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Numerical Model Investigation for Potential Methane Explosion and Benzene Vapor Intrusion Associated with High-Ethanol Blend Releases

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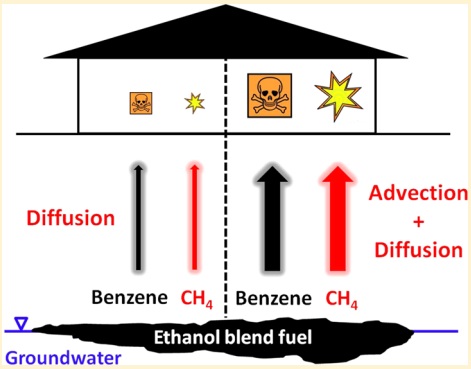
Supporting Information

ABSTRACT: Ethanol-blended fuel releases usually stimulate methanogenesis in the subsurface, which could pose an explosion risk if methane accumulates in a confined space above the ground where ignitable conditions exist. Ethanol-derived methane may also increase the vapor intrusion potential of toxic fuel hydrocarbons by stimulating the depletion of oxygen by methanotrophs, and thus inhibiting aerobic biodegradation of hydrocarbon vapors. To assess these processes, a three-dimensional numerical vapor intrusion model was used to simulate the degradation, migration, and intrusion pathway of methane and benzene under different site conditions. Simulations show that methane is unlikely to build up to pose an explosion hazard (5% v/v) if diffusion is the only mass transport mechanism through the deeper vadose zone. However, if methanogenic activity near the source zone is sufficiently high to cause advective gas transport, then the methane indoor concentration may exceed the flammable threshold under simulated conditions. During subsurface migration, methane biodegradation could consume soil oxygen that would otherwise be available to support hydrocarbon degradation, and increase the vapor intrusion potential for benzene. Vapor intrusion would also be exacerbated if methanogenic activity results in sufficiently high pressure to cause advective gas transport in the unsaturated zone. Overall, our simulations show that current approaches to manage the vapor intrusion risk for conventional fuel released might need to be modified when dealing with some high ethanol blend fuel (i.e., E20 up to E95) releases.



INTRODUCTION

Recent U.S. legislation promoting a higher percentage of ethanol in blended fuel will further stimulate the production and consumption of fuel ethanol.[1] Vapor intrusion risk associated with high-ethanol blend releases (E20 up to E95) has been increasingly recognized as a potential concern.[2] Fuel ethanol releases often stimulate methanogenic activity,[3−9] which may pose an explosion hazard when methane accumulates in a confined or poorly ventilated space at 5% to 15% (v/v). Ethanol-derived methane may also increase the vapor intrusion potential of toxic fuel hydrocarbons by stimulating the depletion of oxygen by methanotrophs and thus inhibiting aerobic biodegradation of hydrocarbon vapors.[3,6,10]

Relative high concentrations of methane have been reported in groundwater (23 to 47 mg/L)[3,11,12] and soil gas (15% to 58% v/v)[10,11] that have been impacted by fuel ethanol spills. Although these studies contribute to the understanding of methane generation and migration in the subsurface, none of them directly assessed methane intrusion and accumulation in overlying buildings. Because of flame quenching within the soil matrix, a methane explosion will not occur in situ in the soil, but may happen when methane accumulates in a confined space above ground where ignitable conditions exist.[5]

Flux chambers have been used to measure methane intrusion and accumulation in confined spaces above fuel ethanol-impacted sites.[3,4] However, flux chamber measurements are not representative of actual vapor flow into buildings, because (1) flux chambers do not have foundations, thus may overestimate the vapor flux into buildings, and (2) flux chambers cannot mimic "building effects" (e.g., depressurization) that play an important role in the vapor subsurface-to-indoor air pathway.[13] Therefore, direct measurements of methane concentrations in the indoor air or model simulations that consider both attenuation across foundations and building effects are

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necessary to assess the potential explosion risk associated with high ethanol blend releases.

CH_4 gas release by ebullition and advection has previously been noted in a variety of environments, including saturated peat,[14] rice fields,[15] sediment,[16] landfills,[17] and aquifers contaminated by petroleum spills.[18,19] Recent field studies show the importance of CH_4 migration by ebullition and advection at sites impacted by ethanol-blend releases.[4,10] Soil gas advection would enhance the upward migration of methane, thus increasing the potential explosion risk. Another knowledge gap is the impact of biogenic methane on the fate and transport of fuel hydrocarbons in the subsurface. Anaerobic biodegradation processes are relatively slow and do not significantly attenuate hydrocarbon vapor migration through the vadose zone.[20] If sufficient oxygen (e.g., >1%) is present in the unsaturated zone, then biodegradation could reduce hydrocarbon concentrations by several orders of magnitude within a relatively short distance (1−2 m).[21,22] However, the consumption of methane by methanotrophs may deplete available soil oxygen, thus inhibiting aerobic hydrocarbon degradation.[3] These processes are still poorly understood.

With improved understanding of vapor intrusion processes, various mathematical models have been developed to assess potential impacts to indoor air quality.[23−31] Although 1-D analytical models such as the Johnson and Ettinger model [23] are simple, fast, and widely used for screening purposes, 3-D numerical models that consider multispecies transport, reaction, and phase partitioning are more accurate and applicable to describe scenarios with complex model domain and boundary conditions.[25,28,32−35] To our knowledge, such 3-D models have not been used to assess the vapor intrusion risk associated with ethanol-blended fuel releases.

In this study, a 3-D numerical vapor intrusion model[25] was used to simulate various scenarios and quantitatively address: (1) the potential for methane accumulation in buildings overlaying ethanol-blended fuel impacted sites, and the associated explosion hazard; (2) the effect of methane (and associated methanotrophic activity) on the vapor intrusion pathway of benzene; and (3) the impact of gas advection on the vapor intrusion pathway of methane and benzene.

MATERIALS AND METHODS

3-D Numerical Model. The 3-D numerical model used in this study was developed by Abreu and Johnson.[25] This finite difference model solves (1) continuity equations that govern the soil gas pressure distribution and the resulting soil gas velocity field; (2) chemical reactive transport equations that account for diffusion, advection, and biodegradation in the subsurface; (3) air flow and chemical transport through foundation cracks; and (4) chemical mixing with indoor air. The soil characteristics (e.g., porosity, water content, permeability, bulk density, and organic carbon content) can be modeled as homogeneous, layered (up to 10 layers) or heterogeneous. This model also allows for different biodegradation kinetics (nonbiodegradation, zero-order, first-order, Monod) and user-defined building characteristics (e.g., foundation cracks position and size, air exchange rate, and building depressuration). Model outputs include soil gas pressure, soil gas velocity and chemical concentration fields, chemical flux, and indoor air concentration. Details about mathematical model development can be found in Abreu (2005).[36] This model has been used in several studies,[25,32,33] and US EPA guidance on vapor intrusion.[37,38]

Simulated Scenarios and Model Input Parameters. This study simulated a symmetrical scenario that includes a single building (10 m × 10 m) located at the center of an open field (48 × 48 m^2) (Figure 1). The building has a 2 m deep

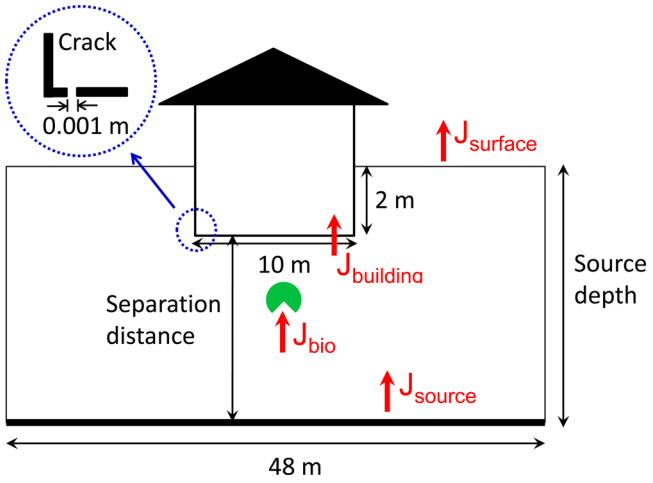

Figure 1. Cross-sectional view of the model domain and the perimeter crack on the building foundation (blue dashed circle). The vapor mass fluxes used in following figures includes flux emitted from the source (J_{source}), flux into the building ($J_{building}$), flux across the soil surface ($J_{surface}$), and flux biodegraded (J_{bio}).

basement and a perimeter crack (1 mm wide) around the entire foundation of the basement (Figure S1 in the Supporting Information, SI). Similar to other numerical modeling studies,[25,28,32,34−36] the building is assumed to be underpressurized relative to atmosphere by 5 Pa. This pressure difference between building indoor air and atmosphere is generated by a building depressurization effect. The contaminant source zone is located at the bottom of the unsaturated zone and spreads across the entire model domain (48 × 48 m^2, Figure 1). Four different source depths (3, 5, 8, and 15 m) were chosen. The 3 m depth represents a shallow vapor source case and 15 m depth represents a deep vapor source case. Since the basement has a depth of 2 m, actual separation distance between source zone and building foundation are 1, 3, 6, and 13 m. All simulations were conducted for homogeneous and steady-state scenarios and the associated model input parameters related to CH_4 and benzene source concentrations, source gas pressure, and separation distance are listed in Table 1 (see Figures 1− 7). Other model input parameters regarding building and foundation, soil properties, contaminant properties, and biodegradation rate constants were selected based on previous studies (SI Table S1).[25,32,33] These biodegradation rate constants are illustrative of the range of values in the literature, but their use does not imply that these values are universally accepted.

On the basis of the overall stoichiometry of ethanol degradation under fermentative methanogenic conditions (2 $CH_3CH_2OH = CO_2 + 3CH_4$), the degradation of ethanol could produce gas with up to 75% (v/v) CH_4 content. Therefore, 75 v/v % (4.91 × 10^2 g/m^3) was chosen as the maximum CH_4 source concentration.

To simulate the CH_4 explosion risk, we considered aerobic CH_4 biodegradation by methanotrophs as it migrates upward through the vadose zone. Since the available oxygen can also be consumed by the biodegradation of other compounds

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Table 1. Simulated Scenarios for Table 2 and Figures 1−7 in the Main Text and Tables S2 and S3 and Figures S2−S8 in the SI

	CH_4 source concentration	TPH source concentration	benzene source concentration	source gas pressure	separation distance
Table 2	75%	200 g/m^3	NA[a]	0 to 200 Pa	3 m
Figure 2	0.015% to 75%	200 g/m^3	NA	0 Pa	1, 3, 6, and 13 m
Figure 3	0.015% to 75%	200 g/m^3	NA	0 Pa	6 m
Figure 4	75%	200 g/m^3	NA	0.1 to 200 Pa	1, 3, 6, and 13 m
Figure 5	0.076% to 75%	NA	0.1 g/m^3	0 Pa	1, 3, 6, and 13 m
Figure 6	0.015% to 75%	NA	0.1 g/m^3	0 Pa	6 m
Figure 7	0.015% to 75%	NA	0.1 g/m^3	0 Pa	6 m
SI Table S2	75%	200 g/m^3	NA	0 to 200 Pa	1, 6, and 13 m
SI Table S3	75%	200 g/m^3	NA	0 to 200 Pa	1, 6, and 13 m
SI Figure S2	0.015% to 75%	200 g/m^3	NA	0 Pa	1 m
SI Figure S3	0.015% to 75%	200 g/m^3	NA	0 Pa	3 m
SI Figure S4	75%	200 g/m^3	NA	0 to 200 Pa	3 m
SI Figure S5	0% to 75%	NA	0.1 g/m^3	0 Pa	6 m
SI Figure S6	0% to 75%	NA	0.1 g/m^3	0 Pa	6 m
SI Figure S7	0% to 75%	NA	0.1 g/m^3	0 Pa	6 m
SI Figure S8	75%	NA	0.1 g/m^3	0.1 to 200 Pa	1, 3, 6, and 13 m

[a]"NA" is the abbreviation for not applicable.

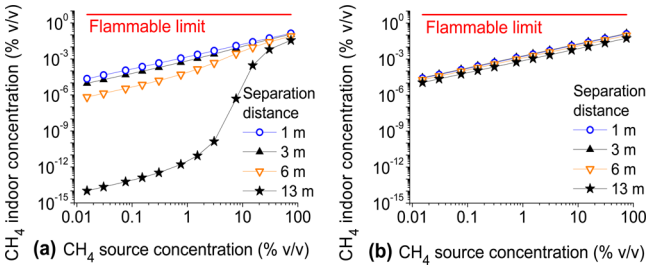

Figure 2. Simulated CH_4 indoor concentrations for different CH_4 source concentrations and separation distances, (a) with and (b) without CH_4 biodegradation. The source was assumed to contain 200 g/m^3 TPH that contribute to the biochemical oxygen demand in the vadose zone. The source pressure is 0 Pa.

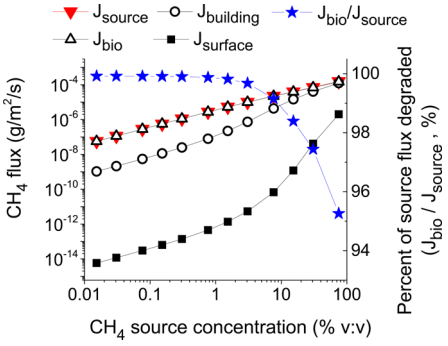

Figure 3. Changes in CH_4 mass flux emitted from the source (J_{source}), flux into the building ($J_{building}$), flux across the soil surface ($J_{surface}$), and flux biodegraded (J_{bio}) with different CH_4 source concentrations. The right *Y*-axis shows the percent of source flux degraded (J_{bio}/J_{source}). The source also contains 200 g/m^3 TPH that contribute to the biochemical oxygen demand in the vadose zone. The source soil gas pressure is 0 Pa. The separation distance is 6 m.

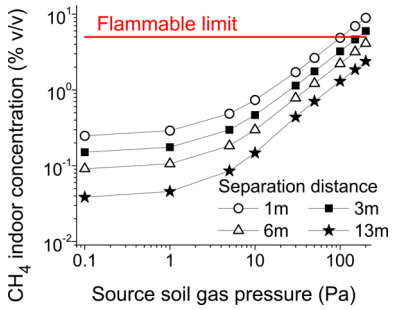

Figure 4. Simulated CH_4 indoor concentrations for different separation distances and source gas pressures. The source contains 75% (v/v) CH_4 and 200 g/m^3 TPH that contribute to the biochemical oxygen demand in the vadose zone. The CH_4 indoor concentration for the source soil gas pressure of 0 Pa can be found in Figure 2a.

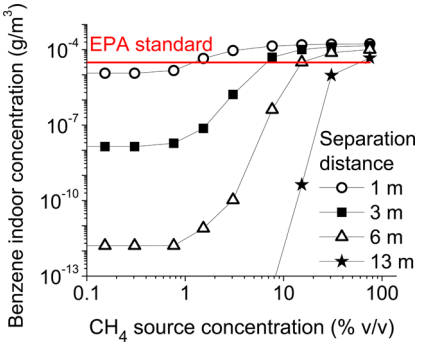

Figure 5. Simulated benzene indoor concentrations for different CH_4 source concentrations and separation distances. The EPA indoor air standard for benzene (3.1×10^{-5} g/m^3) corresponds to a 10^{-4} lifetime risk.[48] The source contains 0.1 g/m^3 benzene, with a source soil gas pressure of 0 Pa.

associated with the release, the model assumes that 200 g/m^3 of the total petroleum hydrocarbons (TPH) were present at the source zone (Table 1). This concentration is representative of nonaqueous phase liquid (NAPL) sources[38,39] and has been used in previous modeling studies.[25,32,36] The properties of these hydrocarbons were assumed to be the same as for benzene vapor (SI Table S1) because model computation slows significantly when running multiple fuel constituents. Benzene was not included as a separate component for these simulations because it has a minor effect on the CH_4 mass fluxes.

To simulate the impacts of CH_4 generation on benzene vapor intrusion potential, 0.1 g/m^3 was chosen as the benzene source concentration as a representative value from a petroleum vapor intrusion database.[40] This concentration falls within the

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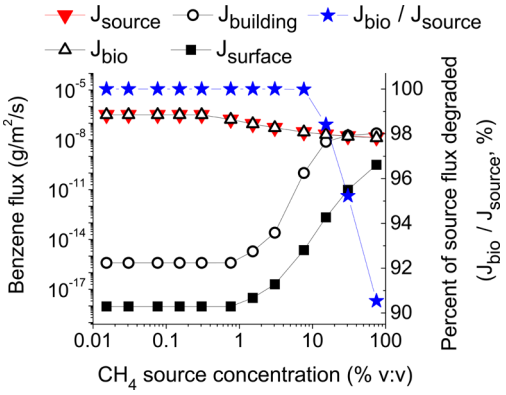

Figure 6. Changes in benzene flux emitted from source (J_{source}), flux into the building basement ($J_{building}$), flux across the soil surface ($J_{surface}$), and flux biodegraded (J_{bio}) for different CH_4 source concentrations. The right *Y*-axis shows the percent of source flux that is biodegraded (J_{bio}/J_{source}). The source contains 0.1 g/m^3 benzene, with a source soil gas pressure of 0 Pa. The separation distance is 6 m.

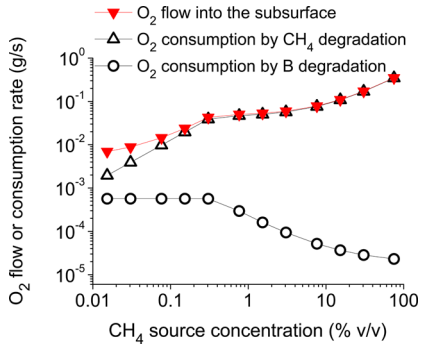

Figure 7. Changes in O_2 consumption by aerobic degradation of benzene (B) and CH_4 with different CH_4 source concentrations. The source contains 0.1 g/m^3 benzene, with a soil gas pressure of 0 Pa. The separation distance is 6 m.

top 25% of benzene vapor concentrations measured near various NAPL sources and complied. Our intent was to use a benzene concentration representative of commonly reported values rather than the maximum value in site investigations. TPH was not included as a component. This shows the effect that CH_4 alone has on benzene attenuation. Including 200 g/m^3 TPH in these cases would directionally, but not significantly, reduce the amount of benzene attenuation. Not including TPH is a more conservative approach for assessing impacts of methane on benzene vapor intrusion.

To simulate the impact of gas advection on migration and intrusion of subsurface CH_4 and benzene, different source gas pressures (0.1, 1, 5, 10, 50, 100, 150, 200 Pa) were selected (Table 1). Note that the higher simulated pressures may be rare in the high-permeability sandy soils assumed here, but were considered to delineate the potential effects of high-ethanol blend releases under a wide range of conditions. To our knowledge, data on soil gas pressures in the source zone of fuel ethanol releases are not available. However, according to a numerical simulation of soil gas data at a crude oil release site, methanogenesis in the source zone could generate about 1 Pa of source pressure.[18] Landfill sites could have as high as several thousand Pa of source pressure.[41] As a readily degradable compound, the release of large volumes of fuel ethanol usually stimulates much stronger methanogenic activity than petroleum hydrocarbons, but is unlikely to be stronger than methanogenesis at landfills. Therefore, the source gas pressure at a fuel ethanol impacted aquifer is likely to be higher than that at a petroleum spill site and smaller than that at a landfill site.

Assumptions and Limitations of This Modeling Study. This modeling study has following assumptions: (1) the source zone is nondepleting and infinite; (2) the building is modeled as a perfectly mixed continuously stirred tank reactor (CSTR); (3) no NAPL phase is present in the transport domain (it could be present at the source zone) and chemicals partition among gas, dissolved and adsorbed phases only; and (4) density-driven advective transport is neglected.

Similar to previous studies,[25,32,33] all simulations reported herein assume homogeneous and steady-state conditions. However, real site geologic conditions are usually heterogeneous, complex, and site-specific.[34] Nonsteady state environmental factors such as barometric pressure fluctuations and wind load on buildings could affect the migration and intrusion of gas contaminant into buildings.[42,43] Although a modified version of the Abreu and Johnson model is capable of simulating vapor intrusion during transient wind load and barometric pressure fluctuations,[44] such simulations are time-consuming and require significant computational resources. Therefore, this study simulates quasi-steady scenarios representing short-term average indoor concentrations during periods of net airflow is into the building enclosure. Finally, note that all simulations assumed perimeter cracks, and results may be different for buildings with more centrally located cracks.

Diffusion in this model follows Fick's law, which presumes low concentrations for each soil gas constituent and that their individual fluxes are independent. This is addressed in these model scenarios by specifying, indirectly, through pressures at the model boundaries, a constituent-independent Darcy velocity field for the soil gas. This is a reasonable assumption for the nearly equimolar (and nearly equal volume) aerobic reactions included in the model domain. Also, the effect of displaced, passive nonreactive soil gases (mainly N_2) on flux estimates is not addressed; this would require a different approach, such as a "dusty gas" model.[45,46]

Finally, the model presumes a separating and attenuating layer of vadose-zone soil between the methanogenic source and the building enclosure. Direct entry of methane gas into a building, such as gas evolution through an untrapped or unvented well, sump, or sewer connected to a building, is not evaluated.

RESULTS AND DISCUSSION

The Explosion Risk for Diffusion-Driven CH_4 Migration Is Negligible. If diffusion is the major mass transport process in the deeper vadose zone (advection may occur in the vicinity of the basement due to building depressurization), CH_4 is unlikely to build up to the lower flammable level (5% v/v) in overlying buildings. CH_4 indoor concentrations are simulated for different CH_4 source concentrations and separation distances, with and without biodegradation (Figure 2). Simulated CH_4 indoor concentrations increase as source concentrations increase and separation distance decreases. However, even under the worse-case scenario examined here (i.e., CH_4 source concentration is 75% v/v, the separation distance is 3 m, and no biodegradation), the simulated CH_4

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Table 2. Simulated Air Flow Rate and CH_4 Flux with Different Source Pressures for a Separation Distance of 3 m[a]

	air flow rate (L/min)			CH_4 flux (g-CH_4/m^2/s)		
pressure (Pa)	Q_{source}	$Q_{surface}$	$Q_{building}$	J_{source}[b]	$J_{surface}$[c]	$J_{building}$[d]
0	0	−0.9[e]	0.9	2.5×10^{-4}	1.2×10^{-5}	1.8×10^{-4}
0.1	1.1	−0.1	1.2	2.5×10^{-4}	1.2×10^{-5}	2.4×10^{-4}
1	4.5	3	1.3	2.8×10^{-4}	1.9×10^{-5}	2.8×10^{-4}
5	20	18	1.9	4.0×10^{-4}	6.9×10^{-5}	4.7×10^{-4}
10	39	36	3	6.0×10^{-4}	1.9×10^{-4}	7.4×10^{-4}
30	114	109	6	1.6×10^{-3}	9.2×10^{-4}	1.8×10^{-3}
50	190	183	9	2.7×10^{-3}	1.8×10^{-3}	2.9×10^{-3}
100	379	366	16	5.4×10^{-3}	4.0×10^{-3}	5.3×10^{-3}
150	568	549	24	8.1×10^{-3}	6.1×10^{-3}	7.8×10^{-3}
200	757	732	31	1.1×10^{-2}	7.9×10^{-3}	1.0×10^{-2}

[a]The source contains 75% (v/v) CH_4 and 200 g/m^3 TPH. [b]J_{source} was calculated by dividing mass flow rate emitted from the source (g-CH_4/s) by the source area (48 m × 48 m). [c]$J_{surface}$ was calculated by dividing mass flow rate across the soil surface (g-CH_4/s) by the soil surface area (48 m × 48 m −10 m × 10 m). [d]$J_{building}$ was calculated by dividing mass flow rate into buildings (g-CH_4/s) by the building foundation area (10 m × 10 m). [e]The negative value for $Q_{surface}$ means the air flows from atmosphere into the soil due to building depressurization effect.

indoor concentration is still much lower (>20-fold) than the lower flammable level for CH_4 (5% v/v) (Figure 2).

Methanotrophic bacteria could significantly attenuate the mass flux of CH_4 in the unsaturated zone and reduce indoor concentrations and the associated explosion risk (compare Figure 2, parts (a) and (b)). Figure 3 shows the simulated scenarios with a separation distance of 6 m and a TPH concentration of 200 g/m^3. If the CH_4 source concentration is lower than 1.5% (v/v), then more than 99% of CH_4 flux emitted from the source (J_{source}) is degraded before reaching the ground surface, and the percent of source flux that is biodegraded (J_{bio}/J_{source}) does not change with increasing CH_4 source concentrations (Figure 3). If the CH_4 source concentration is higher than 1.5% (v/v), then the percentage of source flux that is biodegraded (J_{bio}/J_{source}) decreases as the CH_4 source concentration increases. However, even when the CH_4 source concentration reaches 75% (v/v) and the vapor source is shallow (1 m separation distance), biodegradation still attenuates more than 82% of the upward CH_4 flux (SI Figure S2). Methanotrophic bacteria are widespread in natural environments (they are especially abundant in soil).[47] Our modeling results corroborate previous pilot-scale experimental results[3] and indicate the importance of methanotrophic activity to attenuate CH_4 generated from ethanol plumes and reduce its potential to reach the surface. Note that while the simulated indoor CH_4 concentration does not reach the lower flammable level, the subslab soil gas concentration does (SI Figure S4). This may create other concerns not examined in this study (e.g., CH_4 build up in less ventilated smaller confined spaces).

CH_4 explosion risk in nonpressurized flow can also be assessed using the attenuation factors assembled from the US EPA vapor intrusion database, which contains indoor air measurements of toxic vapors coupled with subslab soil gas, exterior soil gas groundwater, or crawlspace measurements for 913 buildings at 41 sites in 15 U.S. states. [37] By compiling this database, a recent EPA report recommends 0.01 as a conservative subslab attenuation factor (the ratio of indoor air concentration to subslab soil gas concentration, $AF_{subslab} = C_{indoor}/C_{subslab}$) for chlorinated volatile compounds.[37] Using this attenuation factor and assuming that the source of CH_4 concentration is 75% (v/v), the corresponding CH_4 indoor concentration is only 0.75% (v/v), which is much lower than the lower flammable limit.

Potential Explosion Risk Increases Significantly for Advection-Driven CH_4 Migration. A recent field study showed that the accumulation of ethanol-derived methane and carbon dioxide in the source zone could generate a pressure gradient and cause significant advective gas transport in the subsurface.[4] They reported up to 6.3×10^{-3} g/m^2/s of surficial CH_4 efflux and 6% to 22% (v/v) of CH_4 concentration in the flux chamber emplaced at a site impacted by the release of a large volume of denatured fuel-grade ethanol. [4] Our simulations corroborate this field study, indicating that if methanogenic activity near the source zone is sufficiently high to cause significant advective gas transport, CH_4 could build up to flammable levels (>5% v/v) in overlying buildings. Scenarios with different source gas pressures (0, 0.1, 1, 5, 10, 30, 50, 100, 150, and 200 Pa) and separation distances (1, 3, 6, and 13 m) were simulated (Figure 4). SI Figure S4 shows that increases in source pressure significantly change the soil gas pressure field distribution, which may change the subsurface air flow and contaminant mass flux. Table 2 lists the simulated air flow rate and CH_4 flux for the separation distance of 3 m. The simulated air flow rate and CH_4 flux for other separation distances are listed in SI Tables S5 and S6, respectively. Simulated CH_4 indoor concentrations for all separation distances are shown in Figure 4. As source gas pressures increase from 0 to 200 Pa, simulated air flow rates from the source (Q_{source}) for a separation distance of 3 m increased from 0 to 757 L/min (Table 2), resulting in a 44-fold increase in the CH_4 flux emitted from the source (J_{source}) (Table 2). As a result, the simulated CH_4 flux into buildings ($J_{building}$) increases by 56-fold (Table 2), which causes the CH_4 indoor concentrations to increase by more than 60-fold for the separation distance of 3 m (Figure 4). When the separation distance is equal to or less than 3 m and the source gas pressure is higher than 100 Pa, simulated CH_4 indoor concentrations exceed the 5% v/v flammable level, resulting in a potential explosion risk (Figure 4). In this study, we have neglected advective transport due to changes in density. For high CH_4 source concentrations, lower densities relative to air may also contribute to increased upward CH_4 mass fluxes in addition to high source pressures.

To put the simulated CH_4 fluxes data into context, measured CH_4 surficial efflux data in natural and impacted environments are listed in Table 3. The simulated $J_{surface}$ for the 75% (v/v) CH_4 source concentration varied by 6 orders of magnitude with different separation distances and source pressures; e.g., 5.1 ×

Table 3. Measured CH_4 Flux in Natural and Contaminated Environments

environments	flux (g-CH_4/m^2/s)	reference
rice field	5.7×10^{-7} to 1.2×10^{-5}	50,51
wetlands	8.0×10^{-8} to 4.5×10^{-5}	52,53
lagoon	3.1×10^{-9} to 6.8×10^{-5}	54,55
peat	1.0×10^{-7} to 3.6×10^{-5}	56,57
E95[a] impacted aquifer	2.2×10^{-5} to 6.3×10^{-3}	4
landfill	2.4×10^{-8} to 4.6×10^{-2}	58,59

[a]Ethanol denatured with 5% gasoline.

10^{-8} g/m^2/s for 0 Pa source pressure and 13 m separation distance to 1.1×10^{-2} g/m^2/s for 200 Pa source pressure and 1 m separation distance (SI Table S3). Methane mass fluxes lower than 10^{-3} g/m^2/s are typical for natural methanogenic environments (Table 3). Values greater than 10^{-3} g/m^2/s have been observed at landfills and sites impacted by ethanol blend fuel releases (Table 3).

Oxygen Consumption during CH_4 Biodegradation in the Vadose Zone Increases Benzene Vapor Intrusion Potential. Baseline simulations indicate that if there is no CH_4 generation in the source zone, 0.1 g/m^3 of benzene will not cause a vapor intrusion problem even for a shallow source (e.g., 1 m separation distance). However, CH_4 generation near the source could significantly increase benzene indoor concentrations (Figure 5). As CH_4 source concentrations increase from 0 to 75% (v/v), benzene indoor concentrations increase by 15-, 1.0×10^4-, 6.2×10^7-, and 6.3×10^{16}-fold for separation distances of 1, 3, 6, and 13 m, respectively. Although previous studies indicate a low benzene vapor intrusion potential when the separation distance is larger than 10 m,[32,39,40] our simulations infer that if very high CH_4 concentrations (e.g., 75% v/v) are generated and subsequently consumed in the vadose zone (resulting in O_2 depletion), even a separation distance of 13 m may result in some benzene vapor intrusion and possibly exceed the EPA indoor air screening level of 3.1×10^{-5} g/m^3 that corresponds to a 10^{-4} lifetime risk[48] (Figure 5). Note that US EPA provides target indoor air concentrations for three different lifetime risk levels: 10^{-4}, 10^{-5}, and 10^{-6}. Our inferences about the significance of benzene vapor intrusion may be different at other risk levels.

Inhibition of benzene biodegradation as methanotrophs consume vadose-zone oxygen is the major reason for the increase in benzene vapor intrusion. Biodegradation attenuates more than 90% of the benzene flux emitted from the source (Figure 6). As CH_4 source concentrations increase from 0.015% (v/v) to 75% (v/v), the benzene flux that is bioattenuated (J_{bio}) decreases 25-fold, and the percent of benzene source flux that is biodegraded (J_{bio}/J_{source}) decreases from >99.99% to 90.5%. This leads to a significant increase (>-10^7-fold) in the benzene flux intrusion into buildings ($J_{building}$) and transport across the soil surface ($J_{surface}$), despite a decrease in the benzene flux emitted from the source (J_{source}) by at least 22-fold due to a lower benzene concentration gradient between the source and the subslab (Figure 6).

Depletion of O_2 is the major reason for decreases in benzene biodegradation.[49] Under aerobic conditions, CH_4 degrades faster than benzene (see SI Table S1 footnotes). As the CH_4 source concentration increases from 0.015% (v/v) to 75% (v/v), the O_2 consumed by CH_4 degradation increases by 180-fold, thus leading to a rapid decrease (25-fold) in the O_2 that is used for benzene degradation, even though the total O_2 flux entering into the system increases by more than 50-fold due to a lower O_2 concentration gradient between the soil surface and the vapor source (Figure 7). To better illustrate these processes, changes in the concentration distribution of benzene, CH_4, and O_2 with different CH_4 source concentrations for a separation distance of 6 m are shown in SI Figures S5, S6, and S7.

Benzene vapor intrusion could be exacerbated if methanogenic activity is sufficiently high to cause significant advective gas transport. Benzene indoor concentrations were simulated for different source gas pressures (SI Figure S8). As the source gas pressure increases from 0.1 to 200 Pa, the advective gas transport strips more benzene from the source zone and thus increases benzene indoor concentrations by at least 40-fold for all four separation distances (SI Figure S8).

Implications for Site Assessment and Remedial Action. Guidance for assessing health risks associated with vapor intrusion of petroleum hydrocarbon[39]and chlorinated solvents[37] is relatively well established, but guidance for assessing explosion risks associated with methane vapor intrusion from ethanol fuels is limited. Using a 3-D numerical model, this study indicates that methane is unlikely to reach flammable levels in overlying buildings if diffusion is the major mass transfer process in the deeper vadose zone. However, our simulations show that if methanogenic activity is sufficiently strong (as might occur for releases with high ethanol content) to increase gas pressure and cause advective gas transport near the source zone, CH_4 could build up to potentially flammable levels (>5% v/v) in overlying buildings.

The U.S. EPA's guidance document for petroleum vapor intrusion is based on field measurement data at retail service station sites,[39] including sites for which E10 (10% ethanol fuel) would have been used for decades. According to this document, regular gasoline or E10 releases are unlikely to cause a flammability hazard, unless the gasoline is in the building or in direct contact with the foundation. Therefore, the inferences of our simulations are mainly applicable to releases of high-ethanol content fuels, including E20 up to E95.

Conceptual models of vapor intrusion usually assume that diffusion is the major vapor transport mechanism in the deeper vadose zone, and that advection plays an important role only in the vicinity of the building basement (due to building depressurization This study indicates that advective soil gas transport generated from the accumulation of fermentative biogas could play an important role in the subsurface vapor transport. Therefore, gas advection should be considered for fuel ethanol impacted sites or other sites where strong fermentation activities exist. Conditions that are conducive to advective gas migration through the vadose zone include (1) high soil moisture content that inhibits diffusion, (2) a shallow source zone, (3) a soil surface that is paved or covered by a large building foundation that inhibits O_2 inflow, (4) release of high ethanol blends (e.g., E85), and (5) a large volume release where the source is not removed.

The U.S. EPA is trying to establish vertical separation criteria for screening vapor intrusion risk at petroleum release sites. Using available field measurement data, recent EPA guidance indicates that 5.5 to 6.1 m of separation distance could reduce soil benzene concentration below a defined soil gas threshold (100 μg/m^3) at 95% of sites that have an NAPL source present.[39] Although that document is based on comprehensive site data, our modeling results indicate that under our simulated conditions, the presence of high concentrations of CH_4 originating from releases of high ethanol blends may deplete

the available soil O_2 and inhibit benzene aerobic degradation, thus resulting in a higher benzene vapor intrusion potential than suggested in the current EPA guidance for gasoline fuel release sites. If methanogenic activity is sufficiently high to generate advective gas transport, then the benzene intrusion rate would be even higher. Therefore, the proposed EPA separation distance criteria for conventional gasoline releases may not apply to higher ethanol content fuels such as E85 and E95.

■ ASSOCIATED CONTENT

Supporting Information

Details on model input parameters; simulated air flow rates; and CH_4 flux with different source pressures for different separation distances, changes in pressure field distribution, and concentration distribution of benzene, CH_4, and O_2. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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