

Theme of the poster: Theme C: SITE CHARACTERISATION & RISK ASSESSMENT - No PhD work.

VAPOR EMISSIONS FROM CONTAMINATED SOILS INTO BUILDINGS: DEVELOPMENTS OF THE VOLASOIL MODEL FOR A MULTILAYER SOIL

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1. Summary

Soil vapor migration into house, with subsequent inhalation, is often the main exposure pathway to humans at sites contaminated with volatile organic compounds (VOCs). In the case of VOCs contamination, quantification of indoor gas concentrations is therefore essential while assessing risks for human health.

The Johnson & Ettinger model (US EPA, 2003) and the VOLASOIL model (Waitz *et al.*, 1996) are the two models mainly used in France to predict indoor air concentrations. In comparison with Johnson & Ettinger, the VOLASOIL appears more simple and direct: Results are easier to account for, making a conscious and appropriate modelling easier in its field of application.

The VOLASOIL model is conceived for one unsaturated layer (soil or concrete slab) above the pollution source only. We present here developments of the VOLASOIL model for the general case of a multilayer soil, inclusive a multilayer capillary fringe or aquifer for a source in the aquifer. These developments should allow a broader use of VOLASOIL, e.g. for a building with a concrete slab. These developments are illustrated with an application and discussed as regards validity for different cases of source.

2. Introduction

Soil vapor migration into house, with subsequent inhalation, is often the main exposure pathway to humans at sites contaminated with volatile organic compounds (VOCs). In the case of VOCs contamination, quantification of indoor gas concentrations is therefore essential while assessing risks for human health.

The Johnson & Ettinger model (US EPA, 2003) and the VOLASOIL model (Waitz *et al.*, 1996) are the two models mainly used in France to predict indoor air concentrations. In comparison with Johnson & Ettinger, the VOLASOIL appears more simple and direct: the vapor transfer modelling is based only on the Darcy and Fick laws of convection and diffusion. Results are easier to account for, making a conscious and appropriate modelling easier in its field of application. This could help avoiding the use of the model as a "black box".

The VOLASOIL model (Waitz *et al.*, 1996) is conceived for one unsaturated layer (soil or concrete slab) above the pollution source only.

We present here developments of the VOLASOIL model for the general case of a multilayer soil, inclusive a multilayer capillary fringe or aquifer for a source in the aquifer.

After a short presentation of the VOLASOIL model, these developments are presented, then illustrated with an application and discussed as regards validity for different cases of source.

3. Presentation of the VOLASOIL model

3.1. History

The CSOIL model was first issued by the Dutch RIVM in 1994 (van den Berg, 1994). It modelizes the volatile pollutant flux from the soil to the indoor air as a combination of a convective transport within a flux of evaporating soil water, and a diffusion flux in the soil air and the soil water.

The RIVM developed the VOLASOIL model ("VOLASOIL") in 1996 (Waitz *et al.*, 1996) following an evaluation of the 1994 CSOIL model ("CSOIL1994"): Waitz *et al.* observed that measured indoor air concentrations could differ largely from concentrations calculated with CSOIL1994. Large temporal differences were also observed, which Waitz *et al.* considered may have been caused by convective flow of air, which is not incorporated in CSOIL1994. The theoretical evaluation by Waitz *et al.* of the vapor transfer in CSOIL1994, taking into account the American descriptions of Nazaroff (1985) and Johnson and Ettinger (1991), concluded it was not suitable for actual risk assessment. As regards the conceptual modelling, the main differences of VOLASOIL compared to CSOIL1994 are the incorporation of a convective (pressure-driven) flow of soil air, the suppression of the water evaporation flux, and the use of different contaminant scenario's. Besides, the groundwater table is incorporated in VOLASOIL.

The VOLASOIL model is integrated in the Dutch commercial software Risc Human.

3.2. Conceptual model

The conceptual model of VOLASOIL is described (with little additions¹) in Figure 1. It considers:

- four successive compartments: from the bottom to the top, saturated zone (groundwater), capillary fringe, vadose zone (soil and/or floor), indoor air (here in the crawl space, basement, or first floor);
- three flux mechanisms:
 - diffusion in the soil water of the capillary fringe and of the vadose zone;
 - diffusion in the soil air of the capillary fringe and of the vadose zone;
 - convection in the soil air of the vadose zone;

Besides, the multiphase equilibrium between soil air, soil water, and soil, is considered to take place (see right side of Figure 1)².

The different fluxes are not independent: it is the same soil air (or soil water in equilibrium with the soil air) which is simultaneously submitted to the different mechanisms, and the total pollutant flux is constant (steady state model and mass conservation).

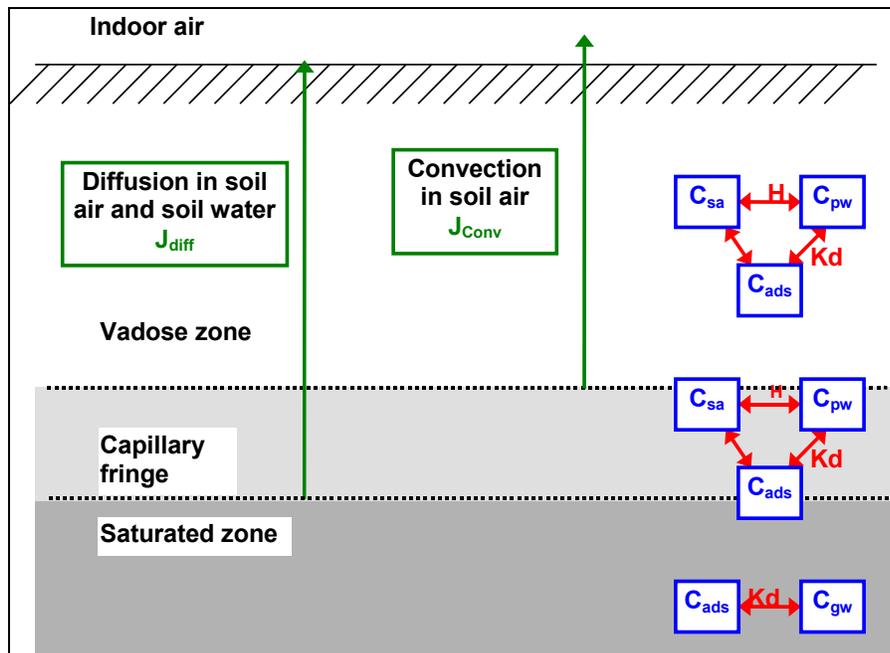


Figure 1: Conceptual model of vapor emission in indoor air (see § 4 for parameter definition)

¹ diffusive flux in soil water within the vadose zone and in soil air within the capillary fringe.

² In the original VOLASOIL model, sorption to soil does not appear. It plays a role here in the discussion of the conceptual development of the multilayer solution (§ 4.4).

4. Development of the VOLASOIL model for the general case of a multilayer soil

We consider here n successive layers of homogeneous soil, indexed from the polluted layer (i=0) up to the surface (i=n for the layer in contact with the indoor air).

4.1. Convection of soil air in the vadose zone

A convective flux of soil air is supposed to occur from the vadose zone into the indoor air, due to pressure difference between the indoor air and the soil air, which is caused by wind and heating effects.

The convective flux of soil air F_{ci} [$L/m^2/s$] is given by the Darcy law (Waitz *et al*, 1996, here with a 1000 facto for unit conversion):

Equation 1
$$F_{ci} = 1000 K_{tot} \frac{\Delta p_{is}}{L}, \text{ with:}$$

| Parameter | Symbol | Unit |
|--|------------------|--------------|
| Convective flux of soil air into the building | F_{ci} | $L/m^2/s$ |
| Air-conductivity | K | $m^3/m/Pa/s$ |
| "Mean" air-conductivity of the vadose zone (soil and/or floor) above the pollution | K_{tot} | $m^3/m/Pa/s$ |
| Pressure difference between the indoor air and the soil air | Δp_{is} | Pa |
| Thickness of the vadose zone above the pollution | $L = (\sum l_i)$ | m |
| Thickness of the layer i | l_i | m |

The air-conductivity of a given layer is described in Waitz *et al*, 1996. for several layers, the mean" air-conductivity is given, as for water conductivity, as a harmonic mean:

Equation 2
$$(\sum l_i) / K_{tot} = \sum l_i / K_i$$

4.2. Convection and diffusion of pollutant, local differential equations

The local equations of the convective and diffusive fluxes of pollutant [$mg/m^2/s$] in soil water / air is respectively given by:

Equation 3
$$J_{conv} = F_{ci} C_{sa}$$

Equation 4
$$J_{pw} = D_{pw} \text{grad}(C_{pw}) \quad (\text{Fick law})$$

Equation 5
$$J_{sa} = D_{sa} \text{grad}(C_{sa}) \quad (\text{Fick law})$$

| Parameter | Symbol | Unit |
|---|------------------|-------------------------------------|
| Pollutant concentration in soil water / air | C_{pw}, C_{sa} | $mg/L_{(pw / sa)}$ |
| Diffusion coefficients in soil water / air (see Milligton-Quirk equations in Waitz <i>et al</i> , 1996) | D_{pw}, D_{sa} | $(mg/m^2/s)/(mg/L_{(pw / sa)} / m)$ |

Writing the air / water equilibrium equation: $C_{pw} = C_{sa} / H$, we get the local expression of the multiphase diffusive flux³, J_{diff} , as a function of the pollutant concentration in soil air:

Equation 6
$$J_{diff} = J_{pw} + J_{sa} = DUa \text{grad}(C_{sa}), \text{ with:}$$

Equation 7
$$DUa = D_{sw} / H + D_{sa}, \text{ and:}$$

| Parameter | Symbol | Unit |
|--|--------|------------------------------|
| Air / water partitioning coefficient (Henry coefficient) | H | $(mg/L_a) / (mg/L_w)$ |
| Multiphase diffusion coefficient in soil expressed from the soil air concentration | DUa | $(mg/m^2/s)/(mg/L_{sa} / m)$ |

Locally, the convective and diffusive fluxes of pollutant [$mg/m^2/s$] add up. Hence the local equation of the total pollutant flux [$mg/m^2/s$]:

Equation 8
$$J_{tot} = J_{diff} + J_{conv} = DUa \text{grad}(C_{sa}) + F_{ci} C_{sa}$$

³ equivalent to J_4 in Waitz *et al*, 1996 (Annex .2.1).

4.3. Convection and diffusion of pollutant, monolayer solution of the differential equations

As a convention, the pollutant concentration in soil air in a layer i is written $C_{sa_i}(z)$ as a function of the depth z from the top of the layer i .

In each layer i , J_{tot} is constant with the depth (steady state model and mass conservation). Hence, deriving Equation 8 in regard to the depth z :

$$\text{Equation 9} \quad DU_{a_i} C_{sa_i}''(z) + F_{ci} C_{sa_i}'(z) = 0 .$$

The solution of that differential equation is:

$$\text{Equation 10} \quad C_{sa_i}(z) = - F_{ci} DU_{a_i} K_i e^{-\frac{F_{ci}}{DU_{a_i}} z} + K_i' ,$$

with K_i and K_i' two constants, which are determined by the conditions at the limits of the layer.

Noting down: $\chi_i = e^{-\frac{F_{ci}}{DU_{a_i}} l_i}$, these limit conditions are:

$$\text{Equation 11} \quad (F_{ci} DU_{a_i}) K_i = (C_{sa_i}(l_i) - C_{sa_i}(0)) / (1 - \chi_i)$$

$$\text{Equation 12} \quad K_i' = C_{sa_i}(0) + (F_{ci} DU_{a_i}) K_i , \text{ hence:}$$

$$\text{Equation 13} \quad K_i' = (C_{sa_i}(l_i) - C_{sa_i}(0) \chi_i) / (1 - \chi_i)$$

Then, substituting in Equation 8 C_{sa} by its expression from Equation 10, and then K_i' by its expression from Equation 13, we get:

$$\text{Equation 14} \quad J_{tot} = F_{ci} K_i' = F_{ci} (C_{sa_i}(l_i) - C_{sa_i}(0) \chi_i) / (1 - \chi_i)$$

This formulation of the total flux for one layer can be found in Waitz *et al*, 1996 p 68 (Equation 74 after neglecting the indoor air concentration) et p 139 (Equation 16), by substituting $C_{sa_i}(0)$ with C_o (surface) and $C_{sa_i}(l_i)$ with C_{sa} (pollution source).

4.4. Convection and diffusion of pollutant, multilayer solution

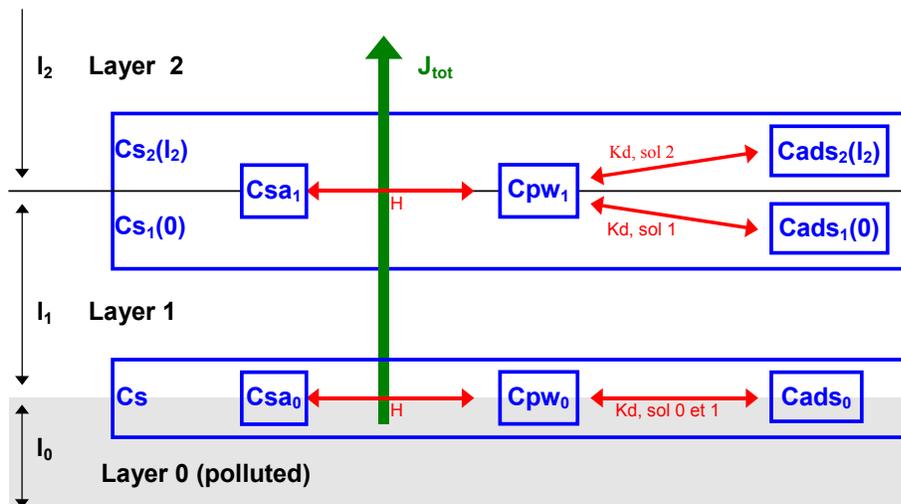


Figure 2: Modelling of diffusion and convection in a multilayer soil

From Equation 14, we get for each layer i :

$$\text{Equation 15} \quad C_{sa_i}(l_i) = F_{ci} J_{tot} (1 - \chi_i) + \chi_i C_{sa_i}(0)$$

The concentrations in soil air, C_{sa} , is continuous: the values of C_{sa} at the top of the layer i and at the bottom of the subsequent layer $i+1$ are equal (cf. Figure 2): $C_{sa_i}(0) = C_{sa_{i+1}}(l_{i+1})$.

We call C_{sa_i} this concentration at the interface: $C_{sa_i} = C_{sa_i}(0) = C_{sa_{i+1}}(l_{i+1})$.

J_{tot} is constant over all layers: for all i , $J_{tot} = J_{tot_i}$.

Equation 15 can then be written, for all i between 1 and n :

$$\text{Equation 16} \quad C_{sa_{i-1}} = F_{ci} J_{tot} (1 - \chi_i) + \chi_i C_{sa_i} .$$

Then, through subsequent substitutions on the n layers from the contaminated layer ($C_{sa_0} = C_{sa_{i=0}}$) to the surface ($C_{sa_{surf}} = C_{sa_n}$):

$$C_{sa_0} = F_{ci} J_{tot} [(1-\chi_1) + \chi_1 ((1-\chi_2) + \chi_2 ((1-\chi_3) + \chi_3 (\dots + \chi_{n-2} ((1-\chi_{n-1}) + \chi_{n-1} (1-\chi_n)) \dots))] + (\prod \chi_i) C_{sa_n} .$$

$$= F_{ci} J_{tot} [1 - (\prod \chi_i)] + (\prod \chi_i) C_{sa_n}$$

and finally, substituting χ_i with its expression:

$$\text{Equation 17} \quad J_{tot} = F_{ci} \frac{C_{sa_0} - e^{-F_{ci} \sum \frac{l_i}{DU_{a_i}}} C_{sa_n}}{1 - e^{-F_{ci} \sum \frac{l_i}{DU_{a_i}}}} .$$

We introduce DU_{eq} [(mg/m²/s)/(mg/L_{sa}/m)] as the mean diffusion coefficient on the n layers expressed from the soil air concentration:

$$\text{Equation 18} \quad \frac{\sum l_i}{DU_{eq}} = \sum \frac{l_i}{DU_{a_i}} .$$

Then, with $L = \sum l_i$ and neglecting the indoor air concentration C_{sa_n} as in VOLASOIL, we get:

$$\text{Equation 19} \quad J_{tot} = \frac{F_{ci}}{1 - e^{-F_{ci} \frac{L}{DU_{eq}}}} C_{sa_0} ,$$

We can check that Equation 19 gives the monolayer flux of VOLASOIL, (Waitz *et al*, 1996, Equation 74 p 69) by substituting the multilayer and multiphase term L/DU_{eq} with the monolayer and monophasic term (L_s/D_{sa}) of VOLASOIL.

When the soil air convective flux F_{ci} tends towards 0, we get: $e^{-F_{ci} \frac{L}{DU_{eq}}} \sim 1 - F_{ci} \frac{L}{DU_{eq}}$, which gives the pollutant flux due to diffusion alone (without convection: $F_{ci} = 0$):

$$\text{Equation 20} \quad J_{diff} = DU_{eq} (C_{sa_0} - C_{sa_n}) / L \sim DU_{eq} C_{sa_0} / L ;$$

In the same way as before, we can check that Equation 20 gives the diffusive monolayer flux $J_{d_{sa}}$ of VOLASOIL (equation 54) and J_2 of CSOIL-1994 (van den Berg, 1994 p 60).

When the mean diffusion coefficient DU_{eq} tends towards 0, we find the convective flux alone:

$$\text{Equation 21} \quad J_{conv} = F_{ci} .$$

Besides, introducing: $x = F_{ci} L/DU_{eq}$, we get:

$$\frac{J_{tot} - (J_{conv} + J_{diff})}{C_{sa_0}} = \frac{x e^{-x} - 1 + e^{-x}}{(1 - e^{-x}) (L / DU_{eq})} = \frac{\frac{x+1}{e^x} - 1}{(1 - e^{-x}) (L / DU_{eq})} < 0, \quad \text{hence: } \underline{J_{tot} < J_{conv} + J_{diff}} .$$

The pollutant transfer caused by the combination of the convection and the diffusion is lower than the addition of the convection and the diffusion considered separately.

4.5. Addition of a (multilayer) capillary fringe

A transfer within the capillary fringe has to be taken into account when the source is a contaminated groundwater. We present here a general solution with convection (in soil air) and diffusion (in soil air and soil water) in the vadose zone and convection (in soil water) and diffusion (in soil air⁴ and soil water) in the capillary fringe. For specific cases, unwanted mechanisms can be suppressed by letting the corresponding parameters (diffusion coefficient, water flux,...) be equal to 0 or tend towards 0.

We follow the transfer from the soil air concentrations at the groundwater surface, $C_{sa_{nap}}$, obtained from the groundwater concentration and the Henry coefficient H .

⁴ Other models than VOLASOIL, e.g. Johnson & Ettinger (1991), take into account a residual diffusion in the soil air of the capillary fringe. This residual diffusion actually increases dramatically the diffusion.

Locally, the convective flux of pollutant J_{pw} [$\text{mg}/\text{m}^2/\text{s}$] in the water flux E_v [$\text{L}/\text{m}^2/\text{s}$, *i.e.* $10^{-3}\text{m}/\text{s}$], is:

$$\text{Equation 22} \quad J_{pw} = E_v C_{pw} = \frac{E_v}{H} C_{sa}.$$

The diffusive fluxes are given as before. The whole set of equations is similar to that of diffusion+convection in the vadose zone (§ 4.2), by substituting;

- the convective soil air flux, F_{ci} , by the convective soil water flux, expressed as an equivalent soil air flux, E_v/H ;
- the soil air concentration at the source in the vadose zone, C_{sa_o} , by the soil air concentration at the groundwater surface, $C_{sa_{nap}}$;
- the indoor air concentration, C_{sa_n} , by the soil air concentration at the bottom of the vadose zone (top of the capillary fringe), C_{sa_o} ;
- the depth of the source and the mean diffusion coefficient in the vadose zone, L and D_{Ueq} , by the thickness and the mean diffusion coefficient of the capillary fringe, L_{cap} and $D_{Ueq_{cap}}$.

The pollutant flux through the capillary fringe is then given by Equation 17 with those substitutions:

$$\text{Equation 23} \quad J_{tot} = \frac{E_v}{H} \frac{C_{sa_{nap}} - e^{\frac{E_v L_{cap}}{H D_{Ueq_{cap}}}} C_{sa_o}}{1 - e^{\frac{E_v L_{cap}}{H D_{Ueq_{cap}}}}}$$

We introduce the following notations:

$$\text{Equation 24} \quad CT_{cap} = \frac{E_v / H}{1 - e^{\frac{E_v L_{cap}}{H D_{Ueq_{cap}}}}} \quad [(\text{mg}/\text{m}^2/\text{s})/(\text{mg}/\text{L})]$$

$$\text{Equation 25} \quad CT_{vad} = \frac{F_{ci}}{1 - e^{-\frac{F_{ci} L}{D_{Ueq}}}}, \quad [(\text{mg}/\text{m}^2/\text{s})/(\text{mg}/\text{L})]$$

$$\text{Equation 26} \quad \chi_{cap} = e^{\frac{E_v L_{cap}}{H D_{Ueq_{cap}}}}$$

The flux of pollutant J_{tot} is constant from the capillary fringe to the vadose zone:

$$\text{Equation 27} \quad J_{tot} = CT_{cap} (C_{sa_{nap}} - \chi_{cap} C_{sa_o}) = CT_{vad} C_{sa_o}, \text{ hence:}$$

$$\text{Equation 28} \quad J_{tot} = \frac{CT_{vad} CT_{cap}}{CT_{vad} + \chi_{cap} CT_{cap}} C_{sa_{nap}}.$$

4.6. Addition of a transfer within the groundwater

A *transfer within* the groundwater and the capillary fringe may be taken into account for a soil contamination in the aquifer and a not-well-mixed aquifer, or when the source is the contaminated groundwater and the attenuation of the contamination at the surface through volatilisation or addition of rainwater at the top of the groundwater.

The modelling is the same as with the capillary fringe, just considering the saturated zone as one more layer (with no soil air) of the capillary fringe.

5. Application

An application was performed with tetrachloroethene – PCE, starting from a real case but extending it to different types of soil and of capillary fringe. 7 cases were thus considered:

- 1: the source is in the soil just under the concrete slab: there is only one layer, like in VOLASOIL;
- 2a: the source is in the soil under the concrete slab and 35 cm of unsaturated sand;
- 2b: the source is in the soil under the concrete slab and 35 cm of unsaturated "standard soil";
- 2c: the source is in the soil under the concrete slab and 35 cm of unsaturated silt;
- 3: the source is in the groundwater under the concrete slab and 35 cm of unsaturated sand⁵ and a sandy capillary fringe, for which three sets of characteristics are considered:

3a: porosities & thickness given in the Johnson & Ettinger spreadsheet of the US EPA;

3b: porosities from the Johnson & Ettinger spreadsheet, thickness from Waitz *et al.*, 1996;

3c: thickness from the Johnson & Ettinger spreadsheet, porosities from ASTM 1995.

The relevant soil and pollutant characteristics are reported in Table 1 and in Table 2. For the concrete slab, a "normal" quality according to Waitz *et al.*, 1996, was considered.

The calculation of the soil air convective flux, of the effective diffusion coefficient of each layer and of the concerned vadose zone, and of the resulting pollutant flux are reported in Table 2 to Table 4. The part of each unsaturated layer in the air-conductivity and in the diffusivity (expressed as "resistances" to convection and to diffusion), and the part of the diffusion in the total flux, are displayed in Table 2, Table 3 and Table 4.

| | | | 1: concrete slab | 2a & 3: concrete slab + sand | 2b: concrete slab + standard soil | 2c: concrete slab + silt |
|---|----------------------|--------------------------------|------------------|------------------------------|-----------------------------------|--------------------------|
| Characteristics of the individual layers of the vadose zone | | | | | | |
| | Permeability | Air conductivity | Thickness | | | |
| | κ | K | li | | | |
| | m2 | (m3/m2/s)/(Pa/m) | m | | | |
| Concrete slab "normal" quality VOLASOIL | - | 9,2E-7 | 0,15 | 0,15 | 0,15 | 0,15 |
| Sand J&E (medium sand VOLASOIL) | 5,0E-11 | 2,3E-6 | | 0,35 | | |
| Standard soil HESP: sand + silt | 1,0E-12 | 4,6E-8 | | | 0,35 | |
| Silt | 3,2E-14 | 1,5E-9 | | | | 0,35 |
| Contribution to the "resistance" to convection of the vadose zone above the pollution: (li / Ki)/(L/Ktot) | | | | | | |
| Concrete slab "normal" quality VOLASOIL | | | 100% | 52% | 2% | 0,1% |
| Sand J&E (medium sand VOLASOIL) | | | 0% | 48% | 0% | 0% |
| Standard soil HESP: sand + silt | | | 0% | 0% | 98% | 0% |
| Silt | | | 0% | 0% | 0% | 99,9% |
| Resulting property of the vadose zone above the pollution | | | | | | |
| Thickness of the vadose zone above the pollution | L | m | 0,15 | 0,50 | 0,50 | 0,50 |
| Mean air-conductivity of the vadose zone above the pollution | Ktot | (m3/m2/s)/(Pa/m) | 9,2E-7 | 1,6E-6 | 6,5E-8 | 2,1E-9 |
| Total "resistance" to convection of the vadose zone above the pollution | L / Ktot | Pa.s/m | 1,6E+5 | 3,1E+5 | 7,7E+6 | 2,4E+8 |
| Air flux calculation | | | | | | |
| Pressure difference between the indoor air and the soil air | DeltaP _{is} | Pa | 4 | 4 | 4 | 4 |
| Convective flux of soil air | Fci | I_{sa} / m2 / s | 2,5E-2 | 1,3E-2 | 5,2E-4 | 1,7E-5 |

Table 1: Soil characteristics regarding convection, calculation of the soil air convective flux

| Parameter | Symbol | Unit | Dry concrete slab | Sand J&E | Standard soil HESP: sand + silt | Silt | Sand capillary fringe J&E spreadsheet | Sand capillary fringe VOLASOIL | Sand capillary fringe ASTM, 1995 |
|---|------------|-----------------------------|-------------------|---------------|---------------------------------|---------------|---------------------------------------|--------------------------------|----------------------------------|
| Properties of the layer | | | | | | | | | |
| Total porosity | n | lvoid/lsoil | 0,02 | 0,375 | 0,4 | 0,45 | 0,375 | 0,375 | 0,38 |
| Water porosity | Vw | lpw/lsoil | 0 | 0,054 | 0,20 | 0,20 | 0,253 | 0,375 | 0,342 |
| Air porosity | Va | lsa/lsoil | 0,02 | 0,321 | 0,20 | 0,25 | 0,12 | 0 | 0,038 |
| Source for soil porosities | | | HESP, 1995 | US EPA, 2003 | HESP, 1995 | | spreadsheet US EPA | Waitz <i>et al.</i> , 1996 | ASTM, 1995 |
| Relative diffusivity in soil air | Dsa/Da | - | 0,0054 | 0,16 | 0,029 | 0,049 | 0,006 | 0 | 1,3E-4 |
| Relative diffusivity in soil water | Dpw/Dw | - | 0 | 0,0004 | 0,029 | 0,023 | 0,073 | 0,27 | 0,19 |
| Properties of the pollutant (PCE) | | | | | | | | | |
| Henry coefficient | H | (mg/la) / (mg/lw) | 7,4E-1 | 7,4E-1 | 7,4E-1 | 7,4E-1 | 7,4E-1 | 7,4E-1 | 7,4E-1 |
| diffusion coefficient in open air | Da | (mg/m2/s)/(mg/la/m) | 7,2E-3 | 7,2E-3 | 7,2E-3 | 7,2E-3 | 7,2E-3 | 7,2E-3 | 7,2E-3 |
| diffusion coefficient in open water | Dw | (mg/m2/s)/(mg/lw/m) | 7,2E-7 | 7,2E-7 | 7,2E-7 | 7,2E-7 | 7,2E-7 | 7,2E-7 | 7,2E-7 |
| Multiphase diffusion coefficient in soil expressed from the soil air concentration | DUa | (mg/m2/s)/(mg/lsa/m) | 3,9E-5 | 1,2E-3 | 2,1E-4 | 3,5E-4 | 4,6E-5 | 2,6E-7 | 1,1E-6 |

Table 2: Soil and pollutant characteristics regarding diffusion in the different layers

⁵ With 35 cm of unsaturated soil under the slab, the depth of the groundwater table is very low. This thickness of unsaturated soil was chosen to illustrate the potential impact of a thin layer of soil under a slab.

| | | | 1: concrete slab | 2a & 3: concrete slab + sand | 2b: concrete slab + standard soil | 2c: concrete slab + silt | Sand capillary fringe J&E spreadsheet | Sand capillary fringe VOLASOIL | Sand capillary fringe ASTM, 1995 |
|--|----------|---------------------------------|--|------------------------------|-----------------------------------|--------------------------|---|--------------------------------|----------------------------------|
| | | | Characteristics of the individual soil layers | | | | | | |
| Multiphase diffusion coefficient in soil expressed from the soil air concentration | | | Thickness | | | | | | |
| DUa (mg/m ² /s)/(mg/l/m) | | | li | | | | | | |
| | | | m | | | | | | |
| Concrete slab "normal" quality VOLASOIL | | | 0,15 | 0,15 | 0,15 | 0,15 | | | |
| Sand J&E | | | | 0,35 | | | | | |
| Standard soil HESP: sand + silt | | | | | 0,35 | | | | |
| Silt | | | | | | 0,35 | | | |
| Sand capillary fringe J&E spreadsheet | | | | | | | 0,17 | | |
| Sand capillary fringe VOLASOIL | | | | | | | | 0,4 | (li from J&E) |
| Sand capillary fringe ASTM, 1995 | | | | | | | | | 0,17 |
| | | | Contribution to the "resistance" to diffusion of the vadose zone above the pollution: (li/DUa)/(L/Dueq) | | | | | | |
| Concrete slab "normal" quality VOLASOIL | | | 100% | 93% | 70% | 79% | | | |
| Sand J&E | | | 0% | 7% | 0% | 0% | | | |
| Standard soil HESP: sand + silt | | | 0% | 0% | 30% | 0% | | | |
| Silt | | | 0% | 0% | 0% | 21% | | | |
| | | | Resulting property of the vadose zone above the pollution | | | | Property of the capillary fringe (index "cap") | | |
| Depth of the pollution source | L | m | 0,15 | 0,50 | 0,50 | 0,50 | 0,17 | 0,40 | 0,17 |
| Mean diffusion coefficient expressed from the soil air concentration | Dueq | (mg/m ² /s)/(mg/l/m) | 3,9E-5 | 1,2E-4 | 9,1E-5 | 1,0E-4 | 4,6E-5 | 2,6E-7 | 1,1E-6 |
| Total "resistance" to diffusion | L / Dueq | (mg/l/s)/(mg/m ² /s) | 3,8E+3 | 4,1E+3 | 5,5E+3 | 4,8E+3 | 3,7E+3 | 1,5E+6 | 1,5E+5 |

Table 3: Calculation of the diffusion characteristics of the vadose zone and the capillary fringe

| | | | 1: concrete slab (VOLASOIL) | 2a: concrete slab + vadose sand | 2b: concrete slab + vadose standard soil | 2c: concrete slab + vadose silt | 3a: concrete slab + Sand (vadose + cap. Fringe J&E) | 3b: concrete slab + Sand (vadose + cap. Fringe VOLASOIL) | 3c: concrete slab + Sand (vadose + cap. Fringe ASTM 1995) |
|---|------------------|---------------------------------|-----------------------------|---------------------------------|--|---------------------------------|---|--|---|
| Concentration at the top of the groundwater | Cgw | mg/lw | | | | | 0,67 | 0,67 | 0,67 |
| Henry coefficient | H | (mg/l/a) / (mg/lw) | | | | | 7,4E-1 | 7,4E-1 | 7,4E-1 |
| Concentration in soil air at the groundwater surface | Csa _g | mg/l/a | | | | | 0,50 | 0,50 | 0,50 |
| Concentration in soil air in a vadose source | Csa _o | mg/l/a | 0,5 | 0,5 | 0,5 | 0,5 | | | |
| | | | Vadose Zone | | | | | | |
| Convective flux of soil air | Fci | l/a / m ² / s | 2,5E-2 | 1,3E-2 | 5,2E-4 | 1,7E-5 | 1,3E-2 | 1,3E-2 | 1,3E-2 |
| Total "resistance" to diffusion in the vadose zone above the pollution | L/Dueq | (mg/l/a)/(mg/m ² /s) | 3,8E+3 | 4,1E+3 | 5,5E+3 | 4,8E+3 | 4,1E+3 | 4,1E+3 | 4,1E+3 |
| Transfer coef. from soil air to vapor emission into the building | CTvad | (mg/m ² /s)/(mg/l/a) | | | | | 1,3E-2 | 1,3E-2 | 1,3E-2 |
| | | | Capillary fringe | | | | | | |
| "Resistance" to diffusion in the capillary fringe | Lcap/ | (mg/l/a)/(mg/m ² /s) | | | | | 3,7E+3 | 1,5E+6 | 1,5E+5 |
| Part in the total "resistance" to diffusion above the groundwater: (Lcap/DUeqcap)/((Lcap/DUeqcap)+(L/DUeq)) | | % | | | | | 47% | 99,7% | 97% |
| Calculation parameter | zcap | - | | | | | 1 | 1 | 1 |
| Transfer coef. from soil air at groundwater surface to emission into the vadose zone | CTcap | (mg/m ² /s)/(mg/l/a) | | | | | 2,7E-4 | 6,5E-7 | 6,5E-6 |
| Total pollutant flux | Jtot | (mg/m ² /s) | 1,2E-2 | 6,4E-3 | 2,7E-4 | 1,1E-4 | 1,3E-4 | 3,27E-7 | 3,3E-6 |
| Diffusive pollutant flux alone | Jdiff | (mg/m ² /s) | 1,3E-4 | 1,2E-4 | 9,1E-5 | 1,0E-4 | 6,4E-5 | 3,26E-7 | 3,2E-6 |
| Part of diffusive flux in the total flux | Jdiff / Jtot | % | 1% | 2% | 33% | 96% | 48% | 99,7% | 97% |

Table 4: Calculation of the pollutant flux

The results of those simulations lead to the following comments:

- Air-conductivities are known only as orders of magnitude, and effective diffusivities with an uncertainty of a factor 2. The results should be considered in a consequent way.
- For the air-conductivity, the VOLASOIL floor of "normal" quality is roughly equivalent to a medium-to-fine sand. A limited layer (< 1 m) of rough sand between the slab and a pollution source will then make little difference in the VOC emission. But for a fine sand or mixed soil, a thin layer (10 cm) will make a difference of an order of magnitude. In such a case, the depth of a source immediately beneath the slab should be very thoroughly assessed, e.g. with PID measures and subsequent analytic confirmation.
- In the vadose zone, diffusion may be restricted by the slab itself, especially for limited soil layers (< 1 m). But this influences significantly the total pollutant flux only when diffusion plays a major role, which is only for quite impermeable soils (roughly: Permeability < 10⁻¹² m², i.e. water-conductivity < 10⁻⁵ m/s).
- A capillary fringe strongly restricts the overall diffusivity from the source to the surface and the total pollutant flux (factor 50 to 20.000 with a sandy soil). The way the capillary fringe is modelled, especially regarding the residual air porosity and diffusion, is essential, with a factor 400 between the Spreadsheet of Johnson & Ettinger by the US EPA and VOLASOIL here. The explanations given by Waitz *et al.*, 1996 and US EPA, 2003, show that VOLASOIL is consequent with the column

experiments that have been performed on the question, whereas Johnson & Ettinger adds more security, for example in order to account for groundwater vertical movements⁶.

6. Discussion of validity for different cases of pollution source

The air-conductivity of the slab in VOLASOIL is often criticised as over-conservative, but no counter-proposals seem available. A representative measure of this parameter is extremely difficult. In any case, when convection is not limited by the soil above the pollution source (medium sand or source immediately beneath the slab), this slab air-conductivity leads to an important flux of soil air (not negligible compared to the room ventilation flux) and an important flux into the building. The steady-state hypothesis of the model can then become unrealistic, and the control of the mass conservation, leading to the integration of the source depletion, can then avoid over-conservative estimates: in our simulations (not reported here) with HVOCs, a sandy soil and a "normal" floor, the steady-state flux into the building from a source immediately beneath the slab summed up after one year in the pollutant quantity present in the two first meters of the soil source. A further mathematical development of VOLASOIL with a depleting source (not reported here) induced a correction of a factor 15 for the average flux over one year.

In contrary to the Johnson & Ettinger model, VOLASOIL does not restrict the depth of influence of the convection. For a deep source (e.g. > 2 m), or for the flux starting from a capillary fringe or from a free phase over the groundwater, it should be asked where that supposed soil air moving upward comes from, and how much pressure difference remains between the source in the soil and the slab. The multilayer development of VOLASOIL does not allow to extend the VOLASOIL modelling to unlimited depths. The development of a VOLASOIL model modified with convection starting only at a given depth would be the same as presented in Section 4.5 for the addition of a capillary fringe. But the opportunity of such a modelling has still to be discussed. Such a modelling might be used to limit over-estimations of risk in some cases of deep sources.

7. Conclusion

The mathematical developments of VOLASOIL for the general case of a multilayer soil and the subsequent simulations and discussions presented here should allow a broader use of VOLASOIL, e.g. for a building with a concrete slab. The depth of the source should nevertheless remain limited, given the uncertainty upon the existence of a convective air flux from deep sources. The way to restrict the depth of influence of the convection in VOLASOIL has been presented here. The opportunity of such a development has still to be discussed.

Further mathematical developments of VOLASOIL, not presented here, were made by INERIS in order to take into account the depletion of the source of pollution. They induce a decrease of a factor 15 of the modelled average flux over one year in the case of a HVOC source situated immediately beneath the building slab.

Besides, the results of the simulations presented here stressed the following points:

- the major impact of the capillary fringe and of the uncertainty in its parameterisation;
- the interest of a thorough assessment of the depth of a shallow source.

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⁶ Mc Hugh *et al.* (2003) note that the Johnson & Ettinger modelling is over-conservatist for a groundwater source: the actual pollutant flux would be limited by the (slow) diffusion in the groundwater.

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