	air-filled porosity of pore i in segment j as a fraction of total column volume (m^3 m^{-3})
η	dynamic viscosity of air (Pa s)
κ	air permeability (m^2)

APPENDIX 2: Temperature correction of vapour pressure and solubility

M.F.W. Waitz

Vapour pressure and solubility

Vapour pressure and solubility are physicochemical properties correlated with each other via the Henry constant. Both vapour pressure and solubility are highly temperature dependent.

Vapour pressure

Vapour pressures will be higher when temperature rises [Chang, 1990]. Three temperature correction methods will be described. Accuracy decreases from A, via B to C.

Method A

The Handbook of Chemistry and Physics [Lide *et al.*, 1993] uses a temperature-dependent formula for calculation of vapour pressures:

$$\log p = -\frac{0.05223\ a}{T} + b \qquad (1)$$

where: p = pressure [mm of mercury (1 mm Hg-pressure ≈ 133.33 Pa)]
T = absolute temperature [K]
a = empirical constant
b = empirical constant

Constants a and b are compoundspecific.

Method B

Constants a and b of Method A are not determined for most organic compounds. In this case an alternative method can be used. Via this method a vapour pressure at a given temperature will be recalculated to a vapour pressure at a different temperature by using the integrated Clausius-Clapeyron equation [Chang, 1990]:

$$Vp_2 = Vp_1 \, e^{\frac{(T_2 - T_1) H_{vap}}{T_1 . T_2 . R}} \qquad (2)$$

where: Vp_1 = vapour pressure at T_1 [Pa]
Vp_2 = vapour pressure at T_2 [Pa]
R = molar gas constant [8.3144 $J.mol^{-1}.K^{-1}$]
H_{vap} = enthalpy of vaporization at 298 K [$J.mol^{-1}$]
T_1 = temperature at known vapour pressure (e.g. 293 K) [K]
T_2 = temperature at unknown vapour pressure (e.g. 283 K) [K]

Enthalpies of vaporization at 298 K can be found in the Handbook of Chemistry and Physics [Lide *et al.*, 1993].

Method C

In all other cases when Method A and Method B cannot be used, the general Method C will give outcome. Sawyer & McCarty [1989] declare that 10°C rise in temperature corresponds with a 1.5 times higher saturated vapour pressure. Equation (3) expresses this analogue to the Arrhenius equation. In general, the equation might be valid between 273 and 333 K but this can be compoundspecific.

$$Vp_2 = Vp_1 \, e^{(0.041 \, (T_2 - T_1))} \qquad (3)$$

where: Vp_1 = vapour pressure at T_1 [Pa]
Vp_2 = vapour pressure at T_2 [Pa]
T_1 = temperature at known vapour pressure [K]
T_2 = temperature at unknown vapour pressure [K]

Solubility

Because solubility and vapour pressure are correlated to each other, temperature correction for solubility will be realised using a temperature correction for the Henry constant.

Van den Berg [1995] and Veerkamp & Ten Berge [1995] use a temperature correction for the Henry constant, which is valid between 273 and 313 K. This correction is derived from an empirical relation obtained by Wolff & Van der Heide [1982]. Applying this relation leads to errors of maximal 10%.

$$\ln H_2 = \ln (Klw_1 \; R \; T_1) + \kappa \; (T_2 - T_1) \tag{4}$$

where:
- H_2 = Henry constant at T_2 [$Pa.m^3.mol^{-1}$]
- Klw_1 = Air—water partitioning coefficient (dimensionless Henry constant) at T_1 [-]
- R = molar gas constant [8.3144 $J.mol^{-1}.K^{-1}$]
- κ = empirical parameter: 0.024 [K^{-1}]
- T_1 = temperature at known Henry constant (e.g. 293 K) [K]
- T_2 = temperature at unknown Henry constant (e.g. 283 K) [K]

The dimensioned Henry constant H_1 is the quotient of vapour pressure and solubility:

$$H_1 = \frac{Vp_1}{S_1} \tag{5}$$

where:
- H_1 = Henry constant at T_1 [$Pa.m^3.mol^{-1}$]
- Vp_1 = vapour pressure at T_1 [Pa]
- S_1 = solubility at T_1 [$mol.m^{-3}$]

Klw_1 is the dimensionless Henry constant at temperature T_1. Klw_1 is derived from the Henry constant (H_1) at temperature T_1:

$$Klw_1 = \frac{H_1}{R \; T_1} \tag{6}$$

where:
- Klw_1 = Air—water partitioning coefficient (dimensionless Henry constant) at T_1 [-]
- H_1 = Henry constant at T_1 [$Pa.m^3.mol^{-1}$]
- R = molar gas constant [8.3144 $J.mol^{-1}.K^{-1}$]
- T_1 = temperature at known Henry constant (e.g. 293 K) [K]

Combination of Equations (4) and (6) and using 0.024 for κ gives:

$$\ln H_2 = \ln \left(\frac{H_1}{R\,T_1} R\,T_1\right) + 0.024\,(T_2 - T_1) \tag{7}$$

Equation (7) may be written as:

$$\ln H_2 = \ln H_1 + 0.024\,(T_2 - T_1) \tag{8}$$

Final temperature correction for the Henry constant is:

$$H_2 = H_1\, e^{(0.024\,(T_2 - T_1))} \tag{9}$$

where: H_2 = Henry constant at T_2 [$Pa.m^3.mol^{-1}$]
H_1 = Henry constant at T_1 [$Pa.m^3.mol^{-1}$]
T_1 = temperature at known Henry constant (e.g. 293 K) [K]
T_2 = temperature at unknown Henry constant (e.g. 283 K) [K]

This temperature correction is an empirical expression of the Arrhenius equation [Chang, 1994; Atkins, 1987], which is based on the assumption that in a closed container the number of collisions between gas molecules increases with higher temperatures.

By using the vapour pressure at T_2 (calculated with one of the former temperature corrections for vapour pressure), and the Henry constant at T_2 (calculated with Equation (9)), the unknown solubility (S_2) at T_2 can be calculated:

$$S_2 = \frac{Vp_2}{H_2} \tag{10}$$

where: S_2 = solubility at T_2 [$mol.m^{-3}$]
Vp_2 = vapour pressure at T_2 [Pa]
H_2 = Henry constant at T_2 [$Pa.m^3.mol^{-1}$]

Application of temperature corrections

The temperature corrections for solubility and vapour pressure will be used for methanol and benzene (Table 1). Three temperature correction methods have been used. Accuracy is decreasing from method A, via B to method C.

***Table 1:** Temperature correction of vapour pressure (Vp), solubility (S) and Henry constant (H) for methanol and benzene*

Temperature corrections	Vp (Pa)	S ($mol.m^{-3}$)	H ($Pa.m^3.mol^{-1}$)
METHANOL			
standard, 20 °C	12 700 [a]	31 000 [b]	0.410
method A, 10 °C	7 132	22 127	0.322
method B, 10 °C	7 252	22 502	0.322
method C, 10 °C	8 467	26 270	0.322
BENZENE			
standard, 20 °C	10 133 [b]	22.788 [b]	445.0
method A, 10 °C	6 031	17.242	350.0
method B, 10 °C	6 203	17.735	350.0
method C, 10 °C	6 755	19.313	350.0

a : Chemiekaartenboek [1991]
b : Verschueren [1983]

Table 1 shows that vapour pressure and solubility of organic compounds decrease significant with lower temperatures. Also Henry constants are decreased at lower temperatures.

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APPENDIX 3: Calculation of K_{oc} from solubility and molecular topology

M.F.W. Waitz

The partitioning coefficient soil—water for organic compounds, corrected for organic carbon K_{oc}, is often calculated from octanol—water partitioning coefficient K_{ow} [Fetter, 1993]. In case of missing K_{ow} values, The K_{oc} can be estimated via the solubility or on basis of molecular topology.

K_{oc} from solubility

Karickhoff [1981] presents an equation for calculating K_{oc} based on solubility corrected for crystal energy:

$$\log K_{oc} = -0.921 \log S - 0.00953\,(MP - 25) - 1.405 \qquad (r^2 = 0.995) \qquad (1)$$

where S is the solubility (in ppm) and MP is melting point (in °C). The equation is valid for rigid hydrophobic organic solutes, which are solids at 25 °C (cyclic aliphatic or aromatic compounds containing less than 5 atoms in a flexible chain). Non-rigid molecules melt at much lower temperatures than rigid molecules of similar molecular weight and are frequently liquids at room temperatures. The crystal correction is either zero or very small in most cases. Therefore Equation (1) is also applicable for non-rigid molecules.

K_{oc} from molecular topology

The applicability of using octanol—water partition coefficient (K_{ow}) and aqueous solubility data to estimate K_{oc} has been questioned because some organic compounds have similar aqueous solubility but very different octanol solubility [Fetter, 1993]. A more fundamental approach has been suggested on the basis of molecular topology.

Sabljić [1987] introduced a molecular connectivity model, which is a very accurate predictive tool for the soil sorption coefficients of a wide range of organic chemicals. The first-order molecular connectivity index $^1\chi$ is related to, and is calculated on the basis of the non-hydrogen part of the molecule. Each non-hydrogen atom has an atomic δ value, which is the number of adjacent non-hydrogen atoms. A connectivity index is calculated for a molecule using the following equation [Sabljić, 1987]:

$$1\chi = \sum (\delta_i \, \delta_j)^{-0.5} \qquad (2)$$

where δ_i and δ_j are the delta values for a pair of adjacent non-hydrogen atoms. The summation takes place over all the bonds between non-hydrogen atoms. The relationship between K_{om} (distribution coefficient for soil organic matter) and $^1\chi$ is given by Equation (3). The K_{om} has to be multiplied by 1.724 in order to convert it to K_{oc}.

$$\log K_{om} = 1\chi \; 0.53 + 0.54 - P_f \qquad (3)$$

This equation is derived for polar organic compounds; the polarity correction factor P_f is known for 17 different groups of polar organics. For non-polar organic compounds the polarity correction factor P_f becomes zero.

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APPENDIX 4: Solutions for stationary transport of trace organics in soils

J.I. Freijer

Solution for stationary transport in a uniform unsaturated soil column

Consider an unsaturated soil column with uniform properties. A contaminant source is positioned somewhere below the soil surface. The source is never exhausted, guaranteeing stationary transport to the surface. It should be stressed that the solution developed cannot be used for dynamic systems where the contaminant disappears from the soil. Under stationary conditions the continuity equation for a conservative compound is

$$\frac{\partial C_T}{\partial t} = -\frac{\partial J_T}{\partial z} = 0 \tag{1}$$

The total flux through the system is given by [Jury *et al.*, 1983; Jury *et al.*, 1990]

$$J_T = -D_{ug}\frac{dC_g}{dz} - D_U\frac{dC_w}{dz} + F_g C_g + F_w C_w \tag{2}$$

where the water flux through the system can be calculated from

$$F_w = -K_w\left(\frac{dh}{dz} + 1\right) \tag{3}$$

and the air flux through the system follows from

$$F_g = -K_g\frac{dp}{dz} \tag{4}$$

The dispersion coefficient in the water phase includes molecular diffusion and mechanical dispersion

$$D_U = D_{uw} + \alpha F_w \tag{5}$$

The liquid—gas partitioning is described by a Henry function

$$C_g = K_H C_w \tag{6}$$

Combination of Eq.(2) and Eq.(6) yields

$$J_T = -D_E \frac{dC_g}{dz} + F_E C_g \tag{7}$$

with

$$D_E = D_{ug} + \frac{D_U}{K_H} \tag{8}$$

$$F_E = F_g + \frac{F_w}{K_H} \tag{9}$$

Rearrangement of Eq.(7) gives

$$-\frac{D_E}{J_T - F_E C_g} dC_g = dz \tag{10}$$

Integrating Eq.(10):

$$\frac{D_E}{F_E} \ln(J_T - F_E C_g) + C_1 = z \tag{11}$$

The upper boundary condition at the surface (z=0) is a known gas concentration, C_{g0}, and thus

$$C_1 = -\frac{D_E}{F_E} \ln(J_T - F_E C_{g0}) \tag{12}$$

Combination of Eqs.(11) and (12) gives

$$\ln\left[\frac{J_T - F_E C_g}{J_T - F_E C_{g0}}\right] = \frac{F_E z}{D_E} \tag{13}$$

$$\frac{J_T - F_E C_g}{J_T - F_E C_{g0}} = \exp\,[F_E z/D_E\,] \tag{14}$$

$$(J_T - F_E C_{g0})\,\exp[F_E z/D_E\,] = J_T - F_E C_g \tag{15}$$

From Eq.(15) it follows that the total flux density can be computed from

$$J_T = \frac{-\,F_E\,(C_g - C_{g0}\,\exp[F_E z/D_E\,])}{\exp[F_E z/D_E] - 1} \tag{16}$$

The concentration as a function of height is given by

$$C_g = C_{g0}\,\exp[F_E z/D_E\,] - J_T/F_E\,(\exp[F_E z\,/\,D_E\,] - 1) \tag{17}$$

Solution for stationary transport in a layered soil column

Assume a soil column consisting of an unsaturated layer above a saturated layer (Fig. 1). Transport through the system is stationary. In the upper, unsaturated layer with thickness L_s a contaminant is transported by advection and diffusion (Eq. (16)). In the lower saturated layer, with thickness L_{gw}, transport is only due to diffusion in the water phase. The source of contaminant is assumed to be inexhaustible and is positioned somewhere below z, in the saturated zone.

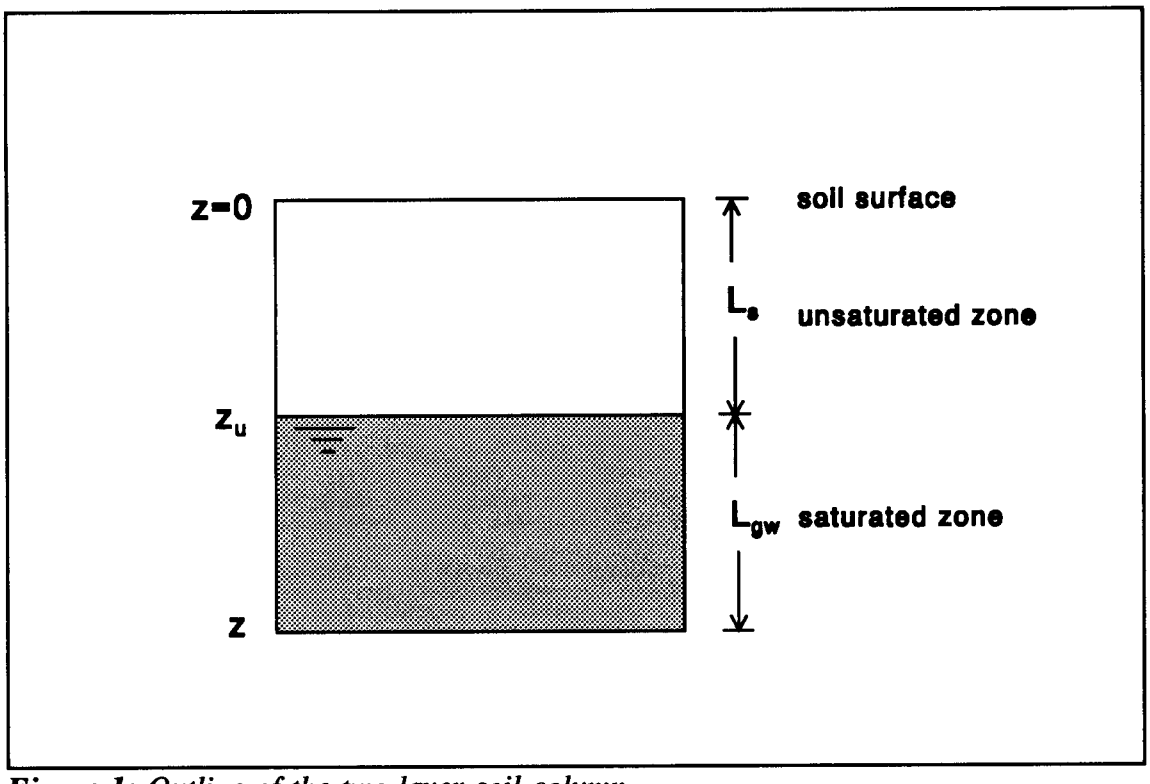

***Figure 1:** Outline of the two-layer soil column.*

The total flux density is given by

$$J_T = -D_{sw} \frac{dC_w}{dz} \tag{18}$$

Integration of Eq.(18) gives

$$C_w = -J_T/D_{sw}\ z + C_1 \tag{19}$$

At the interface with the unsaturated zone (the upper boundary of the saturated layer at $z=z_u$) the concentration in the water phase is equal to C_{wu}

$$C_1 = C_{wu} + J_T/D_{sw}\ z_u \tag{20}$$

Combination of Eqs.(19) and (20) yields

$$C_w - C_{wu} = J_T/D_{sw}\ (z_u - z) \tag{21}$$

The concentration in the gas phase at the interface of the unsaturated and the saturated layer can be found when combining Eqs.(6) and (21)

$$C_{gu} = K_H \{C_w - J_T/D_{sw} (z_u - z)\} \tag{22}$$

The total flux density, J_T, as a function of C_w and z follows from Eqs.(16) and (22)

$$J_T = \frac{- F_E (K_H[C_w - J_T/D_{sw}(z_u - z)] - C_{g0} \exp[F_E z_u/D_E])}{\exp[F_E z_u/D_E] - 1} \tag{23}$$

The thickness of the unsaturated and the saturated layer can be expressed as

$$L_s = -z_u \tag{24}$$

$$L_{gw} = (z_u - z) \tag{25}$$

Combination of Eqs.(23) to (25) and rearrangement yields

$$J_T = \frac{- F_E (K_H[C_w - J_T/D_{sw}L_{gw}] - C_{g0} \exp[-F_E L_s/D_E])}{\exp[-F_E L_s/D_E] - 1} \tag{26}$$

$$J_T - \frac{J_T F_E K_H L_{gw}}{D_{sw}(\exp[-F_E L_s/D_E] - 1)} = \frac{- F_E(K_H C_w - C_{g0} \exp[-F_E L_s/D_E])}{\exp[-F_E L_s/D_E] - 1} \tag{27}$$

$$J_T = \frac{- F_E (K_H C_w - C_{g0} \exp[-F_E L_s/D_E])}{\exp[-F_E L_s/D_E] - 1 - F_E K_H L_{gw}/D_{sw}} \tag{28}$$

References

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

Jury WA, Russo D, Streile G, El Abd J.(1990. Evaluation of volatilization by organic chemicals residing below the soil surface. Water Resources Res. 26:13-20

Notation

C_1	integration constant
C_g	concentration in the gas phase (kg m^{-3})
C_{g0}	concentration in the gas phase at the upper boundary, z=0 (kg m^{-3})
C_w	concentration in the water phase (kg m^{-3})
C_{gu}	concentration in the gas phase at the interface of the unsaturated and the saturated zone, $z=z_u$ (kg m^{-3})
C_{wu}	concentration in the water phase at the interface of the unsaturated and the saturated zone, $z=z_u$ (kg m^{-3})
D_E	effective total diffusion coefficient in unsaturated soil (m^2 s^{-1})
D_{sw}	effective water diffusion coefficient in saturated soil (m^2 s^{-1})
D_{ug}	effective gas diffusion coefficient in unsaturated soil (m^2 s^{-1})
D_{uw}	effective water diffusion coefficient in unsaturated soil (m^2 s^{-1})
D_U	effective water dispersion coefficient in unsaturated soil (m^2 s^{-1})
h	pressure-head (m)
F_E	effective advective air flux density (m^3 m^{-2} s^{-1})
F_g	advective air flux density (m^3 m^{-2} s^{-1})
F_w	water flux density (m^3 m^{-2} s^{-1})
J_T	total flux density of organic contaminant kg m^{-2} s^{-1})
K_g	air conductivity in unsaturated soil (m^2 Pa^{-1} s^{-1})
K_H	Henry gas-water partition coefficient (m^3 m^{-3})
K_w	water conductivity in unsaturated soil (m^3 m^{-2} s^{-1})
L_s	Thickness of the unsaturated layer (m)
L_{gw}	Thickness of the saturated layer from the interface with the unsaturated zone until a given value of z (m)
p	pressure (Pa)
z	height (negative upwards) (m)
z_u	height at the interface of the unsaturated and the saturated zone (m)
α	dispersivity (m)

APPENDIX 5: CSOIL set of formulas

The CSOIL exposure model is developed for the derivation of Intervention Values for soil and groundwater clean-up. These Intervention Values are, for example, based on potential risk assessment for humans exposed to soil contaminants [Van den Berg, 1995]. Physicochemical properties of the contaminant, together with soil properties, plant uptake characteristics, human physical characteristics, human behaviour, climatological/meteorological standards and other assumptions lead to quantification of the potential exposure. The exposure is compared with the human toxicologically based Maximum Permissible Risk (MPR).

Matching the MPR with the soil concentration gives the human toxicologically based Intervention Value (former C-value) for soil and groundwater for a standardized situation [DGM, 1994a,b]. Exceedance of the Intervention Values means "serious soil contamination", an unacceptably increased risk to humans or the environment, taking into account all possible exposure pathways [Van den Berg *et al.*, 1993].

The following formulas have been adjusted on the basis of the TCB [1992] recommendations; the information on the uptake of heavy metals by plants has been adjusted to Bockting and Van den Berg [1992] as well as other information. Mistakes have been corrected.

Appendix 5.1	Formulas fugacity calculations.
Appendix 5.2	Formulas air flux calculations.
Appendix 5.3	Formulas dilution air flux outdoor.
Appendix 5.4	Formulas air concentration calculation .
Appendix 5.5	Formulas crop content.
Appendix 5.6	Formulas calculation concentration in drinking water after permeation.
Appendix 5.7	Formulas for the calculation of the air concentration in the bathroom during showering.
Appendix 5.8	Formulas for the quantification of the exposure.
Appendix 5.9	Primary set of data.
Appendix 5.10	Conversion formulas.

Appendix 5.1 Formulas fugacity calculations

Organic substances

Za = 1 / (R*T)

Za	: fugacity capacity constant air	[$molm^{-3}.Pa^{-1}$]
R	: gas constant	[8.3144 $Pa.m^3.mol^{-1}.K^{-1}$]
T	: temperature	[K]

Zw = S/Vp

Zw	: fugacity constant water	[$mol.m^{-3}.Pa^{-1}$]
S	: water solubility	[$mol.m^{-3}$]
Vp	: vapour pressure pure substance	[Pa]

Zs = Kd * SD * Zw / Vs

Zs	: fugacity capacity constant soil	[$mol.m^{-3}.Pa^{-1}$']
Kd	: distribution coefficient soil—water	[($mol.kg^{-1}$ dry soil)/($mol.dm^{-3}$)]
SD	: mass volume of the dry soil	[kg dry soil.dm^{-3} humid soil]
Vs	: volume fraction solid phase	[-]

Vs = 1 - porosity
= 1 - Va- Vw

Va	: volume fraction air	[-]
Vw	: volume fraction water	[-]

Kd = Koc * foc

Koc	: distribution coefficient soil—water corrected for organic carbon	[($mol.kg^{-1}$ org. C)/($mol.dm^{-3}$)]
foc	: fraction organic carbon	[kg org.C.kg^{-1} dry soil]

Waitz, *et al.* [1996]: The VOLASOIL risk assessment model based on CSOIL for soils contaminated with volatile compounds.

Koc = 0.411 * Kow or: log Koc = 0.989 * log Kow - 0.346

Kow : octanol—water distribution coefficient [(mol.dm^{-3})/(mol.dm^{-3})]

Klw = Za / Zw
= Vp / (S * R * T)

Klw : air—water distribution coefficient [(mol.m^{-3} air)/(mol.m^{-3} water)] [-]

for dissociating organic substances

Kd = Kd * fnd

fnd : fraction non-dissociated substance

fnd = $1 / (1 + 10^{[ph - pKa]})$

pH : acid content of the soil (4-8, as default: 6)
pKa : acid dissociation constant of the substance

Calculation mass fractions

Pa = (Za * Va) / (Za * Va + Zw * Vw + Zs * Vs)
Pw = (Zw * Vw) / (Za * Va + Zw * Vw + Zs * Vs)
Ps = (Zs * Vs) / (Za * Va + Zw * Vw + Zs * Vs)

Pa : mass fraction in soil air [-]
Pw : mass fraction in soil moisture [-]
Ps : mass fraction in solid phase soil [-]

<u>Inorganic substances</u>

Za= 0; Csa = 0; Pa = 0
Pw = 1; Ps = O

Metals and arsenic

Za = 0; Csa = 0; Pa = 0

Pw = Vw / (Vw + Kd * SD)

Ps = 1 - Pw

Calculation concentrations

Csa = Cs * SD * Pa / Va

Csa : soil-air concentration [mol.dm^{-3} or g.m^{-3}]
Cs : initial soil content (total soil content in gas, water, and solid phase) [mol.kg^{-1} dry soil or mg.kg^{-1}]
Cpw = Cs * SD * Pw / Vw

if : Cpw > S then: Cpw = S
Csa= S * Vw * Pa / (Pw * Va)

Cpw : soil-moisture concentration [mol.dm^{-3} or g.m^{-3}]

Appendix 5.2 Formulas air flux calculations

$Dsa = Va^{10/3} * Da / (1-Vs)^2$ with $Da = .036 * (76/M)^{1/2}$

Dsa	: diffusion coefficient in the soil-gas phase	$[m^2.h^{-1}]$
Da	: diffusion coefficient in free air	$[m^2.h^{-1}]$
M	: molecular mass	$[g.mol^{-1}]$

$Dsw = Vw^{10/3} * Dw / (1-Vs)^2$ with $Dw = 3.6 * 10^{-6} * (76/M)^{1/2}$

Dsw	: diffusion coefficient in the soil-water phase	$[m^2.h^{-1}]$
Dw	: diffusion coefficient in free water	$[m^2.h^{-1}]$

$Du = (Pa * Dsa / Va) + (Pw * Dsw / Vw)$

Du	: diffusion coefficient in the soil	$[m^2.h^{-1}]$

J2 = Da * Csa / d
J3 = Cpw * Ev / 24
J4 = Du * Cs * SD / dp
J5 = Du * Cs * SD / (dp - Bh)

if : Cpw > S then : J4 = Du * S * Vw / (dp * Pw)
if : Cpw > S then : J5 = Du * S * Vw / [(dp - Bh)* Pw]

J2	: boundary-layer flux	$[g.m^{-2}.h^{-1}]$
J3	: water-evaporation flux	$[g.m^{-2}.h^{-1}]$
J4	: diffusion flux water-soil to surface level	$[g.m^{-2}h^{-1}]$
J5	: diffusion flux water-soil to crawl space	$[g.m^{-2}h^{-1}]$
Ev	: flux of evaporating water	[Fast *et al.*, 1987: 0.0001 $m^3.m^{-2}.d^{-1}$]
d	: thickness boundary layer	[Jury *et al.*, 1984: 0.005 m]
dp	: mean depth of the contamination	[1.25 m]
Bh	: height of the crawl space	[0.5 m]

if : J3+J4 < J2 then: Jo = J4 + J3
if : J3+J4 >= J2 then: Jo = J2

if : J3+J5 < J2 then: Ji = J5 + J3
if : J3+J5 >= J2 then: Ji = J2

Jo : total soil flux to outdoor air [$g.m^{-2}.h^{-1}$]
Ji : total soil flux to crawl space [$g.m^{-2}.h^{-1}$]

Appendix 5.3 Formulas dilution air flux outdoor

$Vf = Vg * Sz / Lp$

Vf	: dilution velocity	[$m.h^{-1}$]
Vfa	: dilution velocity adult	[$m.h^{-1}$]
Vfc	: dilution velocity child	[$m.h^{-1}$]
Vg	: mean wind velocity	[$m.h^{-1}$]
Sz	: vertical Pasquill dispersion coefficient, related to Pasquill weather stability class D	[m]
Lp	: diameter contaminated area	[100 m]

$Vg = (Vx + V') / 2$

Vx	: wind velocity at x m altitude	[$m.h^{-1}$]
V'	: friction velocity	[$m.h^{-1}$]

$Vx = \ln [Z / Zo] * V' / k$

Z	: breathing altitude	[x m]
Zo	: roughness of the surface area (residential area)	[1.0 -]
k	: von Karman constant	[0.4 -]

$V' = k * V10 / \ln (Z10 / Zo)$

Z10	: altitude	[10 m]
V10	: wind velocity at 10 m altitude	[18 000 $m.h^{-1}$]

$Sz = Co * 0.20 * Lp^{0.76}$

$Co = (10 * Zo) \wedge (0.53 * Lp^{-0.22})$

Co	: correction factor for the roughness length	[-]

model calculation for Lp = 100 m:

		children	adults	
Z	=	1.0	1,5	[m]
V'	=	3127	3127	[$m.h^{-1}$]
V1	=	0	3170	[$m.h^{-1}$]
Vg	=	1563	3148	[$m.h^{-1}$]
Co	=	1.56	1.56	[-]
Sz	=	10.31	10.31	[m]
Vfc	=	161.3		[$m.h^{-1}$]
Vfa	=		324.6	[$m.h^{-1}$]

Appendix 5.4 Formulas air concentration calculation

Coaa = Jo / Vfa

Coaa	: concentration in the outdoor air for an adult at 1.5 m altitude	[$g.m^{-3}$]
Vfa	: dilution velocity adult	[$m.h^{-1}$]

Coac = Jo / Vfc

Coac	: concentration in the outdoor air for a child at 1 m altitude	[$g.m^{-3}$]
Vfc	: dilution velocity child	[$m.h^{-1}$]

Cba = Ji * Bo / (Bv * Vv)

Cba	: concentration in the crawl space air	[$g.m^{-3}$]
Bo	: surface area of the crawl space	[50 m^2]
Bv	: volume of the crawl space	[25 m^3]
Vv	: air-exchange rate (experimental data (Fast *et al.*, 1987): min. 0.03 - max. 7.4 - av. 1.25)	[1.25 h^{-1}]

Cia = fbi * Cba

Cia	: concentration in the indoor air	[$g.m^{-3}$]
fbi	: contribution of the crawl space air to the indoor air as fraction (experimental data (Fast *et al.*, 1987): min. 0 - max. 0.68 - av. 0.11 - 95 perc. 0.39)	[0.1 -]

if : Cia < Coac then: Cia = Coac

Appendix 5.5 Formulas crop content

Deposition

$$Cdp = TSPo * DRo * frs * Cs * [fin / (Yv * fEi)] * \{ 1 - (1 - \exp[- fEi * te]) / (fEi * te)\}$$

Cdp	: crop content originating from deposition	[mg subst.kg^{-1} dw crop]
fin	: fraction interception by crop	[0.4 -]
Yv	: crop yield	[0.28 kg dw.m^{-2}]
fEi	: weathering constant	[0.033 d^{-1}]
TSPo	: concentration particles in outdoor air	[0.07 mg.m^{-3}]
frs	: fraction soil in particles	[0.5 -]
DRo	: deposition velocity	[1 cm.s^{-1} = 864 m.d^{-1}]
te	: growing period crop	[180 d]

$$Cdp = 1.089 * 10^{-3} * Cs$$ [mg.kg^{-1} dw crop]

Crop content

<u>Metals</u>

root crops:

$$Cpr = BCFr * Cs$$

Cpr	: content of the root crop	[mg subst.kg^{-1} dw crop]
BCFr	: bioconcentration factor root	[(mg subst.kg^{-1} dw crop)/(mg subst.kg^{-1} dry soil)]

leafy crops:

$$Cps = BCFs * Cs + Cdp$$

Cps	: content of the leafy crop	[mg subst.kg^{-1} dw crop]

BCFs : bioconcentration factor leafy crop [(mg subst.kg^{-1} dw crop)/(mg subst.kg^{-1} dry soil)]

if no BCFr or BCFs are given:

ln BCFr/s = 2.67 - 1.12 * ln Kd

<u>other inorganic substances</u>

based on high water solubility: concentration in pore-water = concentration in plant moisture

root crops:

Cpr' = Cpw * (1 - fdwr)

Cpr' : content of the root crop [mg subst.kg^{-1} fresh weight crop]
fdwr = ratio dry weight—fresh weight root crops [0.202 kg dw.kg^{-1} fresh]

BCFr' = (1 -fdwr)

BCFr' : bioconcentration factor root [(mg subst.kg^{-1} fresh crop)/(mg subst.dm^{-3} soil moisture)]

leafy crops:

Cps' = Cpw * (1-fdws) + Cdp * fdws

Cps' : content of the leafy crop [mg subst.kg^{-1} fresh weight crop]
fdws = ratio dry weight—fresh weight leafy crops [0.117 kg dw.kg^{-1}l fresh]

BCFs' = (1 - fdws)

BCFs' : bioconcentration factor stem [(mg subst.kg^{-1} fresh crop)/(mg subst.dm^{-3} soil moisture)]

Organic substances

roots:

$BCFr = 10^{(0.77 * \log Kow - 1.52)} + 0.82$

BCFr' : bioconcentration factor root [(mg subst.kg^{-1} fresh crop)/(mg subst.dm^{-3} soil moisture)]

Cpr' = BCFr' * Cpw

Cpr' : content of the root crop [mg subst.kg^{-1} fresh weight crop]

stems:

$BCFs' : [10^{(0.95 * \log Kow - 2.05)} + 0.82] * [0.784 * 10^{(-0.434 * (\log Kow - 1.78)^2/2.44)}]$

BCFs' : bioconcentration factor stem [(mg subst.kg^{-1} fresh crop)/(mg subst.dm^{-3} soil moisture)]

Cps' = BCFs' * Cpw + Cdp * fdws

Cps' : content of the leafy crop [mg subst.kg^{-1} fresh weight crop]

Appendix 5.6 Formulas calculation concentration in drinking water after permeation

$Cmax = Cpw * 2 * Dpe * t / (r * d)$

Cmax	: maximum concentration in the drinking water after t days stagnation	[$mg.dm^{-3}$]
Dpe	: permeation coefficient	[$m^2.d^{-1}$]
t	: time period of water stagnation	[Vonk, 1985a,b: 8 h = 1/3 d]
r	: radius of the pipe	[0.0098 m]
d	: thickness of pipe wall	[0.0027 m]

24 hrs permeation:

$Cdw = Cmax * 3 * pi * r^2 * L / Qwd$

Cdw	: 24 h mean drinking water concentration	[$mg.dm^{-3}$]
t	: in this case 24 h = 1 d, hence correction factor 3	
L	: length of the pipe along which permeation can occur = size location	[100 m]
Qwd	: mean daily water consumption	[500 dm^3]

$Cdw = 4.56 * 10^3 * Dpe * Cpw$ [$mg.dm^{-3}$]

Appendix 5.7 Formulas for the calculation of air concentration in the bathroom during showering

$kwa = [(H_{sh}/RT_{sh}) * kL * kG]/[(H_{sh}/RT_{sh}) * kG + kL)] * [Ad/Vd] * tf$

kwa	: degree of evaporation of the contaminant	[-]
(H_{sh}/RT_{sh})	: air—water distribution coefficient at a temperature of 313 K (T_{sh})	[-]
T_{sh}	: water temperature shower water	[313 K]
kL	: water mass transport coefficient	[$m.s^{-1}$]
kG	: vapour mass transport coefficient	[$m.s^{-1}$]
Ad	: surface area water drop	[m^2]
Vd	: volume water drop	[m^3]
tf	: dropping time drop	[1 s]

temperature correction for the Henry constant:

$\ln H_{sh} = \ln (Klw*R*T_0) + 0.024 * (T_{sh} - T_0)$

H_{sh}	: Henry constant at a temperature of 313 K (T_{sh})	[$Pa.m^3.mol^{-1}$]
H_0	: Henry constant for the reference situation (T_0 = 283-293 K)	[$Pa.m^3.mol^{-1}$]

$Ad = 4 * pi * r^2$

$Vd = 4/3 * pi * r^3$

$Ad/Vd = 3 / r$

r	: radius of the drop	[0.5 mm = 0.0005 m]

$kL = Kl * (44/M)^{1/2} / 3600$ [$m.s^{-1}$]

$kG = Kg * (18/M)^{1/2} / 3600$ [$m.s^{-1}$]

Kl	: liquid phase exchange velocity	[0.2 $m.h^{-1}$]
Kg	: gas phase mass transport coefficient	[29.88 $m.h^{-1}$]

$Cbk = kwa * Vwb * Cdw / (2 * Vbk)$

Waitz, *et al.* [1996]: The VOLASOIL risk assessment model based on CSOIL for soils contaminated with volatile compounds.

Cbk	: concentration in the bathroom air	[g subst.m^{-3}]
Vwb	: volume water consumption	[0.15 m^3]
Vbk	: volume bathroom	[l*b*h = 3*2*2.5 = 15 m^3]

Cbk = kwa * Cdw * 5 * 10^{-3} [g.m^{-3}]

Appendix 5.8 Formulas quantification exposure

Soil ingestion

DI = AID * Cs * fa / W

DI : uptake via soil ingestion [mg subst.kg^{-1}.d^{-1}]
AID : daily intake amount soil [kg dry subst.d^{-1}]
adults : 50 * 10^{-6}
children : 150 * 10^{-6}
W : body weight
adults : 70 kg
children : 15 kg
fa : relative absorption factor, set at 1 [-]
Cs : initial soil content (total soil content in gas, water, and solid phase) [mol.kg^{-1} dry soil or mg.kg^{-1}]

DIa = 50 * 10^{-6} * Cs / Wa
DIc = 150 * 10^{-6} * Cs / Wc

Dermal contact soil

Outdoor exposure via soil, indoor via soil in dust; during sleep no exposure.

DA = A exp * fm * DAE * DAR * Cs * t * tf * frs / W

DA : uptake via dermal contact with soil [mg.kg^{-1}.d^{-1}]
A exp : exposed surface area [m^2]

	indoor	outdoor
adult	0.09	0.17
children	0.05	0.28

fm : matrix factor [0.15 -]

DAE : degree of coverage [mg soil.cm^{-2} = * 0.01 kg.m^{-2}]

	indoor	outdoor
adults	0.056	3.75
children	0.056	0.51

DAR : absorption velocity [h^{-1}]

adults	0.005
children	0.01

t : duration of exposure [h d^{-1}]

	indoor	outdoor
adults	8	8
children	8	8

tf : time fraction exposure [-]

correction of daily to annual average exposure

	indoor	outdoor
adults	1.857	0.143
children	1.143	0.357

frs : fraction soil in dust [-]

frsi: indoor: 0.8

DAa = 5.92 * 10^{-6} * Cs / Wa

DAc = 6.43 * 10^{-6} * Cs / Wc

<u>Inhalation of soil (particles)</u>

IP = ITSP * Cs * fr * fa / W

IP : uptake of inhaled soil particles [mg.kg^{-1}.d^{-1}]

ITSP : amount of inhaled soil particles [kg.d^{-1}]

fr : retention factor particles in lung [0.75 -]

ITSP = TSP * frs * AV * t * ft

TSP : amount of air-suspended particles [mg.m^{-3}]

TSPo: outdoor: 70 ug.m^{-3}

TSPi: indoor: 0.75 * 70 = 52.5 ug.m^{-3}

frs : soil fraction in particles in the air [-]
frso: outdoor: 0.5
frsi: indoor: 0.8

AV : breathing volume [$m^3.d^{-1}$]
AVa: adults : 20 = 0.83 $m^3.h^{-1}$
AVc: children : 7.6 = 0.32 $m^3.h^{-1}$

t : duration of exposure [h]

	indoor	outdoor
adults	8	8
children	16	8

tf : time fraction exposure [-]
correction from daily to annual average exposure

	indoor	outdoor
adults	2.856	0.143
children	1.322	0.357

IPa = 0.625 * 10^{-6} * Cs / Wa
IPc = 0.235 * 10^{-6} * Cs / Wc

Inhalation of air

IV = [AV * Cia * tfi * ti + AV * Coa * tfo * to] * fa * 10^3 / W

IV : uptake of contamination via vapours [$mg.kg^{-1}.d^{-1}$]
Cia : concentration in the indoor air [$g.m^{-3}$]
Coa : concentration in the outdoor air [$g.m^{-3}$]
Coaa : concentration in the outdoor air for an adult [$g.m^{-3}$]
Coac : concentration in the outdoor air for a child [$g.m^{-3}$]
ti/to : daily duration of exposure indoor respectively outdoor
(see Table under inhalation soil particles) [h]
tfi/tfo : annual average time fractions for stay indoor respectively outdoor
(see Table under inhalation soil particles) [-]

IVa = (22.86 * Cia + 1.14 * Coaa) * 0.83 * 1000 / Wa
IVc = (21.14 * Cia + 2.86 * Coac) * 0.32 * 1000 / Wc

Ingestion of crops: leafy and root crops

metals

VI = (Qfvk * Cpr + Qfvb * Cps) * fv * fa / W

VI	: uptake of contaminant via crop	[$mg.kg^{-1}.d^{-1}$]
Qfvk	: daily consumption of root crops	[kg dry $weight.d^{-1}$]
	adults : 0.02761	
	children : 0.01511	
Qfvb	: daily consumption of leafy crops	[kg dry $weight.d^{-1}$]
	adults : 0.01843	
	children : 0.00890	
fv	: fraction contaminated food	[0.1 -]
Cpr	: content of the root crop	[mg $subst.kg^{-1}$ dw crop]
Cps	: content of the leafy crop	[mg $subst.kg^{-1}$ dw crop]

VIa = (0.002761 * Cpr + 0.001843 * Cps) / Wa
VIc = (0.001511 * Cpr + 0.000890 * Cps) / Wc

other (in)organic substances

VI = (Qfvk' * Cpr' + Qfvb' * Cps') * fv * fa / W

Qfvk'	: daily consumption of root crops	[kg fresh $weight.d^{-1}$]
	adults : 0.1367	
	children : 0.0748	
Qfvb'	: daily consumption of leafy crops	[kg fresh $weight.d^{-1}$]
	adults : 0.1578	
	children : 0.0761	
Cpr'	: content of the root crop	[mg $subst.kg^{-1}$ fresh weight crop]
Cps'	: content of the leafy crop	[mg $subst.kg^{-1}$ fresh weight crop]

VIa = (0.01367 * Cpr' + 0.01578 * Cps') / Wa
VIc = (0.00748 * Cpr' + 0.00761 * Cps') / Wc

Ingestion of drinking water

DIw = Qdw * Cdw * fa / W

DIw : intake of contaminated drinking water by drinking [$mg.kg^{-1}.d^{-1}$]
Qdw : daily drinking water intake [$m^3.d^{-1}$]
adults : 0.002 = 2 $dm^3.d^{-1}$
children : 0.001 = 1 $dm^3.d^{-1}$
Cdw : drinking water concentration [$mg.dm^{-3} = g.m^{-3}$]

DIwa = 2 * Cdw / Wa
DIwc = 1 * Cdw / Wc

Inhalation of vapours during showering

IVw = Cbk * AV * td * fa * 1000 / W

IVw : intake contamination by inhaling vapour during showering [$mg.kg^{-1}.d^{-1}$]
Cbk : concentration in the bathroom air [$g.m^{-3}$]
td : duration of stay in the bathroom [h]
15 min. showering + 15 min. drying/dressing = [0.5 h]

IVwa = 2.08 * Cdw * kwa / Wa
IVwc = 0.792 * Cdw * kwa / Wc

Dermal contact during showering

DAw = A tot * f exp * DAR * tdc * (1-kwa) * Cdw * fa / W

DAw : uptake as a result of dermal contact during showering [$mg.kg^{-1}.d^{-1}$]
A tot : exposure surface area = entire body [m^2]
adults : 1.8
children : 0.95

f exp : fraction exposed skin [0.4 -]
DAR : dermal absorption velocity [$(mg.m^{-2})/(mg.dm^{-3}).h^{-1}$]
tdc : contact time = showering time [0.25 $h.d^{-1}$]
(1-kwa) : substance remaining in water after evaporation [-]

DAR = P1 * P2 according to Fiserova-Bergerova & Pierce (1989), with:

P1 = (0.038 + 0.153 * Kow)
P1 = 5000 * P1 / (5000 + P1), maximization according to Brown & Rossi (1989)
P2 = exp (-0.016 * M) / 1.5

DAwa = 0.18 * DAR * (1-kwa) * Cdw / Wa
DAwc = 0.095 * DAR * (1-kwa) * Cdw / Wc

Total exposure

TAD = DIa + DAa + IPa + IVa + VIa + DIWa + IVwa + DAwa
TCH = DIc + DAc + IPc + IVc + VIc + DIWc + IVwc + DAwc

TAD : daily exposure adult [$mg.kg^{-1}.d^{-1}$]
TCH : daily exposure child [$mg.kg^{-1}.d^{-1}$]

DOSIS = (6 * TCH + 64 * TAD) / 70

DOSIS : lifetime mean daily exposure [$mg.kg^{-1}.d^{-1}$]

Appendix 5.9 Primary set of data

Necessary set of data in order to be able to calculate potential exposure.

S	: water solubility	[$mol.m^{-3}$] or [$mg.l^{-1}$]
Vp	: vapour pressure pure substance	[Pa] or [atm] or [mm Hg]
	or	
Klw	: air—water distribution coefficient	[-]
	(this may also be calculated from the other data, see Appendix 1.10)	
M	: molecular mass	[$g.mol^{-1}$]
Kow	: octanol—water distribution coefficient	
	(for organic substances)	[($mol.dm^{-3}$)/$mol.dm^{-3}$)]
Kd	: soil—water distribution coefficient (for metals)	[$dm^3.kg^{-1}$]
Dpe	: permeation coefficient	[$m^2.d^{-1}$]

Waitz, *et al.* [1996]: The VOLASOIL risk assessment model based on CSOIL for soils contaminated with volatile compounds.

Appendix 5.10 Conversion formulas

Klw = Vp / (S * R * T)

Vp = Klw * S * R * T

R_1 = 8.3144 $Pa.m^3.mol^{-1}.K^{-1}$
R_2 = $8.206*10^{-5}$ $m^3.atm.mol^{-1}.K^{-1}$

if H is given as [$Pa.m^3.mol^{-1}$] then: Klw = H / (R_1 * T)

if H is given as [$atm.m^3.mol^{-1}$] then: Klw = H / (R_2 * T) or:
Klw = H * 1.013 * 10^5 / (R_1 * T)

1 mm Hg pressure = 133.33 Pa = $1.316*10^{-3}$ atm

if S is given in [$mg.l^{-1}$] then: S = S / M [$mol.m^{-3}$]

M : molecular mass [$g.mol^{-1}$]

foc = 0.58 * fom or fom = 1.724 * foc or OS = 172.4 * foc

fom : fraction of mass organic matter
OS : percentage organic matter

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APPENDIX 6: Comparing VOLASOIL and CSOIL with measurements

Note: all calculations are performed with the standard scenarios (CSOIL: house with garden; VOLASOIL (version 1.6): groundwater contamination (well-mixed layer) except for case VII, scenario F).

CASE I

Circumstances

contamination:	benzene
groundwater concentration:	4.7 µg l^{-1} (0.1588 mg kg^{-1} ds. CSOIL input)
groundwater table:	2.20 m-mv
soil profile:	medium coarse sand, mixed with debris (z: 0.5 m; kappa: 10^{-10} m^2)
measuring period:	summer; 25°C (air pressure differences 1 Pa)
concentration outdoor air:	1 µg m^{-3}
distance measurements air—groundwater:	8.5 m

Calculations

Case I					
	Measured (µg m^{-3})	CSOIL (µg m^{-3})	c/m*	VOLASOIL (µg m^{-3})	c/m*
Conc. crawl space (basement)	4.4	9.0	2	21	5
Conc. indoor	3	0.90	0.3	0.45	0.2

* = calculated concentration/measured concentration

CASE II

Circumstances

contamination:	benzene
groundwater concentration:	160 µg l^{-1} (5.4 mg kg^{-1} ds. CSOIL input)
groundwater table:	2.20 m-mv
soil profile:	medium coarse sand, mixed with debris (z: 0.5 m; kappa: 10^{-10} m^2)
measuring period:	summer; 25°C (air pressure differences 1 Pa)
concentration outdoor air:	3 µg m^{-3}!
distance measurements air-groundwater:	6 m

Calculations

Case II					
	Measured (µg m^{-3})	CSOIL (µg m^{-3})	c/m*	VOLASOIL (µg/m^3)	c/m*
Conc. crawl space	2	305	150	704	350
Conc. indoor	3	30.5	10	15.2	5

* = calculated concentration/measured concentration

CASE III

Circumstances

contamination:	tetrachloroethene (PER)
groundwater concentration:	1100 µg l^{-1} (107 mg kg^{-1} ds. CSOIL input)
groundwater table:	5.0 m-mv
soil profile:	loam, mixed with debris (z: 0.6 m; kappa: $10^{-13.5}$ m^2)
measuring period:	september; 13°C (air pressure differences 2 Pa)
concentration outdoor air:	<0.63 µg m^{-3}
distance measurements air—groundwater:	30 m

Calculations

Case III					
	measured (µg m^{-3})	CSOIL (µg m^{-3})	c/m*	VOLASOIL (µg m^{-3})	c/m*
Conc. crawl space	10	2490	250	293	30
Conc. indoor	<1	249	250	12.4	10

* = calculated concentration/measured concentration

Waitz, *et al.* [1996]: The VOLASOIL risk assessment model based on CSOIL for soils contaminated with volatile compounds.

CASE IV

Circumstances

contamination:	tetrachloroethene (PER)
groundwater concentration:	57000 µg l^{-1} (5534 mg kg^{-1} ds. CSOIL input)
groundwater table:	22 m-mv
soil profile:	sand with loam (z: 0.5 m; kappa: $10^{-10.5}$ m^2)
measuring period:	winter (air pressure differences 2 Pa)
concentration outdoor air:	low
distance measurements air—groundwater:	10 m

Calculations

Case IV					
	Measured (µg m^{-3})	CSOIL (µg m^{-3})	c/m*	VOLASOIL (µg m^{-3})	c/m*
Conc. crawl space	4700	7980	2	42712	9
Conc. indoor	2200	798	0.4	1808	0.8

* = calculated concentration/measured concentration

CASE V

Circumstances

contamination:	tetrachloroethene (PER)
groundwater concentration:	geometric mean = 81 µg l^{-1} (7.9 mg kg^{-1} ds. CSOIL input)
groundwater table:	0.9 m-mv
soil profile:	sand (z: 0.5 m; kappa: $10^{-10.5}$ m^2)
depth crawl space:	0.75 m-mv
measuring period:	unknown
concentration outdoor air:	unknown
distance measurements air—groundwater:	± 5 m

Calculations

Case V					
	Measured (µg m^{-3})	CSOIL (µg m^{-3})	c/m*	VOLASOIL (µg m^{-3})	c/m*
Conc. crawl space	948	3610	4	126550	130
Conc. indoor	194	361	2	5358	30

* = calculated concentration/measured concentration

CASE VI

Circumstances

contamination:	trichloroethene (TRI)
groundwater concentration:	4000 µg l^{-1} (496 mg kg^{-1} ds. CSOIL input)
groundwater table:	22 m-mv
soil profile:	sand with loam (z: 0.5 m; kappa: $10^{-10.5}$ m^2)
measuring period:	winter (air pressure differences 2 Pa)
concentration outdoor air:	low
distance measurements air—groundwater:	10 m

Calculations

Case VI					
	Measured (µg m^{-3})	CSOIL (µg m^{-3})	c/m*	VOLASOIL (µg m^{-3})	c/m*
Conc. crawl space	280	1230	4	1369	5
Conc. indoor	150	123	0.8	58	0.4

* = calculated concentration/measured concentration

CASE VII

Circumstances

contamination:	vinylchloride (VC) at ± 0.5 m below groundwater table
groundwater concentration:	11000 µg l^{-1} (148 mg kg^{-1} ds. CSOIL input)
groundwater table:	2.6 m-mv
soil profile:	fine sand with little loam (z: 0.38 m; kappa: $10^{-12.5}$ m^2)
measuring period:	summer
concentration outdoor air:	< 14 µg m^{-3}
distance measurements air—groundwater:	± 30 m

Calculations

Case VII					
	Measured (µg m^{-3})	CSOIL (µg m^{-3})	c/m*	VOLASOIL (µg m^{-3})	c/m*
Conc. crawl space	< 14	54600	± 4000	31	± 2
Conc. indoor	< 14	5460	± 400	1.3	± 0.1

* = calculated concentration/measured concentration

APPENDIX 7: UNCSAM results of sensitivity and uncertainty analysis

```
 #1 28-nov-95 11:56:04
 #2 UNCSAM-TABUNC [RIVM] Version 1.2, [Okt 3, 1995]
 #3 Copyright (c) RIVM/CWM, 1995

                    GENERAL     INFORMATION


 *** Uncertainty measures of file: 951128-g.tab
Title: VOLASOIL (version 1.5); 28 november 1995

  Number of parameters                  :  18
  Number of model-outcomes              :   3
  Number of runs                        : 200

Separation-index for Kolmogorov-Smirnov analysis: 0.900
Largest VIF for original regression             : 0.103E+01
Largest VIF for rank-regression                 : 0.102E+01

             ****       A:   Ordinary Regression Summary     ****

  ==============================================================================
                   d.f. ||  CIA           ||  CCA           ||  CSA           |
  Sum  Sq. Reg.  ||   18 ||    0.635E-01  ||    0.437E+00  ||    0.643E+01  |
  Mean Sq. Reg.  ||   18 ||    0.353E-02  ||    0.243E-01  ||    0.357E+00  |
  ------------------------------------------------------------------------------
  Sum  Sq. Error ||  181 ||    0.234E-01  ||    0.295E+01  ||    0.160E-03  |
  Mean Sq. Error ||  181 ||    0.129E-03  ||    0.163E-01  ||    0.883E-06  |
  ------------------------------------------------------------------------------
  Sum  Sq. Total ||  199 ||    0.869E-01  ||    0.339E+01  ||    0.643E+01  |
  Mean Sq. Total ||  199 ||    0.437E-03  ||    0.170E-01  ||    0.323E-01  |
  ------------------------------------------------------------------------------
       R2        || ---- ||    0.731E+00  ||    0.129E+00  ||    0.100E+01  |
       R2adj.    || ---- ||    0.704E+00  ||    0.424E-01  ||    0.100E+01  |
  ==============================================================================

             ****       B:   Rank Regression Summary     ****

  ==============================================================================
                   d.f. ||  CIA           ||  CCA           ||  CSA           |
  Sum  Sq. Reg.  ||   18 ||    0.545E+06  ||    0.600E+06  ||    0.665E+06  |
  Mean Sq. Reg.  ||   18 ||    0.303E+05  ||    0.333E+05  ||    0.369E+05  |
  ------------------------------------------------------------------------------
  Sum  Sq. Error ||  181 ||    0.122E+06  ||    0.671E+05  ||    0.157E+04  |
  Mean Sq. Error ||  181 ||    0.672E+03  ||    0.371E+03  ||    0.870E+01  |
  ------------------------------------------------------------------------------
  Sum  Sq. Total ||  199 ||    0.667E+06  ||    0.667E+06  ||    0.667E+06  |
  Mean Sq. Total ||  199 ||    0.335E+04  ||    0.335E+04  ||    0.335E+04  |
  ------------------------------------------------------------------------------
       R2        || ---- ||    0.818E+00  ||    0.899E+00  ||    0.998E+00  |
       R2adj.    || ---- ||    0.800E+00  ||    0.889E+00  ||    0.997E+00  |
  ==============================================================================
```

Information on the NRC (sensitivity analysis)

PARAMETER	CIA NRC	CIA Rank	CCA NRC	CCA Rank	CSA NRC	CSA Rank
M	285.4762	1	4220.5816	1	0.1034	4
Vp	-68.6362	2	-198.4285	2	0.9569	3
S	14.7665	3	54.1664	3	-1.0007	1
dg	-1.7651	4	-2.7920	6	0.0000	10
Csw	1.1415	5	6.0428	4	1.0001	2
vri	-0.8252	6	-0.5384	16	0.0000	18
Δpcs	0.6731	7	0.7715	14	0.0000	16
Vi	0.5509	8	-1.3403	9	-0.0003	5
Af	0.5420	9	3.0666	5	-0.0002	6
κ	0.3942	10	1.4327	8	0.0000	17
z	0.3508	11	0.1626	17	0.0000	12
dc	0.3065	12	0.8352	12	-0.0001	9
Vc	-0.1831	13	0.1461	18	-0.0001	8
Aof	0.1502	14	-2.1216	7	0.0000	11
Lf	0.0979	15	-1.3225	10	0.0000	15
Δpic	0.0579	16	-0.6069	15	0.0000	13
vrc,b	-0.0481	17	-0.7830	13	0.0000	14
n	0.0132	18	0.9563	11	0.0001	7

Information on the SRC (uncertainty analyses)

PARAMETER	CIA SRC	CIA Rank	CCA SRC	CCA Rank	CSA SRC	CSA Rank
Δpcs	0.7723	1	0.1992	1	-0.0001	12
vri	-0.3176	2	-0.0466	10	0.0000	16
κ	0.1287	3	0.1053	5	0.0000	17
S	0.0579	4	0.0478	9	-0.0981	2
dg	-0.0557	5	-0.0198	15	0.0000	15
Aof	0.0554	6	-0.1759	2	-0.0003	10
Af	0.0515	7	0.0656	7	-0.0005	4
Δpic	0.0482	8	-0.1137	4	-0.0004	6
dc	0.0462	9	0.0283	11	-0.0005	5
Csw	0.0453	10	0.0540	8	0.9939	1
z	0.0355	11	0.0037	18	0.0001	14
vrc,b	-0.0328	12	-0.1200	3	-0.0001	13
Vp	-0.0325	13	-0.0211	14	0.0113	3
Vi	0.0226	14	-0.0124	16	-0.0004	9
Vc	-0.0223	15	0.0040	17	-0.0004	8
M	0.0202	16	0.0671	6	0.0002	11
Lf	0.0092	17	-0.0280	12	0.0000	18
n	0.0016	18	0.0261	13	0.0004	7

Information on the NRRC (sensitivity analysis)

PARAMETER	CIA NRRC	CIA Rank	CCA NRRC	CCA Rank	CSA NRRC	CSA Rank
Δpcs	0.6298	1	0.4067	3	-0.0029	12
vri	-0.4978	2	-0.0152	17	0.0024	13
κ	0.1982	3	0.0775	7	-0.0018	15
Δpic	0.1580	4	-0.5918	2	-0.0041	11
Aof	0.1400	5	-0.5935	1	0.0048	7
Af	0.1349	6	0.1355	4	0.0080	3
vrc,b	-0.1288	7	-0.0866	5	0.0048	8
dc	0.1285	8	0.0616	8	0.0051	5
dg	-0.1151	9	-0.0510	9	0.0004	17
S	0.0819	10	-0.0156	16	-0.0921	2
z	0.0706	11	0.0329	13	-0.0015	16
Csw	-0.0464	12	0.0117	18	0.9951	1
Vc	0.0356	13	-0.0451	12	0.0067	4
Vi	-0.0270	14	-0.0230	14	0.0045	10
M	0.0185	15	-0.0178	15	0.0049	6
Lf	-0.0183	16	0.0483	11	-0.0023	14
Vp	0.0131	17	-0.0484	10	0.0045	9
n	-0.0021	18	0.0825	6	0.0002	18

Information on the SRRC (uncertainty analysis)

PARAMETER	CIA SRRC	CIA Rank	CCA SRRC	CCA Rank	CSA SRRC	CSA Rank
Δpcs	0.6298	1	0.4067	3	-0.0029	12
vri	-0.4978	2	-0.0152	17	0.0024	13
κ	0.1982	3	0.0775	7	-0.0018	15
Δpic	0.1580	4	-0.5918	2	-0.0041	11
Aof	0.1400	5	-0.5935	1	0.0048	7
Af	0.1349	6	0.1355	4	0.0080	3
vrc,b	-0.1288	7	-0.0866	5	0.0048	8
dc	0.1285	8	0.0616	8	0.0051	5
dg	-0.1151	9	-0.0510	9	0.0004	17
S	0.0819	10	-0.0156	16	-0.0921	2
z	0.0706	11	0.0329	13	-0.0015	16
Csw	-0.0464	12	0.0117	18	0.9951	1
Vc	0.0356	13	-0.0451	12	0.0067	4
Vi	-0.0270	14	-0.0230	14	0.0045	10
M	0.0185	15	-0.0178	15	0.0049	6
Lf	-0.0183	16	0.0483	11	-0.0023	14
Vp	0.0131	17	-0.0484	10	0.0045	9
n	-0.0021	18	0.0825	6	0.0002	18

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#1 16-nov-95 11:53:30
#2 UNCSAM-BASICS [RIVM] Version 1.2, [Okt 3, 1995]
#3  Copyright (c) RIVM/CWM, 1995

**** Basic Statistics of file: 951116-a.bam


     Title:  VOLASOIL (version 1.5); 16 november 1995
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parameter	mean	st. dev.	c.v.
M	7.81100E+01	7.09617E-03	9.08484E-05
Vp	6.29470E+03	3.83133E+00	6.08659E-04
S	2.29522E+01	1.15637E-01	5.03815E-03
Csw	3.00042E+01	1.53204E+00	5.10608E-02
κ	5.05104E-12	2.11971E-12	4.19658E-01
dg	1.49992E+00	6.08601E-02	4.05756E-02
z	4.89996E-01	6.36938E-02	1.29988E-01
Vi	1.50037E+02	7.92809E+00	5.28409E-02
Vc	2.49947E+01	3.91185E+00	1.56507E-01
dc	4.00058E-01	7.75059E-02	1.93737E-01
vrc,b	1.74546E+01	1.52857E+01	8.75743E-01
vri	7.04280E+01	3.48495E+01	4.94825E-01
Af	4.99763E+01	6.10441E+00	1.22146E-01
Lf	9.99864E-02	1.21126E-02	1.21142E-01
Aof	2.75029E-02	1.30288E-02	4.73727E-01
n	9.99847E+00	1.56018E+00	1.56041E-01
Δpic	2.96828E+00	3.17813E+00	1.07070E+00
Δpcs	3.99786E+00	5.89761E+00	1.47519E+00

parameter	abs. dev.	variance	skewness	curtosis
M	5.64712E-03	5.03556E-05	8.38003E-03	-7.67464E-02
Vp	3.05443E+00	1.46791E+01	2.84406E-02	-1.01479E-01
S	9.23781E-02	1.33718E-02	9.07351E-03	-1.91045E-01
Csw	1.21973E+00	2.34714E+00	5.33128E-02	-7.72625E-02
κ	1.69276E-12	4.49316E-24	-6.33839E-03	-1.88744E-01
dg	4.84805E-02	3.70396E-03	-2.50707E-02	-9.74010E-02
z	5.50246E-02	4.05690E-03	-6.58165E-05	-1.21928E+00
Vi	6.26162E+00	6.28546E+01	1.30057E-01	2.98107E-01
Vc	3.11348E+00	1.53026E+01	-1.01261E-02	-6.29189E-02
dc	6.19856E-02	6.00717E-03	1.57333E-02	-2.19781E-01
vrc,b	1.25085E+01	2.33653E+02	1.00582E+00	-9.70121E-03
vri	2.95545E+01	1.21449E+03	5.80292E-01	-8.21612E-01
Af	4.85014E+00	3.72639E+01	-8.60682E-02	3.01210E-02
Lf	9.67031E-03	1.46714E-04	-2.00109E-02	-1.65810E-01
Aof	1.12562E-02	1.69751E-04	2.46423E-04	-1.21805E+00
n	1.24332E+00	2.43415E+00	-2.94666E-02	-1.06187E-01
Δpic	2.40171E+00	1.01005E+01	1.62925E+00	2.17973E+00
Δpcs	3.55256E+00	3.47818E+01	3.60537E+00	1.66157E+01

parameter	2.5 perc.	25 perc.	75 perc.	97.5 perc.
M	7.80956E+01	7.81052E+01	7.81148E+01	7.81242E+01
Vp	6.28705E+03	6.29211E+03	6.29729E+03	6.30224E+03
S	2.27192E+01	2.28739E+01	2.30310E+01	2.31870E+01
Csw	2.69175E+01	2.89664E+01	3.10330E+01	3.31001E+01
κ	8.39766E-13	3.61543E-12	6.49377E-12	9.25397E-12
dg	1.37724E+00	1.45860E+00	1.54101E+00	1.62234E+00
z	3.85014E-01	4.35131E-01	5.45166E-01	5.95407E-01
Vi	1.34049E+02	1.44701E+02	1.55248E+02	1.65449E+02
Vc	1.70499E+01	2.23637E+01	2.76466E+01	3.26661E+01
dc	2.47108E-01	3.46799E-01	4.52636E-01	5.55350E-01
vrc,b	1.30583E+00	5.01141E+00	2.65370E+01	5.50923E+01
vri	2.61580E+01	4.01128E+01	9.65502E+01	1.43468E+02
Af	3.79173E+01	4.58633E+01	5.41334E+01	6.23252E+01
Lf	7.58167E-02	9.17523E-02	1.08300E-01	1.24048E-01
Aof	6.01433E-03	1.62185E-02	3.88577E-02	4.90271E-02
n	6.89914E+00	8.93553E+00	1.10486E+01	1.31128E+01
Δpic	1.10226E-01	7.11170E-01	4.09277E+00	1.25109E+01
Δpcs	1.71736E-01	8.80744E-01	4.50434E+00	2.34325E+01

parameter	50 perc.	mean	minimum	maximum
M	7.81100E+01	7.81100E+01	7.80907E+01	7.81309E+01
Vp	6.29470E+03	6.29470E+03	6.28470E+03	6.30615E+03
S	2.29521E+01	2.29522E+01	2.26473E+01	2.32714E+01
Csw	2.99966E+01	3.00042E+01	2.60152E+01	3.46290E+01
κ	5.04524E-12	5.05104E-12	-6.93769E-13	1.06687E-11
dg	1.50015E+00	1.49992E+00	1.32351E+00	1.66747E+00
z	4.90183E-01	4.89996E-01	3.80955E-01	5.99005E-01
Vi	1.50000E+02	1.50037E+02	1.29066E+02	1.78699E+02
Vc	2.50084E+01	2.49947E+01	1.39075E+01	3.65654E+01
dc	4.00203E-01	4.00058E-01	1.95660E-01	6.10019E-01
vrc,b	1.22502E+01	1.74546E+01	1.03729E+00	5.94476E+01
vri	6.24540E+01	7.04280E+01	2.51356E+01	1.49637E+02
Af	4.99995E+01	4.99763E+01	2.99526E+01	6.61784E+01
Lf	1.00010E-01	9.99864E-02	6.58706E-02	1.31758E-01
Aof	2.74944E-02	2.75029E-02	5.07023E-03	4.99018E-02
n	9.99577E+00	9.99847E+00	5.34142E+00	1.41407E+01
Δpic	1.75575E+00	2.96828E+00	3.86494E-02	1.44473E+01
Δpcs	2.00556E+00	3.99786E+00	4.63628E-02	4.50072E+01

```
 #1 28-nov-95 11:54:27
 #2 UNCSAM-BASICS [RIVM] Version 1.2, [Okt 3, 1995]
 #3 Copyright (c) RIVM/CWM, 1995

**** Basic Statistics of file: 951128-g.bim

     Title:   simulation data from file: 951128-g.sgn
```

parameter	mean	st. dev.	c.v.
CIA	1.62556E-02	2.08998E-02	1.28570E+00
CCA	2.28515E-02	1.30536E-01	5.71239E+00
CSA	3.49852E+00	1.79739E-01	5.13757E-02

parameter	abs. dev.	variance	skewness	curtosis
CIA	1.33437E-02	4.36803E-04	3.04541E+00	1.14463E+01
CCA	2.95673E-02	1.70398E-02	1.29010E+01	1.73019E+02
CSA	1.42320E-01	3.23060E-02	6.04834E-02	-4.06192E-02

parameter	2.5 perc.	25 perc.	75 perc.	97.5 perc.
CIA	8.83726E-04	4.77050E-03	1.76570E-02	8.69487E-02
CCA	1.97259E-04	1.59424E-03	1.26596E-02	1.18378E-01
CSA	3.10385E+00	3.37392E+00	3.62412E+00	3.85412E+00

parameter	50 perc.	mean	minimum	maximum
CIA	8.75300E-03	1.62556E-02	9.36713E-05	1.35348E-01
CCA	4.66693E-03	2.28515E-02	1.07619E-04	1.81063E+00
CSA	3.49576E+00	3.49852E+00	3.03501E+00	4.03894E+00

MODELLED CONCENTRATIONS BY UNCSAM

	CSA [g.m-3]	CCA [g.m-3]	CIA [g.m-3]
NUMBER:	200	200	200
MEAN:	3.49852022709	0.022851461	0.016255641
MINIMUM	3.03500706169	0.000107619	0.000093671
MAXIMUM	4.03893548411	1.810629791	0.135348274
	3.576864e+00	1.762551e-02	8.723049e-03
	3.788825e+00	5.128893e-03	6.310257e-03
	3.450784e+00	1.410561e-03	1.022312e-02
	3.436226e+00	1.625659e-03	1.144138e-02
	3.774245e+00	2.904817e-02	4.212725e-02
	3.102809e+00	3.857735e-04	1.457314e-02
	3.646197e+00	5.921440e-03	4.143517e-02
	3.519062e+00	4.507543e-03	4.496825e-03
	3.319854e+00	1.428358e-03	5.873603e-03
	3.478851e+00	2.976088e-03	1.048183e-02
	3.484449e+00	2.028156e-03	1.890325e-02
	3.073575e+00	8.297826e-02	4.337768e-02
	4.038935e+00	2.969267e-03	1.149828e-02
	3.779127e+00	1.265811e-03	9.112995e-03
	3.721487e+00	2.970872e-02	5.586297e-03
	3.479255e+00	1.218079e-02	1.627616e-02
	3.560756e+00	1.156794e-02	6.998038e-03
	3.271546e+00	4.742823e-03	1.664164e-03
	3.550578e+00	1.049626e-03	4.602844e-03
	3.253903e+00	3.016574e-03	5.403135e-03
	3.567753e+00	6.220073e-04	2.514119e-03
	3.493738e+00	5.238061e-03	1.425373e-03
	3.572278e+00	1.099746e-01	8.756440e-03
	3.494076e+00	1.968716e-03	2.936307e-03
	3.595493e+00	1.675229e-01	1.343296e-01
	3.417339e+00	6.473731e-03	4.572648e-03
	3.352462e+00	2.585171e-03	2.281299e-02
	3.319720e+00	3.053434e-03	4.923915e-02
	3.343875e+00	1.332656e-03	2.798291e-02
	3.532898e+00	2.548086e-02	1.032569e-02
	3.373893e+00	1.733757e-02	7.195087e-03
	3.397268e+00	7.645448e-03	1.195361e-02
	3.626966e+00	2.254993e-02	1.454215e-02
	3.499890e+00	1.565453e-03	4.114241e-03
	3.035007e+00	1.211930e-02	9.402832e-03
	3.343210e+00	1.647070e-03	9.656885e-03
	3.706316e+00	4.591030e-03	3.688252e-02
	3.465958e+00	6.197809e-03	1.113262e-02
	3.626279e+00	2.245843e-03	4.952878e-03
	3.524860e+00	1.810630e+00	4.757598e-02
	3.493821e+00	2.857842e-03	7.104578e-03
	3.661548e+00	1.175769e-02	4.402367e-03
	3.822609e+00	7.531859e-03	2.270395e-03
	3.874271e+00	5.806781e-03	9.855563e-03

CSA [g.m-3]	CCA [g.m-3]	CIA [g.m-3]
3.675495e+00	2.430456e-04	8.230718e-03
3.627800e+00	6.823961e-03	2.363769e-02
3.436601e+00	4.898542e-02	1.936279e-02
3.666131e+00	1.580034e-02	1.419950e-02
3.456877e+00	3.041934e-02	1.119453e-02
3.428343e+00	1.185931e-01	1.324364e-02
3.555488e+00	3.932695e-03	1.668956e-02
3.886369e+00	2.016933e-03	1.642725e-02
3.377656e+00	1.983633e-03	2.147743e-02
3.266374e+00	6.687373e-04	7.502548e-03
3.379374e+00	2.845595e-02	4.530371e-02
3.736561e+00	6.662698e-03	3.364728e-02
3.483144e+00	3.075008e-03	2.400829e-03
3.594056e+00	5.802932e-03	6.748980e-03
3.374007e+00	3.123930e-03	1.668555e-02
3.578838e+00	1.961527e-04	6.748412e-03
3.398313e+00	2.657896e-04	4.286011e-03
3.449095e+00	8.747562e-02	1.353483e-01
3.553221e+00	2.518134e-02	2.802977e-03
3.546745e+00	1.821050e-02	1.011040e-03
3.584209e+00	4.511967e-03	7.326723e-03
3.630269e+00	9.102236e-03	4.394517e-02
3.545604e+00	3.096050e-03	8.649252e-03
3.610107e+00	3.683842e-04	1.778914e-02
3.144449e+00	3.343673e-02	9.940415e-04
3.493734e+00	3.675665e-04	2.024478e-03
3.695333e+00	6.227227e-03	1.295152e-02
3.378939e+00	6.725328e-03	2.575066e-03
3.617630e+00	1.240912e-03	4.658869e-03
3.636382e+00	5.095466e-04	2.931888e-03
3.497106e+00	2.285377e-03	2.414984e-02
3.637332e+00	2.928606e-02	2.382082e-02
3.655385e+00	3.068715e-03	8.985663e-02
3.432179e+00	1.273914e-03	4.755568e-03
3.635992e+00	4.988721e-02	2.413834e-02
3.612079e+00	1.564312e-02	2.449292e-03
3.660716e+00	4.228626e-03	1.422332e-02
3.516010e+00	1.363290e-04	5.770743e-03
3.363083e+00	1.925034e-02	9.367132e-05
3.579221e+00	9.626432e-03	5.410530e-03
3.515288e+00	3.173210e-03	8.451616e-04
3.481228e+00	2.584680e-03	2.171121e-02
3.353720e+00	5.603791e-04	1.186957e-02
3.730782e+00	1.124038e-02	6.772061e-03
3.606437e+00	6.199213e-04	1.122944e-02
3.750800e+00	2.476110e-02	4.791979e-03
3.445298e+00	1.059232e-02	1.705079e-02
3.407431e+00	9.418987e-04	3.696775e-03
3.499372e+00	1.604512e-03	1.913773e-02
3.241335e+00	6.914359e-03	1.966185e-02
3.366575e+00	1.590819e-03	1.074089e-02
3.481622e+00	2.817700e-03	1.658759e-02
3.507095e+00	5.789159e-03	2.834684e-02

CSA [g.m-3]	CCA [g.m-3]	CIA [g.m-3]
3.443949e+00	1.452838e-03	1.683864e-02
3.399937e+00	7.768240e-03	2.669646e-02
3.183631e+00	1.886944e-02	2.666492e-02
3.655725e+00	7.448114e-04	1.266067e-02
3.350477e+00	1.657417e-02	6.047975e-02
3.509641e+00	2.862200e-03	3.191086e-02
3.395857e+00	3.609492e-03	3.736890e-03
3.452434e+00	1.274443e-02	8.750562e-03
3.480991e+00	1.467783e-02	3.677327e-03
3.479899e+00	1.164531e-02	3.000414e-03
3.263304e+00	1.083337e-03	7.643331e-03
3.556137e+00	6.817412e-03	1.102392e-02
3.471041e+00	4.293209e-04	1.214160e-02
3.225464e+00	1.860042e-02	1.486502e-02
3.631534e+00	1.787174e-04	6.716394e-03
3.410730e+00	3.288454e-03	4.665526e-03
3.628869e+00	3.469293e-02	4.997507e-03
3.284662e+00	7.361914e-03	9.006340e-03
3.336289e+00	6.135133e-03	3.328568e-02
3.364692e+00	1.859749e-02	4.415317e-02
3.304416e+00	4.533369e-03	1.347536e-02
3.323063e+00	3.767605e-02	1.688204e-02
3.269625e+00	2.475679e-04	1.749572e-02
3.244119e+00	4.387526e-03	6.310202e-03
3.417028e+00	5.190476e-03	8.630927e-03
3.565980e+00	1.240522e-02	5.084521e-03
3.613436e+00	2.669581e-04	1.407271e-02
3.679165e+00	1.089665e-02	4.155745e-03
3.572798e+00	1.261418e-03	6.907294e-03
3.745555e+00	3.814700e-04	6.059223e-03
3.101880e+00	1.335960e-03	8.470076e-03
3.377556e+00	1.552846e-03	3.544948e-03
3.433686e+00	5.089628e-02	1.157446e-02
3.702706e+00	4.130640e-04	4.135759e-03
3.631773e+00	1.452954e-03	3.338114e-02
3.545984e+00	2.404128e-04	3.864722e-03
3.351149e+00	2.395515e-03	1.741900e-02
3.810911e+00	2.978037e-02	7.057411e-03
3.353208e+00	1.474870e-03	8.455852e-03
3.406862e+00	2.231888e-03	6.177381e-03
3.495094e+00	2.706312e-03	4.341957e-03
3.791690e+00	9.448483e-03	5.199383e-03
3.217934e+00	1.170122e-02	2.871897e-02
3.983215e+00	4.609152e-04	1.452787e-02
3.556373e+00	1.076192e-04	4.242343e-03
3.295969e+00	1.430555e-04	5.484814e-03
3.824708e+00	2.936737e-01	8.755446e-03
3.654975e+00	5.350749e-03	6.991341e-02
3.512280e+00	9.705734e-04	6.330301e-03
3.329663e+00	3.231004e-03	1.846964e-02
3.452482e+00	6.371978e-02	3.434465e-02
3.215765e+00	6.776577e-04	9.231122e-03
3.443831e+00	1.249097e-01	6.677224e-02

CSA [g.m-3]	CCA [g.m-3]	CIA [g.m-3]
3.448950e+00	5.577618e-02	1.013386e-01
3.205797e+00	6.612271e-03	3.000484e-03
3.295036e+00	1.477093e-02	4.295037e-02
3.163876e+00	8.152463e-03	4.121517e-02
3.261311e+00	4.252098e-03	5.392205e-03
3.762465e+00	1.630306e-02	1.417626e-02
3.573770e+00	7.884485e-04	4.763342e-03
3.789903e+00	1.001696e-02	4.828884e-03
3.601076e+00	7.281253e-03	6.298892e-02
3.558365e+00	1.309937e-02	9.619464e-03
3.322966e+00	5.081162e-03	6.171380e-03
3.828389e+00	3.358705e-04	1.220487e-02
3.669605e+00	5.438112e-03	8.413453e-04
3.417627e+00	4.429256e-03	1.106723e-02
3.664199e+00	5.737183e-02	1.522901e-02
3.406903e+00	6.252242e-03	5.112475e-02
3.195990e+00	1.695545e-03	3.569490e-03
3.599438e+00	2.561976e-03	7.767119e-02
3.284252e+00	1.960224e-03	8.387845e-03
3.417554e+00	7.017774e-03	8.718657e-02
3.512770e+00	3.144065e-03	4.020839e-03
3.525544e+00	2.783300e-04	1.271782e-02
3.501244e+00	1.231633e-02	7.474972e-03
3.088805e+00	3.629740e-03	2.877243e-02
3.362649e+00	2.637604e-03	3.766071e-03

MODELLED CONCENTRATIONS BY UNCSAM

CSA Conc. [g.m-3]	Number	Fraction	CCA Conc. [g.m-3]	Number	Fraction
3.0	0	0.0%	0	0	0.0%
3.1	3	1.5%	0.01	137	68.5%
3.2	6	3.0%	0.02	30	15.0%
3.3	18	9.0%	0.03	13	6.5%
3.4	32	16.0%	0.04	5	2.5%
3.5	46	23.0%	0.05	2	1.0%
3.6	36	18.0%	0.06	3	1.5%
3.7	33	16.5%	0.07	2	1.0%
3.8	17	8.5%	0.08	0	0.0%
3.9	7	3.5%	0.09	2	1.0%
4.0	1	0.5%	0.1	0	0.0%
4.1	1	0.5%	0.11	1	0.5%
4.2	0	0.0%	0.12	1	0.5%
> 4.2	0	0.0%	0.13	1	0.5%
			> 0.130	3	1.5%

CIA Conc. [g.m-3]	Number	Fraction	Cum. Number	Cum. %
0	0	0.0%	0	0
0.002	14	7.0%	14	7
0.004	21	10.5%	35	17.5
0.006	35	17.5%	70	35
0.008	21	10.5%	91	45.5
0.01	19	9.5%	110	55
0.012	14	7.0%	124	62
0.014	7	3.5%	131	65.5
0.016	9	4.5%	140	70
0.018	12	6.0%	152	76
0.02	5	2.5%	157	78.5
0.022	2	1.0%	159	79.5
0.024	3	1.5%	162	81
0.026	2	1.0%	164	82
0.028	3	1.5%	167	83.5
0.03	4	2.0%	171	85.5
0.032	1	0.5%	172	86
0.034	3	1.5%	175	87.5
0.036	2	1.0%	177	88.5
0.038	2	1.0%	179	89.5
0.04	0	0.0%	179	89.5
0.042	2	1.0%	181	90.5
0.044	4	2.0%	185	92.5
0.046	2	1.0%	187	93.5
0.048	1	0.5%	188	94
0.05	1	0.5%	189	94.5
0.052	1	0.5%	190	95
0.054	0	0.0%	190	95
0.056	0	0.0%	190	95
0.058	0	0.0%	190	95
0.06	0	0.0%	190	95
0.062	1	0.5%	191	95.5
0.064	1	0.5%	192	96
0.066	0	0.0%	192	96
0.068	1	0.5%	193	96.5
0.07	1	0.5%	194	97
0.072	0	0.0%	194	97
0.074	0	0.0%	194	97
0.076	0	0.0%	194	97
0.078	1	0.5%	195	97.5
0.08	0	0.0%	195	97.5
0.082	0	0.0%	195	97.5
0.084	0	0.0%	195	97.5
0.086	0	0.0%	195	97.5
0.088	1	0.5%	196	98
0.09	1	0.5%	197	98.5
0.092	0	0.0%	197	98.5
0.094	0	0.0%	197	98.5
0.096	0	0.0%	197	98.5
0.098	0	0.0%	197	98.5
0.1	0	0.0%	197	98.5
> 0.10	3	1.5%	200	100
	200			

APPENDIX 8: Modified CSOIL exposure time equations

M.F.W. Waitz

The CSOIL exposure time calculations of inhalation of volatile compounds in air depends on the indoor/outdoor concentration of air, daily duration of indoor/outdoor exposure, annual average time fractions for residential time indoors/outdoors, relative absorption factors and human physiological characteristics such as breathing volume and body weight [Van den Berg, 1995]. Application of CSOIL exposure time calculations for site-specific risk assessment is difficult due to complicated exposure time calculations. In CSOIL daily duration of exposure indoor/outdoor (t) are closely correlated with the annual average time fractions (tf) for stay indoor/outdoor. They cannot be separated and are difficult to understand. Using following exposure calculations, CSOIL exposure time equations could be modified.

Multiplication of daily exposure durations and time fractions give exposure times. These values, easier to apply, are used below. Intake of volatile soil contaminants by adults or children is calculated by:

$$IV_a = \frac{(Cia\ T_{i,a} + Coa\ T_{o,a})\ \ AV_a\ \ fa\ 1000}{W_a} \qquad (1)$$

$$IV_c = \frac{(Cia\ T_{i,c} + Coa_c\ T_{o,c})\ \ AV_c\ \ fa\ 1000}{W_c} \qquad (2)$$

where:
- IV_a = intake of contaminants through inhalation of air, adult [$mg.kg^{-1}.d^{-1}$]
- IV_c = intake of contaminants through inhalation of air, child [$mg.kg^{-1}.d^{-1}$]
- Cia = concentration indoor air [$g.m^{-3}$]
- Coa_a = concentration outdoor air, for an adult at breathing height [$g.m^{-3}$]
- Coa_c = concentration outdoor air, for a child at breathing height [$g.m^{-3}$]
- $T_{i,a}$ = daily indoor exposure time, adult [$h.d^{-1}$]
- $T_{i,c}$ = daily indoor exposure time, child [$h.d^{-1}$]
- $T_{o,a}$ = daily outdoor exposure time, adult [$h.d^{-1}$]
- $T_{o,c}$ = daily outdoor exposure time, child [$h.d^{-1}$]
- AV_a = breathing volume, adult [$m^3.d^{-1}$]
- AV_c = breathing volume, child [$m^3.d^{-1}$]
- fa = relative absorption factor of contaminants in lungs [-; default set at 1]
- W_a = body weight, adult [kg]
- W_c = body weight, child [kg]

Intake of volatile compounds depends on the concentration in indoor and outdoor air, time spent indoors and outdoors, breathing volume, absorption of contaminants in lungs and body weight. Values of above-mentioned parameters are different for children than for adults (see Table 1).

***Table 1:** Parameters for calculation of intake of volatile soil contaminants by adults and children [Van den Berg, 1995; Linders, 1990]*

Parameters		Adult	Child
breathing volume	AV	20 $m^3.d^{-1}$ = 0.83 $m^3.h^{-1}$	7.6 $m^3.d^{-1}$ = 0.32 $m^3.h^{-1}$
daily indoor exposure time	T_i	22.85 $h.d^{-1}$	21.15 $h.d^{-1}$
daily outdoor exposure time	T_o	1.14 $h.d^{-1}$	2.86 $h.d^{-1}$
body weight	W	70 kg	15 kg
breathing height	Z^*	1.5 m	1.0 m

* : see outdoor-air concentration

Daily indoor/outdoor exposure times can be changed without difficulty. For example, calculation of exposure times are given (Table 2) for the standard scenario (house with garden) used for assessing Intervention Values.

***Table 2:** Sample calculations of daily indoor/outdoor exposure times*

Exposed	Exposure location	Weekday			Weekend			Week	Day
		days	hours	total hours	days	hours	total hours	total hours	mean hours
		[-]	[h.d^{-1}]	[h]	[-]	[h.d^{-1}]	[h]	[h.w^{-1}]	[h.d^{-1}]
adult	indoor	5	24	120	2	20	40	160	22.86
	outdoor	5	0	0	2	4	8	8	1.14
child	indoor	5	22	110	2	19	38	148	21.14
	outdoor	5	2	10	2	5	10	20	2.86

Lifelong average daily exposure to volatile soil contaminants is calculated by using Equation (3), according to the current set of formulas. The exposure is the weighted average of the intake of contaminants through inhalation of air for an adult and a child. The human lifetime is 6 years for a child and 64 years for an adult.

$$DOSE_{IV} = \frac{6\ IV_c + 64\ IV_a}{70} \qquad (3)$$

where: $DOSE_{iv}$ = lifelong average daily exposure to volatile soil [mg.kg^{-1}.d^{-1}]
IV_a = intake of contaminants through inhalation of air, adult [mg.kg^{-1}.d^{-1}]
IV_c = intake of contaminants through inhalation of air, child [mg.kg^{-1}.d^{-1}]I

Waitz, *et al.* [1996]: The VOLASOIL risk assessment model based on CSOIL for soils contaminated with volatile compounds.

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