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Estimating the oxygenated zone beneath building foundations for petroleum vapor intrusion assessment

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Graphical abstract

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Supplementary Material

The detailed development of this new analytical model, and further comparisons with a 3-D numerical model and with field data are available in the supplementary material.

A spreadsheet of the new analytical model developed in this work is available in the supplementary material or at www.pvtools.net.

Abstract

Previous studies show that aerobic biodegradation can effectively reduce hydrocarbon soil gas concentrations by orders of magnitude. Increasingly, oxygen limited biodegradation is being included in petroleum vapor intrusion (PVI) guidance for risk assessment at leaking underground storage tank sites. The application of PVI risk screening tools is aided by the knowledge of subslab oxygen conditions, which, however, are not commonly measured during site investigations. Here we introduce an algebraically explicit analytical method that can estimate oxygen conditions beneath the building slab, for PVI scenarios with impervious or pervious building foundations. Simulation results by this new model are then used to illustrate the role of site-specific conditions in determining the oxygen replenishment below the building for both scenarios. Furthermore, critical slab-width-to-source-depth ratios and critical source depths for the establishment of a subslab “oxygen shadow” (i.e. anoxic zone below the building) are provided as a function of key parameters such as vapor source concentration, effective diffusion coefficients of concrete and building depth. For impervious slab scenarios the obtained results are shown in good agreement with findings by previous studies and further support the recommendation by U.S. EPA about the inapplicability of vertical exclusion distances for scenarios involving large buildings and high source concentrations. For pervious slabs, results by this new model indicate that even relatively low effective diffusion coefficients of concrete can facilitate the oxygen transport into the subsurface below the building and create oxygenated conditions below the whole slab foundation favorable for petroleum vapor biodegradation.

1 Introduction

The accidental release of petroleum hydrocarbons into the subsurface may cause petroleum vapor intrusion (PVI), a process by which vapors of petroleum chemicals migrate from subsurface to overlying buildings [1]. The resulting indoor air quality problem from these vapors can pose potential threats to human health [2–4]. The difference between PVI and vapor intrusion (VI) involving other volatile contaminants (typically chlorinated compounds), is the potential of petroleum hydrocarbons to biodegrade in the presence of oxygen [5]. As described in the recent guidance on petroleum vapor intrusion issued by the United States Environmental Protection Agency (U.S. EPA) [6] and Interstate Technology & Regulatory Council (ITRC) [7] the potential threats of PVI to residents' health can be indeed significantly reduced or eliminated in oxygen-rich soils due to the occurrence of aerobic biodegradation by soil microbes. It is well known that microorganisms can oxidize petroleum hydrocarbons to carbon dioxide while utilizing electron acceptors such as molecular oxygen [8, 9]. Unlike recalcitrant compounds such as chlorinated solvents, a large number of petroleum hydrocarbon are susceptible to aerobic biodegradation at rates that are quite rapid with respect to rates of physical transport by diffusion and advection [21–22], leading to vapors attenuation by several orders of magnitude within a few meters [2, 10–18]. Based on this, U.S. EPA and ITRC guidances [6,7] proposed vertical screening distances (i.e. the thickness of clean biologically active soil between the source and the overlying receptor) beyond which the potential for PVI can be considered negligible. In these guidance documents no particular concerns are addressed to sources underlying an open ground surface. In such scenarios, indeed, oxygen can readily penetrate into the subsurface and create oxygenated conditions favorable for petroleum vapor biodegradation [19]. Conversely, both U.S.EPA and ITRC guidances highlight that a key aspect to be evaluated is the establishment of oxygenated soil zones beneath large buildings [1]. An impervious slab can potentially act as a surface cap reducing the migration of oxygen into the soil beneath the slab, and consequently, limiting the attenuation of vapor concentrations due to aerobic biodegradation [20]. In most PVI conceptual site models (CSMs), atmospheric oxygen at ground surface beyond the building perimeter is considered as the primary source of oxygen in the subsurface [1, 30–31]. For instance, in different analytical PVI models [20, 21, 23–28] and in a series of numerical modeling studies conducted by Abreu and Johnson [30] and Abreu *et al.* [31], this migration pathway was considered the only mechanism of oxygen replenishment in the subsurface below the building. However, U.S. EPA [6] suggests that diffusive transport through permeable concrete slabs can also enhance the oxygen availability in the subsurface and reports values for the effective diffusion coefficient for oxygen through permeable concrete slabs in the range of 1.08 to 15.6 cm²/h. Although these effective diffusion coefficients of concrete are significantly lower than the ones typical of soils [32–34], the net flux of oxygen through the slab might be significant if the building size is large enough to make the diffusive oxygen flux from open ground surface beyond foundation edge, negligible towards the middle of the subslab zone. Furthermore, wind or changes in barometric pressure may also periodically facilitate oxygen transport into the subsurface beneath the building foundation [35–37].

Though these studies provided some basis regarding possible oxygen migration pathways into the subsurface, there has been no algebraically explicit analytical solution that can be used by practitioners to easily estimate oxygen profiles beneath the building. To address this need, in this study we present an explicit analytical solution that can be used to predict subslab oxygen conditions in a two-dimensional (2-D) PVI scenario with either impervious or pervious building foundation surrounded by open ground surface. Accounting for building footprint size, the new model can predict oxygen availability beneath and adjacent to the building slab as a function of key parameters such as source strength, source depth, slab dimension and building features. The solution presented in this work can also be easily coupled to vapor intrusion tools such as BioVapor or integrated into an analytical solution for vapor transport as shown by Yao *et al.* [38]. In this work, after a brief description of the analytical solution method, simulation results from this new model are compared with those from a more rigorous three-dimensional (3-D) numerical model. These results are then used to illustrate the relationship between a subslab “oxygen shadow” (i.e. anoxic zone below the building) and the petroleum vapor source concentration and depth, building foundation size for both impervious and pervious building foundations. For the reader’s convenience, we have also prepared a spreadsheet of this new model.

2 Method development

The next sections report the model derived for the estimation of the 2-D aerobic/anaerobic interface profile beneath and adjacent to building foundations (see Fig. 1). The analytical solution was obtained by introducing a combined oxygen and hydrocarbon variable that couples vapor transport and reaction in the aerobic zone. In this way it is possible to describe the 2-D problem with a Laplace’s equation and hence to derive the expression for the estimation of the position of the aerobic/anaerobic interface using the Schwarz-Christoffel mapping method [39–40]. The analytical solution was derived with either impervious or pervious building foundation. Namely, for an impervious slab (see Section 2.1), atmospheric oxygen at ground surface beyond the building perimeter was considered as the primary source of oxygen in the subsurface. Conversely, for a pervious slab, it was considered that oxygen replenishment below the building can also occur as a result of diffusion through the building foundation. In this case, the oxygen conditions below the building foundations are simulated by combining the results returned by the model developed for an impervious slab (Section 2.1) with the ones obtained from the analytical solution described in Section 2.2 that was derived assuming that oxygen diffusion from the building is the primary source of oxygen in the subsurface. It is worth noting, that the solution proposed in this work focuses on the estimation of the 2-D aerobic/anaerobic interface profile beneath and adjacent to building foundations, but, as shown by Yao *et al.* [38], this approach can be further extended to derive soil gas concentration profiles for both hydrocarbons and oxygen in the subsurface.

2.1 Oxygen diffusion from open ground surface, beyond the building edge

In 2-D PVI scenarios, in the absence of transience, leaching, sorption, and gaseous advection, the soil gas transport of oxygen and hydrocarbon vapors can be described by equations representing a coupled balance of diffusion D and biodegradation R [41]:

$$\begin{cases} D_i \nabla^2 c_i = R_i & \text{(hydrocarbons)} \\ D_o \nabla^2 c_o = \sum \delta_i R_i & \text{(oxygen)} \end{cases} \quad (1a)(1b)$$

where the subscripts i and o refer to the vapor phase hydrocarbons (of which there may be more than one) and oxygen, respectively. c is the concentration of the species in the soil-gas phase, R the reaction rate of that species, δ_i the stoichiometric mass of oxygen consumed per mass of hydrocarbon i reacted and D the effective porous medium diffusion coefficients for the different species.

When the petroleum vapor concentration is low, the aerobic biodegradation of petroleum hydrocarbons can usually be described by a first order reaction rate law, i.e. neglecting the influence of oxygen concentration on the aerobic reaction rate (pseudo first-order biodegradation rate) [42]. The reaction is assumed to occur only when the oxygen concentration in soil gas is higher than a specific threshold level and so the rate R in equation (1) is represented by:

$$\begin{cases} R_i = k_i c_i & (c_o > c_o^{\min}) \\ R_i = 0 & (c_o \leq c_o^{\min}) \end{cases} \quad (2a)(2b)$$

where $c_o^{\min}$ is the minimum oxygen concentration (e.g. 1% v/v) below which aerobic

biodegradation of hydrocarbons stops, or slows down to negligibly low rates, $k_i = \frac{\lambda_i \theta_w}{H_i}$ is the reaction rate constant for the soil gas concentration of hydrocarbon i , λ_i the degradation rate of hydrocarbon i in water phase, θ_w the moisture content and H_i the Henry's law constant of hydrocarbon i .

The reaction term R can be eliminated by reorganizing equations (1a) and (1b) to a Laplace's equation:

$$\nabla^2 (c_o - \frac{\sum \delta_i D_i \nabla^2 c_i}{D_o}) = 0 \quad (3)$$

Equation (3) can be normalized by defining a new variable $w(x, z)$:

$$\begin{cases} \nabla^2 w(x, z) = 0 \\ w(x, z) = \frac{c_o - c_o^{\min} + \frac{\sum \delta_i D_i (c_i^s - c_i)}{D_o}}{c_o^{\text{atm}} - c_o^{\min} + \frac{\sum \delta_i D_i c_i^s}{D_o}} \end{cases} \quad (4a)(4b)$$

where c_o^{atm} is the atmospheric oxygen concentration and c_i^s the petroleum vapor source concentration. Note that in the case of a hydrocarbons mixture, in the summation (Σ) of equation (4b) should be included all the degradable compounds present in the source.

Now the two-dimensionality of the analysis is reflected in the reduction of the problem to x-z coordinates, with the boundary conditions as shown in Fig. 2:

$$\begin{cases} w(x, 0)=0 \\ w(x > \frac{L_{\text{slab}}}{2}, L)=1 \end{cases} \quad (5a)(5b)$$

and

$$\begin{cases} \frac{d}{dx}w(0, z)=\frac{d}{dz}w(x \leq \frac{L_{\text{slab}}}{2}, L)=0 \\ w(+\infty, z)=\frac{z}{L} \end{cases} \quad (6a)(6b)$$

The value of $w(x, z)$ at the aerobic/anaerobic interface, w_a , and the anaerobic zone thickness $L_b(x = +\infty)$ can be obtained by solving equations (3–6) when $x \rightarrow +\infty$ [21]:

$$\begin{cases} w_a = \frac{\frac{\sqrt{k_i/D_i}L_b(x=+\infty)}{1+\sqrt{k_i/D_i}L_b(x=+\infty)}}{1+\frac{D_o(c_o^{\text{atm}}-c_o^{\text{min}})}{\Sigma\delta_i D_i c_i^s}} \\ \frac{L_b}{L}(x=+\infty) \approx \frac{1}{1+\frac{D_o(c_o^{\text{atm}}-c_o^{\text{min}})}{\Sigma\delta_i D_i c_i^s}} \end{cases} \quad (7a)(7b)$$

To solve equation (4), we have followed an approach similar to the one used by Shen *et al.* [44] for the estimation of 2-D concentration profiles for non-degradable compounds. Specifically, to solve the Laplace's equation we have used the Schwarz-Christoffel mapping method [39–40] with the boundary conditions reported in Fig. 2. The detailed mathematical derivations are provided in the Supplementary Information. Making reference to the boundary conditions, it should be noted that here we have considered an impervious slab (i.e. no-flux boundary) and steady-state diffusion and consumption in a homogeneous 2-D soil domain. Under these conditions, the relation between the dependent variable w and its contour coordinates (x, z) is:

$$\left(\frac{\Omega \cdot \cos(\pi \frac{z}{L}) \cosh(\pi \frac{x}{L}) - \Omega + 1}{\cos(\pi \cdot w(x, z))} \right)^2 - \left(\frac{\Omega \cdot \sin(\pi \frac{z}{L}) \sinh(\pi \frac{x}{L})}{\sin(\pi \cdot w(x, z))} \right)^2 = 1 \quad (8)$$

with:

$$\Omega = \frac{1}{\cosh^2(\pi \cdot \frac{L_{\text{slab}}}{4L})} \quad (9)$$

where L is the vertical distance from the source to the bottom of the slab and L_{slab} the slab width (footprint) of the building. Substitute $x < \frac{L_{slab}}{2}$ and $z = L$ into equations (8–9), and the variable $((x < \frac{L_{slab}}{2}, L))$ immediately below the foundation bottom can be obtained:

$$w(x < \frac{L_{slab}}{2}, L) = \frac{1}{\pi} \arccos(1 - \Omega \cdot (1 + \cosh(\pi \frac{x}{L}))) \quad (10)$$

Similarly, the position of aerobic/anaerobic interface can be obtained by substituting $w(x, z_a(x)) = w_a$ into equations (8) and (9):

$$Z_a(x) = \begin{cases} \frac{L}{\pi} \arccos(\frac{a}{b} + \sqrt{\frac{a^2}{b^2} + \frac{c}{b}}), & \text{if } w_a \leq \frac{1}{2} \\ \frac{L}{\pi} \arccos(\frac{a}{b} + \sqrt{\frac{a^2}{b^2} + \frac{c}{b}}), & \text{if } w_a > \frac{1}{2} \end{cases} \quad (11a)(11b)$$

where

$$\begin{cases} a = \frac{\Omega \cdot (\Omega - 1) \cdot \cosh(\frac{\pi x}{L})}{\cos^2(\pi \cdot w_a)} \\ b = (\frac{\Omega \cdot \cosh(\pi \frac{x}{L})}{\cos(\pi \cdot w_a)})^2 + (\frac{\Omega \cdot \sinh(\pi \frac{x}{L})}{\sin(\pi \cdot w_a)})^2 \\ c = 1 + (\frac{\Omega \cdot \sinh(\pi \frac{x}{L})}{\sin(\pi \cdot w_a)})^2 - \frac{(\Omega - 1)^2}{\cos^2(\pi \cdot w_a)} \end{cases} \quad (12a)(12b)(12c)$$

Hence the aerobic layer depth from the building foundation, $L_a(x)$ is equal to:

$$L_a(x) = L - Z_a(x) \quad (13)$$

At the center of the building ($x = 0$) the aerobic layer depth can be derived from equations (11–13) as follows:

$$L_a(0) = L(1 - \frac{1}{\pi} \arccos(\frac{\Omega + \cos(\pi \cdot w_a - 1)}{\Omega})) \quad (14)$$

Note that when $L_a(0) = L$ this indicates that oxygen rich conditions are established down to the source depth, while for $L_a(0) = 0$, the occurrence of a completely anaerobic condition in the vadose zone beneath the slab is expected. For scenarios involving a building foundation depth ($d_f > 0$), the above equations can be still used (see Fig. 2d) simply considering that oxygen concentrations at the foundations depth will be lower than the atmospheric values expected at the open ground surface. Specifically, assuming that in a homogeneous soil the oxygen concentration decreases linearly with increasing depth [44], the model for a basement scenario can be applied by assuming that the variable w_a decreases linearly with increasing slab depth:

$$w_a = \frac{\frac{\sqrt{k_i/D_i} L_b (x=+\infty)}{1 + \sqrt{k_i/D_i} L_b (x=+\infty)}}{\frac{D_o(c_o^{\text{atm}} - c_o^{\text{min}})}{\sum \delta_i D_i c_i^s} \left(1 - \frac{d_f}{d_s - L_b(x=+\infty)}\right) + 1} \quad (15)$$

where d_s is the vertical source distance from open ground and d_f the slab depth from open ground. It is easily checked that for $d_f = 0$, equation (15) is equivalent to the solution given by equation (7). It is worth noting that equation (15) represents only an approximation of the oxygen behavior expected in scenarios involving a building foundation depth ($d_f > 0$) as the presence of a basement will probably create non-linear oxygen depth profiles not considered in the model.

2.2 Oxygen diffusion through a pervious slab

In cases where diffusive flux through the pervious slab could be an alternative oxygen migration pathway into the soil, the oxygen mass balance beneath the pervious foundation can be written as follows:

$$\left\{ \begin{array}{l} \frac{\sum \delta_i D_i c_i^s}{L_b} = \frac{D_o(c_o^{\text{ss}} - c_o^{\text{min}})}{L_a} \\ \frac{D_o(c_o^{\text{ss}} - c_o^{\text{min}})}{L_a} = \frac{D_o^{\text{slab}}(c_o^{\text{atm}} - c_o^{\text{ss}})}{L_{ck}} \end{array} \right. \quad (16a)(16b)$$

where L_{ck} is the thickness of the slab, D_o^{slab} the overall diffusivity of oxygen through foundation slab and c_o^{ss} the subslab oxygen concentration. The aerobic zone thickness can be obtained by solving equation (16):

$$L_a = \frac{D_o^{\text{slab}} L (c_o^{\text{atm}} - c_o^{\text{min}}) + L_{ck} \sum \delta_i D_i c_i^s}{D_o(c_o^{\text{atm}} - c_o^{\text{min}}) + \sum \delta_i D_i c_i^s} \left(\frac{D_o}{D_o^{\text{slab}}} \right) \quad (17)$$

It should be noted that equation (17) is independent of foundation footprint size since oxygen diffusive flux from the open ground surface beyond the building edge is neglected here. In practice, for a pervious slab the subslab oxygen conditions are determined by a combination of diffusion through the foundation slab and diffusion from open ground surface beyond the foundation edge. Hence, the 2-D aerobic/anaerobic interface profile for a pervious foundation slab can be estimated by using the higher value of L_a obtained from equation (13) and equation (17).

3 Partial Validation

In this section simulation results from this new model are compared with those from a more rigorous 3-D numerical model for partial validation. Specifically, in order to assess the capability of the analytical model to predict oxygen availability beneath and adjacent to building foundations, in Fig. 3 the results provided by the new method are compared with those reported in Abreu and Johnson [30] using a three-dimensional (3-D) numerical model

with the same input parameters (see Table 1). Namely, Fig. 3 shows the normalized oxygen iso-concentration contour curves simulated by Abreu and Johnson for a slab-on-grade (left) and basement scenario (right), assuming a benzene vapor source located at a depth of 8 m bgs and a first-order biodegradation rate of $\lambda_b = 0.18 \text{ h}^{-1}$, with different source vapor concentrations ($c_b^s = 200, 100$ and 20 g/m^3). In the same figure, the predicted position of the aerobic/anaerobic interface by the analytical model (dashed red lines) is compared with the normalized oxygen concentration of 0.05 (corresponding to an oxygen concentration of 13.7 g/m^3 , i.e. the threshold oxygen value below which aerobic biodegradation is no longer significant) returned by the 3-D numerical model. In these simulations the foundation slab was considered impervious to soil gas flow except for through a perimeter crack area in the 3-D numerical model.

From Fig. 3 it can be seen that for both slab-on-grade and basement scenarios, the aerobic layer depth calculated using the new analytical model follows closely the trend predicted by the 3-D numerical simulations, though with a tendency of the analytical method to provide slightly more conservative results. This slight discrepancy can be ascribed to some simplifying assumptions employed in the analytical model. First, the analytical model doesn't account for the presence of a perimeter crack area in the foundation slab that can affect the oxygen replenishment below the building foundation. Second, due to the 2-D nature of the analytical solution, the model presented in this work, differently from the 3-D numerical solution, assumes infinitely long rectangular building along y axis.

Regardless of the above limitations, the comparisons shown in Fig. 3 (and the further comparisons reported in the Supplementary Material) clearly highlight that the analytical method presented here provides a simple tool to assess the oxygen conditions beneath and adjacent to building foundation slabs and hence to assess whether a site might develop a subslab oxygen shadow, which may reduce the potential for aerobic biodegradation. Furthermore, the predicted oxygen conditions beneath the foundation by the new 2-D analytical method can be used as inputs in existing VI screening tools such as BioVapor (an illustrative demonstration is reported in the Supplementary Material) or integrated into an analytical solution for vapor transport as reported by Yao *et al.* [38]. This can be easily done using the spreadsheet attached to this paper which implements the model described in this work.

4 Results and discussion

In Section 4.1 simulation results from this new model are used to evaluate the role of site-specific parameters in determining oxygenated soils beneath and adjacent to the building foundation. Then, in Section 4.2, the relationship between a subslab “oxygen shadow” (i.e. anoxic zone below the building) and the petroleum vapor source concentration and depth, building foundation size for both impervious and pervious building foundations is investigated.

4.1 Role of site-specific conditions in determining oxygenated zone below the building

Figs. 4–6 show the predicted 2-D aerobic/anaerobic interface profile beneath and adjacent to building foundations as a function of source concentrations and depths for a building

footprint size of 10 m, 15 m and 20 m, respectively. The simulation results were obtained assuming either an impervious (left) or pervious slab (right). For the latter scenario, to highlight the cases where oxygen diffusion through the slab is the primary source of oxygen in the subsurface, the aerobic/anaerobic interface was shown as dotted lines. For these simulations, the chemical properties of benzene were assumed as representative of petroleum hydrocarbons and the effective diffusion coefficients in the soil were calculated by assuming the soil properties of a sand (see Table 1). As to the oxygen diffusion coefficient through the slab, a value of $5 \text{ cm}^2/\text{h}$ was assumed as representative of the average values reported in the literature [6]. The other input parameters used for these simulations are reported in Table 1. Making reference to the results reported in these figures it can be noticed that the presence of the building can significantly affect the oxygen availability below building foundations. This is particularly significant in the case of large buildings and shallow sources. For instance, making reference to a slab size of 20 m and a source depth of 3 m (see Fig. 6), it can be noticed that the oxygen availability beneath the impervious slab is drastically reduced toward the center of building, up to creating an “oxygen shadow” even in the case of a relatively low source concentration of 10 g/m^3 . Conversely, for smaller footprint buildings and large source depths, the establishment of oxygenated conditions is almost insensitive to the presence of the building. Indeed, looking at Fig. 4 (i.e. slab size of 10 m) it can be noticed that for a source depth of 10 m the aerobic/anaerobic interface profile for source concentrations of 10, 20 or 50 g/m^3 is almost horizontal. Moreover, from these results it can be observed that for an impervious slab, as already highlighted by Knight and Davis [20], the oxygen availability in the subsurface basically depends on the slab width to source depth ratio. Indeed, the profiles shown in Fig. 4 for a slab size of 10 m and a source depth of 3 m (i.e. $L_{\text{slab}}/L = 3.3$) are essentially the same of the ones obtained assuming a slab width of 15 m and a source depth of 5 m (i.e. $L_{\text{slab}}/L = 3$ as shown in Fig. 5). As to the simulations carried out assuming a pervious slab, the results reported in these figures clearly show that for all cases with vapor source concentrations lower than 100 g/m^3 the oxygen diffusion through foundations was high enough to create an oxygenated zone below the whole building foundation (i.e. no “oxygen shadow”). Besides, even for vapor source concentrations of 200 g/m^3 , simulation results show that the oxygen replenishment from the building is high enough to create an oxygenated zone provided that the vapor source is located at least 5 meter below the building foundations. These results also highlight that for a pervious slab, oxygen diffusion through the slab is the primary source of oxygen in the subslab near to the building center (see dotted lines in Figs. 4–6). This is particular evident in the case of high source concentrations and large slab sizes, i.e. when the oxygen diffusion from ground surface beyond the building perimeter is not high enough to create an oxygenated zone under the entire subslab zone. Conversely, at the foundation perimeter in all simulated cases oxygen diffusion from ground surface beyond building perimeter is the primary source of oxygen in the subsurface. Here it should be however considered that the solution proposed in this work is based on the assumption of an infinitely large building in all directions. The consequence of this is that the right hand graphs in Figs. 4–6 all have flat (constant) oxygen profiles under the building. Conceptually, the oxygen concentration profile would not be zero at a fixed constant depth below a building. This behavior can be expected only for very large buildings.

Another aspect that should be considered in the evaluation of oxygen conditions beneath impervious slabs is the depth of foundations below ground surface. The simulations discussed above were indeed run assuming a slab-on-grade scenario (i.e. $d_f = 0$). In the case of a basement scenario (i.e. $d_f > 0$) the above considerations are still valid although in this case it should be considered that for the same vertical source-building separation distance the oxygen availability is lower compared to that in a slab-on-grade scenario. Fig. 7 shows a comparison of the 2-D aerobic/anaerobic interface profile calculated for a building size of 15 m for a slab-on-grade ($d_f = 0$) or basement ($d_f = 2$ m) scenario. From this comparison it can be observed that although the simulated profiles are quite similar, in the basement scenario the oxygen availability beneath building foundation is more limited than that in the slab-on-grade scenario. It is worth noting that for pervious slab cases the foundations depth doesn't affect the oxygen replenishment from indoor air since oxygen diffusion from building depends only on the vertical source-building separation distance (simulations not shown for sake of conciseness).

4.2 Critical slab size and source depth for the development of subslab oxygen shadow

To generalize the results discussed above, a conservative estimate of the critical slab size ($L_{slab,c}$) above which the development of an oxygen shadow at the center of the impervious building is expected can be obtained by substituting $L_a(0) = 0$ into equations (10–12):

$$\frac{L_{slab,c}}{L} = \frac{4}{\pi} \ln\left(\cot\left(\frac{\pi w_a}{4}\right)\right) \quad (18)$$

with w_a defined as in equation (15).

Similarly, in the case of a pervious slab foundation, the critical vertical source-building separation distance (L_c) below which the development of an oxygen shadow below the building is expected, can be obtained by substituting $L_a = 0$ into equation (17):

$$L_c = \frac{L_{ck} \sum \delta_i D_i c_i^s}{D_o^{slab} (c_o^{atm} - c_o^{min})} \quad (19)$$

The application of equation (18) and equation (19) is shown in Fig. 8 for a sandy (Fig. 8a, b) and clay soil (Fig. 8c, d). Namely, Fig. 8a and Fig. 8c show the critical slab width to source depth ratio ($L_{slab,c}/L$) calculated with equation (18) as a function of the vapor source concentration for a slab-on-grade scenario ($d_f = 0$) and two basement scenarios ($d_f = 0.25d_s$ and $d_f = 0.5d_s$). On the other hand, Fig. 8b and Fig. 8d show the critical vertical building-source distance (L_c) calculated with equation (19) as a function of vapor source concentration for different oxygen diffusion coefficients through the slab that were selected based on the values reported in the U.S.EPA's PVI guidance [6]. These simulations were performed again by employing the chemical properties of benzene (the other input parameters are reported in Table 1). From Fig. 8a it can be observed that the establishment of an "oxygen shadow" at the center of the building strongly depends on the source depth and vapor source concentration. For instance, in the case of a vapor source concentration of

10 g/m³, from Fig. 8a it can be easily checked that the critical slab width to source depth ratio is $L_{slab,c}/L \approx 4$ and $L_{slab,c}/L \approx 3$ for a slab-on-grade and basement scenario, respectively. This means that if the source is located 5 m below building foundations, for slab sizes less than 20 m (slab-on-grade) or 15 m (basement), the oxygen diffusion from the open ground surface would be expected to create an oxygenated zone under the entire subslab zone, i.e. making petroleum vapor intrusion risks not significant. Conversely, for a vapor source concentration of 100 g/m³ and a source depth of 5 m, Fig. 8a shows that for slab sizes larger than 7.5 m (slab-on-grade, $L_{slab,c}/L \approx 1.5$) or 2.5 m (basement, $L_{slab,c}/L \approx 0.5$) an oxygen shadow at the center of the building is expected, i.e. highlighting that further investigations might be needed to evaluate the subslab oxygen conditions. As it can be observed from the trends shown in Fig. 8a and Fig. 8c, the above considerations are valid for both sandy and clay soils. Indeed, as already highlighted by Knight and Davis [20], the establishment of oxygenated zone beneath impervious slabs is independent of the soil type as the oxygen replenishment from open ground only depends on the ratio of the diffusion coefficients of oxygen and vapor into the soil (D_o/D_v) that for a sand or a clay remains constant and equal to the ratio of the diffusion coefficients of oxygen and vapor in air. Finally, as already shown in Fig. 7, from Fig. 8a and Fig. 8c it can be observed that for impervious scenarios the depth of the foundations (d_f) does not seem to play such significant role on PVI (i.e., it does not matter much if is a slab-on-grade or basement scenario).

The above results are in line with the previous findings of Knight and Davis [20]. Indeed, as also shown in the Supplementary Material, Knight and Davis [20] have drawn similar conclusions about the critical slab width to source depth ratio in the case of slab-on-grade scenarios. The good agreement with the results obtained by Knight and Davis [20] using a model based on an instantaneous reaction (i.e. rapid compared to soil vapor diffusion in the subsurface) also highlights that the degradation rate constant (that in this work was assumed to be equal to 0.18 h⁻¹) plays only a limited role in the establishment of oxygenated conditions below the building. This latter consideration is also in line with previous findings by Abreu and Johnson [30] that have shown that the degradation rate does not affect the general oxygen profile. Similarly, the results obtained in this work are in good agreement with the results obtained from 3-D numerical simulations by Abreu *et al.* [1]. Moreover, Abreu *et al.* [1] have found that for a vapor source of 10 g/m³ and a source depth of 4.6 m (15 ft), the critical slab size for the establishment of an oxygen shadow below building foundation is 20 m (66 ft) on the shorter side. It can be readily checked that the latter simulation corresponds to a slab width to source depth ratio of $L_{slab,c}/L \approx 4.3$ that is in line with the one that can be estimated from Fig. 8a and Fig. 8c. The results reported in this work hence further support the recommendation of U.S.EPA to not adopt for LNAPL sources, the vertical exclusion distance of 4.6 m (15 ft) beneath impervious slabs characterized by a building width higher than 20 m (66 ft) on the shortest side.

For a pervious slab, the above criteria are instead not sufficient to evaluate if an oxygen shadow is expected below the building. For such cases, the other aspect to be evaluated is indeed the oxygen diffusion through the pervious slab. Here, the evaluation can be performed using Fig. 8b and Fig. 8d. Namely, based on the vapor source concentration and the source depth, it can be evaluated if the oxygen diffusion through building is high enough to create an oxygenated zone beneath the foundation. For instance, considering the same

scenario discussed above for the impervious slab scenario (i.e. 100 g/m^3 at a depth of 5 m), from Fig. 8b and Fig. 8d it can be easily checked that for effective oxygen diffusion coefficients through the slab higher than $2 \text{ cm}^2/\text{h}$ (sandy soil) or $1 \text{ cm}^2/\text{h}$ (clay soil), oxygen replenishment from building is high enough to create an oxygenated zone under the entire building foundations. It is interesting to note that compared to the impervious slab scenario, for a pervious slab the type of soil strongly influences the re-oxygenation under the building. Indeed, looking at Fig. 8b and Fig. 8d it can be observed that for the same oxygen diffusion coefficient through the slab (D_o^{slab}), the oxygen replenishment in the case of the clay soil is significantly higher compared to a sandy soil. This is due to the fact that for clay soil the vapor diffusive flux from the source (responsible of oxygen consumption in the subsurface) is significantly lower with respect to that in a sandy soil scenario. Overall these results highlight the key role played by this oxygen replenishment mechanism, suggesting that future research efforts could be addressed to accurately evaluating the oxygen diffusion coefficients through pervious slabs as a function of the physical characteristics of the concrete foundations slab, the nature of the cement, the cement/water ratios and the concrete production processes.

5 Conclusions

Estimates from the analytical method proposed in this work replicate quite well the predicted oxygen profiles from more sophisticated 3-D numerical models. The different simulations carried out allowed to evaluate the critical parameters affecting the establishment of anoxic zones beneath impervious or pervious building foundation slabs. Namely, it was found that for impervious slabs the critical parameters affecting the oxygen replenishment below the building are the slab size to source depth ratio (L_{slab}/L) and the source concentration. For instance, for vapor source concentrations lower than 10 g/m^3 , it was found that for $L_{\text{slab}}/L > 4$ (slab-on-grade) and $L_{\text{slab}}/L > 3$ (basement), an “oxygen shadow” (i.e. anoxic zone) below the building is expected. These results are not only in line with previous findings of Knight and Davis [20] and Abreu *et al.* [1], but further support the recommendation of U.S. EPA about the inapplicability of vertical exclusion distances for large buildings and high source concentrations. For pervious slabs, instead, it was found that even relatively low effective diffusion coefficients of concrete (e.g. D_{slab} of $1\text{--}2 \text{ cm}^2/\text{h}$) can facilitate the oxygen transport into the subsurface below the building and create oxygen-rich conditions below the whole slab foundation (i.e. no “oxygen shadow”). In this view, the accurate assessment of diffusion coefficients through the slab plays a key role in the correct evaluation of oxygen availability below the building and hence future efforts could be made to address this issue.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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Abbreviations

PVI	Petroleum Vapor Intrusion
UST	Underground Storage Tank
3-D	three-dimensional
2-D	two-dimensional 1-D, one-dimensional
VI	Vapor Intrusion
US EPA	United States Environmental Protection Agency
ITRC	Interstate Technology & Regulatory Council
CO₂	carbon dioxide
O₂	oxygen
CSM	conceptual site model

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Highlights

- A 2-D analytical model for estimating subslab oxygen availability is presented
- The analytical model replicates quite well 3-D numerical results
- The role of pervious and impervious foundations slab is investigated
- The site parameters affecting the development of subslab oxygen shadow are examined

Figure 1.
Conceptual modeling scenario.

Figure 2.

2-D analytical model domain for an impervious slab with the boundary conditions (B.C.) for (a) hydrocarbon vapors, (b) oxygen (c) composite hydrocarbon vapor and oxygen variable w for a slab-on-grade scenario and (d) composite hydrocarbon vapor and oxygen variable w for a basement scenario.

Figure 3.

Comparison between the normalized oxygen concentration results provided by the 3-D numerical model of Abreu and Johnson [30] and by the analytical model developed in this paper for a slab-on-grade scenario (left hand panels) and for a basement scenario (right hand panels). The dashed red lines indicate the aerobic layer depths predicted by the analytical model, which should be compared with the normalized oxygen iso-concentration contour curve of 0.05 iso-concentration contour curves obtained by Abreu and Johnson. Oxygen

contours are normalized to source atmospheric concentration. (Figure adapted from Abreu and Johnson [30]).

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Building size ($L_{\text{slab}} = 10 \text{ m}$)

Figure 4.

2-D aerobic to anaerobic interface profiles simulated by the model developed in this work as function of different vapor source concentrations and source depths for an impervious and pervious slab. In these simulations a slab width of 10 m was considered. Solid Lines: oxygen diffusion from open ground; Dashed lines: oxygen diffusion from building.

Building size ($L_{\text{slab}} = 15 \text{ m}$)

Figure 5.

2-D aerobic to anaerobic interface profiles simulated by the model developed in this work as function of different vapor source concentrations and source depths for an impervious and pervious slab. In these simulations a slab width of 15 m was considered. Solid Lines: oxygen diffusion from open ground; Dashed lines: oxygen diffusion from building.

Building size (L_{slab}) = 20 m

Figure 6.

2-D aerobic to anaerobic interface profiles simulated by the model developed in this work as function of different vapor source concentrations and source depths for an impervious and pervious slab. In these simulations a slab width of 20 m was considered. Solid Lines: oxygen diffusion from open ground; Dashed lines: oxygen diffusion from building.

Figure 7.

2-D aerobic to anaerobic interface profiles simulated by the model developed in this work as function of different vapor source concentrations for (a) slab-on-grade or (b) basement scenario. The simulations were run assuming a source located 5 m below building foundations and a slab size of 15 m.

Figure 8.

(a, c) Impervious slab (oxygen from open ground beyond the building edge): critical slab width to source depth ratio ($L_{slab,c}/L$) above which the development of an oxygen shadow is expected (i.e. $L_a = 0$) at the center of an impervious slab ($x = 0$) for different building foundations depths (df) as a function of vapor source concentration and (b, d) Pervious slab (oxygen from building): critical source vertical distance from the bottom of the foundations (L_c) below which the development of an oxygen shadow is expected below the building for

different effective diffusion coefficients of concrete (D_{slab}) as a function of vapor source concentration. The simulations were run for a sandy (a,b) and (c,d) clay soil.

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Table 1

Input Parameters. Unless otherwise noted in figures, the data used in this work are those used by Abreu and Johnson [30].

Parameter	Symbol	Unit	Figure 3	Figure 4-6	Figure 7	Figure 8
Source depth	d_s	m	8	3, 5, 10	5 (slab-on-grade) 7 (basement)	-
Soil porosity	θ_i	-	0.35	0.375	0.375	0.375 (sand) 0.459 (clay)
Moisture-filled porosity	θ_w	-	0.07	0.054	0.054	0.054 (sand) 0.215 (clay)
Vapor source concentration	C_b^s	g/m ³	20, 100, 200	10-200	10-200	0.1-1000
Biodegradation rate constant of benzene in water	λ_b	h ⁻¹	0.18	0.18	0.18	0.18
Vapor diffusion coefficient in the vadose zone	D_b	m ² /h	$3.73 \cdot 10^{-3}$	$5.12 \cdot 10^{-3}$	$5.12 \cdot 10^{-3}$	$5.12 \cdot 10^{-3}$ (sand) $1.37 \cdot 10^{-3}$ (clay)
Foundations depth	d_f	m	0.2 (slab-on-grade) 2 (basement)	0	0 (slab-on-grade) 2 (basement)	-
Slab size	L_{slab}	m	10	10, 15, 20	15	-
Foundations thickness	L_{ck}	m	0.15	0.15	0.15	0.15
Oxygen atmospheric concentration	C_o^{atm}	g/m ³	279	279	279	279
Reaction threshold of oxygen	C_o^{min}	g/m ³	13.7	13.7	13.7	13.7
Ratio of oxygen to benzene consumed	δ_b	gO ₂ /gHC	3	3	3	3
Oxygen diffusion coefficient in the vadose zone	D_o	m ² /h	$8.48 \cdot 10^{-3}$	$1.16 \cdot 10^{-2}$	$1.16 \cdot 10^{-2}$	$1.16 \cdot 10^{-2}$ (sand) $2.12 \cdot 10^{-3}$ (clay)
Oxygen diffusion coefficient through the slab	D_o^{slab}	m ² /h	0	0 (impervious) $5 \cdot 10^{-4}$ (pervious)	0	0 (impervious) $1 \cdot 10^{-4}$ – $1 \cdot 10^{-3}$ (pervious)

Nomenclature

λ_b	Degradation rate of benzene in water phase	h^{-1}
λ_i	Degradation rate of hydrocarbons in water phase	h^{-1}
δ_b	Stoichiometric mass of oxygen consumed per mass of benzene	g_{O_2}/g_{HC}
δ_i	Stoichiometric mass of oxygen consumed per mass of hydrocarbons	g_{O_2}/g_{HC}
θ_i	Porosity of the soil	-
θ_w	Water-filled porosity of the soil	-
A_b	Foundations area	m^2
C_b^s	Vapor source concentration of benzene	g/m^3
c_i	Concentration of hydrocarbons in the soil-gas phase	g/m^3
C_i^s	Vapor source concentration of hydrocarbons	g/m^3
c_o	Concentration of oxygen in the soil-gas phase	g/m^3
C_o^{atm}	Oxygen concentration in the atmosphere	g/m^3
C_o^{min}	Minimum oxygen concentration to sustain biodegradation	g/m^3
C_o^{ss}	Subslab concentration of oxygen	g/m^3
d_f	Depth of the building foundation below ground surface	m
d_s	Depth of contaminant source below ground surface	m
D_b	Effective porous medium diffusion coefficient of benzene	m^2/h
D_i	Effective porous medium diffusion coefficient of hydrocarbons	m^2/h
D_o	Effective porous medium diffusion coefficient of oxygen	m^2/h
D_o^{slab}	Overall diffusivity of oxygen through the foundations slab	m^2/h
H_i	Henry's law constant of hydrocarbons	-
K_i	First-order reaction rate constant for hydrocarbons	h^{-1}
L	Source vertical distance from the bottom of the foundations	m
L_a	Thickness of the aerobic zone in the subsurface	m
L_b	Thickness of the anaerobic zone in the subsurface	m
L_c	Critical source vertical distance from the bottom of the foundations	m
L_{ck}	Thickness of the slab	m
L_{slab}	Slab width of the building	m
$L_{slab,c}$	Critical slab width of the building	m
R_i	Loss rate of hydrocarbons due to biodegradation (first-order kinetic)	$g/(m^3 h)$
w	Constituent oxygen and hydrocarbons variable	-
w_a	Constituent oxygen and hydrocarbons variable at the interface	-
x	Coordinate in the horizontal direction	m
z	Coordinate in the vertical direction	m

z_a Position of the aerobic to anaerobic interface m

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