

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[1, 2?]. 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.

Although it is recognized that sorption may be used to treat indoor air contaminants, and passive sorption tube samplers are used prolifically in VI 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[3].

Over the years many VI sites have been investigated for their potential exposure risk. Most of these are conducted by private industries but a few notable academic ventures exist as well. Two well-known examples of these are the studies of "Sun Devil Manor" near Hill Air Force Base in Utah, and a building in Indianapolis, Indiana. Both of these sites were outfitted with a wide variety of instrumentation to investigate the VI drivers at these sites.

30 These studies yielded some of the richest VI datasets available and gave
31 invaluable insights, in particular in the application of CPM[4] and sub-slab
32 depressurization (SSD) mitigation systems[5, 6]. However, neither of these
33 studies considered the role of sorption had at these sites.

34 The potential impact of sorption may perhaps be most significant in the
35 application of the controlled pressure method and various mitigation schemes.
36 The controlled pressure method (CPM) is the forced over- and depressur-
37 ization of a building to max- and minimize the contaminant entry to the
38 building. This aids the investigator to ascertain the worst-case VI scenario
39 and help identify potential indoor contaminant sources[7, 4]. However, if
40 the building has a large capacity to sorb contaminant vapors onto various
41 materials, these may be sorbed and desorbed in response to the changing
42 condition, potentially preventing corresponding changes in indoor air con-
43 taminant concentrations. The same is true for various mitigation schemes,
44 while they may successfully prevent contaminant vapors from entering the
45 house, these may still be released from the interior over an unknown period
46 of time[1, 2].

47 In the past VI models have been used to gain insight into VI when no field
48 or experimental data has been available. Previously examples of VI modeling
49 studies are the role of rainfall in VI[8], or drivers of temporal variability in
50 some of the aforementioned sites[9]. However, while many VI models include
51 a sorption term in the governing equation for contaminant transport in soils,
52 none have explored the role of sorption in VI. The reason for this is two-fold.
53 First, there has been a general lack of interest in sorption and VI thus far.
54 Secondly, the vast majority of VI modeling efforts and studies has focused
55 on steady-state analyses of VI, and sorption only affects soil contaminant
56 transport in time-dependent scenarios.

57 To bridge this knowledge gap we will begin to explore the role of sorp-
58 tion in VI through a combined effort of experimental and simulation work.
59 Sorption data of TCE on various common indoor materials and Appalian
60 soil will be measured in a flow-chamber experiment. These sorption data
61 will then be incorporated into a three-dimensional finite element model of
62 VI. For this purpose we will consider a prototypical VI scenario where a free-
63 standing house with a basement is overlying a homogenously contaminated
64 groundwater source. Using this model we will investigate how the dynamic
65 contaminant transport is affected in general by sorption, how indoor sorp-
66 tion materials affect indoor air concentration as the building’s pressurization
67 fluctuates and how indoor air concentration are affected by indoor materials

68 following successful mitigation of the structure.

69 **2. Methods**

70 *2.1. Experimental Setup*

71 The TCE dynamic sorption process of different building materials were
72 determined by use of a method schematically shown in Figure 1. This method
73 involved a selected material contained in an adsorption column through which
74 TCE-containing gas was passed, and subsequent thermal desorption and mea-
75 surement of the total amount of adsorption. During the adsorption part of
76 the process, stainless steel tubes were packed with building materials held in
77 place by glass wool. The amount of building material normally held in the
78 tube was around 1 g. It was determined that neither the glass wool nor the
79 stainless steel tube would retain significant amounts of TCE. The sample-
80 containing tubes were first exposed desired low concentrations of TCE in
81 nitrogen, which were then allowed to interact with the flow for varying pe-
82 riods of time. The typical flow rate of the nitrogen was 60 ml/min and the
83 concentrations of TCE was around 1.1 ppbv. All of these adsorption experi-
84 ments were conducted at room temperature. After a given time of exposure
85 to the TCE-containing flow, that flow was stopped, and the sample tube
86 was attached to a sorbent tube placed downstream of the sample tube. The
87 sample tube was arranged such that the direction of the nitrogen flow in
88 the subsequent desorption process was opposite that of the TCE-containing
89 nitrogen flow during the adsorption process. During the thermal desorption
90 step, the sample containing tube was covered by a heating mantle which per-
91 mitted its heating at 100 °C. This allowed fully desorbing the TCE which
92 had been held on the sample into a pure nitrogen flow, which carried it to
93 the room temperature downstream sorbent tube, where it was again fully
94 adsorbed. These tubes fully capture all of the TCE desorbed, from the sam-
95 ples, and the amount of TCE was analyzed by Gas Chromatography (GC)
96 with an Electron Capture Detector(ECD).

97 *2.2. Numerical Model*

98 To investigate the role of sorption in VI, we consider a simple VI scenario.
99 Here we consider a house with a 10 by 10 m footprint, with the foundation
100 bottom located 1 m below ground surface (bgs). The sole contaminant source
101 is an uniformly TCE contaminated groundwater located 4 bgs, and the soil
102 surrounding the house is assumed to homogenous and of a singular type. All

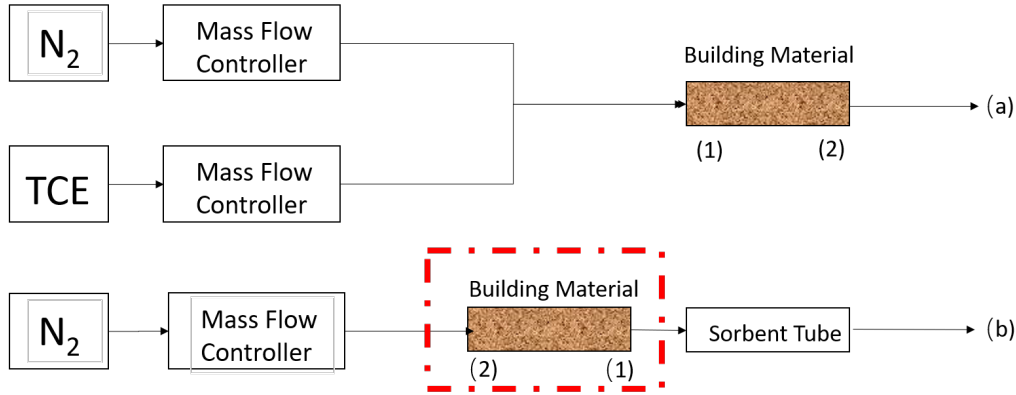


Figure 1: Schematic of experimental setup.

Figure 2: The vapor intrusion model

contaminant vapors are assumed to enter the house through breaches in the foundation, modeled as a 1 cm wide crack that runs along the perimeter of the house. Finally we assume that sorption processes can occur both in the soil matrix and in the indoor environment (on various indoor materials).

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

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

These physics are implemented in COMSOL Multiphysics, a commercial finite-element method package, which is used to solve our model. It is important to note that the indoor environment is implicitly modeled, but instead only given by the CSTR equation; the soil domain is explicitly modeled.

2.2.1. Vadose Zone Moisture Content

Since the contaminant transport occurs through three-phased the vadose zone, it is important that we correctly account for soil moisture content and its effect on advective and diffusive transport. In this modeled scenario, we

123 assume that the soil moisture is at steady-state and does not change, and
 124 thus the soil moisture content is given by the retention model developed by
 125 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.

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

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

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

126 Se is the saturation, and ranges from 0 to 1, which represent completely un-
 127 to fully saturated; z is the elevation above the groundwater in meters; θ_r ,
 128 θ_s , θ_w , and θ_g are the residual moisture content, saturated porosity (or just
 129 porosity), and water and air filled porosities respectively. All units are in
 130 volume of phase divided by the volume of soil; k_r is the relative permeability
 131 of water, which modifies the saturated permeability. This too ranges from 0
 132 to 1, indicating completely im- and permeable respectively. $1 - k_r$ gives the
 133 relative permeability of air.

134 2.2.2. Gas Flow In The Vadose Zone

135 The gas flow in the vadose zone is governed by a modified version of
 136 Darcy's Law. Originally, Darcy's Law was developed to describe flow in
 137 saturated porous media, but since we're interested in flow in unsaturated
 138 media, modification is necessary. An effective permeability that depends
 139 on the relative permeability from van Genuchten is introduced to allow for
 140 correct flow profiles in unsaturated porous media.

141 The vapor flow governing equation is given by

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

142 Here ρ is the fluid density; ∇ is the del operator; κ is the saturated per-
 143 meability; μ is the fluid viscosity; and p is the fluid pressure. We assume

144 that the contaminant vapors are so dilute that the gas flow properties can
 145 be taken to be those of air, and specifically at 20 °C and all the transport
 146 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.

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

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

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

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

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

151 2.2.3. Mass Transport In The Vadose Zone

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

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

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

157 In this work, we consider sorption between the soil and vapor phases, as
 158 a function of the water contaminant concentration, through linear sorption
 159 (9).

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

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

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

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

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

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

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

174 Here the j_{ck} is the molar contaminant flux into the building in $\text{mol}/(\text{m}^2 \cdot \text{s})$;
 175 D_{air} is the contaminant diffusion coefficient in pure air in m^2/s ; L_{slab} is the
 176 thickness of the foundation slab in m. The flux expression changes if there
 177 is a bulk flow into the building, i.e. $u_{ck} \geq 0$, or out of the building.

178 *Retardation factor.* As the contaminants are transported through the vadose
 179 zone, the partitioning between the various phases increases the contaminant
 180 residency time, retarding the transport of contaminants. This effect is rep-
 181 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 .

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

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

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

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

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

189 Where the porosity fractions are the water and gas phase tortuosity terms;
 190 D_{air} and D_{water} are the contaminant diffusion coefficient in air and water
 191 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.

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

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

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

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

192 $\vec{n} \cdot \vec{N}$ is the dot product between the boundary normal vector and the contam-
 193 inant flux; j_{ck} is the contaminant vapor flux into the building. We assume
 194 that only contaminants in the gas phase enter the building, and dividing j_{ck}
 195 by K_H we get proper accounting in terms of the water phase concentration.

196 *Initial Conditions.* For a steady-state condition the initial conditions don't
 197 matter, but are set to be zero everywhere. For transient simulations in this
 198 work, the steady-state solution is always used as an initial condition.

Table 1: Transport properties and model parameters

199 *2.2.4. Indoor Environment*

200 The indoor air space is modeled as a continuously stirred tank reactor
 201 (CSTR) given by (20). Contaminants are assumed to only enter through the
 202 foundation crack, represented by n_{entry} , which is calculated by integrating
 203 the contaminant flux over the foundation crack boundary. The product of
 204 air exchange rate, which govern how many house volumes are exchanged with
 205 the outside per time unit, and indoor air contaminant concentration gives the
 206 contaminant exit rate. The sorption of contaminant is given by the sorption
 207 reaction term in (22) and the sorbed contaminant concentration is given by
 208 (21).

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

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

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

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

214 *Fitting Kinetic Parameters.* To calculate the indoor sorption rate we need k_1
 215 and k_2 . These values are found by solving (22) numerically and then finding
 216 the best k_1 and k_2 by fitting them to the experimental data via least square.
 217 We use Runge-Kutta method of order 5(4) as the numerical solve, which
 218 is implemented together with the least square method in the SciPy python
 219 package[10].

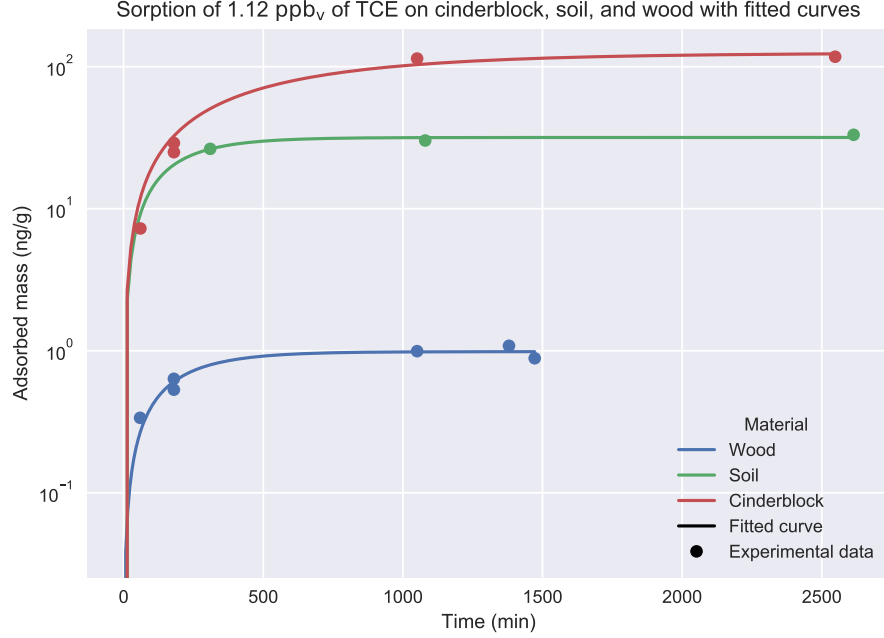


Figure 3

Table 2: Fitted kinetic sorption parameters based on sorption experiment data.

Material	k_1 (1/hr)	k_2 (1/hr)	K
Wood	0.32	44.90	$7.10 \cdot 10^{-3}$
Drywall	0.41	87.94	$4.65 \cdot 10^{-3}$
Carpet	0.26	58.74	$4.42 \cdot 10^{-3}$
Paper	0.04	88.37	$4.55 \cdot 10^{-4}$
Soil	0.34	2636.57	$1.30 \cdot 10^{-4}$
Cinderblock	0.10	4175.16	$2.40 \cdot 10^{-5}$

220 3. Results & Discussion

221 3.1. Kinetic Sorption Model

222 4. Conclusions

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 225 ronmental Research and Development Program and Environmental Security

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227 Declaration of interest: none

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