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Simulated Soil Vapor Intrusion Attenuation Factors Including Biodegradation for Petroleum Hydrocarbons

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Abstract

Aerobic biodegradation can contribute significantly to the attenuation of petroleum hydrocarbons vapors in the unsaturated zone; however, most regulatory guidance for assessing potential human health risks via vapor intrusion to indoor air either neglect biodegradation in developing generic screening levels or allow for only one order of magnitude additional attenuation for aerobically degradable compounds, which may be overly conservative in some cases. This paper describes results from three-dimensional numerical model simulations of vapor intrusion for petroleum hydrocarbons to assess the influence of aerobic biodegradation on the attenuation factor for a variety of source concentrations and depths for residential buildings with basements and slab-on-grade construction. The simulations conducted in this study provide a framework for understanding the degree to which bioattenuation will occur under a variety of scenarios and provide insight into site conditions that will result in significant biodegradation. This improved understanding may be used to improve the conceptual model of contaminant transport, guide field data collection and interpretation, and estimate semi-site-specific attenuation factors for combinations of source concentrations, source depth, oxygen distribution, and building characteristics where site conditions reasonably match the scenarios simulated herein.

Introduction

Subsurface migration of volatile compounds and vapor intrusion to indoor air is a potential exposure pathway for human occupants of buildings over or near contaminated soils and ground water. In the past decade, there has been a significant increase in attention directed to vapor intrusion issues and several new regulatory guidance documents have been developed by state and federal agencies and stakeholder groups for assessment and management of vapor intrusion risks (e.g., USEPA 2002; ITRC 2007). These guidance documents generally provide a framework for screening sites to assess whether vapor intrusion poses no significant risk or may require further evaluation, including assessment, remediation, or exposure controls.

Most regulatory guidance documents use conservative assumptions to account for uncertainties in the screening process (i.e., tending to err on the side of caution by overestimating rather than underestimating potential risks). This results in decisions to conduct detailed vapor intrusion investigation more frequently than may be necessary. It is expected that screening procedures will improve as we learn more about the processes affecting vapor intrusion. To date, most vapor intrusion screening procedures either assume that biodegradation does not occur or assume that biodegradation reduces concentrations of petroleum hydrocarbons by a consistent factor of 10 at all sites (e.g., NJDEP 2005). Both approaches are admittedly simple and are intended to be conservative for most petroleum release sites (i.e., tending to err on the side of caution).

Many petroleum hydrocarbons are metabolized by ubiquitous, naturally occurring soil microbes provided that sufficient oxygen is present in the subsurface. A growing body of work, including modeling studies (DeVaull 2007; Abreu and Johnson 2006), field investigations (Hers et al. 2000, Connor et al. 2006, McAlary et al. 2007, Lundegard et al. 2008, Pasteris et al. 2002), and literature reviews (Roggemans et al. 2001), indicates that under some conditions aerobic biodegradation in the unsaturated zone can significantly attenuate petroleum hydrocarbon vapors. The magnitude of bioattenuation of hydrocarbon vapors is related to the availability of oxygen, subsurface hydrocarbon concentration distribution, and hydrocarbon source concentration and depth. This mathematical modeling study is intended to provide insight to the significance of bioattenuation for a wide range of scenarios. However, this paper is limited by size constraints imposed by the journal,

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and a more complete set of simulations will be presented in a forthcoming API document (API 2009).

Approach

A three-dimensional mathematical model was used to simulate a range of scenarios to develop relationships between the site-specific conditions and the vapor intrusion attenuation factor (α), which is defined as the indoor air concentration of a chemical divided by its subsurface vapor source concentration at a specified depth. The development and use of the numerical model is described in detail in Abreu and Johnson (2005, 2006) and Abreu (2005). In brief, the numerical model simultaneously solves transient equations for the soil-gas pressure field (from which the advective flow field is computed), transient advective and diffusive transport and reaction of multiple chemicals (including oxygen) in the subsurface, flow and chemical transport through foundation cracks, and chemical mixing indoors. Inputs to the model include geometry descriptors (e.g., building footprint, foundation depth, crack locations and widths, source depth), chemical properties, kinetic parameters, the indoor-outdoor pressure differential, oxygen concentration at ground surface, and the chemical vapor concentrations at the vapor source. The model uses a finite-difference numerical method to solve the model partial differential equations and boundary conditions. The numerical accuracy of the code has been demonstrated through the comparison of model predictions with other analytical and numerical model results, and the code has been shown to be capable of fitting field-measured vertical soil-gas profiles.

For these simulations, the advective transport is a result of the pressure difference between the building and soil-gas pressures. In this study, the indoor air–soil-gas pressure coupling is simulated by assuming a constant 5 Pa building gauge pressure (underpressurization). In most single-family residences, the building pressure fluctuates in response to changes in wind and weather. In some cases, buildings are positively pressurized, which can contribute oxygen-rich air to the subsurface immediately below the building (Luo et al. 2006), in which case there would potentially be additional biodegradation immediately below the building than that shown by the simulation results.

The site-specific conditions and the physical settings considered were selected to cover a wide range of potential conditions that might be encountered at hydrocarbon release sites. The conceptual model for the simulations represents typical residential homes with an aerially extensive source directly beneath the building (i.e., lateral separation between the source and the building was not considered). Both basement and slab-on-grade construction scenarios were considered and foundation cracks were assumed to be present around the perimeter of the 10 × 10 m structure. Examples of the model domain for each foundation scenario are presented in Figures 1 and 2. The domain was symmetrical, so one quarter of the domain was simulated for computational efficiency.

Based on a review of the literature (DeVaull 2007; Abreu and Johnson 2006; Johnson et al. 1999), three key parameters were selected for this evaluation because they are considered to have the most significant influence on bioattenuation:

- Vapor source concentration
- Source depth
- Biodegradation rates.

A series of model simulations were performed over a range of values for these parameters to generate sufficient information to assess the expected relationship between the attenuation factor and the various combinations of the three key parameters. Homogeneous soil properties and steady-state conditions were simulated in this application of the model. Several other scenarios (e.g., consideration of nonhomogeneous soils) may also have a significant effect on bioattenuation, but are not included in this paper. Simulations have been performed to assess the importance of other parameters on bioattenuation and are presented in the companion document (API 2009).

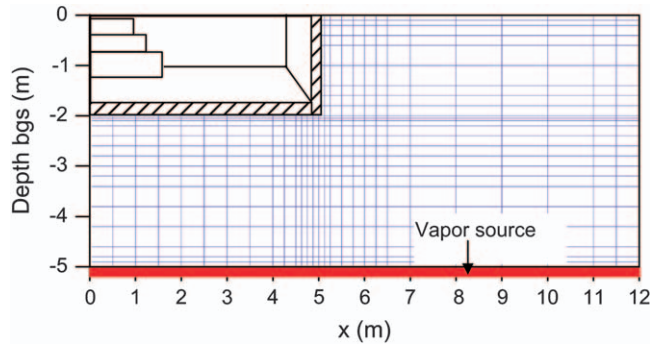

Figure 1. Vertical cross section of sample model domain showing the grid refinement for basement scenario.

Conditions Simulated

Unless otherwise specified in the text and figures, the model input parameters common to all simulations are listed in Table 1. These parameter values are the same as those used in Abreu and Johnson (2006) with some exceptions listed subsequently.

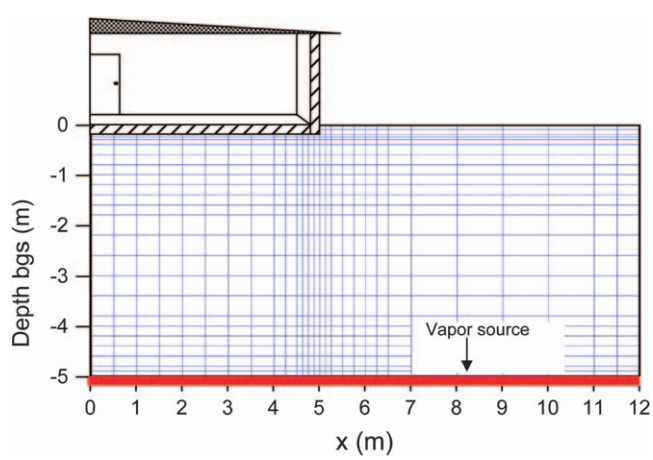

Figure 2. Vertical cross section of sample model domain showing the grid refinement for slab-on-grade scenario.

Table 1
Model Input Parameters (unless otherwise noted in the text or figures)

Building/foundation parameters
Length: 10 m
Width: 10 m
Depth in soil:
- 0.2 m (slab-on-grade type)
- 2.0 m (basement type)

Foundation thickness: 0. 15 m
Enclosed space volume: 244 m^3
Indoor air mixing height: 2.44 m
Air exchange rate: 0.5 h^{-1}
Crack width: 0.001 m
Total crack length: 39 m
Crack location:
- Perimeter

Building pressure: 5 Pa below atmospheric pressure

Soil Properties
Homogeneous sandy soil
Soil bulk density: 1660 kg/m^3
Moisture-filled porosity: 0.054 m^3water/m^3soil
Total soil porosity: 0.375 m^3voids/m^3soil
Soil gas permeability: 1E-11 m^2

Soil domain[1] dimensions in (x,y,z) directions
- 12 × 12 m × (1 to 12 m depths)

Hydrocarbon vapor source properties
Location: base of vadose zone
Source size: entire domain footprint

Hydrocarbon properties
Overall effective diffusion coefficient for transport in the porous media: 5.12E-3 m^2/h
Overall effective diffusion coefficient for transport in the crack: 3.17E-2 m^2/h
Atmospheric concentration: 0.0 mg/L

Oxygen properties

Overall effective diffusion coefficient for transport in porous media: 1.16E-2 m^2/h
Overall effective diffusion coefficient for transport in the crack: 7.2E-2 m^2/h
Ratio of oxygen to hydrocarbon consumed:
- 3 kg-oxygen/kg-hydrocarbon

Threshold concentration: 1% vol/vol
Atmospheric concentration: 21% vol/vol

Others
Dynamic viscosity of air: 0.0648 kg/m/h

[1]The symmetrical scenario domain includes only a quarter of the building footprint (5 × 5 m footprint area) in the simulation.

Vapor Source Concentration

The vapor source concentrations considered in this study ranged from 4 to 400,000 μg/L-vapor. This represents sources ranging from vapor concentrations in equilibrium with low-concentration dissolved phase plumes to those in equilibrium with nonaqueous phase liquid (NAPL) sources. There are typically hundreds of individual chemicals in a gasoline mixture. For simplicity, the source was simulated as a single component representing the sum of concentrations of all hydrocarbons in the mixture. The properties of benzene were used in the simulations because it is typically an important contributor to total risk and it has physical and chemical properties similar to other petroleum hydrocarbons typically considered in vapor intrusion assessments. Therefore, the range of source concentrations simulated will encompass a broad range of source concentrations encountered at hydrocarbon release sites.

Depth of Source below the Building Foundation

The depth of the source below the building foundation ranged from 1 to 10 m. This encompasses a range of shallow source depths that is of interest for many vapor intrusion investigations at petroleum hydrocarbon sites.

Biodegradation Rates

DeVaull (2007) compiled 84 data sets of reported biodegradation rates for aromatic hydrocarbons measured by multiple investigators. The data included biodegradation rates for individual chemicals benzene, toluene, ethylbenzene and xylene (BTEX), trimethylbenzene, and naphthalene, as well as rates for mixed BTEX chemicals (i.e., degradation rates calculated based on total BTEX concentrations rather than individual constituents). For aromatics, DeVaull reported average water-phase, first order degradation rates (λ) ranging from 0.4 to 2 h^{-1}, with a geometric mean of 0.79 h^{-1}. The values of λ considered in this work are as follows:

- 2 h^{-1}, the upper bound average rate reported by DeVaull.
- 0.79 h^{-1}, the geometric mean rate reported by DeVaull.
- 0.079 h^{-1}, which is a factor of about 5 times lower than the lower-bound average rate reported by DeVaull.

The no-biodegradation case ($\lambda = 0$) was also included in this work to indicate the difference in fate and transport between conditions favoring degradation and those where degradation is not expected (e.g., evaluation for nondegradable compounds).

Aliphatic hydrocarbons generally have higher aqueous degradation rates than aromatic hydrocarbons, based on available data reviewed to date. DeVaull (2007) reported average water-phase λ values for aliphatics ranging from 4 to 1,100 h^{-1}, with a geometric mean of 71 h^{-1}. Although aliphatics have faster degradation rates, they also have higher dimensionless Henry's law constants, so they partition less into the aqueous phase where degradation occurs. Additional

simulations conducted for a companion report (API 2009) show that the results of simulations assuming a single aromatic component source are very similar to these assuming multiple components (gasoline) source provided that the total petroleum hydrocarbon concentrations of both sources are the same. This indicates that the faster degradation rates for the aliphatics are counterbalanced by their lower solubility, so the net effect of degradation is similar for the aliphatics and aromatics.

The minimum oxygen concentration for biodegradation to occur is a user-defined input to the model. In this study, the oxygen threshold was assumed to be 1% vol/vol. This threshold was chosen based on previous published biodegradation studies. Field data reported in Roggemans et al. (2001) show decreasing oxygen concentration with depth until reaching a constant value of 2% vol/vol. Additionally, Bordon and Bedient (1986) report that aerobic biodegradation is observed when the oxygen concentration in ground water is greater than 100 μg/L-water (vapor equilibrium oxygen concentration of 0.24% vol/vol). In practice, it is difficult to accurately measure very low oxygen concentrations, and it is possible that the threshold is below these reported values. If microorganisms can degrade hydrocarbons in the presence of less than 1% oxygen, then these simulations would underestimate the influence of bioattenuation.

Results

The results show the simulated effect of biodegradation on the attenuation factor and subsurface distribution of hydrocarbons and oxygen for a wide variety of scenarios, including a range of source concentrations and depths that would reasonably be expected to be encountered in vapor intrusion assessments for petroleum hydrocarbon release sites. The three-dimensional model output illustrating the hydrocarbon and oxygen soil vapor concentrations distribution is presented as two-dimensional contour plots on vertical cross sections through the center of the building. In these plots, hydrocarbon concentrations are normalized by the source zone vapor concentration and oxygen concentrations are normalized by atmospheric oxygen concentration (i.e., 21% vol/vol).

The predicted vapor intrusion attenuation factors for the scenarios studied assuming a hydrocarbon source (with properties of pure benzene) are presented in Tables 2 and 3 for the basement and slab-on-grade scenarios, respectively.

Effect of Source Concentration

Soil-gas concentration distributions and attenuation factors for hydrocarbon undergoing biodegradation with a first-order biodegradation rate of $\lambda = 0.79\ h^{-1}$ and vapor source concentrations of 100, 1000, and 10,000 μg/L are shown in Figure 3 for basement scenarios and in Figure 4 for slab-on-grade scenarios, all with a source depth of 5 m below ground surface (bgs). This range of source concentrations was selected to represent dissolved ground water plumes at various concentrations. Figures 3 and 4 show that for vapor source concentration ranging from 100 to 10,000 μg/L at a depth of 5 m bgs on homogeneous subsurface, the model predicts aerobic conditions (i.e., oxygen concentrations greater than 1% v/v, or normalized oxygen concentrations greater than 0.05) beneath the entire building footprint; therefore, biodegradation occurs without oxygen limitations throughout the subsurface. The simulated α-values for the basement and slab-on-grade scenarios are about 5.5E-10 and 4.1E-14, respectively. These values are several orders of magnitude lower than the calculated attenuation factors for the no degradation scenarios (α-value = 1.1E-3 and 6.3E-4 for the basement and slab-on-grade scenarios, respectively). These calculations show 6 to 10 orders of magnitude attenuation attributable to biodegradation, which is much greater than the 0 or 1 order of magnitude assumed currently in regulatory guidance documents.

When comparing predicted α-values for the different building types in Figures 3 and 4, it should be noted that the source-foundation separation distance is different for these two scenarios (i.e., the source is 2 m closer to the basement than the slab-on grade). Also, the oxygen transport distance for the basement scenario is greater than that for the slab-on-grade scenario. Because of these factors, the hydrocarbon concentration beneath the foundation for the slab-on-grade scenario is less than that for the basement scenario. Consequently, the α-values for slab-on-grade scenarios in Figure 4 are about four orders of magnitude smaller than for basement scenarios in Figure 3. However, if the attenuation factors are compared based on the separation distance between the source and the floor of the building (see Tables 2 and 3), they are generally within an order of magnitude, which is relatively small compared to the range of attenuation factors simulated.

The scenarios presented in Figures 3 and 4 indicate that sufficient oxygen to support biodegradation is present throughout the region immediately beneath the building. However, scenarios with higher hydrocarbon source concentrations will result in increased oxygen utilization, and oxygen availability may limit the degree of biodegradation. An example of this is shown on Figure 5, which shows simulations for a source concentration of 100,000 μg/L (i.e., nearly saturated vapor source) at various depths below a basement. The simulations show depleted oxygen concentrations beneath the building for shallow, highly concentrated sources; however, oxygen is predicted to migrate beneath the building foundation for deeper sources, even when they are highly concentrated. This demonstrates the importance of understanding the oxygen distribution as part of a site assessment for vapor intrusion at petroleum hydrocarbon release sites.

Figures 3, 4, and 5 shows that when the source concentration is relatively high, the predicted oxygen concentrations beneath the building may be lower than those outside the building footprint because of oxygen consumption during microbial activity. The simulations here assume steady-state soil-gas flow into the building, and this is a simplification of real-world conditions. If a building has pressure that fluctuates between being higher and lower than the soil-gas pressure, then the flux of oxygen to the region beneath the building will increase to some degree,

Table 2
Attenuation Factor Results for Single Component Source Basement Scenarios

Vapor Source Concentration (mg/L)	Biodegradation Rate (h^{-1})	Vapor Source Depth below Foundation (m)						
		1	2	3	4	5	7	10
		Equivalent Vapor Source Depth below Ground Surface (m)						
		3	4	5	6	7	9	12
400	0	1.3E-03	1.3E-03	1.1E-03	1.0E-03	9.1E-04	7.4E-04	5.7E-04
	0.079	1.2E-03	1.0E-03	8.0E-04	6.2E-04	4.7E-04	2.4E-04	6.4E-05
	0.79	1.2E-03	1.0E-03	7.9E-04	6.2E-04	4.6E-04	2.3E-04	3.3E-05
	2	1.2E-03	1.0E-03	7.9E-04	6.2E-04	4.6E-04	2.3E-04	2.9E-05
200	0	–	–	1.1E-03	1.0E-03	9.1E-04	7.4E-04	5.6E-04
	0.079	–	–	5.2E-04	3.1E-04	1.7E-04	2.8E-05	5.0E-07
	0.79	–	–	5.0E-04	2.7E-04	1.1E-04	1.9E-06	8.6E-12
	2	–	–	5.0E-04	2.7E-04	1.0E-04	4.0E-07	4.4E-15
100	0	1.3E-03	1.3E-03	1.1E-03	1.0E-03	9.0E-04	7.4E-04	5.6E-04
	0.079	8.9E-04	4.6E-04	2.0E-04	6.6E-05	1.5E-05	5.2E-07	6.5E-09
	0.79	8.7E-04	3.6E-04	8.7E-05	5.5E-06	7.8E-08	3.6E-12	2.4E-17
	2	8.7E-04	3.5E-04	6.7E-05	1.5E-06	3.2E-09	1.4E-15	9.5E-23
40	0	1.3E-03	1.3E-03	1.1E-03	1.0E-03	9.0E-04	7.4E-04	5.6E-04
	0.079	5.6E-04	1.6E-04	3.2E-05	4.8E-06	8.3E-07	2.7E-08	1.8E-10
	0.79	3.5E-04	1.1E-05	9.0E-08	2.4E-10	2.7E-12	2.8E-16	3.6E-22
	2	3.1E-04	2.2E-06	2.6E-09	2.5E-13	7.5E-16	2.7E-21	1.5E-29
10	0	1.3E-03	1.3E-03	1.1E-03	1.0E-03	9.0E-04	7.4E-04	5.6E-04
	0.079	4.4E-04	8.0E-05	1.3E-05	2.1E-06	3.4E-07	8.3E-09	3.1E-11
	0.79	1.5E-05	6.8E-08	5.9E-10	2.3E-12	2.3E-14	1.2E-18	2.8E-25
	2	1.8E-06	5.8E-10	7.1E-13	2.1E-16	5.8E-19	8.2E-25	–
4	0	1.3E-03	1.3E-03	1.1E-03	1.0E-03	9.0E-04	7.4E-04	5.6E-04
	0.079	4.4E-04	8.0E-05	1.3E-05	2.1E-06	3.4E-07	8.3E-09	3.1E-11
	0.79	1.5E-05	5.8E-08	5.5E-10	1.5E-12	1.0E-14	5.0E-19	7.7E-26
	2	1.1E-06	2.7E-10	6.1E-13	6.8E-17	1.5E-19	1.2E-25	–
1	0	1.3E-03	1.3E-03	1.1E-03	1.0E-03	9.0E-04	–	–
	0.079	4.4E-04	8.0E-05	1.3E-05	2.1E-06	3.4E-07	–	–
	0.79	1.5E-05	5.8E-08	5.5E-10	1.5E-12	1.0E-14	–	–
	2	1.1E-06	2.7E-10	6.1E-13	6.8E-17	1.5E-19	–	–
0.4	0	1.3E-03	1.3E-03	1.1E-03	1.0E-03	9.0E-04	7.4E-04	5.6E-04
	0.079	4.4E-04	8.0E-05	1.3E-05	2.1E-06	3.4E-07	8.3E-09	3.1E-11
	0.79	1.5E-05	5.8E-08	5.5E-10	1.5E-12	1.0E-14	5.0E-19	7.7E-26
	2	1.1E-06	2.7E-10	6.1E-13	6.8E-17	1.5E-19	1.2E-25	–
0.04	0	1.3E-03	1.3E-03	1.1E-03	1.0E-03	9.0E-04	7.4E-04	–
	0.079	4.4E-04	8.0E-05	1.3E-05	2.1E-06	3.4E-07	8.3E-09	–
	0.79	1.5E-05	5.8E-08	5.5E-10	1.5E-12	1.0E-14	5.0E-19	–
	2	1.1E-06	2.7E-10	6.1E-13	6.8E-17	1.5E-19	1.2E-25	–
0.004	0	1.3E-03	1.3E-03	1.1E-03	1.0E-03	–	–	–
	0.079	4.4E-04	8.0E-05	1.3E-05	2.1E-06	–	–	–
	0.79	1.5E-05	5.8E-08	5.5E-10	1.5E-12	–	–	–
	2	1.1E-06	2.7E-10	6.1E-13	6.8E-17	–	–	–

and the oxygen deficient zone may not develop to the same extent. Potential differences in conditions beneath and beside a building should be considered when selecting locations and depths for sample collection.

Vapor intrusion attenuation factors (α) are presented in Figure 6 for a broader range of source concentrations and first-order biodegradation rates (0.079, 0.79, and 2 h^{-1}) for a basement scenario with source depth of 5 m bgs. For reference, the calculated attenuation factors assuming no biodegradation are also included in this figure. The dependence of α on concentration for a slab-on-grade building is similar to that shown in Figure 6, but there is more attenuation for the slab-on-grade scenario (see Tables 2 and 3). For very high vapor source concentrations, the α-value approaches the no-biodegradation case as a result of oxygen depletion beneath the foundation. For low vapor source concentration ranges (less than approximately 10,000 μg/L), α-values are relatively unaffected by changes in hydrocarbon vapor source concentration because there are oxygen-rich conditions throughout the subsurface (see Figures 3 and 4) and degradation is no longer limited by the oxygen availability. For source vapor concentrations greater than about 10,000 μg/L, oxygen transport limitations may inhibit the contribution of biodegradation,

Table 3
Attenuation Factor Results for Single Component Source Slab-on-Grade Scenarios

Vapor Source Concentration (mg/L)	Biodegradation Rate (h^{-1})	Vapor Source Depth below Foundation (m)						
		1	2	3	4	5	7	10
		Equivalent Vapor Source Depth below Ground Surface (m)						
		1	2	3	4	5	7	10
400	0	1.4E-03	1.1E-03	8.7E-04	7.3E-04	6.3E-04	4.8E-04	3.5E-04
	0.079	1.1E-03	6.3E-04	3.8E-04	2.3E-04	1.3E-04	3.4E-05	2.5E-06
	0.79	1.0E-03	5.2E-04	2.6E-04	1.1E-04	4.0E-05	1.9E-06	1.3E-09
	2	1.0E-03	5.1E-04	2.4E-04	8.9E-05	2.6E-05	3.6E-07	1.2E-11
100	0	1.4E-03	1.1E-03	8.7E-04	7.3E-04	6.3E-04	4.8E-04	3.5E-04
	0.079	8.2E-04	2.5E-04	7.0E-05	1.5E-05	3.2E-06	1.6E-07	2.4E-09
	0.79	4.1E-04	2.4E-05	9.0E-07	1.1E-08	1.5E-10	4.3E-14	6.8E-19
	2	3.1E-04	6.8E-06	6.0E-08	1.2E-10	1.9E-13	1.5E-18	4.5E-25
40	0	1.4E-03	1.1E-03	8.7E-04	7.3E-04	6.3E-04	4.8E-04	3.5E-04
	0.079	7.6E-04	1.4E-04	2.6E-05	4.1E-06	7.6E-07	2.3E-08	1.6E-10
	0.79	1.0E-04	1.1E-06	1.3E-08	3.7E-11	9.5E-13	3.9E-17	1.2E-22
	2	4.0E-05	3.9E-08	1.3E-10	8.9E-15	1.3E-16	4.1E-23	2.1E-30
10	0	1.4E-03	1.1E-03	8.7E-04	7.3E-04	6.3E-04	4.8E-04	3.5E-04
	0.079	7.5E-04	1.4E-04	2.3E-05	3.3E-06	5.5E-07	1.2E-08	4.7E-11
	0.79	6.2E-05	3.7E-07	3.0E-09	2.8E-12	4.9E-14	5.2E-19	2.8E-25
	2	8.4E-06	5.5E-09	8.9E-12	1.1E-16	1.1E-18	3.3E-26	–
4	0	1.4E-03	1.1E-03	8.7E-04	7.3E-04	6.3E-04	4.8E-04	3.5E-04
	0.079	7.5E-04	1.4E-04	2.3E-05	3.3E-06	5.5E-07	1.2E-08	4.7E-11
	0.79	6.2E-05	3.7E-07	3.0E-09	2.8E-12	4.1E-14	3.4E-19	1.1E-25
	2	8.4E-06	5.5E-09	8.6E-12	8.1E-17	5.9E-19	1.3E-26	–
1	0	1.4E-03	1.1E-03	8.7E-04	7.3E-04	6.3E-04	4.8E-04	–
	0.079	7.5E-04	1.4E-04	2.3E-05	3.3E-06	5.5E-07	1.2E-08	–
	0.79	6.2E-05	3.7E-07	3.0E-09	2.8E-12	4.1E-14	3.4E-19	–
	2	8.4E-06	5.5E-09	8.6E-12	8.1E-17	5.9E-19	1.2E-26	–
0.4	0	1.4E-03	1.1E-03	8.7E-04	7.3E-04	6.3E-04	4.8E-04	3.5E-04
	0.079	7.5E-04	1.4E-04	2.3E-05	3.3E-06	5.5E-07	1.2E-08	4.7E-11
	0.79	6.2E-05	3.7E-07	3.0E-09	2.8E-12	4.1E-14	3.4E-19	1.0E-25
	2	8.3E-06	5.5E-09	8.6E-12	8.1E-17	6.0E-19	1.2E-26	–
0.04	0	1.4E-03	1.1E-03	8.7E-04	7.3E-04	6.3E-04	4.8E-04	–
	0.079	7.5E-04	1.4E-04	2.3E-05	3.3E-06	5.5E-07	1.2E-08	–
	0.79	6.2E-05	3.7E-07	3.0E-09	2.8E-12	4.1E-14	3.5E-19	–
	2	8.4E-06	5.5E-09	8.6E-12	8.1E-17	5.9E-19	1.2E-26	–
0.004	0	1.4E-03	1.1E-03	8.7E-04	7.3E-04	–	–	–
	0.079	7.5E-04	1.4E-04	2.3E-05	3.3E-06	–	–	–
	0.79	6.2E-05	3.7E-07	3.0E-09	2.8E-12	–	–	–
	2	8.4E-06	5.5E-09	8.6E-12	8.1E-17	–	–	–

and above this level the attenuation factor is dependent on the hydrocarbon source concentration.

Effect of Building Foundation Type

Figure 7 shows simulations for a 100,000 μg/L source concentration at a depth of 7 m for both slab-on-grade and basement scenarios. When considering a basement scenario, the attenuation factor is higher because (1) the foundation is farther from the ground surface (i.e., oxygen diffusive path length is longer) and (2) to some extent the foundation is closer to the source (i.e., hydrocarbon diffusive path length is shorter). For the scenarios considered in this figure, these factors lead to a reduction in the calculated attenuation factor by more than six orders of magnitude.

Effect of Source Depth

Figure 8 shows the variation of the basement scenario α-value as a function of source depth for the range of biodegradation rates considered in this study and a vapor source concentration of 10,000 μg/L. For an average degradation rate ($\lambda = 0.79\ h^{-1}$), the simulations show about 100-fold additional attenuation compared to the no-biodegradation case, with a source only 1 m below the foundation. At a depth of 2 m, the attenuation factor is about 1E-7, at which point the indoor air concentration attributable to vapor intrusion would be less than 0.001 μg/L, which is near or below risk-based target concentrations or background levels for most hydrocarbons. For conditions specified in Table 1, the attenuation factors are insensitive to vapor source concentrations below 10,000 μg/L (as shown

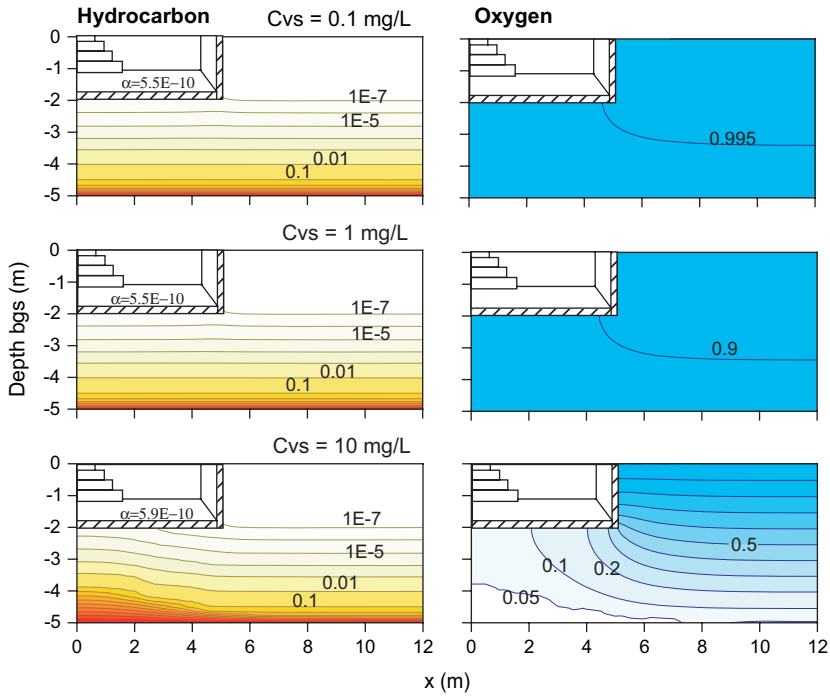

Figure 3. Effect of low vapor source concentration (Cvs) on soil-gas concentration distribution and vapor intrusion attenuation factors (α) for basement foundation scenarios and hydrocarbon biodegradation rate $\lambda = 0.79\ h^{-1}$. Hydrocarbon and oxygen concentrations are normalized by source and atmospheric concentrations, respectively.

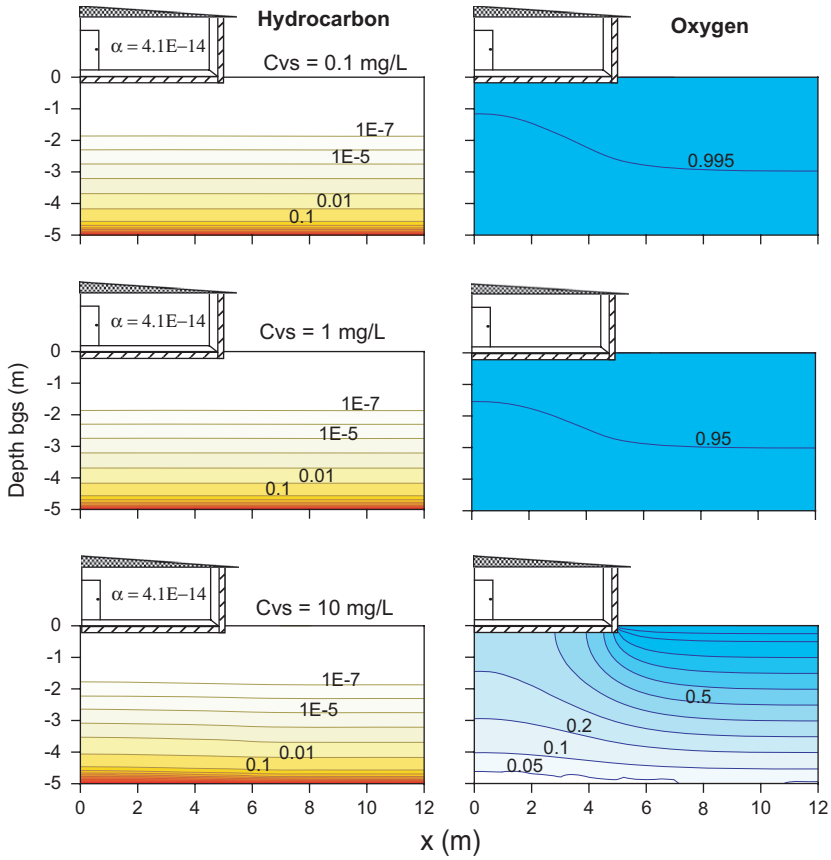

Figure 4. Effect of low vapor source concentration (Cvs) on soil-gas concentration distribution and vapor intrusion attenuation factors (α) for slab-on-grade foundation scenarios and hydrocarbon biodegradation rate $\lambda = 0.79\ h^{-1}$. Hydrocarbon and oxygen concentrations are normalized by source and atmospheric concentrations, respectively.

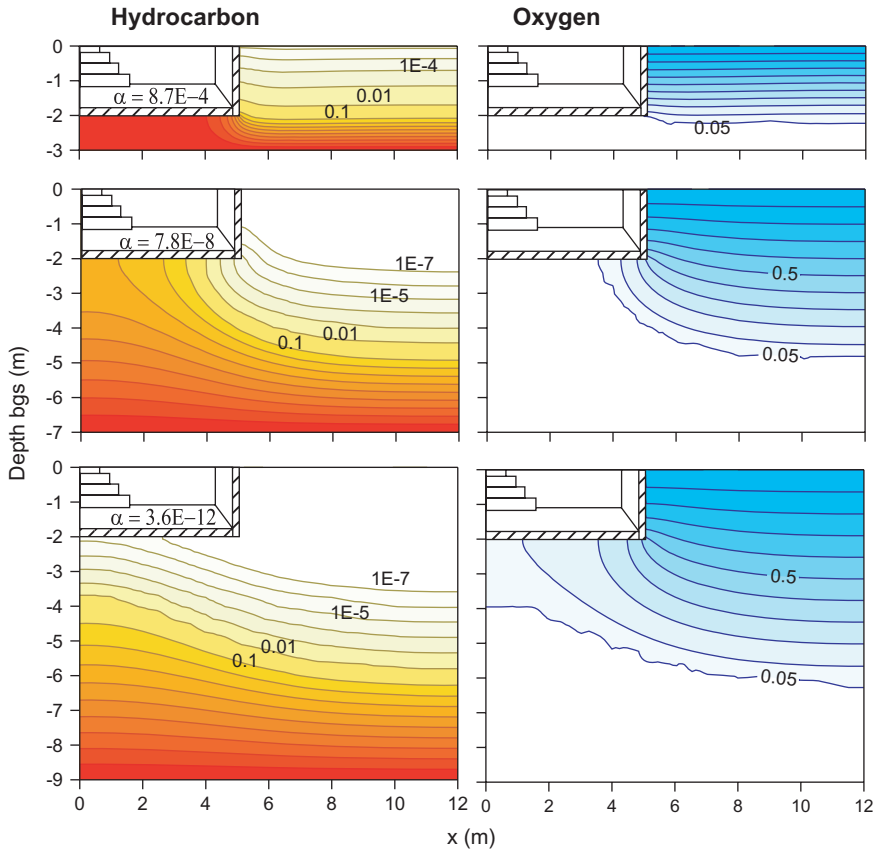

Figure 5. Effect of source depth on the soil-gas concentration distribution and vapor intrusion attenuation factors (α) for basement scenarios with a high vapor source concentration of 100,000 μg/L and biodegradation rate λ = 0.79 h^{-1}. Hydrocarbon and oxygen concentrations are normalized by source and atmospheric concentrations, respectively.

on Figure 6); therefore, the results presented in Figure 8 are applicable to scenarios with vapor source concentrations ≤ 10,000 μg/L. Note that these figures show the α-value as a function of depth below the foundation, not depth below ground surface, so a plot for the slab-on-grade scenario is very similar (see Tables 2 and 3). The no-degradation case is also plotted to highlight the effect of biodegradation on the α-value.

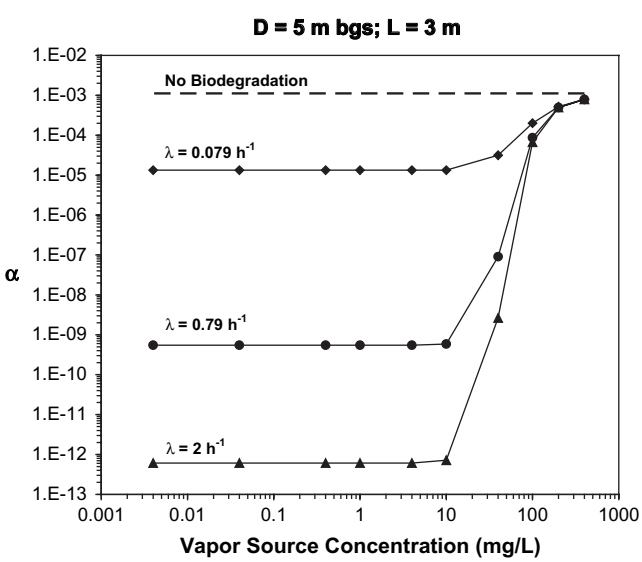

Figure 6. Influence of soil vapor source concentration and first-order biodegradation rates (λ) on vapor intrusion attenuation factors (α, indoor air VOC concentration divided by source vapor concentration) for basement scenarios, homogeneous sand soil and source depth (D) of 5 m bgs (source-foundation separation L = 3 m).

Pure Compounds vs. Hydrocarbon Mixtures

Most petroleum hydrocarbons are a mixture of hundreds of compounds, all of which contribute to the demand for oxygen. A series of simulations performed to compare the scenario of a single component to that of a typical gasoline are presented in the companion document (API 2009) and example results are presented here. One representative simulation is shown in Figure 9, which shows a source concentration of 40,000 μg/L and a source depth of 4 m below a slab-on-grade foundation. The vertical concentration profile of the pure benzene vapor scenario is similar to those for aromatics (benzene, toluene, ethylbenzene, and xylenes), and the oxygen distribution is virtually identical for the two scenarios.

These findings indicate that the results from the single-component source simulations may be used to assess vapor intrusion for other compounds with similar degradation rates in petroleum mixtures at hydrocarbon release sites. For sites with hydrocarbon mixtures, the sum of all hydrocarbon concentrations in the mixture, or the total petroleum hydrocarbon (TPH) concentration (including methane), should be used to select an applicable attenuation factor from Tables 2 and 3.

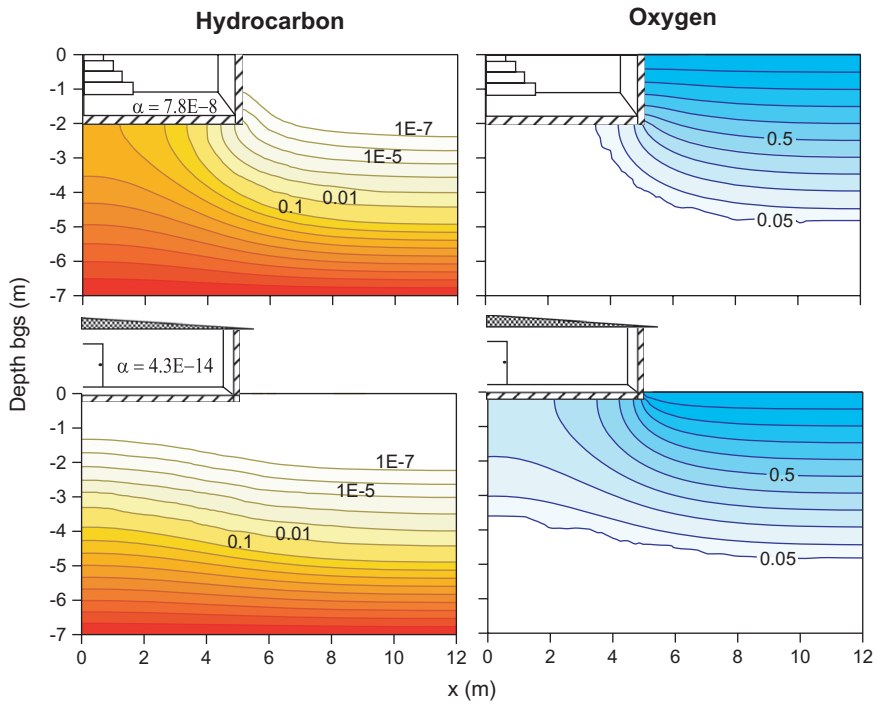

Figure 7. Effect of building type on soil-gas concentration distribution for high vapor source concentration (100,000 µg/L) and biodegradation rate $\lambda = 0.79\ h^{-1}$. Hydrocarbon and oxygen concentrations are normalized by source and atmospheric concentrations, respectively.

Discussion

Biodegradation contributes to the attenuation factor to varying degrees, depending very strongly on the site conditions. Shallow, high concentration sources may have relatively little attenuation via biodegradation (similar to assumptions in current regulatory screening guidance for vapor intrusion), but deeper sources and lower-concentration sources can have many orders of magnitude more attenuation.

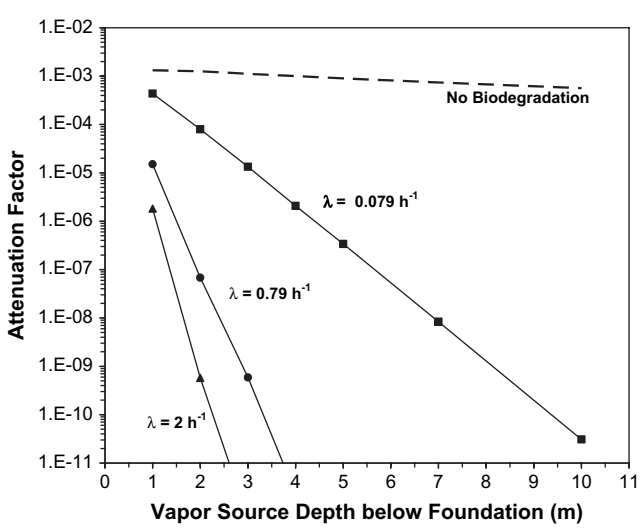

Figure 8. Attenuation factors as a function of source depth below foundation and first-order biodegradation rate for basement scenarios with perimeter cracks and 10,000 µg/L vapor source concentration. This graph is applicable to all sources with vapor concentration ≤ 10,000 µg/L.

The model simulations in this study help elucidate the expected dependence of the attenuation factor on the source concentration, depth, and biodegradation rate and can be used to estimate the attenuation factor for compounds with degradation rates similar to those used in these simulations and locations where site conditions are similar to those listed in Table 1.

A conceptual model of the fate and transport of chemicals should form the foundation for any vapor intrusion assessment. Conceptual models are developed using available site-specific information, theoretical knowledge of physical chemical and biological processes and mechanisms affecting fate and transport, and experience gained from other sites with similar chemicals and geologic conditions. The simulations presented in this paper can be used to refine a site conceptual model for petroleum release sites by incorporating the influence of biodegradation on vapor intrusion and attenuation.

The findings of this study also may help in the design of an investigation program. Where biodegradation occurs, there are dramatic decreases in hydrocarbon concentrations over very narrow ranges of depth; therefore, vertical profiles of hydrocarbon vapor and oxygen concentrations can provide valuable information regarding the biodegradation process. Comparisons of measured oxygen and hydrocarbon profiles to the model results can be used to assess whether the simulations are representative of site conditions, and support the use of α-values that incorporate biodegradation.

The attenuation factors presented in this study can be used to estimate site-specific soil vapor screening levels for biodegradable compounds, providing there is sufficient

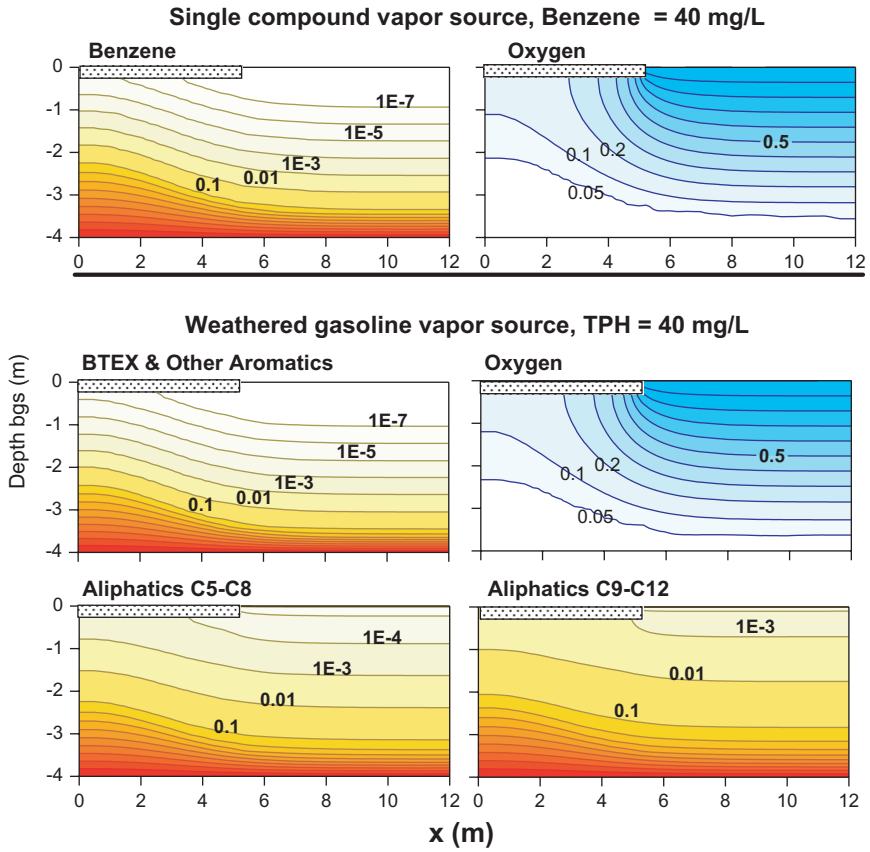

Figure 9. Effect of multicomponent source on soil-gas distribution and oxygen consumption in the subsurface for dissolved ground water source scenario. For comparison purposes two source types are illustrated: single- and multicomponent sources. Each is located underneath a slab-on-grade scenario at 4 m bgs; and each source has 40,000 µg/L total vapor concentration.

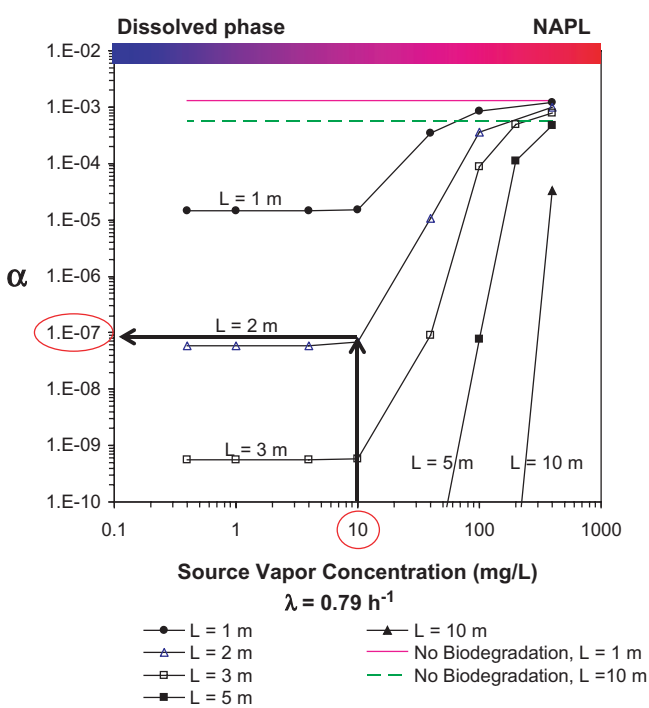

Figure 10. Use of the chart to select a semi-site-specific attenuation factor. For a source concentration of 10,000 µg/L and a source-building separation of 2 m, the attenuation factor would be about 1E-7.

site-specific information available to characterize the source depth, source concentration, and presence of oxygenated conditions, and verify that the geologic and building conditions are similar to those simulated herein. This is analogous to selecting a semi site-specific attenuation factor for nondegradable compounds presented in the draft OSWER guidance on vapor intrusion (USEPA 2002).

At most sites, it should be relatively easy to estimate or measure the source concentrations and depth, two of the key parameters studied here. Biodegradation rates can also be derived from matching a mathematical model to vertical profiles of hydrocarbon and oxygen concentrations (Johnson et al. 1999; Ettinger and McAlary 2005). Alternatively, a range of literature values for biodegradation rate (e.g., DeVaull 2007) may be used to assess the potential significance of biodegradation on the vapor intrusion pathway (for example, when conducting an uncertainty analysis), providing that the model used appropriately couples transport of both oxygen and hydrocarbons.

In cases of low-concentration deep sources with oxygen-rich conditions, biodegradation may provide several orders of magnitude more attenuation than necessary to yield a condition of no significant risk (i.e., ample factor of safety to account for variation between the simulated and site-specific attenuation factors), in which case the model simulations may help support decisions regarding which sites, or portions of sites, are low priority for vapor intrusion assessment

or can be screened out altogether. In cases of high-concentration shallow sources with oxygen-depleted conditions, it may be apparent that the attenuation is unlikely to be sufficient, and the model simulations may support a management decision for additional assessment or preemptive mitigation. For intermediate conditions at sites where the conditions are similar to the model assumptions and inputs used in this paper, the model simulations presented herein may help guide the selection of site-specific attenuation factor or help select the key data required to verify the conceptual model, and gain a better understanding of the potential for vapor intrusion risks.

It is instructive to compare the vertical profiles of hydrocarbon and oxygen concentrations beneath and beside the buildings in Figures 3 and 4. A practical consideration in vapor intrusion assessments is understanding whether soil vapor samples collected beside a building (a.k.a. near-slab samples [NJDEP 2005]) are representative of the gas concentrations beneath the building. The simulations show that the vertical soil-gas concentration profiles outside the building footprint and beneath the building are not necessarily similar. Calculated soil-gas concentrations beneath and beside the building are predicted to be more similar to one another with increasing depth. Further research would help verify these simulations and help practitioners in selecting appropriate depths for near-slab soil-gas samples.

Example Application

This section provides a practical example to demonstrate how the results of this study could be applied for screening a single-family residential building with moderate to low hydrocarbon concentrations to assess the potential for vapor intrusion. The example considers a residential structure with a 2-m-deep basement located above ground water containing dissolved hydrocarbons and TPH vapor concentrations of 10,000 μg/L and vapor concentrations of

Step	Activities	Example Application
1. Conceptualize	Collect data to verify that site conditions reasonably match model scenarios. Use theory and experience to assess whether model is relevant and proceed only if it is, or with a reasonable degree of caution and data collection to compensate for differences between model scenarios and site conditions.	The example scenario was developed to be consistent with model formulation, but in general this assumption should not take this for granted.
2. Identify site-specific inputs	Collect data to establish vapor source concentrations, depth, geologic conditions, and building type.	The site-specific inputs considered in this evaluation are: Source concentration: 10,000 μg/L (concentrations of individual constituents are listed in Table 4) Building construction: basement Depth to ground water: 4 m Degradation rate constant: 0.79 h^1 assumed
3. Look up attenuation factor	Refer to Table 2 or 3, or Figure 8 and select the appropriate attenuation factor. The TPH source vapor concentration should be used in this evaluation (not the concentration of an individual constituent, unless it is a single component source).	Figure 10 illustrates the use of the vapor intrusion attenuation factor summary figure in estimating the α-value for site conditions. For this example, an α-value of about 1E-7 is supported.
4. Calculate indoor air concentrations for individual constituents	Multiply the source vapor concentrations by the site-specific attenuation factor identified in the previous step.	Results are presented in Table 4.
5. Assess potential risks	Compare the predicted indoor air concentrations to target risk-based indoor air concentrations or calculate risks using the predicted indoor air concentrations, and consider uncertainty. If risks are unacceptable or marginal, consider additional data collection (vertical soil-gas profiles, subslab or indoor air sampling) or preemptive mitigation.	In this example, risk-based concentrations from the USEPA vapor intrusion guidance (assuming 1E-06 target risk level for carcinogens) are used. The predicted indoor air concentrations for the individual constituents are below risk-based target levels.
6. Ground-truth with data	Using a conceptualization of the site conditions informed by expectations from these model results, collect necessary and sufficient data to verify site conditions.	Collect necessary and sufficient number of soil-gas or indoor air samples and consider vertical profiles of soil vapor concentrations for hydrocarbons, and fixed gases (O_2, CO_2, CH_4) to support assessment of hydrocarbon fate and transport.

Table 4
Example Calculations

Compound	Source Vapor Concentration (μg/L)	Predicted IA (μg/m^3)	Target IA (μg/m^3)
Benzene	10	0.001	0.31
Toluene	100	0.01	400
Ethylbenzene	30	0.003	2.2
Xylene	150	0.015	7,000
Naphthalene	20	0.002	3

individual constituents as listed in Table 4. The vadose zone is composed of homogeneous sandy soil and the depth to ground water is 4 m (i.e., source-building separation of 2 m). The following steps would be appropriate for assessing the potential for vapor intrusion:

For the conditions described in this example, the predicted indoor air concentrations are more than two orders of magnitude lower than the target indoor air concentrations, which indicates the risk via vapor intrusion would most likely be negligible, providing there are no barriers to entry for atmospheric oxygen to the subsurface. Verification with appropriate data collection is nevertheless an important consideration, but this screening level assessment would indicate that risks are unlikely to be significant, and it may be appropriate to customize the scope of data collection accordingly.

Although typical sites often have additional complexities (geologic heterogeneity, nonsteady flow conditions, different building geometries, complex contaminant source distribution, and so on), the model simulations may help identify scenarios where attenuation of degradable compounds is likely to be much more significant than current regulatory screening levels. At a minimum, the conceptualization of the site conditions and selection of an approach for investigation and remediation should benefit from consideration of the theoretical analysis provided by the mathematical model.

Conclusions

Based on the results of the modeling assessment summarized here, the following conclusions are offered:

- Provided that soils are oxygenated beneath a building, aerobic biodegradation will reduce the concentrations of aerobically degradable petroleum hydrocarbons and the potential risks from vapor intrusion to indoor air up to several orders of magnitude compared to nondegrading compounds. The magnitude of the reduction will depend on site-specific conditions, especially the source concentrations, source depth, and oxygen distribution and degradation rates, which should be considered in the development of a conceptual site model for each site. The simulations presented here should help formulate conceptual models for a variety of sites, and help with screening, prioritization, and selection of data collection strategies for vapor intrusion assessments at petroleum release sites.
- Oxygen supply and degradation rates are likely to be sufficient to mitigate potential risks from vapor intrusion for low vapor concentration sources with a minimal source–building separation. Sites with higher source concentrations may also be mitigated by biodegradation to some degree depending on site-specific conditions, particularly the source–building separation distance. There appears to be a theoretical source–building separation distance beyond which degradation will mitigate vapor intrusion risks regardless of how high the source concentration is, although this may vary with site-specific conditions. Shallow and higher concentration hydrocarbon sources are more likely to pose a potential risk due to vapor intrusion, especially where the oxygen demand is greater than the oxygen supply and anaerobic conditions occur beneath the building.
- Simulations presented in this paper represent a wide range of source concentrations and depth that may be encountered where vapor intrusion assessments are required at sites with petroleum hydrocarbon releases. The results presented in Tables 2 and 3 provide a theoretical basis for estimating site-specific attenuation factors. Providing site conditions match the scenarios simulated, these tables may help identify scenarios where current regulatory approaches are overly conservative using generic attenuation factors derived from data for nondegrading compounds or adjusting screening levels by a factor of 10 to account for biodegradation regardless of the site-specific conditions. Many sites have complexities (e.g., geologic heterogeneity) that are not included in these simplified simulations, so expectations from these simulations should be verified with some degree of site-specific data collection, proportional to the complexity and potential risks.

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