

# Hydrocarbon and Oxygen Transport in the Vicinity of a Building Overlying a NAPL Source Zone

Hong Luo, Paul Dahlen, Paul C. Johnson

Ira A. Fulton Schools of Engineering, School of Sustainable Engineering and the Built Environment, Arizona State Univ., POB 875306, Tempe, AZ 85287, 480-965-0055, 480-965-0557 (fax), [hong.luo@asu.edu](mailto:hong.luo@asu.edu); [paul.dahlen@asu.edu](mailto:paul.dahlen@asu.edu); [paul.c.johnson@asu.edu](mailto:paul.c.johnson@asu.edu) .

## Abstract

Within the context of developing guidelines for assessing petroleum-impacted sites for vapor intrusion pathway significance, the concepts of “exclusion criteria” and an “exclusion distance” are often introduced. The concept is that one uses site criteria (i.e. depth to source, soil setting, etc.) to exclude the need to conduct further pathway assessment, rather than sample chemical concentrations in soil gas or indoor air. This is appealing, particularly for petroleum-impacted sites, because modeling results and field studies suggest that there will be some settings where vapor transport is significantly attenuated by aerobic biodegradation. Three-dimensional modeling results have been used by some to propose depth and source concentration combinations that can be assumed to have *de minimis* risks. The potential weakness of this approach is that base-case simplified geologies are often used and it is assumed that the base-case inputs are inherently conservative. Case studies are needed to validate modeling results and that is the intent of this work. Soil gas concentrations were monitored in the vicinity of a one-story 2100 ft<sup>2</sup> building having a basement extending 5 ft below ground surface (BGS). Non aqueous-phase liquid (NAPL) impacted soils are first encountered at about 9.2 m (30 ft) BGS to 10.6 m (35 ft) BGS. The data show relatively uniform and elevated (60 – 160 mg/L) hydrocarbon vapor concentrations and depleted O<sub>2</sub> beneath and around the building foundation, which is not anticipated by simplistic scenario modeling results. Detailed soil respiration and air permeability test results suggest two possible reasons for the observed behavior, a) significant background O<sub>2</sub> uptake in surface soils or b) physically limited O<sub>2</sub> transport from the atmosphere. Soil O<sub>2</sub> uptake rates at four locations at the depth of 0-4.0 ft BGS around building foundation ranged from 2 - 25 mg-O<sub>2</sub>/kg-soil/day. There also was a silt/clay zone between 2 - 5 ft BGS and 7-8 ft BGS with an air permeability of less than 10<sup>-14</sup> m<sup>2</sup>. The results from this study showed that simplistic generic scenario modeling results should be used with caution, and that factors reducing O<sub>2</sub> transport from the atmosphere to the subsurface can significantly affect the vapor distribution at petroleum hydrocarbon sites.

## INTRODUCTION

Within the context of developing guidelines for assessing petroleum-impacted sites for vapor intrusion pathway significance, the concepts of “exclusion criteria” and an “exclusion distance” are often discussed. In this approach, one uses criteria (i.e. source depth, lateral distance between building and source) to exclude the need to conduct further pathway assessment, rather than sample chemical concentrations in soil gas or

indoor air. For example, ATSM (2008)<sup>1</sup> uses “30 ft in any linear direction” as the “critical distance” for dissolved petroleum hydrocarbon plume cases in Tier 1 site exclusion/site screening. Several states have also adopted exclusion distances in their vapor intrusion guidance<sup>2</sup>. Guidance for New Hampshire, New Jersey, Connecticut and Massachusetts include a 30-ft exclusion distance for biodegradable vapor sources and other guidance includes exclusion distances ranging from 40 ft to 100 ft. Some authors have also discussed this approach being applied to the site screening process, after considering site experiences and modeling results<sup>3,4</sup>.

This is an appealing concept, particularly for petroleum-impacted sites, because modeling results and field studies suggest that there will be some settings where vapor transport is significantly attenuated by aerobic biodegradation<sup>4,5,6,7</sup>. There are questions, however, concerning the implementation of this approach. For example, which data and modeling results should be considered in establishing the criteria, and how robust are the results? To date, there has been a reliance on “generic” numerical simulation results from simplified scenarios, and arguments that the model inputs for those simplified scenarios are inherently conservative. To increase the confidence in the use of the exclusion criteria approach, case studies are needed to test the robustness of the exclusion criteria and to assess whether or not simplified scenario simulation is inherently conservative and leads to reasonable results. That is the motivation for the study described below.

## **SITE DESCRIPTION AND EXPERIMENTAL METHODS**

The study site is a single-story, 16.8 m x 11.6 m (55 ft x 38 ft), concrete and masonry office building with basement. A central air conditioning system serves the building and the heating and blower units are in the basement. The concrete basement foundation extends 1.5 m (5 ft) below ground surface (BGS) and is about 12 cm thick. While some cracks in the foundation are evident, no full-thickness foundation cracks were visually apparent. There is a chiller system sump in the northeast corner of the basement.

The ground surface is predominantly native soils with grass except on the western side of the building where there is an asphalt/concrete parking lot. Based on exterior soil cores, the shallow (<3.0 m or <10 ft) geology around the building transitions from an organic rich silt root zone to a dense silt/clay and then to coarse sands, gravels, and cobbles. Soils deeper than 10 ft BGS are mainly fine-medium sand and gravels. Beneath the building, soil cores were not possible and geologic information is based solely on shallow materials visible beneath the slab and the cuttings from boreholes. Those materials were fine to medium sands, gravels, and cobbles.

The building overlies petroleum hydrocarbon-impacted soils that extend laterally well beyond the foundation footprint. Due to local groundwater level fluctuations over time and the large volume of petroleum hydrocarbons released in this area, non-aqueous phase liquid (NAPL) light-end petroleum distillate (e.g. gasoline-range petroleum hydrocarbons) is possibly smeared from about 9.2 m to 13.7 m (30 ft to 45 ft) BGS. Hydrocarbon-impacted soils were first encountered during drilling at depths at about 9.2 m (30 ft) BGS to 10.6 m (35 ft) BGS.

A soil gas monitoring network which included permanent depth-discrete multi-level sampling points was designed and installed, with sampling locations shown in Figure 1. Beneath the foundation, sampling points were installed at sub-slab or 1.5 m (5 ft) BGS and 3 m (10 ft) BGS at all locations, and exterior sampling points were installed to 0.7, 1.5, 2.3, 3.0, 3.7, 4.5, 6.1, 7.6, and 9.1 m (2.5, 5.0, 7.5, 10, 12.5, 15, 20, 25, 30 ft) BGS depths. Snapshots of the soil gas concentrations were conducted using all sampling points on site; soil respiration test and soil air permeability test were conducted in the lab.

## RESULTS AND DISCUSSION

Using data available prior to the detailed study around the building, a “generic” simulation using the modified three-dimensional Abreu and Johnson model (2005v)<sup>8</sup> was conducted. The inputs for the generic simulation included site-specific source depth and source vapor concentration, the actual building size and air mixing volume, and soil properties comparable to those considered conservative by some proposing exclusion distance based on non-site-specific modeling<sup>7</sup>. These inputs are shown in Table 1. The resulting soil gas concentration (TPH and O<sub>2</sub>) distributions at a cross-section through the center of the building are shown in Figure 2. These show that, in the case of a 160 mg/L vapor source located at about 30 ft (9.2 m) BGS, the predicted TPH concentrations at the sub-slab depth are non-uniform and range from less than 0.001 mg/L at the building foundation edges to about 20 mg/L beneath the center of the building. O<sub>2</sub> concentrations of up to 4% v/v are present immediately beneath the building foundation. The attenuation factor (indoor air/source concentration)  $\alpha=1.2 \times 10^{-6}$  and these results are similar to other modeling studies that are publically available and some field study results<sup>5,7,9</sup>.

The actual site data are shown in Figures 3 and 4. The former presents plan-view contour plots of soil gas TPH and O<sub>2</sub> concentrations at the sub-slab depth (5 ft BGS), while the latter presents contour plots of soil gas TPH and O<sub>2</sub> concentrations at two vertical cross sections defined in Figure 1. In contrast to the generic modeling results, the measured soil gas TPH concentrations are relatively uniform, ranging from 60 – 90 mg/L beneath the foundation and extending out at those levels at the sub-slab depth around building foundation. O<sub>2</sub> is depleted beneath and around the building foundation.

In comparing the measured soil gas distribution and the results of generic modeling for this site, it is clear that the generic modeling did not anticipate the oxygen depletion and relatively uniform and high TPH concentrations at the sub-slab depth. Thus, it is clear that at least in this case, the use of generic modeling results and exclusion distance criteria from generic modeling would not be appropriate.

To better understand the site-specific factors that might be most responsible for the differences between the generic modeling results and actual measured soil gas concentration distributions, oxygen uptake (soil respiration) and soil air permeability were measured in the lab using soil cores and effective diffusion coefficients were measured in situ.

Oxygen uptake tests were conducted using cores collected from 0.5 ft to 10 ft BGS at four locations around the building, and the results are shown in Figure 5. This figure indicates that O<sub>2</sub> uptake rates ranged from 2 - 25 mg-O<sub>2</sub>/kg-soil/day for shallow soil (0-4

ft BGS), while those for the deeper soils (4 – 10 ft BGS) are typically less than 1 mg-O<sub>2</sub>/kg-soil/day. The elevated O<sub>2</sub> uptake associated with the shallow soils would result in a reduction of oxygen available for biodegradation around and beneath the building, although the significance of those rates would have to be examined through simulation.

Soil air permeability test results are shown in Figure 6. There exist two lower permeability zones at about 2-5 ft BGS and 7-8 ft BGS around the building having air permeabilities of less than 10<sup>-14</sup> m<sup>2</sup>, which is about 100 to 1000 times less permeable than materials in other intervals. It is possible that the low permeability layers might also limit the downward oxygen transport from the atmosphere, although previous modeling results suggest that it is the diffusion coefficient properties of the layers and not the permeability that most influences gas distributions.

Model simulations were conducted using measured site-specific values as inputs to see if they would be significantly different than the generic modeling results. A picture of the model domain is shown in Figure 7. Notable changes from the generic inputs include: (1) a concrete parking lot at the west side the building simulated as a no-flux boundary; (2) measured soil gas permeabilities and measured chemical effective diffusion coefficients. The simulated soil gas distributions using these site-specific inputs are shown in Figures 8a and 8b. In comparing Figures 8 and 4, it is clear that the model results generated using more site-specific inputs better resemble the measured soil gas distributions than those for the generic inputs. The attenuation factor for the site-specific case is about 100X larger (i.e., 100X higher indoor modeled concentrations) than for the generic case.

Considering only the building-source separation distance of 30 ft to 35 ft BGS, as is done in the exclusion criteria approach, this site likely would have been excluded using the approaches suggested by some that argue that the generic modeling results are conservative. That clearly is not the case for this site as the measured data show little attenuation between the source and sub-slab region and foundation, and the attenuation factors differ by 100X between the generic and site-specific model runs (attenuation factors were not measured at the site). Furthermore, there is nothing atypical about this site, in terms of what would be known about it from a basic site investigation. Thus, the results of this study show that generic modeling-based exclusion criteria may fail in some circumstances, and in cases where it is not clear from basic site data that the generic modeling results would not be appropriate.

This study illustrates that it is critical to develop a better understanding of the sensitivity of soil gas distributions to site conditions and the sensitivity of model output to changes in inputs before developing vapor intrusion pathway site exclusion criteria.

## **CONCLUSION**

In this work, a site with conditions that would be excluded from vapor pathway assessment using exclusion criteria developed from generic modeling results was studied. In contrast to generic modeling results that anticipate sub-slab oxygen and significant contaminant attenuation between the source and foundation, the measured concentrations showed depleted sub-slab oxygen, little attenuation, and relatively little spatial variability in contaminant concentrations at the sub-slab depth. Soil oxygen uptake and air

permeability tests conducted on soil cores revealed elevated oxygen uptake in shallow soils and two lower permeability zones, both of which would reduce the oxygen transport to beneath the building (and needed for aerobic biodegradation). Modeling results incorporating site-specific conditions more closely resembled the measured data and the modeled attenuation factors differed by 100X between the generic and site-specific modeling. The results from this study showed that simplistic generic scenario modeling results should be used with caution, and that it is critical to develop a better understanding of the sensitivity of soil gas distributions to site conditions and the sensitivity of model output to changes in inputs and to verify the results with test sites before developing vapor intrusion pathway site exclusion criteria from model output.

## **ACKNOWLEDGEMENT**

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Table. 1 Inputs used to generate Figure 6.2 and Figure 6.8.

<b>Building/foundation parameters<sup>(1)</sup></b>	<b>Soil Properties for site-specific simulation</b>
Length: 16.8 m	Soil Layer 1: 0 to 1.5 m BGS
Width: 11.6 m	soil permeability to soil gas flow ( $K_g$ ) = $10^{-15}$ m <sup>2</sup>
Depth in soil: 1.5 m (basement type)	Soil bulk density ( $\rho_b$ ): 1500 kg/m <sup>3</sup>
Foundation thickness ( $d_{ck}$ ): 0.15 m	Mass fraction of organic carbon in the soil ( $f_{oc}$ ): 0.02 kg-oc/kg-soil
Enclosed space volume ( $V_b$ ): 582.5 m <sup>3</sup>	Moisture-filled porosity ( $\phi_w$ ): 0.268 m <sup>3</sup> water/m <sup>3</sup> soil
Air exchange rate ( $A_{ex}$ ): 0.5 h <sup>-1</sup>	Total soil porosity ( $\phi_T$ ): 0.45 m <sup>3</sup> voids/m <sup>3</sup> soil
Crack width ( $w_{ck}$ ): 0.01 m	Average effective diffusion coefficient: 0.0015 cm <sup>2</sup> /s
Total crack length: 28 m	Soil Layer 2: 1.5 m to 7.7 m BGS
Crack location: perimeter	soil permeability to soil gas flow ( $K_g$ ) = $10^{-11}$ m <sup>2</sup>
Indoor-outdoor pressure difference: 5 Pa	Soil bulk density ( $\rho_b$ ): 1700 kg/m <sup>3</sup>
<b>Chemical-specific properties:</b>	Mass fraction of organic carbon in the soil ( $f_{oc}$ ): 0.001 kg-oc/kg-soil
Source vapor concentration ( $C_{ng}^{source}$ ): 160 mg/L <sub>vapor</sub>	Moisture-filled porosity ( $\phi_w$ ): 0.12 m <sup>3</sup> water/m <sup>3</sup> soil
Molecular diffusion coefficient in air ( $D_{\eta}^a$ ):	Total soil porosity : 0.35 m <sup>3</sup> voids/m <sup>3</sup> soil
3.17E-2 m <sup>2</sup> /h	Average effective diffusion coefficient: 0.0054 cm <sup>2</sup> /s
Molecular diffusion coefficient in water ( $D_{\eta}^w$ ):	Soil Layer 3: 7.7 m to 9.2 m BGS
3.53E-6 m <sup>2</sup> /h	soil permeability to soil gas flow ( $K_g$ ) = $10^{-11}$ m <sup>2</sup>
Henry's Law constant ( $H_i$ ): 0.228 m <sup>3</sup> water/m <sup>3</sup> vapor	Soil bulk density ( $\rho_b$ ): 1700 kg/m <sup>3</sup>
Sorption coefficient of chemical $i$ to organic carbon ( $K_{oc, \eta}$ ): 61.7 kg/kg-oc	Mass fraction of organic carbon in the soil ( $f_{oc}$ ): 0.001 kg-oc/kg-soil
<b>Aerobic Biodegradation Simulations:</b>	Moisture-filled porosity ( $\phi_w$ ): 0.165 m <sup>3</sup> water/m <sup>3</sup> soil
Biodegradation rate: 0.18 1/h	Total soil porosity ( $\phi_T$ ): 0.35 m <sup>3</sup> voids/m <sup>3</sup> soil
Stoichiometric ratio (g-oxygen/g-carbon): 3	Average effective diffusion coefficient: 0.0027 cm <sup>2</sup> /s
Minimum O <sub>2</sub> concentration (g/cm <sup>3</sup> ) to needed for reaction to happen: 1.37E-2 kg/m <sup>3</sup>	<b>Contaminant vapor source properties<sup>(1)</sup></b>
<b>Soil Properties for generic simulation</b>	Location: 9.2 m BGS, across the bottom of the model domain
For cases of soil permeability to soil gas flow ( $K_g$ ) = $10^{-11}$ m <sup>2</sup>	Source size: 30 m x 30 m
Soil bulk density ( $\rho_b$ ): 1700 kg/m <sup>3</sup>	<i>(1)Only a quarter of the domain was simulated in the generic simulation, which is 24 m x 24 m.</i>
Mass fraction of organic carbon in the soil ( $f_{oc}$ ): 0.001 kg-oc/kg-soil	
Moisture-filled porosity ( $\phi_w$ ): 0.07 m <sup>3</sup> water/m <sup>3</sup> soil	
Total soil porosity ( $\phi_T$ ): 0.35 m <sup>3</sup> voids/m <sup>3</sup> soil	

Figure 1. Map of site surface features, soil gas sampling locations and alignment of cross sections A-A and B-B in Figure 4a-4b.

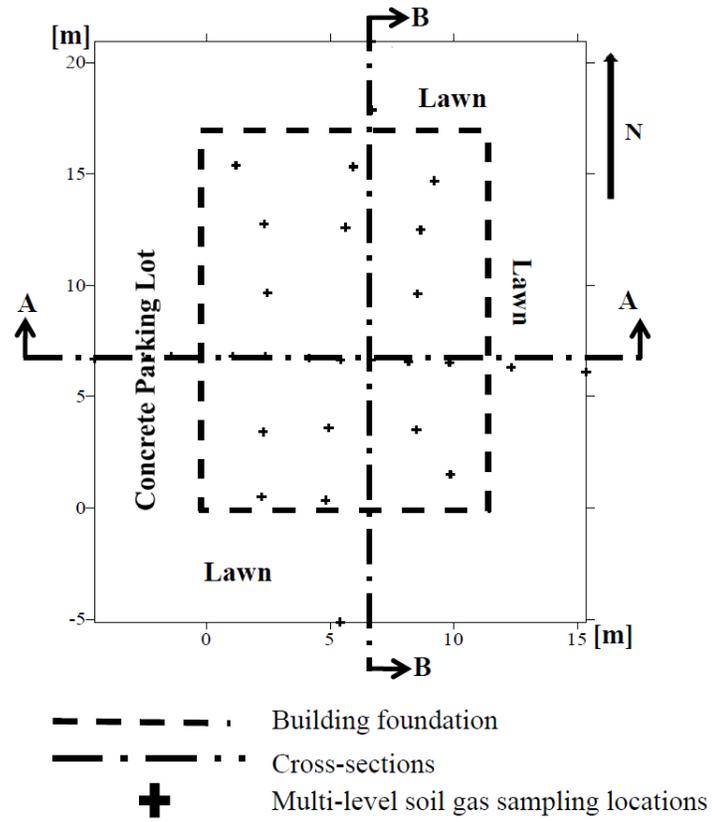


Figure 2. Contour plots of soil gas TPH and O<sub>2</sub> concentrations at A-A cross section through the center of building based on generic simulation results.

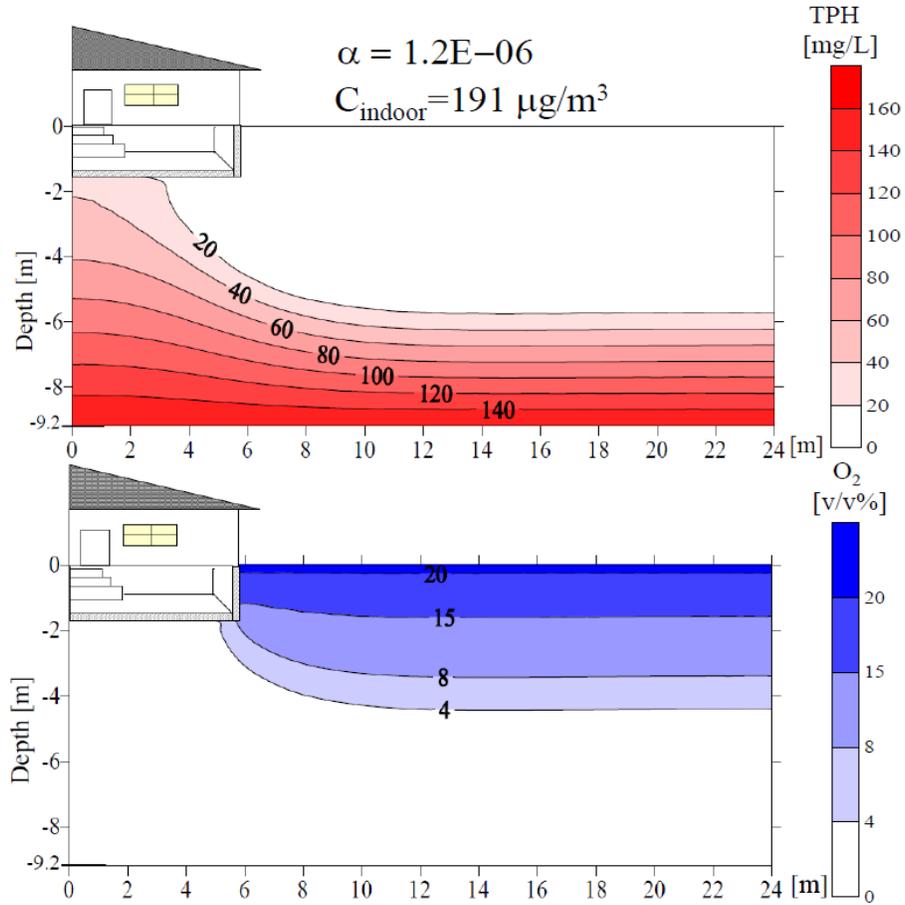


Figure 3. Plan view of soil gas TPH concentrations and soil gas O<sub>2</sub> concentrations at sub-slab depth (5ft BGS) measured on site.

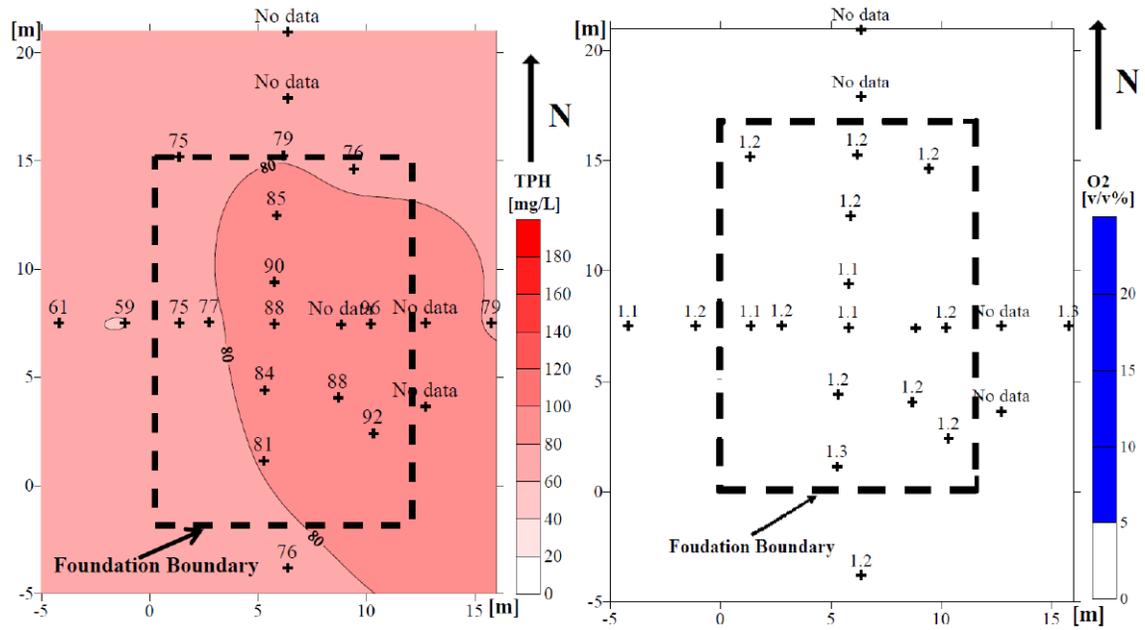


Figure 4 (a) Contour plots of soil gas TPH concentrations and O<sub>2</sub> concentrations at cross-section A-A, and (b) Contour plots of soil gas TPH concentrations and O<sub>2</sub> concentrations at cross-section B-B.

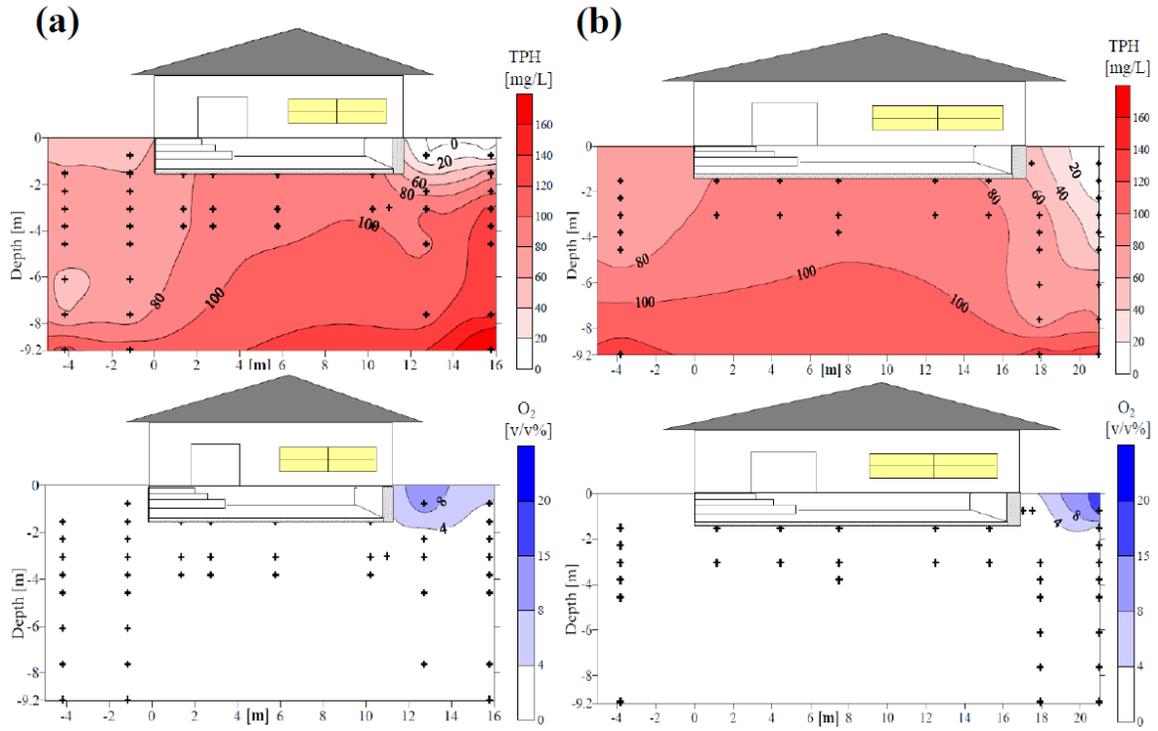


Figure 5. Soil O<sub>2</sub> consumption rate at different depths of four locations near building foundation.

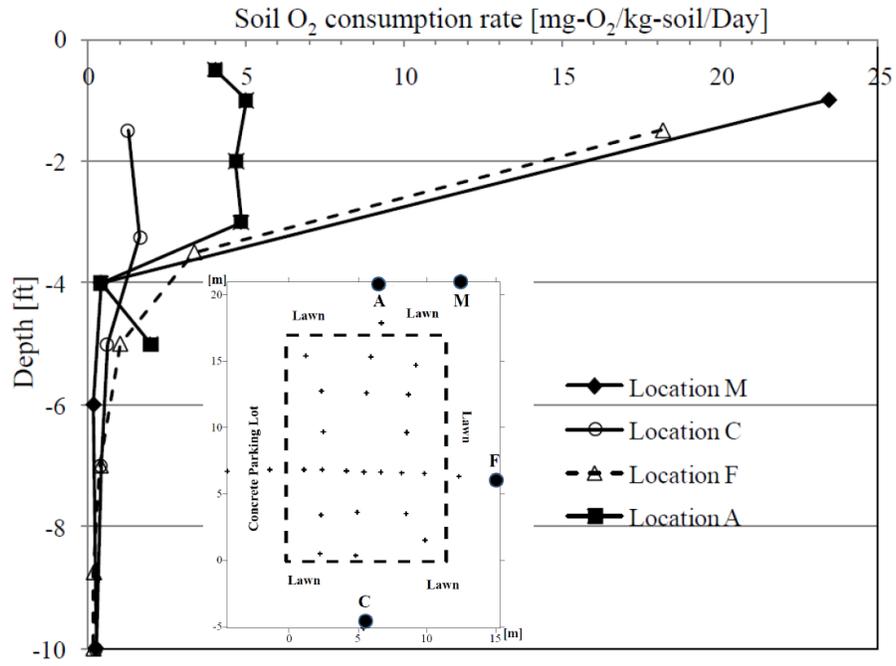


Figure 6. Soil air permeability at different depths of four locations near building foundation.

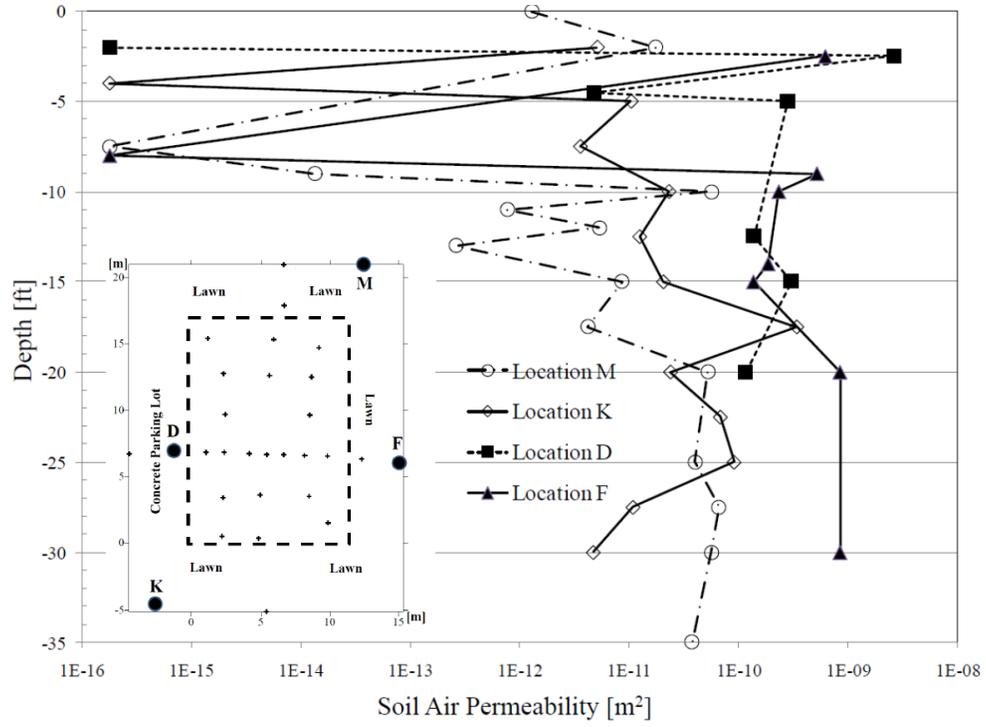


Figure 7. Conceptual picture of the site-specific simulation model domain.

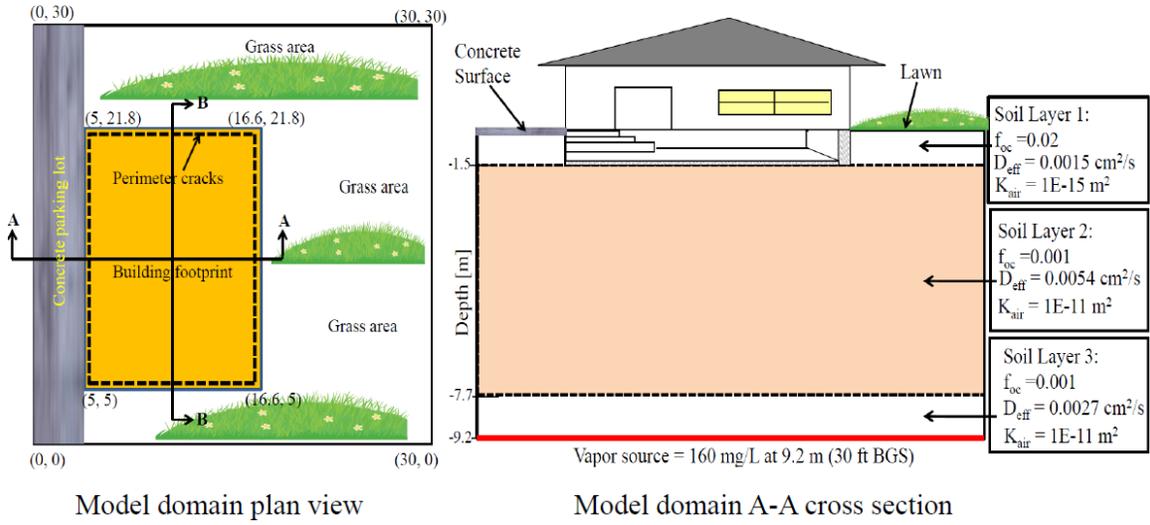


Figure 8. (a) Contour plots of soil gas TPH concentrations and O<sub>2</sub> concentrations at cross-section A-A, and (b) Contour plots of soil gas TPH concentrations and O<sub>2</sub> concentrations at cross-section B-B, using site-specific data as part of the inputs. Inputs are shown in Table 1.

