Published in final edited form as:

Environ Sci Technol. 2015 October 06; 49(19): 11577–11585. doi:10.1021/acs.est.5b01314.

A petroleum vapor intrusion model involving upward advective soil gas flow due to methane generation

Yijun Yao^{a,b,c}, Yun Wu^{a,b,c}, Yue Wang^{a,b,c}, Iason Verginelli^d, Tian Zeng^{a,b,c}, Eric M. Suuberg^e, Lin Jiang^f, Yuezong Wen^{a,b,c,*}, and Jie Ma^{g,*}

^aMOE Key Lab of Environmental Remediation and Ecosystem Health, College of Environmental and Resource Sciences, Zhejiang University, Hangzhou 310058, China

^bResearch Center for Air Pollution and Health, Zhejiang University, Hangzhou 310058, China

^cInstitute of Environmental Science, Zhejiang University, Hangzhou 310058, China

^dLaboratory of Environmental Engineering, Department of Civil Engineering and Computer Science Engineering, University of Rome "Tor Vergata", Via del Politecnico, 1 00133 Rome, Italy

^eSchool of Engineering, Brown University, RI 02912, USA

^fBeijing Municipal Research Institute of Environmental Protection, Beijing 100037, China

^gState Key Laboratory of Heavy Oil Processing, Beijing Key Lab of Oil & Gas Pollution Control, China University of Petroleum-Beijing, Beijing 102249, China

Abstract

At petroleum vapor intrusion (PVI) sites with the presence of significant methane generation, upward advective soil gas transport might be observed. To evaluate the health and explosion risks under such scenarios, a one-dimensional analytical model is introduced in this study. This new model accounts for both advective and diffusive soil gas transport, coupled with a piecewise first-order aerobic biodegradation limited by oxygen availability. The predicted results of the new model are shown to be in good agreement with the simulation results by a three-dimensional numerical model, suggesting that this analytical model is suitable for cases with open ground surface beyond foundation edge as the primary oxygen source. This new analytical model indicates that the major contribution of upward advection to indoor air concentration could be limited to the increase of soil gas entry rate, since the oxygen in soil might already be depleted due to the associated high methane source vapor concentration.

Graphical Abstract

Corresponding author: Phone: +86-571-88982470; fax: +86-571-88982470; wenyuezhong@zju.edu.cn (Wen, Y); Phone: +86-10-89744284; fax: +86-10-89734285; majie@cup.edu.cn (Ma, J).

Web Enhanced Object

A spreadsheet of the new analytical model is available free of charge via the Internet at <http://pubs.acs.org>.

Supporting Information

The calculated results by analytical and numerical results to generate Figures 2–3 are available free of charge via the Internet at <http://pubs.acs.org>.

Introduction

Subsurface vapor intrusion (VI) is a process by which the volatile compounds (VOC), released from contaminated soil and groundwater, migrate into the enclosed space of the building on the surface, inducing negative effects on residents (1–2). In particular, the subsurface to indoor air vapor intrusion pathway of organic compounds such as petroleum hydrocarbons, which can be released in the subsurface due to the leakage of underground storage tanks, has gained increased attention in recent years as a potential mechanism for long-term exposure to VOCs (3). To identify the houses that can be threatened by those hydrocarbon vapors, U.S. Environmental Protection Agency (EPA) recently proposed screening criteria of vertical separation distance based on the aerobic biodegradation potential of petroleum hydrocarbons (4–5). However, EPA also warned that such criteria might not be conservative enough for sites with the presence of significant methane generation (4). Indeed in such scenarios, PVI potential can be increased due to oxygen consumption by methane bio-oxidation as well as the upward advective soil gas flow caused by the accumulation of fermentative gas (methane and carbon dioxide) in the source zone (6–9). Moreover, methane intrusion (MI) may also pose an explosion hazard in the enclosed space of the building above the contamination plume (9–16).

Though there have been some literatures studying health risks caused by petroleum vapor intrusion (PVI) and the associated MI for the explosion risk in indoor environment (9,11,13,15–16), only a few of them involved upward soil gas advection. For instance, Salanitro *et al.* in 1989 conducted a soil column experiment by imposing a constant soil gas advection to study the biodegradation of aromatic hydrocarbons in unsaturated soil (17). Moyer *et al.* performed a biodegradation experiment by subjecting intact soil cores, which were collected from an aviation gasoline release site, to an upward flow of nitrogen, oxygen, water vapor, and hydrocarbon vapors (18–19). In a recent study conducted by Ma *et al.* (9), a three dimensional (3-D) numerical model was employed to simulate the influence of vapor source concentration of methane and soil gas pressure build-up by ethanol-blended fuel release fermentation on VI potential of both methane and benzene. The authors reported that if the methanogenic activity is sufficiently strong to increase gas pressure and cause advective gas transport near the source zone, methane could build up to potentially flammable levels (> 5% v/v) in overlying buildings. Furthermore based on the different simulations carried out the same authors showed that the presence of high concentrations of methane may deplete oxygen and inhibit benzene aerobic degradation, thus resulting in a higher benzene vapor intrusion potential. Though these studies provided some basic

understandings of the influence of upward advection in risk assessments of PVI and MI, up to now there has been few simple, effective model including upward advection.

Indeed, most of the current analytical mathematical models, used as PVI screening tool, such as BioVapor, AAMB and the Verginelli & Baciocchi Model (20–22), are based on the assumption that diffusion dominates source-to-subslab soil gas transport. For example, in a previous study, BioVapor was used to simulate soil gas concentrations of methane and benzene in the absence of upward advective soil gas flow (13). In the presence of upward advective soil gas flow, the subslab vapor concentrations and soil gas entry rate into the building can be significantly increased, raising the potential of PVI and MI (9). Under such scenarios, the explosion hazards of MI and health risks of PVI would be underestimated by using models that neglect upward advective soil gas flow.

In this study, we will introduce a one-dimensional (1-D) analytical model as a screening tool in the risk assessment of PVI and MI for cases involving upward advection due to significant methane generation. Independent of building operational conditions, this new model can be operated easily to predict subslab vapor concentration for both methane and hydrocarbons, in the presence or absence of upward advective soil gas flow. Simulation results by this new model would be compared with those of a 3-D numerical model (9, 23–24), and used to investigate the role of upward advection in the risk assessment of PVI and MI.

Model development

In a 1-D PVI (and MI) scenario, the general governing equations for soil vapor transport in steady-state are shown as equations (T1–T2) in Table 1, for cases without and with upward advective soil gas flow, respectively. As employed in previous models (9, 20–22, 24), a piecewise aerobic biodegradation is assumed here, shown as equation (T3) in Table 1, which means that a first-order reaction occurs if the oxygen concentration is larger than 1% v/v, otherwise, there is no reaction. The boundary conditions for contaminants and oxygen are shown in equation (T4) in Table 1. The effective diffusivities of contaminants and oxygen in soil are calculated according to the Millington and Quirk equation (25) and the soil permeability can be obtained based on moisture content and soil type according to van Genuchten equation (26), as employed in the EPA spreadsheet of the Johnson-Ettinger model (27). In this model, the contaminant concentration at open ground surface and oxygen flux at the bottom are assumed to be zero. The transport length L of oxygen from open ground surface to subslab source zone can be estimated according to a recent study by Verginelli and Baciocchi (21), as shown in equation (T5) and Figure 1. In short, this analytical model is designed for application in a scenario involving a building with an impermeable foundation surrounded by open ground surface, where the atmosphere is regarded as the primary oxygen source.

Analytical model in the absence of significant upward advective soil gas flow

If the source-to-subslab soil gas transport is dominated by diffusion, the position of aerobic/anoxic interface can be determined by assuming instantaneous reaction and a stoichiometric mass balance according to Roggemans equation (28):

$$\frac{\sum \delta_i D_i c_i^s}{L_b} = D_o \frac{c_o^{\text{atm}} - c_o^{\text{min}}}{L - L_b} \quad (1)$$

The thickness of anoxic zone L_b can be obtained by solving this equation, and the result is shown as equation (T6) in Table 1. To reach a fully anoxic subslab condition, the position of aerobic/anoxic interface should be above the bottom of the building foundation, which means $L_b > (d_s - d_f)$. In such scenarios, the methane and petroleum chemicals can be handled as non-biodegradable contaminants such as PCE and TCE (29). Thus the contaminant subslab vapor concentration can be estimated according to a previously developed method, as shown in equation (T8). Conversely, if the calculated anoxic zone thickness $L_b < (d_s - d_f)$, the following equation is given to estimate the subslab vapor concentration:

$$D_i \frac{d^2 c_i}{dz^2} = \frac{\lambda_i \theta_w}{H_i} c_i \quad (2)$$

$$\text{with boundary conditions } \begin{cases} \frac{dc_i}{dz} = 0, z = d_s - d_f \\ c_i = \frac{c_i^s}{1 + L_b \sqrt{\frac{\lambda_i \theta_w}{H_i D_i}}}, z = L_b \end{cases} \quad (3)$$

The subslab vapor concentration is approximated as $c_i|_{z=d_s-d_f}$ as shown in equation (T8). Based on the calculated subslab vapor concentration, the indoor air concentration can be calculated by using either an empirical attenuation factor (AF) or the traditional equation of continued stirred tank (CST) (27, 30), as shown in equation (T12). The soil gas entry rate into the enclosed space can be given using Nazaroff equation (31), as shown in equation (T10).

Analytical model in the presence of upward advective soil gas flow

At sites with the presence of significant methane generation, a pressure gradient may be observed between source and ground surface, inducing upward advective soil gas transport in the vadose zone (9, 14). In equation (T2), the constant soil gas velocity can be estimated using the following equation:

$$u = \frac{k_p p_s}{\mu L} \quad (4)$$

It should be noted that although the source pressure p_s could be in principle estimated as a function of methane generation rate and soil permeability, in this study, similarly to a previous numerical work (9), p_s is required as an independent input of the model. An alternative way to estimate the upward soil gas velocity is to use the soil gas concentrations

of nitrogen measured at different depths (32, 33). Moreover, the Peclet number can be used to identify the dominant transport mechanism:

$$Pe = \frac{uL}{D_m} \quad (5)$$

It is generally assumed that diffusion dominates the soil gas transport if $Pe < 1$ (32). In the presence of upward advection due to significant methane generation, the thickness of the anaerobic zone can be obtained by assuming methane as the major oxygen consumer. Using a stoichiometric mass balance and an instant reaction at the aerobic/anoxic interface, we have an equation similar to equation (1) (27–28):

$$u\delta_m \frac{c_m^s \exp\left(\frac{uL_b}{D_m}\right)}{\exp\left(\frac{uL_b}{D_m}\right) - 1} = u \frac{c_o^{\text{atm}} - c_o^{\text{min}} \exp\left(\frac{u(L-L_b)}{D_o}\right)}{\exp\left(\frac{u(L-L_b)}{D_o}\right) - 1} \quad (6)$$

By assuming $D_m \approx D_o$, the position of the aerobic/anaerobic interface can be obtained by solving equation (6), as shown in equation (T7) in Table 1. If the calculated L_b is larger than $d_s - d_f$, the subslab vapor concentration is approximated to be equal to the source vapor concentration (i.e. no attenuation). Otherwise, the following equation needs to be solved to estimate the subslab vapor concentration:

$$D_i \frac{d^2 c_i}{dz^2} = u \frac{dc_i}{dz} + \frac{\lambda_i \theta_w}{H_i} c_i \quad (7)$$

$$\text{with boundary conditions } \begin{cases} \frac{dc_i}{dz} = 0, z = d_s - d_f \\ uc_i - D_i \frac{d^2 c_i}{dz^2} = \frac{uc_i^s \exp\left(\frac{uL_b}{D_i}\right) - c_i}{\exp\left(\frac{uL_b}{D_i}\right) - 1}, z = L_b \end{cases} \quad (8)$$

The subslab vapor concentration is approximated as $c_i|_{z=d_s-d_f}$ as shown in equation (T9). It is worth noting that since the soil gas entry rate into the building can be increased by upward soil gas flow (9), the generic attenuation factor previously recommended by U.S. EPA (34) may no longer be appropriate to estimate indoor air concentration in the presence of significant upward advective soil gas flow. Furthermore, although the traditional CST equation can still be used to calculate the indoor air concentration, the soil gas entry rate into the building can be estimated by using a modified Nazaroff equation, as shown in equation (T11) in Table 1.

Results and discussions

Comparison with 3-D simulations

Figures 2–3 show the comparison between 3-D simulations (9) and the new analytical model for the predicted soil gas entry rate into the building and indoor air concentrations, respectively. The parameters employed to generate Figures 2–3 are shown in Table 2 (9, 24), and the statistical results of the comparisons are shown in Table 3. In Figures 2–3, the black line is the 45° line, showing where ideal agreement with the 3-D simulations would be found. It can be seen that most of the soil gas entry rates predicted by the analytical model fall in a range of 0.5–2 times of the simulated results by the 3-D numerical model, revealing a good agreement. Figure 2 also indicates that the changes of source vapor pressure (in a range of 0–200 Pa) and vertical building-source separation distance can cause a variation of the predicted soil gas entry rate (and the resulting indoor air concentration) up to 2 orders of magnitude. It is worth mentioning that although van Genuchten equation is recommended to calculate the soil permeability, for this comparisons, to be consistent with the 3-D simulations, a constant soil permeability of 10^{-11} m^2 was used.

Figure 3 reports a comparison of predicted methane (3a) and benzene (3b) indoor air concentrations from 3-D numerical simulations (9) and the new analytical model developed in this study. It should be noted that for this comparison in both models to calculate the indoor air concentration, the traditional CST equation (equation (1)) was used. Points of different colors represent different simulated scenarios, as explained in the figures. Making reference to the obtained results it can be noticed that the predictions of the soil gas entry rates and chemical indoor concentrations by this new analytical model are generally in good agreement with the 3-D numerical results, especially for cases involving positive source vapor pressures (see “Advection & diffusion and biodegradation”). In those cases, the predicted indoor air concentrations are within a range of 1–2 times of the simulated results by 3-D numerical models.

Conversely, from Figure 3(b) it can be seen that in a few diffusion-dominated cases with very low indoor air concentrations the analytical model tends to overestimate the attenuation expected in the subsurface. This result can be mainly ascribed to the fact that for such scenarios, the blocking effect of the building foundation considered in the analytical model, which prevents atmospheric oxygen from entering the soil matrix, is not relevant in the presence of a deep and low-concentration vapor source (35). Nonetheless, the difference in predicted indoor concentration between two models becomes significant only when the oxygen can penetrate into deep soil in the subslab zone, which is unlikely to occur when there are strong fermentation/methanogenesis activities in the source zone. Overall, the comparison between the 1-D analytical predictions and 3-D numerical simulations shown in Figures 2–3 suggests that this new analytical model can provide a simple and effective way to predict methane and hydrocarbons indoor air concentrations for explosion and health risk screenings at sites in the presence of significant upward advection.

Sensitivity analysis

A sensitivity test was applied to the developed model by calculating the responses of source-to-indoor air concentration attenuation factors to $\pm 10\%$ parameter change of given values shown beside the Y axis (36–38) shown in Figure 4. The obtained results indicate that the factor that has the highest influence on the calculated attenuation factor is source vapor depth, followed by source vapor pressure, methane source vapor concentration and building size. On the other hand, the results reported in Figure 4 show that this analytical model, in line with other previous studies (38–41), is relatively insensitive to benzene source vapor concentration, reaction kinetics and building foundation properties (except for the footprint size). According to the development of the model, the increase of the moisture content can decrease the effective diffusivities of soil gas and the upward advection, but increasing the biodegradation rate. In sum, a higher moisture content would lead to lower source-to-indoor air concentration attenuation factors with current conditions, similar to models based on diffusion dominated transport (20–22, 42). Finally, it should be noted the influence of indoor air exchange rate is not significant here, differently from the sensitivity analysis results of the Johnson-Ettinger model in Johnston *et al.* (40–41), where different variations of indoor air exchange rate were employed.

Influences of upward advection on health risk assessment of PVI

Figure 5 presents the sensitivity of source-to-indoor air concentration attenuation factor of benzene to methane source vapor concentration and Peclet number in cases involving only benzene and methane. Making reference to the results reported in Figure 5, it can be noticed that the attenuation factor of benzene increases with methane source vapor concentration, due to the decrease of aerobic zone thickness, until complete oxygen depletion, which explains the horizontal lines in the presence of higher methane source vapor concentration (e.g. $>20\%$ v/v). This is true also in the case of $Pe = 0$ that suggests that in the presence of methane, even in the absence of upward advection, the PVI potential is significantly increased due to the high oxygen consumption in the soil (9, 13). The same figure also highlights that increasing the Peclet number, leads to a higher attenuation factor while reached at lower methane source vapor concentration. The latter result is mainly due to the increased soil gas entry rate by upward advection. Employing a CST assumption to calculate the indoor air concentration, it would be easy to find that changing the Peclet number from 0 to 20 the benzene indoor air concentration increases of roughly one order of magnitude. A similar conclusion was also reached in a previous study (32).

Influences of upward advection on safety hazard assessment of MI

Compared to the health risk by long term exposure to low-concentration toxic chemicals (e.g., benzene), the explosion risk assessment of methane should include the worst-case short-term conditions (43). Therefore when the traditional CST equation is used to predict short-term maximum indoor air concentrations, more conservative input parameters should be employed than those usually adopted to predict the health risks of petroleum products. Moreover, according to the statistical analysis of U.S. EPA's VI database by EPA and other researchers, after minimizing the influences of background sources, the observed subslab-to-indoor air concentration attenuation factors varies from 1 to 10^{-4} (34, 44). It should be noted

that most datasets recorded in U.S. EPA's VI database were obtained at sites contaminated by chlorinated chemicals, and in those cases there should be no upward advective soil gas flow that can increase the soil gas entry rate into the building (and the subslab-to-indoor air concentration attenuation factor). Considering the worst cases recorded in the EPA database, which is no attenuation from subslab to indoor air, an appropriate way might be to employ the minimum explosion concentration of methane, 5% v/v, as the screening value of subslab methane vapor concentration for the explosion risk assessments of MI (43, 32). It should be noted that the identification of lower explosion limited (LEL) level of methane in the subslab zone might cause but does not essentially mean the explosion risk in the indoor space.

The results in Figure 6 suggest that at high methane source vapor concentrations (e.g. > 20 % v/v), the predicted subslab methane vapor concentration would exceed 5% in all cases, resulting in a potential explosion risk. It is however worth mentioning that the identification of lower explosion limited (LEL) level of methane in the subslab zone might cause but does not essentially mean the explosion risk in the indoor space. Indeed, as discussed above, methane could be attenuated through the building foundations, leading to indoor concentrations significantly lower than the ones detected in the subslab. The overlap of the curves indicates the independence of methane subslab vapor concentration on upward advection, which, however, may contribute to a higher indoor air concentration by increasing the soil gas entry rate, as discussed before.

The estimate of methane source vapor concentration required to deplete subslab oxygen

Since the biodegradation rate of methane in soil is usually much higher than petroleum hydrocarbons (9,45–46), in the scenarios where source vapor concentration of methane is much higher than that of hydrocarbons, methane can be assumed as the only contaminant consuming oxygen even in the absence of upward advection. For such scenarios equation (T6) can be used to calculate the critical methane source vapor concentration required to reach a complete anoxic condition in subslab zone (i.e. the thickness of anoxic zone equals the vertical source-building separation, $L_b = d_s - d_f$):

$$c_m^{s,cri} = \frac{D_o(c_o^{atm} - c_o^{min})}{D_m \delta_m \left(\frac{L}{d_s - d_f} - 1 \right)} \quad (9)$$

Figure 7 shows the calculated $c_m^{s,cri}$ as a function of vertical source-building separation ($d_s - d_f$) in the absence of upward advection. The calculated results suggest that a complete anoxic condition in subslab zone can be reached, regardless of the building foundation type, for cases with $d_s - d_f = 6$ m and $c_m^{s,cri} > 20\%$. Similar findings were also reported by Ma *et al.* (9). It should be noted that this conclusion is limited by the assumptions employed in the analytical model, such as infinite emission source of methane and limited oxygen migration pathway (i.e. only diffusion from the open ground surface beyond the foundation edge). A field experiment indicated that some preferential lateral advection below the foundation or vertical advection through the foundation might help maintain high oxygen level (19%) immediately below the foundation even in the presence of 13% v/v methane at 2–3 m below the foundation (47).

Limitations of this model

In this study an explicit algebraic solution is introduced as a screening tool for cases involving upward advective soil gas flow due to methane generation. The different comparisons carried out in this work highlighted that the developed model can replicate quite well the results obtained by 3-D numerical simulations. According to the predictions of this model, oxygen in subslab zone would be depleted by the associated high methane source vapor concentration with upward advection due to significant methane generation, and the major contribution to indoor air concentrations might only be the increase of the soil gas entry rate (increase of about one order of magnitude when the Peclet number changes from 0 to 20).

However, due to the conservative assumptions of vapor source distribution and oxygen migration pathway, the results obtained using this new screening model can be in some cases overestimated. For example, this new analytical model was developed based on an infinite source plume at the bottom (9, 39), though the source plume size is considered in the calculations of soil gas entry rate, as shown in equation (T11). This assumption for cases where only a part of building footprint is actually overlying the source plume can over-predict the hydrocarbon emissions mainly due to an underestimation of the presence of oxygen in the soil. Furthermore, in the analytical model it is assumed that oxygen migrates into the soil only by diffusion from the open ground surface beyond foundation edge (23–24, 39), while in practice there is a possibility of alternative pathways, including lateral advection inward from the edge of the foundation due to wind effect, and vertical diffusion and advection through foundation cracks followed by some lateral spreading mechanism in subslab zone (47). Moreover, with respect to more sophisticated 3-D numerical models, the analytical model is also incapable of simulating complex contamination scenarios involving transient transport, soil heterogeneities, and preferential pathways.

Finally, it is worth pointing out that although the results of the analytical model presented in this work were found to be consistent with those returned by more sophisticated 3-D simulations, practitioners should be paid particular caution to use these results as a definitive answer of the vapors behavior expected in the field in the presence of advective flows. Indeed due to the lack of experimental data, both the numerical and analytical model cannot be considered validated but rather they can only provide a first screening to be verified with further field investigations.

Acknowledgments

This work was funded in the part by the National Natural Science Foundation of China (no. 21307108, no. 21407180 and no. 21320102007), National Institute of Environmental Health Sciences (no. P42ES013660), National public fund for environmental protection (no. 201409047), Scientific Research Fund of Zhejiang Provincial Education Department (no. Y201326597), Science Foundation of China University of Petroleum-Beijing (no. 2462014YJRC016), and the Fundamental Research Funds for the Central Universities (no. 2014QNA6010).

References

1. Liu J, Zhao M, Zhuang S, Yang Y, Liu W. Low concentrations of o,p'-DDT inhibit gene expression and prostaglandin synthesis by estrogen receptor-independent mechanism in rat ovarian cells. *Plos One*. 2012; 7(11)

2. Liu J, Xiong K, Ye X, Zhang J, Yang Y, Liu J. Toxicity and bioaccumulation of bromadiolone to earthworm *Eisenia fetida*. *Chemosphere*. 2015; 135:250–256. [PubMed: 25965004]
3. U.S. EPA. PVI Database. Petroleum Vapor Intrusion (PVI) Compendium. 2012. <http://www.epa.gov/oust/cat/pvi/>
4. U.S. EPA. Evaluation of empirical data to support soil vapor intrusion screening criteria for petroleum hydrocarbon compounds. Washington, DC: Office of Underground Storage Tanks, U.S. Environmental Protection Agency; 2013. http://www.epa.gov/oust/cat/pvi/PVI_Database_Report.pdf
5. Lahvis MA, Hers I, Davis RV, Wright J, DeVaul GE. Vapor intrusion screening at petroleum UST sites. *Ground Water Monit. Rem.* 2013; 33:53–67.
6. Amos RT, Mayer KU, Bekins BA, Delin GN, Williams RL. Use of dissolved and vapor-phase gases to investigate methanogenic degradation of petroleum hydrocarbon contamination in the subsurface. *Water Resour. Res.* 2005; 41(2)
7. Molins S, Mayer KU, Amos RT, Bekins BA. Vadose zone attenuation of organic compounds at a crude oil spill site Interactions between biogeochemical reactions and multicomponent gas transport. *J. Contam. Hydrol.* 2010; 112(1–4):15–29. [PubMed: 19853961]
8. Lundegard PD, Sweeney RE, Ririe GT. Soil gas methane at petroleum contaminated sites: forensic determination of origin and source. *Environ. Forensics*. 2000; 1(1):3–10.
9. Ma J, Luo H, DeVaul GE, Rixey WG, Alvarez PJI. Numerical model investigation for potential methane explosion and benzene vapor intrusion associated with high-ethanol blend releases. *Environ. Sci. Technol.* 2014; 48(1):474–481. [PubMed: 24354291]
10. Freitas JG, Fletcher B, Aravena R, Barker JF. Methane production and isotopic fingerprinting in ethanol fuel contaminated sites. *Ground Water*. 2010; 48(6):844–857. [PubMed: 20070380]
11. Jewell KP, Wilson JT. A new screening method for methane in soil gas using existing groundwater monitoring wells. *Ground Water Monit. Rem.* 2011; 31(3):82–94.
12. Jourabchi, P., Hers, I., Mayer, KU., Devaul, GE., Kolhatkar, RV. Numerical modeling study of the influence of methane generation from ethanol-gasoline blends on vapor intrusion. The second International Symposium on Bioremediation and Sustainable Environmental Technologies; Jacksonville, FL, US. 2013.
13. Ma J, Rixey WG, DeVaul GE, Stafford BP, Alvarez PJJ. Methane bioattenuation and implications for explosion risk reduction along the groundwater to soil surface pathway above a plume of dissolved ethanol. *Environ. Sci. Technol.* 2012; 46(11):6013–6019. [PubMed: 22568485]
14. Sihota NJ, Mayer KU, Toso MA, Atwater JF. Methane emissions and contaminant degradation rates at sites affected by accidental releases of denatured fuel-grade ethanol. *J. Contam. Hydrol.* 2013; 151:1–15. [PubMed: 23685780]
15. Wilson JT, Toso M, Mackay D, Sieyes ND, DeVaul GE. What's the deal with methane at LUST spill sites? Part 1. L.U.S.T Line. 2012; 71 6–8 and 13.
16. Wilson JT, Toso M, Mackay D, Sieyes ND, DeVaul GE. What's the deal with methane at LUST spill sites? Part 2: vapor intrusion. L.U.S.T Line. 2013; 72 5–11 and 21–22.
17. Salanitro, JP., Western, MM., Kemblowski, MW. the 4th National Conference on Petroleum Contaminated Soils. University of Massachusetts at Amherst; 1989 Sep. Biodegradation of aromatic hydrocarbons in unsaturated soil microcosms.
18. Moyer, EE. Ph. D. Thesis. University of Massachusetts; 1993. Investigation of diffusion and biodegradation of vapor phase petroleum hydrocarbons.
19. Moyer, E., Ostendorf, D., Richards, R., Goodwin, S. In Situ Aeration: Air Sparging, Bioventing, and Related Remediation Processes. Columbus, OH: Battelle Press; 1995. Hydrocarbon biodegradation kinetics in an intact unsaturated zone soil core; p. 433–440.
20. DeVaul GE. Indoor vapor intrusion with oxygen-limited biodegradation for a subsurface gasoline source. *Environ. Sci. Technol.* 2007; 41(9):3241–3248. [PubMed: 17539532]
21. Verginelli I, Baciocchi R. Vapor intrusion screening model for the evaluation of risk-based vertical exclusion distances at petroleum contaminated sites. *Environ. Sci. Technol.* 2014; 48(22):13263–13272. [PubMed: 25329246]
22. Yao Y, Yang F, Suuberg EM, Provoost J, Liu W. Estimation of contaminant subslab concentration in petroleum vapor intrusion. *J. Hazard. Mater.* 2014; 279:336–347. [PubMed: 25124892]

23. Abreu LDV, Johnson PC. Effect of vapor source-building separation and building construction on soil vapor intrusion as studied with a three-dimensional numerical model. *Environ. Sci. Technol.* 2005; 39(12):4550–4561. [PubMed: 16047792]
24. Abreu LDV, Johnson PC. Modeling the effect of aerobic biodegradation on soil vapor intrusion into buildings - influence of degradation rate, source concentration, and depth. *Environ. Sci. Technol.* 2006; 40(7):2304–2315. [PubMed: 16646467]
25. Millington RJ, Quirk JP. Permeability of porous solids. *Trans. Faraday Soc.* 1961; 57:1200–1207.
26. Van Genuchten M. Th. A closed-form equation for predicting the hydraulic conductivity of unsaturated soils. *Soil Sci. Soc. Am. J.* 1980; 44:892–898.
27. Johnson PC, Ettinger RA. Heuristic model for predicting the intrusion rate of contaminant vapors into buildings. *Environ. Sci. Technol.* 1991; 25(8):1445–1452.
28. Roggemans, S., Bruce, CL., Johnson, PC. Vadose zone natural attenuation of hydrocarbon vapors: an empirical assessment of soil gas vertical profile data; API Technical Bulletin No. 15. Washington, DC: American Petroleum Institute; 2002. <http://www.api.org/environment-health-and-safety/clean-water/ground-water/vapor-intrusion/vi-publications/~media/7341022C36094FE58DE0682193BC3A6C.ashx>
29. Yao Y, Pennell KG, Suuberg EM. Estimation of contaminant subslab concentration in vapor intrusion. *J. Hazard. Mater.* 2012; 231–232:10–17.
30. Yao Y, Shen R, Pennell KG, Suuberg EM. A review of vapor intrusion models. *Environ. Sci. Technol.* 2013; 47(6):2457–2470. [PubMed: 23360069]
31. Nazaroff WW. Predicting the rate of ²²²Rn Entry from soil into basement of a dwelling due to pressure-driven air flow. *Radiat. Prot. Dosim.* 1988; 24:199–202.
32. DeVaul, G. the 24th Annual International Conference on Soil, Water, Energy, and Air. San Diego, CA, US: Mission Valley Marriott; 2014. Vapor intrusion of methane the challenge of low-risk sites. https://iavi.rti.org/attachments/WorkshopsAndConferences/10_DeVaul_VI_of_Methane_Challengel.pdf
33. Thorstenson DC, Pollock DW. Gas transport in unsaturated zones: Multicomponent systems and the adequacy of Fick's laws. *Water Resour. Res.* 1989; 25(3):477–507.
34. U.S. EPA. EPA's vapor intrusion Database: evaluation and characterization of attenuation Factors for chlorinated volatile organic compounds and residential buildings. Washington, DC: Office of Solid Waste and Emergency Response, U.S. Environmental Protection Agency; 2012. http://www.epa.gov/oswer/vaporintrusion/documents/OSWER_2010_Database_Report_03-16-2012_Final.pdf
35. U.S. EPA. 3-D modeling of aerobic biodegradation of petroleum vapors: effect of building area size on oxygen concentration below the slab. Washington, DC, USA: U.S. Environmental Protection Agency; 2013. <http://www.epa.gov/oust/cat/pvi/building-size-modeling.pdf>
36. Zhang J, Zeng L, Cheng C, Chen D, Wu L. Efficient Bayesian experimental design for contaminant source identification. *Water Resour. Res.* 2015; 51(1):576–598.
37. Shi L, Zeng L, Tang Y, Cheng C, Yang J. Uncertainty quantification of contaminant transport and risk assessment with conditional stochastic collocation method. *Stoch. Env. Res. Risk. A.* 2013; 27(6):1453–1464.
38. Ellison AM. An introduction to Bayesian inference for ecological research and environmental decision-making. *Ecol. Appl.* 1996; 6(4):1036–1046.
39. Hers I, Zapf-Gilje R, Evans D, Li L. Comparison, validation, and use of models for predicting indoor air quality from soil and groundwater contamination. *Soil Sed. Contam.* 2002; 11(4):491–527.
40. Johnston JE, Gibson JM. Probabilistic approach to estimating indoor air concentrations of chlorinated volatile organic compounds from contaminated groundwater: A case study in San Antonio, Texas. *Environ. Sci. Technol.* 2011; 45(3):1007–1013. [PubMed: 21162557]
41. Johnston JE, Sun Q, Gibson JM. Updating Exposure Models of Indoor Air Pollution Due to Vapor Intrusion: Bayesian Calibration of the Johnson-Ettinger Model. *Environ. Sci. Technol.* 2014; 48(4):2130–2138. [PubMed: 24422490]
42. Johnson PC. Identification of application-specific critical inputs for the 1991 Johnson and Ettinger vapor intrusion algorithm. *Ground Water Monit. Rem.* 2005; 25(1):63–78.

43. Eklund, B. Proposed Regulatory Framework for Evaluating the Methane Hazard Due to Vapor Intrusion. Presented at the AWMA Vapor Intrusion Conference; 2010, September 29–30; Chicago, IL. <http://events.awma.org/education/Final%20Papers/1-Eklund.pdf>
44. Yao Y, Wu Y, Suuberg EM, Provoost J, Shen R, Ma J, Liu W. Vapor intrusion attenuation factors relative to subslab and source, reconsidered in light of background data. *J. Hazard. Mater.* 2015; 286:553–561. [PubMed: 25618001]
45. Lundegard PD, Johnson PC, Dahlen P. Oxygen transport from the atmosphere to soil gas beneath a slab-on-grade foundation overlying petroleum-impacted soil. *Environ. Sci. Technol.* 2008; 42(15): 5534–5540. [PubMed: 18754472]
46. Verginelli I, Baciocchi R. Modeling of vapor intrusion from hydrocarbon-contaminated sources accounting for aerobic and anaerobic biodegradation. *J. Contam. Hydrol.* 2011; 126(3–4):167–180. [PubMed: 22115083]
47. DeVaul, G., McHugh, TE., Newberry, P. User's Manual "BioVapor: a 1-D Vapor Intrusion Model with Oxygen-Limited Aerobic Biodegradation". Washington, DC: American Petroleum Institute; 2010. <http://www.api.org/downloads/BioVapor-Users-Guide.pdf>

FIGURE 1.
Conceptual scenario of the screening model

FIGURE 2.

Comparison of soil gas entry rate (Q_b) into the building by using the 3-D numerical model (9) and the analytical model proposed in this study.

(a)

(b)

FIGURE 3.

Comparison of predicted indoor air concentration of (a) methane and (b) benzene using the 3-D model (9) (X-axis) and the analytical methods proposed in this paper (Y-axis).

FIGURE 4.
Sensitivity analysis of model parameters on predicted contaminants source-indoor air concentration attenuation factors.

FIGURE 5.

Sensitivity of benzene source-to-subslab indoor air concentration attenuation factor to methane source vapor concentration for cases with different Peclet numbers ($d_s = 3$ m, $d_f = 0.2$ m and $c_b^s = 10 \text{ g/m}^3$)

FIGURE 6.

Sensitivity of methane subslab vapor concentration to methane source vapor concentration for cases with different Peclet numbers ($d_s = 3 \text{ m}$ and $d_f = 0.2 \text{ m}$; the red line refers to the $5\% \text{ v/v}$ flammable limit of methane in air).

FIGURE 7.

The dependence of critical methane source vapor concentration required for a subslab oxygen depletion zone on vertical source-building separation distance for different building foundations (Full basement: $d_f = 2\text{ m}$; Partial basement: $d_f = 1\text{ m}$; Slab-on-grade: $d_f = 0.2\text{ m}$; the red line refers to the 6 m vertical screening distance suggested by U.S. EPA (4))

TABLE 1

Equations of the screening model

	Diffusion and piecewise aerobic biodegradation	Advection & diffusion and piecewise aerobic biodegradation
Governing equation	$D_i \frac{d^2 c_i}{dz^2} = R_i$	(T1) $D_i \frac{d^2 c_i}{dz^2} = u \frac{dc_i}{dz} + R_i$
Biodegradation rate	$R_i = \begin{cases} \frac{\lambda_i \theta_w}{H_i} c_i, c_o \geq c_o^{\min} \\ 0, c_o < c_o^{\min} \end{cases}, R_o = \begin{cases} \sum \left(\frac{\delta_i \lambda_i \theta_w}{H_i} c_i \right), c_o \geq c_o^{\min} \\ 0, c_o < c_o^{\min} \end{cases}$	
Boundary conditions	$\begin{cases} \frac{dc_i}{dz} = 0, z = d_s - d_f \\ c_i = c_i^s, z = 0 \end{cases}; \begin{cases} c_o = c_o^{\text{atm}}, z = L \\ c_o = c_o^{\min}, z = L_b \\ \frac{dc_o}{dz} = 0, z = 0 \end{cases}$	
Oxygen transport length L	$d_s + (d_f + L_{\text{slab}}) \left(\frac{\pi}{2} - 1 \right)$	
Anoxic zone thickness L_b	(T6) $\frac{L}{\frac{D_o(c_o^{\text{atm}} - c_o^{\min})}{\sum \delta_i D_i c_i^s} + 1}$	$\frac{D_o}{u} \ln \left(\frac{\exp \left(\frac{uL}{D_o} \right) \left(\frac{\delta_m c_m^s}{c_o^{\text{atm}}} + \frac{c_o^{\min}}{c_o^{\text{atm}}} \right) + 1 + \sqrt{\left(\exp \left(\frac{uL}{D_o} \right) \right)}}{2} \right)$
Subslab concentration	(T8) $\frac{c_i^{\text{sub}}}{c_i^s} = \begin{cases} \sqrt{\frac{d_f}{d_s}}, L_b \geq d_s - d_f \\ \frac{1}{\left(1 + L_b \sqrt{\frac{\lambda_i \theta_w}{H_i D_i}} \right) \cosh \left(\sqrt{\frac{\lambda_i \theta_w}{H_i D_i}} (d_s - d_f - L_b) \right)}, L_b < d_s - d_f \end{cases}$	$\begin{cases} 1, L_b \geq \\ \frac{\in \exp \left(\frac{\beta}{z} \right)}{\sinh \left(\varepsilon \frac{\beta}{z} \right) + \in \cdot \cosh \left(\varepsilon \frac{\beta}{z} \right) + \frac{\varepsilon^2 - 1}{2} (1 - \exp(-\gamma)) \sinh \left(\varepsilon \frac{\beta}{2} \right)}, L_b < \end{cases}$
Soil gas entry rate Q_b	(T10) $\frac{2\pi k_p \Delta p L_{ck}}{\mu \ln \left(\frac{2d_f}{w_{ck}} \right)}$	$\frac{2\pi k_p (\Delta p + p_s) L_{ck}}{\mu \ln \left(\frac{2(d_s - d_f)}{w_{ck}} \right)} \frac{\text{atan} \left(\frac{L_s}{2(d_s - d_f)} \right)}{\frac{\pi}{2}}$
Indoor air concentration	$\frac{c_i^{\text{in}}}{c_i^{\text{sub}}} = \begin{cases} a_{\text{sub}}^{\text{in}}, AF \\ \frac{Q_b}{V_b A_e}, CST \end{cases}$	

TABLE 2

Input parameters used in Figures 2–3 (9, 24).

Building/ Foundation parameters	Chemical properties:
Foundation footprint size: 10 m X 10 m	Contaminant type: benzene and methane
Depth of foundation (d_f): 2 m	Effective diffusivity of benzene in soil (D_b): $1.03 \times 10^{-6} \text{ m}^2/\text{s}$
Crack width (W_{ck}): 0.001 m	Henry's law constant of (H_b): 0.228
Thickness of crack (d_{ck}): 0.15 m	First order degradation rate constant of benzene in water (λ_b): 0.18 h^{-1}
Crack location : perimeter	Stoichiometric coefficient of benzene to oxygen (δ_b): 7.5 mol-oxygen/mol-benzene
Disturbance pressure (P): 5 Pa	
Soil properties	
Soil permeability (k_p): 10^{-11} m^2	Effective diffusivity of methane in soil (D_m): $2.29 \times 10^{-6} \text{ m}^2/\text{s}$
Viscosity of soil gas (μ): $1.8 \times 10^{-6} \text{ kg/m/s}$	Henry's law methane constant of (H_m): 29.9
Soil bulk density (ρ_b): 1700 kg/m^3	First order degradation rate constant of methane in water (λ_m): 82 h^{-1}
Total porosity (θ): 0.35	Stoichiometric coefficient of methane to oxygen (δ_m): 2 mol-oxygen/mol-methane
Water-filled porosity (θ_w): 0.07	
Vapor source properties	Effective diffusivity of oxygen in soil (D_o): $2.34 \times 10^{-6} \text{ m}^2/\text{s}$
Depth to source (d_s): 3, 5, 8, 15 m	Henry's law constant of oxygen (H_o): 31.6
Location: base of vadose zone	Minimum oxygen concentration required for biodegradation to occur ($C_o^{\min}$): 1% v/v
Size: entire domain footprints	

Statistical results for the comparison between the analytical predictions and numerical simulations (the units of Q_b , c_m^{in} and c_b^{in} are L/min, % v/v and g/m³, respectively)

TABLE 3

Variables	Scenarios	Number of calculations	Standard deviation	Maximum deviation	Pearson correlation coefficient (significance)
$\log(Q_b)$		40	0.36	0.36	0.95(0.00)
	No biodegradation	48	0.15	0.21	0.99(0.00)
$\log(\text{cmin})$	Diffusion and biodegradation	48	0.62	1.79	0.99(0.00)
	Advection & diffusion and biodegradation	36	0.29	0.62	0.97(0.00)
$\log(\text{cbin})$	Diffusion and biodegradation	48	1.43	1.82	0.99(0.00)
	Advection & diffusion and biodegradation	36	0.26	0.61	0.97(0.00)

Nomenclature

Symbol	Unit	Parameter
M_b	—	Mass unit of benzene
M_i	—	Mass unit of chemical i
M_m	—	Mass unit of methane
M_o	—	Mass unit of oxygen
$\alpha_{\text{sub}}^{\text{in}}$	—	Subslab-to-indoor air concentration attenuation factor
δ_b	$M_o M_b^{-1}$	Stoichiometric conversion factor of benzene
δ_i	$M_o M_i^{-1}$	Stoichiometric conversion factor of chemical i
δ_m	$M_o M_m^{-1}$	Stoichiometric conversion factor of methane
λ_b	T^{-1}	First order biodegradation rate to benzene in water phase
λ_i	T^{-1}	First order biodegradation rate to chemical i in water phase
λ_m	T^{-1}	First order biodegradation rate to methane in water phase
θ_t	—	Total porosity of the soil
θ_w	—	Moisture filled porosity of the soil
μ	$M L^{-1} T^{-1}$	Viscosity of soil gas
ρ_b	$M L^{-3}$	Soil bulk density of soil
p	$M L^{-1} T^{-2}$	Pressure difference between indoor air and atmosphere
A_e	T^{-1}	Air exchange rate of intruded zone
c_b^{in}	$M_b L^{-3}$	Indoor air concentration of benzene
c_b^s	$M_b L^{-3}$	Vapor source concentration of benzene
c_i	$M_i L^{-3}$	Concentration of chemical i in the soil gas phase
c_i^{in}	$M_i L^{-3}$	Indoor air concentration of chemical i
c_i^s	$M_i L^{-3}$	Source vapor concentration of chemical i
c_i^{sub}	$M_i L^{-3}$	Subslab vapor concentration of chemical i
c_m^{in}	$M_m L^{-3}$	Indoor air concentration of methane
c_m^s	$M_m L^{-3}$	Source vapor concentration of methane
$c_m^{s,\text{cri}}$	$M_m L^{-3}$	Critical methane source vapor concentration required to deplete oxygen in soil
c_o	$M_o L^{-3}$	Soil gas concentration of oxygen
c_o^{atm}	$M_o L^{-3}$	Oxygen concentration in the atmosphere

Symbol	Unit	Parameter
$C_{O_{\min}}$	$M_o L^{-3}$	Minimum oxygen concentration required for biodegradation
d_{ck}	L	Thickness of crack
d_f	L	Depth of the building foundation below ground surface
d_s	L	Depth of contaminant source below ground surface
D_b	$L^2 T^{-1}$	Effective porous medium diffusivity of benzene
D_i	$L^2 T^{-1}$	Effective porous medium diffusivity of chemical i
D_m	$L^2 T^{-1}$	Effective porous medium diffusivity of methane
D_o	$L^2 T^{-1}$	Effective porous medium diffusivity of oxygen
H_b	—	Henry's Law constant of benzene
H_i	—	Henry's Law constant of chemical i
H_m	—	Henry's Law constant of methane
H_o	—	Henry's Law constant of oxygen
k_p	L^2	Soil permeability
L	L	Total transport length of oxygen
L_b	L	Thickness of anoxic zone
L_{ck}	L	Total crack length
L_s	L	Half length of contaminant source plume side
L_{slab}	L	Half length of the building footprint side
p_s	$M L^{-1} T^{-2}$	Source vapor pressure
P_e	—	Peclet number
Q_b	$L^3 T^{-1}$	Soil gas entry rate into the enclosed space
R_i	$M_i L^{-3} T^{-1}$	Reaction rate of chemical i
R_o	$M_o L^{-3} T^{-1}$	Reaction rate of oxygen
u	$L T^{-1}$	Velocity of upward soil gas flow in steady state
V_b	L^3	Volume of intruded zone
W_{ck}	L	Width of the crack
Z	L	Coordinate in the vertical direction