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Estimation of contaminant subslab concentration in petroleum vapor intrusion

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Abstract

In this study, the development and partial validation are presented for an analytical approximation method for prediction of subslab contaminant concentrations in PVI. The method involves combining an analytic approximation to soil vapor transport with a piecewise first-order biodegradation model (together called the analytic approximation method, including biodegradation, AAMB), the result of which calculation provides an estimate of contaminant subslab concentrations, independent of building operation conditions. Comparisons with three-dimensional (3-D) simulations and another PVI screening tool, BioVapor, show that the AAMB is suitable for application in a scenario involving a building with an impermeable foundation surrounded by open ground surface, where the atmosphere is regarded as the primary oxygen source. Predictions from the AAMB can be used to determine the required vertical source-building separation, given a subslab screening concentration, allowing identification of buildings at risk for PVI. This equation shows that the “vertical screening distance” suggested by U.S. EPA is sufficient in most cases, as long as the total petroleum hydrocarbon (TPH) soil gas concentration at the vapor source does not exceed 50–100 mg/L. When the TPH soil gas concentration of the vapor source approaches a typical limit, i.e. 400 mg/L, the “vertical screening distance” required would be much greater.

Keywords

Petroleum vapor intrusion; Analytical model; Vertical screening distances; Aerobic biodegradation

1. Introduction

Leakage is unfortunately quite common for underground storage tanks (USTs) containing petroleum products, generating contamination plumes that can extend far from the tank [1]. These contamination plumes can serve as the source of petroleum hydrocarbons soil vapors, which can migrate into buildings built atop such plumes. This migration process is termed petroleum vapor intrusion (PVI). PVI can not only cause negative health effects for building occupants from inhalation of toxic chemicals, but can also pose other potential threats to safety, i.e. explosion [2]. The major difference between PVI and vapor intrusion (VI) involving other volatile contaminants, such as chlorinated solvents, is the biodegradation potential of petroleum hydrocarbon vapors in soil [3].

In PVI, the indoor air contaminant concentration is always the key concern. Due to the difficulties in both gaining access as well as accurately measuring indoor air concentrations, models are often used as preliminary screening tools to provide reasonable estimates of indoor contaminant concentrations. The application of models is particularly popular in petroleum impacted sites, where there is great concern about possible non-PVI background concentrations of petroleum hydrocarbons in the structures of concern. Most of these model-based screening tools [4,5] are one-dimensional (1-D) as they can be more easily applied, compared to multi-dimensional numerical models. Fig. 1 shows a brief development history of 1-D PVI screening tools. The most significant difference among these models is the nature of the assumption concerning biodegradation during soil vapor transport. Based on the same source-to-subslab-to-indoor air pathway, first proposed by Johnson and Ettinger (J-E) in 1991 [6], these screening tools share a common limitation that the vapor transport depends on the operational parameters of the building of concern atop the contaminant vapor source. The operational conditions of buildings, such as the indoor air exchange rate, are usually quite difficult to quantitatively predict a priori. This intrinsic character of such models can result in incorrect predictions of entry rates, as shown by Yao et al. [9].

To avoid such uncertainties associated with building operational parameters (such as indoor air exchange rate and depressurization), contaminant subslab concentration is sometimes used as the indicator of PVI potential [10,11]. Though the subslab concentration is indirectly related to human exposure, it still plays an important role in determining indoor air contaminant concentration. In previous studies, a series of analytical approximation methods (AAMs) were developed, which can provide estimates of contaminant subslab concentration in VI scenarios involving no biodegradation [12,13]. This approach assumed that the influence of a building foundation on contaminant subslab concentration could be approximated as involving mainly the “blocking” or “capping” effect of the building foundation on diffusional transport of contaminant to the atmosphere. This approach works, because it is mainly diffusion, rather than soil gas advection, that determines subsurface vapor profiles (in the absence of biodegradation and preferential pathways). In this study, this same approach will be applied to develop a new method for PVI by including a piecewise first-order aerobic biodegradation reaction rate term. This new method, here called the analytical approximation method including biodegradation (AAMB), will provide an estimate of contaminant subslab concentration in PVI situations, without the need to know building operational conditions. This new model will not only be compared with

another two PVI models, but also be used to examine the recently proposed vertical screening distances with the U.S. EPA's PVI database.

2. Method development

2.1. The “AAMB” conceptual model

In a typical VI scenario with a homogenous groundwater source at the bottom of a domain of interest, and a building surrounded by open surface on top, the general soil gas concentration profile of non-biodegradable contaminants is determined by diffusion from the source at the bottom to the open ground surface. This VI scenario has often been simulated with three-dimensional (3-D) numerical models [14–16], and a typical result is shown in Fig. 2(a). In such a scenario, due to a longer diffusion path of source-to-subslab-to-atmosphere compared to that of source-to-atmosphere (where there is no building), the contaminant subslab soil vapor concentration will be higher than that at the same depth under open ground. This increase in subslab concentration caused by the existence of a largely impermeable building foundation is defined as the “blocking” or “capping” effect. Note that the foundation is considered impermeable despite the potential for vapor intrusion, simply because the resistance to vapor flow into the structure is very high compared with diffusion through soil; this “blocking” or “capping” effect exists even when there is actually vapor intrusion taking place into the structure.

As shown in Fig. 2(a), due to this “blocking” effect, the perimeter subslab non-biodegradable contaminant concentration c^{ss} ($[M/L^3]$) at d_f below ground surface roughly equals the concentration at a deeper position under the open ground. The choice to focus on a perimeter subslab concentration is somewhat arbitrary, but it reflects the common approach in VI modeling assuming a perimeter foundation crack as the foundation entry breach through which contaminants enter. A recent paper has shown that the assumption regarding the nature of this foundation entry breach is not critical to the analysis [19]. It has also been shown in a recent study [12] that the depth under open ground at which the concentration approaches that of the subslab perimeter is $(d_f d_s)$, where d_f ($[L]$) and d_s ($[L]$) are the depth of building foundation and source, respectively.

The non-biodegradable contaminant concentration profile in the soil outside the influence of building foundation is

$$\frac{c}{c^s} = \frac{d}{d_s} \quad (1)$$

where c^s is the non-biodegradable contaminant source vapor concentration $[M/L^3]$, c is the non-biodegradable contaminant soil gas concentration $[M/L^3]$ and d is the depth below ground surface $[L]$. This just reflects the linear profile resulting from diffusion in a uniform diffusivity medium.

Therefore the contaminant subslab concentration can also be approximated by combining the result in Eq. (1) with the above cited approximation, yielding

$$\frac{c^{ss}}{c^s} \approx \left(\frac{d_f}{d_s} \right)^{0.5} \quad (2)$$

The above equation was termed the analytical approximation method (AAM) [12], and it was further modified to include a lateral source-building separation (AAML) [13]. This form of the approximation was derived for a 2-D geometry, and a small correction of the exponent from 0.5 to 0.7 better approximated the 3-D results [12]. This correction is not considered further here, because in application to the biodegradation case, it will be subject to another empirical readjustment.

In Fig. 2(b), a PVI scenario was simulated using a 3-D numerical model that included coupled petroleum hydrocarbon contaminant soil vapor and oxygen transport processes. The model is described in Abreu and Johnson [17,18]. In that case, an aerobic biodegradation was assumed to occur when oxygen concentration was larger than 1% v/v, and there was no reaction below that oxygen limit. All other settings were similar to those used in generating Fig. 2(a). In Fig. 2(b), a similar shape of the contour curves is observed as those in Fig. 2(a), suggesting that the blocking effect also plays a role in determining soil gas concentration profile in this PVI scenario. Based on this observation, a new model involving the “blocking” or “capping” effect of building foundation was developed to estimate contaminant subslab concentration in PVI scenarios involving a piecewise first-order aerobic biodegradation. This situation is illustrated in Fig. 2(b) showing that the hydrocarbon contaminant perimeter subslab concentration falls on an iso-concentration contour, which extends to some position deeper in the soil, outside of the area of influence of building foundation.

According to this picture, similar to Eq. (2), the perimeter subslab concentration in a scenario described in Fig. 2(b) is assumed to be approximated as

$$\frac{c_h^{ss}}{c_h^s} \approx \frac{c_h}{c_h^s} \left(\text{at the depth of } \frac{d}{d_s} = \left(\frac{d_f}{d_s} \right)^r \right) \quad (3)$$

where c_h^{ss} is the perimeter subslab hydrocarbon concentration [M/L^3], c_h^s is the hydrocarbon soil gas concentration at the source [M/L^3], c_h is the hydrocarbon concentration in a 1-D scenario with uniform effective diffusivity, which is used to describe the diffusion through the pore space of porous media, such as soil. The influence of a piecewise first-order biodegradation term is discussed below. In Fig. 2(b), c_h refers to the hydrocarbon concentration in the soil, where it is assumed to be measured beyond the influence of the building foundation. Thus, $(c_h/c_h^s) (d/d_s = (d_f/d_s)^r)$ is the normalized concentration of hydrocarbon contaminants at a normalized depth of $(d_f/d_s)^r$ and r is the semi-empirical parameter used to describe the “blocking” or “capping” effect of the building foundation. The relationship between c_h and c_h^{ss} is assumed to be similar to that between c and c^s in Eq. (2), as shown in Fig. 2(a), but it is important to note that here, the influence of biodegradation must now enter the calculation (i.e., both the subslab contaminant

concentration and the concentrations in the soil outside of the building footprint are lower than they would be in the absence of biodegradation).

The values of r in Eq. (3) were obtained through fitting the full 3-D numerical model results (as shown and discussed in Section 3.1) with the trial-and-error method. In the range of 0–1 different values were substituted into Eq. (3) to make the best agreement between predicted perimeter subslab concentrations and those from the 3-D simulations (the differences for most cases do not exceed one order of magnitude). The detailed calculations are shown in Tables S1 and S2 in supplemental materials. Finally, the semi-empirical perimeter subslab concentration approximation in Eq. (3) becomes:

$$\frac{c_h^{ss}}{c_h^s} = \begin{cases} \frac{c_h}{c_h^s} \left(\frac{d}{d_s} = \left(\frac{d_f}{d_s} \right)^0 .5 \right) & \text{for basement cases} \\ \frac{c_h}{c_h^s} \left(\frac{d}{d_s} = \left(\frac{d_f}{d_s} \right)^0 .35 \right) & \text{for slab-on-grade cases} \end{cases} \quad (4)$$

Before showing the details of development of these relationships, it is instructive to briefly consider their consequence. Take the scenario in Fig. 2(b) for example, $d_f = 2$ m and $d_s = 8$ m, so $\sqrt{d_f d_s} = 4$ m. For the moment, still using Eq. (2), this would mean that the contaminant perimeter subslab concentration at a depth of 2 m below ground surface should equal that at a depth of 4 m, when probed far away from the building. This result is also consistent with Eq. (4) for a basement scenario, meaning that the biodegradation processes do not influence the general shape of the contours in the deeper soil. The details of how the biodegradation process enters the calculation is the subject of the following section.

When it comes to the slab-on-grade case, the situation is different from the basement case. In Fig. 2(c), the contour lines become more horizontal with the decrease of the foundation depth. This might have been anticipated, since the diffusion path of oxygen to beneath the structure is shorter, so that the oxygen is able to penetrate the vadose zone beneath the foundation more easily. This is reflected in the lower contaminant concentrations beneath the slab. However, the “blocking” or “capping” effect of building foundation exists regardless of the depth of foundation and source, since even when d_f approaches 0, this diffusion barrier still exists at the surface. Thus, while the basic character of the approximation for the shape of the contours around the building remains, the more effective penetration of oxygen to beneath the building results in the flattening of the profiles and a decrease in the absolute values of the subslab concentration. Thus, the value of r in Eq. (3) had to be modified from 0.5 for basement cases to 0.35 for slab-on-grade cases, as illustrated in Fig. 2(c). Note that there is almost an order of magnitude difference between the predictions of subslab contaminant concentration in the full 3-D modeled cases shown in Fig. 2(b) and (c), and this is reflected in the approximation.

2.2. The 1-D contaminant concentration profile involving a piecewise aerobic biodegradation

In Fig. 2(b) and (c), the soil gas concentration profile far away from any influence of building foundation can be described using a 1-D soil vapor transport scenario, as illustrated

in Fig. 3. The difference relative to what was done in obtaining the far-field approximation such as used in Fig. 2(a) is that now allowance needs to be made for biodegradation.

According to Roggemans et al. [20], the vadose zone can be divided into an aerobic and an anoxic zone, and the position of the aerobic/anoxic interface is determined by a minimum oxygen concentration limit for aerobic biodegradation to be possible. This is taken to be 1% v/v in this study, as has been also used in other studies [5,18]. A first-order reaction with respect to contaminant concentration is assumed to occur in the aerobic zone, and as Fig. 3 shows there is no explicit oxygen concentration dependence included in the rate law used in this model. No reaction is assumed in the anoxic zone where oxygen concentration is so low (i.e., <1%) that reaction cannot take place at any significant rate. The consequences of such a restrictive biodegradation reaction rate expression have been explored in another publication [21].

In Fig. 3, c_h is the hydrocarbon contaminant soil vapor concentration [M/L^3], c_o is the oxygen concentration [M/L^3], d_s , d_i and l are the source depth [L], aerobic/anoxic interface depth [L] and anoxic zone thickness [L], respectively, c_h^i is the hydrocarbon soil vapor concentration at the aerobic/anoxic interface [M/L^3], λ is the first-order reaction rate constant in water [$1/T$], ϕ_w is the water filled porosity, H is the Henry's law constant of hydrocarbon, D_h and D_o are the effective diffusivity of hydrocarbon and oxygen in soil, respectively, β is the stoichiometric conversion factor between oxygen and hydrocarbon, c_h^s is the hydrocarbon source vapor concentration [M/L^3], and z is the distance from the hydrocarbon vapor source [L]. The reference to water in the above reflects the fact that it is believed that the biodegradation reactions can actually only take place in a liquid water phase within the soil, which is why the partitioning of hydrocarbon into the water phase is significant.

Two mass balance equations are set up to solve for two variables: the depth of the interface d_i [L] and the contaminant concentration at the interface: c_h^i [M/L^3]. The first equation is based on the continuity of contaminant mass transport, while the second is a consequence of mass balance considering oxygen consumption. These are shown in the following equations, respectively.

$$\frac{d^2 c_h}{dz^2} = \begin{cases} \frac{\lambda \phi_w}{D_h H} c_h & z > l \\ 0 & z < l = d_s - d_i \end{cases} \quad (5)$$

$$\frac{d^2 c_h}{dz^2} = \frac{D_o}{\beta D_h} \frac{d^2 c_o}{dz^2} \quad (6)$$

For Eq. (5), if $l < z < d_s$, $(d^2 c_h / dz^2) = (\lambda \phi_w / D_h H) c_h$ is subject to the boundary conditions are: $c_h(z=0) = c_h^s$ and $c_h(z=l) = c_h^i$. The solution of Eq. (6) was given by DeVaul [5]:

$$c_h = \begin{cases} \frac{\exp(-Ed_i)\exp(E(Z-l)) - \exp(Ed_i)\exp(-E(z-l))}{\exp(-Ed_i) - \exp(Ed_i)} c_h^i & z > l \\ c_h^s + \frac{c_h^i - c_h^s}{l} z & z < l = d_s - d_i \end{cases} \quad (7)$$

where $E = \sqrt{\lambda\phi_w/D_h H}$. And

$$\left. \frac{dc_h}{dz} \right|_{z=l} = \frac{c_h^i - c_h^s}{l} = c_h^i E \frac{\exp(-Ed_i) + \exp(Ed_i)}{\exp(-Ed_i) - \exp(Ed_i)} \approx -c_h^i E \quad (8)$$

The approximation shown in Eq. (8) applies if $Ed_i \gg 0$. In most cases, this assumption can be utilized, as the biodegradation rate of hydrocarbon is relatively fast. For example, using the parameters in Table 1, and assuming $d_i = 1$ m,

$$\sqrt{0.18 \text{ h}^{-1} \times 0.25/3.73 \times 10^{-3} (\text{m}^2/\text{h}) \times 0.228 \times 1 \text{ m}} \approx 7.7$$

As for Eq. (6), the boundary conditions are

$$\left(c_h - \frac{D_o}{\beta D_h} c_o \right) \Big|_{z=d_s} = -\frac{D_o}{\beta D_h} c_o^{atm}$$

and $(c_h - (D_o/\beta D_h) c_o)_{z=0} = c_h^s - 0.05 (D_o/\beta D_h) c_o^{atm}$. So the solution of Eq. (6) is

$$c_h - \frac{D_o}{\beta D_h} c_o = -\frac{c_h^s + 0.95 (D_o/\beta D_h) c_o^{atm}}{d_s} z + c_h^s - 0.05 \frac{D_o}{\beta D_h} c_o^{atm} \quad (9)$$

and

$$\left(c_h - \frac{D_o}{\beta D_h} c_o \right) \Big|_{z=l} = c_h^i - 0.05 \frac{D_o}{\beta D_h} c_o^{atm} = -\frac{c_h^s + 0.95 (D_o/\beta D_h) c_o^{atm}}{d_s} l + c_h^s - 0.05 \frac{D_o}{\beta D_h} c_o^{atm} \quad (10)$$

And the simultaneous solution of Eqs. (8) and (10) to eliminate l gives

$$\begin{cases} \frac{c_h^i}{c_h^s} \approx \frac{1 + (D_o/\beta D_h)(0.95 c_o^{atm}/c_h^s)}{Ed_s} \\ \frac{1}{d_s} \approx \frac{1}{1 + (D_o/\beta D_h)(0.95 c_o^{atm}/c_h^s)} - \frac{1}{Ed_s} \end{cases} \quad (11)$$

$l > 0$ requires $1 + (D_o/\beta D_h)(0.95 c_o^{atm}/c_h^s) < Ed_s$, otherwise it means oxygen is abundant in the whole model domain and there is no aerobic/anoxic interface.

The substitution of Eq. (11) into Eq. (7) gives the contaminant soil vapor concentration profile in the area under the open ground surface:

$$\frac{c_h}{s_h^s} \approx \begin{cases} \frac{1+(D_o/\beta D_h)(0.95c_o^{atm}/c_h^s)}{d_s E} \exp\left(-E\left(z - \frac{d_s}{1+(D_o/\beta D_h)(0.95c_o^{atm}/c_h^s)} + \frac{1}{E}\right)\right) & \text{for } z > \frac{d_s}{1+(D_o/\beta D_h)(0.95c_o^{atm}/c_h^s)} - \frac{1}{E} \text{ (aerobic zone)} \\ 1 - \frac{z}{d_s} \left(1 + \frac{D_o}{\beta D_h} \frac{0.95c_o^{atm}}{c_h^s}\right) & \text{for } z \leq \frac{d_s}{1+(D_o/\beta D_h)(0.95c_o^{atm}/c_h^s)} - \frac{1}{E} \text{ (anoxic zone)} \end{cases} \quad (12)$$

if $1 + (D_o/\beta D_h)(0.95c_o^{atm}/c_h^s) < Ed_s$ or $c_h/c_h^s \approx e^{(-Ez)}$ if
 $1 + (D_o/\beta D_h)(0.95c_o^{atm}/c_h^s) \geq Ed_s$ (pure aerobic zone).

Consider the consequence of this assumption for the basement scenario. In that case, the AAMB involves a combination of Eqs. (4) and (12). For example, in the scenario shown in Fig. 2(b),

$$\frac{c_h^{ss}}{c_h^s} \approx \frac{c_h}{c_h^s} \left(\frac{d}{d_s} = \left(\frac{d_f}{d_s} \right)^{0.5} \right) = \frac{c_h}{c_h^s} \left(\frac{d}{8 \text{ m}} = \left(\frac{2}{8} \right)^{0.5} \right) = \frac{c_h}{c_h^s} (z=4 \text{ m}).$$

As

$$l \approx \frac{8 \text{ m}}{1 + (8.48 \times 10^{-3} \text{ (m}^2/\text{h)}) / 3 \times 3.73 \times 10^{-3} \text{ (m}^2/\text{h)}) (0.95 \times 279 \text{ mg/L} / 200 \text{ (mg/L)})} - \frac{1}{\sqrt{(0.18 \text{ h}^{-1} \times 0.28 / 3.73 \times 10^{-3} \text{ (m}^2/\text{h)}) \times 0.228}} \approx 3.86 \text{ m} < 4 \text{ m}$$

so

$$\begin{aligned} & \frac{c_h}{c_g^s} (z=4\text{m}) \\ & \approx \frac{1 + (8.48 \times 10^{-3} \text{ (m}^2/\text{h)}) / 3 \times 3.73 \times 10^{-3} \text{ (m}^2/\text{h)}) (0.95 \times 279 \text{ (mg/L)}) / 200 \text{ (mg/L)})}{\sqrt{(0.18\text{h}^{-1} \times 0.28 / 3.73 \times 10^{-3} \text{ (m}^2/\text{h)}) \times 0.228}} \times 8\text{h} \\ & \exp\left(-\sqrt{\frac{0.18\text{h}^{-1} \times 0.28}{3.73 \times 10^{-3} \text{ (m}^2/\text{h)}) \times 0.228}} \left(4\text{m} - \frac{8\text{m}}{1 + (8.48 \times 10^{-3} \text{ (m}^2/\text{h)}) / 3 \times 3.73 \times 10^{-3} \text{ (m}^2/\text{h)}) (0.95 \times 279 \text{ (mg/L)}) / 200 \text{ (mg/L)})} + \frac{1}{\sqrt{0.18\text{h}^{-1} \times 0.28 / 3.73 \times 10^{-3} \text{ (m}^2/\text{h)}) \times 0.228}}\right)\right) \approx 0.01 \end{aligned}$$

This prediction fits the perimeter subslab concentration from the 3-D simulation shown in Fig. 2(b) (approximately 0.01) well. It will be shown below for a much broader range of cases that the approximation in Eq. (4) works reasonably well. A sensitivity test of AAMB is provided in Supplemental materials.

In short, AAMB was developed as a simplified screening tool, based on assumptions of a homogenous soil, a single uniform source, and impermeable building foundation. It should

also be emphasized that the only oxygen consumption that takes place is that associated with oxidation of contaminant vapor, i.e., there is no baseline soil oxygen demand.

3. Results and discussions

3.1. Comparison with BioVapor and the ASU model

In this study, the predictions by AAMB are examined with respect to predictions from another 1-D VI screening tool, BioVapor, as well as those from the 3-D simulations using the ASU VI model that includes biodegradation [5,18]. Readers are directed to the corresponding references for more details regarding these two models [5,17,18,22]. All these models employ the same assumption of a piecewise first-order aerobic biodegradation rate. It should be noted that in BioVapor there are two options for setting the upper boundary conditions for oxygen transport in soil, one involving setting the flux and the other the maximum concentration. Here the boundary condition of specified maximum oxygen concentration is employed, and the latest version of BioVapor released in 2010 was used [22].

To permit comparison of indoor air contaminant concentration predictions, just as in BioVapor, the Nazaroff equation was also used to calculate soil gas entry rate into the structure in the AAMB [23]:

$$Q_s = \frac{2\pi k}{\mu_g} \frac{\Delta p L_{ck}}{\ln(2d_f/w_{ck})} \quad (13)$$

where Q_s is the soil gas entry rate (L^3/T), and the indoor air concentration could be calculated using the following equation:

$$c_h^{in} \approx \frac{J_s}{V_b A_e} = \frac{Q_s c_h^{ss} \left(\exp(Q_s d_{ck}/A_{ck} D_h^{ck}) / \exp(Q_s d_{ck}/A_{ck} D_h^{ck}) - 1 \right)}{C_b A_e} \quad (14)$$

where J_s is the contaminant entry rate [M/T] and A_{ck} is the area of the crack [L^2]. The perimeter crack assumption is employed in both BioVapor and the ASU model, so use of Eqs. (13) and (14) is consistent for the comparison.

Fig. 4 shows the comparison of predicted normalized subslab and indoor air concentrations for biodegradable contaminant vapors, obtained using the AAMB and ASU models. The dashed line is the 45° line, showing where ideal agreement with the 3-D simulation would be found. The 3-D simulation data in Fig. 4 were obtained from the Supplemental materials for a paper by Abreu and Johnson [18]. The subslab crack contaminant concentrations for the 3-D simulations were indirectly back-calculated from the simulated contaminant indoor air concentration attenuation factors and other model parameters provided in that work.

In Fig. 4 the majority of the predictions by the AAMB fall within one order of magnitude of the predictions from the 3-D model. This is to be expected, since the fitting of the exponent in the AAMB model Eq. (4) was based upon the whole set of predictions from the ASU model. The fact that the results deviate at low contaminant concentrations is a consequence of the fact that the majority of the available results with which to fit the exponent were at

higher concentrations. Since the goal was to find a single value of the exponent, no attempt was made to adjust the exponent for different concentrations levels. What these results confirm is that AAMB is able to capture the major characteristics of PVI scenarios involving an impermeable building foundation surrounded by open ground, for both basement and slab-on-grade scenarios. There is a tendency toward over-prediction in the case of basement scenarios involving low concentrations, and a tendency toward under-prediction in the case of slab-on-grade scenarios, at low concentrations. It should be noted that here, “low concentrations” refers to low normalized concentration, a situation that would exist when the vapor source is relatively deep. Hence, the less accurate predictions would tend to occur in generally lower risk scenarios, involving inherently significant attenuations.

The comparison between the predictions of the ASU model and BioVapor model is shown in Fig. 5. In general, there is a trend toward over-prediction of attenuation (or under-prediction of concentrations) by BioVapor. This is caused by different assumptions concerning the major source of oxygen. In the ASU model (and its AAMB approximation), the source of oxygen is the atmosphere at the open ground surrounding the building of concern, while in BioVapor the 1-D nature of the model effectively requires that the downward air flow through the building foundation is the major source of oxygen. With the latter assumption, a more significant attenuation by biodegradation underneath the building is expected, since the diffusion pathway of oxygen is shorter than in the other models that invoke a capping or blocking effect of the foundation.

The effect related to the strength of the oxygen source is the most significant in cases with high contaminant vapor source concentrations at shallow depths, because of oxygen occlusion from beneath the building foundation [24]. This results in predictions of limited attenuation beneath the foundation, as shown in Fig. 2(b). But because of its structure, BioVapor must assume that there is an aerobic biodegradation zone in the 1-D source-to-subslab pathway. This is the case, independent of the strength of the vapor source, so the over-prediction of attenuation by BioVapor seems inevitable. Fig. 5(c) and (d) shows that when using BioVapor, with an oxygen source concentration assumed to be much lower than atmospheric, the predictions of subslab and indoor air concentration approach those from the ASU model and the AAMB approximation. This is because the assumption of a low surface oxygen concentration in the 1-D model begins to mirror the occlusion of oxygen from beneath the building, a feature that is inherent in the 3-D model and the AAMB approximation to it.

Another question explored here concerns the role of building foundation type (basement or slab-on-grade). In BioVapor, what really matters is only the separation between the source and the building slab. Again, because of the 1-D nature of the BioVapor model, the depth of foundation itself does not play a role (except for its being used in the Nazaroff equation to calculate soil gas entry rate, such as is done in the J-E model). In the ASU model (and AAMB), as the atmosphere is the major source of oxygen, the depth of the building foundation directly affects oxygen concentration beneath the foundation, which has a significant effect in determining both subslab and indoor air concentrations. As shown in Tables S1 and S2 in supplemental materials, between cases no. 21 ($d_s = 5$ m and $d_f = 2$ m) “basement” and no. 75 ($d_s = 3$ m and $d_f = 0.2$ m) “slab-on-grade”, there is a one order of

magnitude difference between these scenarios in predicted subslab and indoor air concentration predicted by both the AAMB and the ASU models. In contrast to this, there is almost no difference between those cases, in terms of the predictions from BioVapor. This difference is not as clearly visible in Fig. 5, because in that representation of the results, different source depths are mixed on the plots.

In short, in scenarios involving an impermeable building foundation surrounded by open ground surface and vapor sources directly underneath the concerned building, AAMB will provide predictions that reasonably approximate a full 3-D simulation (and, thus, actual field conditions), particularly for the key case of shallow sources. The BioVapor model will generally be less reliable as a predictor of subslab concentrations, because of the inherent difficulty in capturing the diffusion of oxygen from around a building, with a 1-D model structure. BioVapor might provide better predictions in a case in which there is reason to believe that the structure actually serves as a source of subslab oxygen (such that the occlusion of oxygen is somehow counteracted).

3.2. Comparison with field data

Fig. 6 presents a measured soil gas concentration profiles of total petroleum hydrocarbon (TPH) and oxygen in a vertical cross-section from a study by Luo et al. [25]. On the left side of these figures, marked the B side, the similarity of shape of soil gas concentration contours to what was shown in Fig. 2(b) can be observed, indicating the usual “blocking” or “capping” effect of the building foundation. The oxygen concentration profile is consistent with the open ground surface on B side, and the concrete building foundation appears to approximate impermeable behavior. The geology from about 0 to 2 m below ground surface is predominantly silty medium to fine sands according to the original reference, and is here assumed to be roughly uniform such that the AAMB model can be applied. According to the sensitivity analysis in the supplemental materials, the calculated subslab concentration is not sensitive to contaminant diffusivity and reaction rate constant. In other words, in this method the differences among the TPH chemicals are not significant. Also, the stoichiometric ratio of oxygen to contaminant is obtained based on the assumption of a complete biodegradation into carbon dioxide and water, so this ratio is assumed to be relatively constant independent of chemical types in TPH. Here the physical and chemical properties of TPH are assumed to be modeled by those of benzene, and unless specified, the parameters are the same as those given in Table 1.

The source zone definition offered by the study's authors is adopted here, and the specified parameters are shown as follows: $c_h^s = 60 \text{ mg/L}$, $d_s = 0.85 \text{ m}$, $d_f = 0.125 \text{ m}$, $\lambda = 0.18 \text{ h}^{-1}$. Thus,

$$\begin{aligned}\frac{c_h^{ss}}{c_h^s} &\approx \frac{c_h}{c_h^s} \left(\frac{d}{0.85 \text{ m}} = \left(\frac{0.125}{0.85} \right)^{0.35} \right) \\ &= \frac{c_h}{c_h^s} (z=0.42 \text{ m}). \quad Asl \approx \frac{0.85 \text{ m}}{1 + \left(8.48 \times 10^{-3} (\text{m}^2/\text{h}) / 3 \times 3.73 \times 10^{-3} (\text{m}^2/\text{h}) \right) (0.95 \times 279 (\text{mg/L}) / 60 (\text{mg/L}))} \\ &\quad - \frac{1}{\sqrt{(0.18 \text{ h}^{-1} \times 0.28 / 3.73 \times 10^{-3} (\text{m}^2/\text{h}) \times 0.228)}} \approx 0.06 \text{ m} < 0.42 \text{ m},\end{aligned}$$

so

$$\begin{aligned}\frac{c_h}{c_h^s} (z=0.42 \text{ m}) &\approx \frac{1 + (8.48 \times 10^{-3} (\text{m}^2/\text{h}) / 3 \times 3.73 \times 10^{-3} (\text{m}^2/\text{h})) (0.95 \times 279 (\text{mg/L}) / 60 (\text{mg/L}))}{\sqrt{(0.18 \text{ h}^{-1} \times 0.28 / 3.73 \times 10^{-3} (\text{m}^2/\text{h}) \times 0.228)}} \times 0.85 \text{ m} \\ &\quad \exp \left(- \sqrt{\frac{0.18 \text{ h}^{-1} \times 0.28}{3.73 \times 10^{-3} (\text{m}^2/\text{h}) \times 0.228}} \right. \\ &\quad \left. \left(0.42 \text{ m} - \frac{0.85 \text{ m}}{1 + (8.48 \times 10^{-3} (\text{m}^2/\text{h}) / 3 \times 3.73 \times 10^{-3} (\text{m}^2/\text{h})) (0.95 \times 279 (\text{mg/L}) / 60 (\text{mg/L}))} \right. \right. \\ &\quad \left. \left. + \frac{1}{\sqrt{(0.18 \text{ h}^{-1} \times 0.28 / 3.73 \times 10^{-3} (\text{m}^2/\text{h}) \times 0.228)}} \right) \right) \approx 0.045\end{aligned}$$

and $c_h^{ss} \approx 2.7 \text{ mg/L}$. This result is in agreement with the measured perimeter subslab concentration ($<10 \text{ mg/L}$) shown in Fig. 6.

3.3. The roles of vertical source-building separations in vapor concentration attenuation processes

In Fig. 7(a), the source-to-indoor air contaminant concentration attenuation factors are presented as a function of vapor source depth, for the same three assumptions regarding reaction kinetics ($\lambda = 0.018, 0.18, 1.8 \text{ h}^{-1}$), with the same vapor source concentration and foundation depth, $c_h^s = 100 \text{ mg/L}$ and $d_f = 2 \text{ m}$. The two curves of $\lambda = 0.18$ and 1.8 coincide in cases with a shallow vapor source, suggesting that the vadose zone beneath the foundation slab is in an anoxic condition, and biodegradation does not play a significant role in determining subslab contaminant concentration in such scenarios. In general, the attenuation factors all increases exponentially with the vapor source depth (or, as plotted in Fig. 7(a), the normalized contaminant concentrations decrease), as the diffusion path becomes longer. The very significant influence of vertical diffusion distance on subslab contaminant concentration confirms that this parameter can justifiably be used to identify buildings that are in danger of vapor intrusion, and that a criterion based upon the screening limits for contaminant subslab concentration is supported.

In practice, U.S. EPA and some investigators have suggested that $30\text{--}100 \text{ }\mu\text{g}/\text{m}^3$ be set as the screening limit for benzene subslab concentration [10,11]. Based on this, the minimum source depth required for subslab benzene concentration to reach the screening limit of $100 \text{ }\mu\text{g}/\text{m}^3$ could be estimated using the AAMB. The source is assumed to be unweathered

gasoline of non-aqueous phase liquids (NAPL) containing 1% v/v benzene in gas phase above the water table, and different components of the contaminant source/soil vapor are assumed to share the same physical and chemical characteristics as benzene [18,26]. The reaction rate constant $\lambda = 0.18 \text{ h}^{-1}$ and other assumed parameters are shown in Table 1. The predicted results are shown in Fig. 7(b), which shows the calculated source depth required for benzene subslab concentration to reach $100 \mu\text{g}/\text{m}^3$ using the AAMB, or Eqs. (4) and (12). It should be noted that the calculations presented in Fig. 7(b) were based on benzene source vapor concentrations, which were multiplied by 100 to obtain the source vapor concentrations of TPH. Two fitting curves are made, based on the calculations for basement and slab-on-grade cases.

$$d_s = \begin{cases} 0.049c_{TPH}^s + 3.15, & d_f = 2 \text{ m} \\ 0.025c_{TPH}^s + 1.72, & d_f = 0.2 \text{ m} \end{cases} \quad \left(1 \text{ mg/L} \leq c_{TPH}^s \leq 400 \text{ mg/L}\right) \quad (15)$$

where c_{TPH}^s is the source soil vapor concentration of total petroleum hydrocarbon (TPH) (mg/L). In practice, vertical source-building separation is more generally cited by investigators, and can be easily obtained from the above:

$$L_s = \begin{cases} 0.049c_{TPH}^s + 0.15, & d_f = 2 \text{ m} \\ 0.025c_{TPH}^s + 1.52, & d_f = 0.2 \text{ m} \end{cases} \quad \left(1 \text{ mg/L} \leq c_{TPH}^s \leq 400 \text{ mg/L}\right) \quad (16)$$

where L_s is the vertical source-building screening distance (m).

In a recent report by U.S. EPA, a 4–6 m vertical “safe distance”, defined as the vertical distance from the sample position to the bottom of the building foundation, was proposed for screening out the danger of PVI, based on subslab screening limits for benzene concentration of $50\text{--}100 \mu\text{g}/\text{m}^3$ [10]. This conclusion was reached from a statistical analysis of U.S. EPA's PVI database [2]. There were few field measurements higher than $100 \mu\text{g}/\text{m}^3$ when the distance from the source was more than 4 m [11]. According to Eq. (16), this recommended distance seems to be adequate for most hydrocarbon sources as long as the equilibrium source vapor concentration of TPH is less than 100 mg/L. However, when the TPH soil vapor concentrations of the hydrocarbon sources approach the typical physical limit, i.e. 400 mg/L, which is approximately the pure component vapor pressure of benzene at room temperature, the required “safe vertical distance” would have to be much greater according to Eq. (16). This condition is not reflected in the PVI database, since the number of measurements at least 4 m above vapor source was quite limited. This issue deserves further examinations.

4. Conclusion

The AAMB provides a simple, analytical screening tool for cases of PVI. Its results indicate a good approximation to the results of full 3-D calculations that include the effects of biodegradation. The comparisons of AAMB with a full 3-D model (which used a commonly assumed biodegradation model) and field measurements suggest that the AAMB is suitable for application in a scenario involving a single homogenous source, constant soil properties and an impermeable building foundation surrounded by open ground surface (and assuming

no other sinks for oxygen except for biodegradation of contaminant vapor). A simple equation was developed and allows examining recommended vertical source-building separation screening distances. The results support an approach involving the definition of a “safe vertical distance” between source and building, but caution that this might need to be greater than presently recommended, if PVI involves a strong vapor source with an equilibrium TPH soil vapor concentration larger than 100 mg/L.

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Highlights

- A petroleum new vapor intrusion (PVI) hazard assessment tool is introduced.
- The application of this PVI tool does not require building operational conditions.
- The new PVI tool permits easy estimates of subslab concentrations.
- A simple equation is developed to estimate vertical screening distances.
- The 4–6 m screening distances proposed by EPA may not be enough in some cases.

Fig. 1.

(a) Scheme of vapor intrusion pathway [8] and (b) a development history of 1-D VI screening tools involving biodegradation based on the J-E model.

Fig. 2.

Simulated normalized vapor concentration profile for (a) a typical basement scenario involving no biodegradation, (b) a typical basement scenario involving a piecewise first-order biodegradation and (c) a typical slab-on-grade scenario involving a piecewise first-order biodegradation [16,17]. The dashed arrows connect points on the iso-concentration contours, one end showing the value at the assumed perimeter crack in the subslab, and the other end showing where the same concentration is achieved in the soil far removed from the influence of the building. Reprinted with permission.

Fig. 3.
Conceptual scenario for 1-D contaminant and oxygen transport.

Fig. 4. Comparison between results from AAMB and 3-D simulations involving a piecewise aerobic biodegradation [18]. (a) Predicted subslab concentrations. (b) Predicted indoor air concentrations.

Fig. 5.

Comparison between results from The ASU model [18] and BioVapor [10]. $x_o^{max} = c_o^{atm}$ in (a) and (b) and $c_o^{max} = 0.2c_o^{atm}$ in (c) and (d).

Fig. 6. Measured O_2 and TPH soil gas distribution for vertical cross-section B–B' of the building studied [25]. Dashed lines beneath building foundation are the estimated source zone. Reprinted from ref 25 with permission.

Fig. 7.

(a) The predicted influence of vapor source depth on normalized contaminant indoor air concentration with different reaction rate constants ($\lambda=0.018, 0.18$ and 1.8 h^{-1}) by AAMB;
 (b) the source depth required for benzene subslab concentration to reach 100 ug/m^3 using AAMB. (In (a), $c_h^s=100 \text{ mg/L}$; in (b), $\lambda=0.18 \text{ h}^{-1}$).

Table 1

Model parameters used to generate Figure 2(b) and 2(c), Figure 4, Figure 5 and Figure 7, unless otherwise noted in the text or figures [18].

Building/foundation parameters	Chemical vapor properties
Foundation foot print length: 10 m, width: 10 m	Contaminant: Benzene, C_6H_6
Depth of foundation (df): 0.2 and 2 m	Diffusivity of benzene in crack (D_h^{ck}): $3.17 \times 10^{-2} \text{ m}^2/\text{h}$
Crack/foundation slab thickness (d_{ck}): 0.15 m	
Crack width (w_{ck}): 0.001 m	Effective diffusivity of benzene in soil (D_h): $3.73 \times 10^{-3} \text{ m}^2/\text{h}$
Total crack length (L_{ck}): 39 m ²	Diffusivity of oxygen in crack (D_o^{ck}): $7.2 \times 10^{-2} \text{ m}^2/\text{h}$
Volume of intruded area (V_b): 174 m ³	Effective diffusivity of oxygen in soil (D_o): $8.48 \times 10^{-3} \text{ m}^2/\text{h}$
Air exchange rate in intruded volume (A_e): 0.5 h ⁻¹	Contaminant source concentration (c_c^s): 20, 100, 200 mg/L
Depth to groundwater/source from open ground surface (d_s): 1-14 m bgs	Oxygen concentration in atmosphere (c_o^{atm}): 279 mg/L
Pressure difference at the crack (p): 5 and 20 Pa	Henry's Law constant (H_c): 0.228
Biodegradation constants	Soil vapor flow properties
First-order reaction rate constant to the contaminant concentration in water (λ): 1.8, 0.18, 0.018 h ⁻¹	Viscosity of air/soil vapor (μ_g): 0.0648 kg/m/h
	Soil permeability (k): 10^{-11} m^2
Ratio of oxygen to hydrocarbon consumed (β): 3 kg oxygen/kg hydrocarbon	Total soil porosity (ϕ): 0.35
	Soil porosity filled with gas (ϕ_w): 0.07