

Sorption Paper Title

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Abstract

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1. Introduction

Many vapor intrusion (VI) contaminants has the capacity to sorb onto soil and various common indoor materials, but the role and more importantly - the consequences of these sorption processes in VI are poorly understood. The migration of contaminant vapors from its source into the affected building and potential indoor sources are usually the prime concern in VI investigations. Rarely is the sorbed contaminant vapors in the soil or indoor considered in an investigation, but these may potentially act as a capacitor, storing and releasing contaminant vapors in response to a change in contaminant concentration. Consequently, contaminant vapors may be much more persistent at a site that has undergone remediation, potentially reducing the effectiveness of mitigation systems, or impeding site investigations.

Measuring contaminant sorption onto materials or soils is not a regular part of VI investigations and thus very little is known of the potential impact of this. In this paper we will therefore begin to explore this topic through a combined effort of gathering experimental sorption data and incorporating it into three-dimensional finite element models of VI scenarios. These type of models have been used extensively before and are useful to illuminate some of these issues. The potential impact of sorption may perhaps be most significant in the application of the controlled pressure method and various mitigation schemes.

The controlled pressure method (CPM) is the sequential forced over- and depressurization of a building which in theory max- and minimizes the

contaminant entry to the building. Helping the investigator to ascertain the worst-case VI scenario and help identify potential indoor contaminant sources. However, if the building has a large capacity to sorb contaminant vapors onto various materials, these may be ad-/absorbed and desorbed in response to the changing condition, potentially preventing corresponding changes in indoor air contaminant concentrations. The same is true for various mitigation schemes, while they may successfully prevent contaminant vapors from entering the house, these may still be released from the interior over an unknown period of time.

2. Methods

2.1. Experimental Setup

The TCE dynamic sorption process of different building materials were determined by use of a method schematically shown in Figure 1. This method involved a selected material contained in an adsorption column through which TCE-containing gas was passed, and subsequent thermal desorption and measurement of the total amount of adsorption. During the adsorption part of the process, stainless steel tubes were packed with building materials held in place by glass wool. The amount of building material normally held in the tube was around 1 g. It was determined that neither the glass wool nor the stainless steel tube would retain significant amounts of TCE. The sample-containing tubes were first exposed desired low concentrations of TCE in nitrogen, which were then allowed to interact with the flow for varying periods of time. The typical flow rate of the nitrogen was 60 ml/min and the concentrations of TCE was around 1.1 ppbv. All of these adsorption experiments were conducted at room temperature. After a given time of exposure to the TCE-containing flow, that flow was stopped, and the sample tube was attached to a sorbent tube placed downstream of the sample tube. The sample tube was arranged such that the direction of the nitrogen flow in the subsequent desorption process was opposite that of the TCE-containing nitrogen flow during the adsorption process. During the thermal desorption step, the sample containing tube was covered by a heating mantle which permitted its heating at 100 °C. This allowed fully desorbing the TCE which had been held on the sample into a pure nitrogen flow, which carried it to the room temperature downstream sorbent tube, where it was again fully adsorbed. These tubes fully capture all of the TCE desorbed, from the sam-

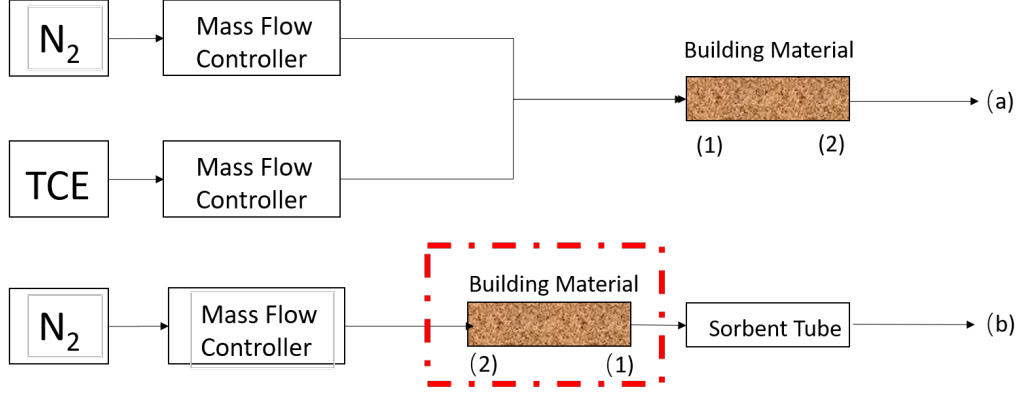


Figure 1: Schematic of experimental setup.

65 ples, and the amount of TCE was analyzed by Gas Chromatography (GC)
 66 with an Electron Capture Detector(ECD).

67 2.2. Numerical Model

68 To investigate the role of sorption in VI, we consider a simple VI scenario.
 69 Here we consider a house with a 10 by 10 m footprint, with the foundation
 70 bottom located 1 m below ground surface (bgs). The sole contaminant source
 71 is an uniformly TCE contaminated groundwater located 4 bgs, and the soil
 72 surrounding the house is assumed to homogenous and of a singular type. All
 73 contaminant vapors are assumed to enter the house through breaches in the
 74 foundation, modeled as a 1 cm wide crack that runs along the perimeter of
 75 the house. Finally we assume that sorption processes can occur both in the
 76 soil matrix and in the indoor environment (on various indoor materials).

77 Modeling this scenario requires us to simulate a couple of physics, many
 78 of which depend and interact with each other. The governing equations and
 79 the physics they govern are:

- 80 1. van Genuchten retention model - soil moisture.
- 81 2. Darcy's Law - air flow in the porous media.
- 82 3. Transport equation - contaminant transport in porous media.
- 83 4. Continuously stirred tank reactor (CSTR) - contaminant concentration
 84 in the indoor environment.

85 These physics are implemented in COMSOL Multiphysics, a commercial
 86 finite-element method package, which is used to solve our model. It is impor-

Figure 2: The vapor intrusion model

87 tant to note that the indoor environment is implicitly modeled, but instead
88 only given by the CSTR equation; the soil domain is explicitly modeled.

89 2.2.1. Vadose Zone Moisture Content

90 Since the contaminant transport occurs through three-phased the vadose
91 zone, it is important that we correctly account for soil moisture content and
92 its effect on advective and diffusive transport. In this modeled scenario, we
93 assume that the soil moisture is at steady-state and does not change, and
94 thus the soil moisture content is given by the retention model developed by
95 van Genuchten.

The van Genuchten retention model gives the soil water saturation as a function of elevation above groundwater. In turn this gives the water and gas filled porosities, and the relative permeability of the soil matrix.

$$\text{Se} = \begin{cases} \frac{1}{(1+\alpha z^n)^m} & z < 0 \\ 1 & z \geq 0 \end{cases} \quad (1)$$

$$\theta_w = \begin{cases} \theta_r + \text{Se}(\theta_s - \theta_r) & z < 0 \\ \theta_s & z \geq 0 \end{cases} \quad (2)$$

$$k_r = \begin{cases} \text{Se}^l [1 - (1 - \text{Se}^{\frac{1}{m}})]^2 & z < 0 \\ 0 & z \geq 0 \end{cases} \quad (3)$$

96 Se is the saturation, and ranges from 0 to 1, which represent completely un-
97 to fully saturated; z is the elevation above the groundwater in meters; θ_r ,
98 θ_s , θ_w , and θ_g are the residual moisture content, saturated porosity (or just
99 porosity), and water and air filled porosities respectively. All units are in
100 volume of phase divided by the volume of soil; k_r is the relative permeability
101 of water, which modifies the saturated permeability. This too ranges from 0
102 to 1, indicating completely im- and permeable respectively. $1 - k_r$ gives the
103 relative permeability of air.

104 2.2.2. Gas Flow In The Vadose Zone

105 The gas flow in the vadose zone is governed by a modified version of
106 Darcy's Law. Originally, Darcy's Law was developed to describe flow in
107 saturated porous media, but since we're interested in flow in unsaturated

media, modification is necessary. An effective permeability that depends on the relative permeability from van Genuchten is introduced to allow for correct flow profiles in unsaturated porous media.

The vapor flow governing equation is given by

$$\frac{\partial}{\partial t}(\rho\theta_s) + \nabla \cdot \rho \left(- \frac{(1 - k_r)\kappa}{\mu} \nabla p \right) = 0 \quad (4)$$

Here ρ is the fluid density; ∇ is the del operator; κ is the saturated permeability; μ is the fluid viscosity; and p is the fluid pressure. We assume that the contaminant vapors are so dilute that the gas flow properties can be taken to be those of air, and specifically at 20 °C and all the transport properties may be found in Table 1.

Boundary Conditions. To solve (4) we assign the atmosphere boundary (see Figure 2) to be at reference pressure and act as a gauge, i.e. zero pressure. The foundation crack boundary is assigned the indoor-outdoor pressure difference value. Remaining boundaries are no-flow boundary conditions.

$$\text{Atmosphere} \quad p = 0 \text{ (Pa)} \quad (5)$$

$$\text{Foundation crack} \quad p = p_{\text{in/out}} \text{ (Pa)} \quad (6)$$

$$\text{All other} \quad -\vec{n} \cdot \rho_{\text{air}} \vec{u} = 0 \text{ (kg/(m}^2 \cdot \text{s))} \quad (7)$$

Here \vec{n} and \vec{u} are the boundary normal and gas velocity vectors.

Initial Conditions. For steady-state problems, the initial conditions don't matter, but is simply zero for the entire domain. When solving transient, the initial conditions are given by the steady-state solution.

2.2.3. Mass Transport In The Vadose Zone

Contaminants in the vadose zone exist in three phases - gaseous, solved in water, and sorbed onto soil particles. While there are three distinct phases, the water and gas phases are related via Henry's Law (8).

$$c_g = K_H c_w \quad (8)$$

Where c_g and c_w are the gas and water phase concentrations respectively in mol/m³; K_H is the dimensionless Henry's Law constant.

127 In this work, we consider sorption between the soil and vapor phases, as
 128 a function of the water contaminant concentration, through linear sorption
 129 (9).

$$c_s = \rho_b c_g = \frac{\rho}{1 - \theta_t} K_H c_w \quad (9)$$

130 Here the c_s is the solid phase concentration in mol/kg; ρ_b is the bulk density
 131 of the soil kg/m³, which is given by the density ρ and the total soil porosity θ_t .
 132 Using these two relations we can express the total contaminant concentration
 133 in terms of the water contaminant concentration.

134 Mass transport in the vadose zone is governed by diffusion and advection
 135 and is given by (10).

$$R \frac{\partial c}{\partial t} = \nabla \cdot [D_{\text{eff}} \nabla c] - K_H \vec{u} \cdot \nabla c \quad (10)$$

136 The first term in (10) gives the change in contaminant water concentration
 137 with respect to time, modified by the *retardation factor*, R , which is discussed
 138 below; The second is the effective diffusive flux which is modified by the
 139 effective diffusion coefficient D_{eff} which is also discussed below. The third is
 140 the advective flux where \vec{u} is the soil-gas velocity from Darcy's Law, which
 141 when multiplied with K_H gives the gas phase concentration advective flux.

142 *Contaminant entry into the building.* The contaminant enters the building
 143 through a combination of advection and diffusive fluxes and is given by (11).

$$j_{ck} = \begin{cases} u_{ck} c_g - \frac{D_{\text{air}}}{L_{\text{slab}}} (c_{in} - c_g) & u_{ck} \geq 0 \\ u_{ck} c_{in} - \frac{D_{\text{air}}}{L_{\text{slab}}} (c_{in} - c_g) & u_{ck} < 0 \end{cases} \quad (11)$$

144 Here the j_{ck} is the molar contaminant flux into the building in mol/(m² · s);
 145 D_{air} is the contaminant diffusion coefficient in pure air in m²/s; L_{slab} is the
 146 thickness of the foundation slab in m. The flux expression changes if there
 147 is a bulk flow into the building, i.e. $u_{ck} \geq 0$, or out of the building.

148 *Retardation factor.* As the contaminants are transported through the vadose
 149 zone, the partitioning between the various phases increases the contaminant
 150 residency time, retarding the transport of contaminants. This effect is rep-
 151 resented by R which is the retardation factor (12).

$$R = \theta_w + \theta_g K_H + \rho_b K_H K_{\text{ads}} \quad (12)$$

Here θ_w , θ_g are the water and gas filled soil porosities; K_{ads} is the solid-gas phase sorption isotherm in m^3/kg . The diffusive and advective transport retardation is proportional to the inverse of R .

$$D_{\text{retarded}} = \frac{D_{\text{eff}}}{R} \quad (13)$$

$$\vec{u}_{\text{retarded}} = \frac{\vec{u}}{R} \quad (14)$$

152 It should be noted that the soil-gas velocity, \vec{u} , is not retarded in of itself,
 153 but rather just the contaminant being transported through advection, giving
 154 a effective bulk velocity.

155 *Effective diffusivity.* The effective diffusivity in the vadose zone varies with
 156 the soil moisture content, from being close to that in water when fully sat-
 157 urated and vice versa. Millington-Quirk developed (15) which describes the
 158 effective diffusivity in variably saturated porous media.

$$D_{\text{eff}} = D_{\text{water}} \frac{\theta_w^{\frac{7}{3}}}{\theta_t^2} + \frac{D_{\text{air}}}{K_H} \frac{\theta_g^{\frac{7}{3}}}{\theta_t^2} \quad (15)$$

159 Where the porosity fractions are the water and gas phase tortuosity terms;
 160 D_{air} and D_{water} are the contaminant diffusion coefficient in air and water
 161 respectively in m^2/s .

Boundary Conditions. A few boundary conditions are required to solve (10). In this model, the sole contaminant source is assumed to be the homogenously contaminated groundwater, which we assume to have a fixed concentration. The atmosphere acts as a contaminant sink, and any contaminant that makes it to this boundary is infinitely diluted, thus this is simply a zero concentration boundary condition. Contaminants leave the soil domain and enter the building through a combination of advective and diffusive gas phase transport. The last boundary condition is applied to all other boundaries and is a no-flow boundary.

$$\text{Groundwater} \quad c_w = 0 \text{ (mol/m}^3\text{)} \quad (16)$$

$$\text{Atmosphere} \quad c_w = c_{gw} \text{ (mol/m}^3\text{)} \quad (17)$$

$$\text{Foundation crack} \quad -\vec{n} \cdot \vec{N} = -\frac{j_{ck}}{K_H} \text{ (mol/(m}^2 \cdot \text{s))} \quad (18)$$

$$\text{All other} \quad -\vec{n} \cdot \vec{N} = 0 \text{ (mol/(m}^2 \cdot \text{s))} \quad (19)$$

162 $\vec{n} \cdot \vec{N}$ is the dot product between the boundary normal vector and the contam-
 163 inant flux; $j_c k$ is the contaminant vapor flux into the building. We assume
 164 that only contaminants in the gas phase enter the building, and dividing j_{ck}
 165 by K_H we get proper accounting in terms of the water phase concentration.

166 *Initial Conditions.*

167 2.2.4. Indoor Environment

168 The indoor air space is modeled as a continuously stirred tank reactor
 169 (CSTR) given by (20). Contaminants are assumed to only enter through the
 170 foundation crack, represented by n_{entry} , which is calculated by integrating
 171 the contaminant flux over the foundation crack boundary. The product of
 172 air exchange rate, which govern how many house volumes are exchanged with
 173 the outside per time unit, and indoor air contaminant concentration gives the
 174 contaminant exit rate. The sorption of contaminant is given by the sorption
 175 reaction term in (22) and the sorbed contaminant concentration is given by
 176 (21).

$$V_{\text{bldg}} \frac{\partial c_{\text{in}}}{\partial t} = n_{\text{entry}} - A_e c_{\text{in}} V_{\text{bldg}} + r_{\text{sorb}} V_{\text{mat}} \quad (20)$$

$$V_{\text{mat}} \frac{\partial c_{\text{sorb}}}{\partial t} = -r_{\text{sorb}} V_{\text{mat}} \quad (21)$$

$$r_{\text{sorb}} = k_1 c_{\text{sorb}} - k_2 c_{\text{in}} \quad (22)$$

177 Here V_{bldg} and V_{mat} are the indoor control volume and volume of indoor
 178 material in m^3 ; c_{in} and c_{sorb} are the indoor and sorbed (onto the indoor mate-
 179 rial) contaminant concentrations in mol/m^3 ; n_{entry} is the contaminant entry
 180 rate in mol/s ; r_{sorb} sorption rate in $\text{mol}/(\text{m}^3 \cdot \text{s})$; k_1 and k_2 are desorption
 181 and sorption reaction constants in $1/\text{s}$.

182 *Fitting Kinetic Parameters.* To calculate the indoor sorption rate we need k_1
 183 and k_2 . These values are found by solving (22) numerically and then finding
 184 the best k_1 and k_2 by fitting them to the experimental data via least square.
 185 We use Runge-Kutta method of order 5(4) as the numerical solve, which
 186 is implemented together with the least square method in the SciPy python
 187 package[?].

Table 1: Transport properties and model parameters

188 **3. Results & Discussion**

189 **4. Conclusions**

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194 Declaration of interest: none

195 **References**