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DIFFERENTIAL MIGRATION OF METHANE AND ATTENUATION OF SULFUR ODORANT IN SOIL

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Abstract: *In the practice of natural gas distribution network operation, a frequent discrepancy is observed between instrumentally detectable methane and the intensity of the odor associated with the sulfur odorant. In underground leaks, the soil may remain olfactively impregnated near the source, while at the surface or along preferential pathways, methane is predominantly measured. In non-specialist language, the phenomenon is sometimes explained by the phrase "the soil acts as an osmotic filter, and the mercaptan remains in the soil because its molecule is larger than that of methane." However, this formulation is scientifically improper.*
This paper reframes the phenomenon within the correct terminology of gas transport in porous media. Advection controlled by the pressure gradient, molecular and effective diffusion, sorption on mineral and organic surfaces, partial dissolution in pore water, chemical oxidation, and biological attenuation are analyzed separately. Based on the properties of methane and a model mercaptan such as methanethiol, as well as on the literature regarding odor fade, it is demonstrated that the difference in molecular mass and kinetic size can have at most a secondary role. The dominant explanatory mechanism is the selective interaction of sulfur odorant compounds with the porous medium and the reactive phases within it, combined with chemical transformations that reduce the intensity of the olfactory signal.
The applied conclusion is that the absence of a strong odor does not exclude the presence of methane in a dangerous concentration. For this reason, the assessment of an underground leak must be based on instrumental detection, on the interpretation of geotechnical conditions, and on understanding the odorant attenuation phenomenon, not exclusively on olfactory perception.

Keywords: *methane; mercaptans; methanethiol; tert-butyl mercaptan; odor fade; porous media; adsorption; oxidation; diffusion; advection; natural gas; underground leak*

Nomenclature

Symbol	Meaning	Observation
C	concentration	concentration of a gaseous species in the gas phase
D_{eff}	effective diffusion coefficient	includes effects of porosity, tortuosity, and water saturation
q_g	apparent velocity of the gas phase	advective parameter related to the pressure gradient
R_i	attenuation/reactivity term	includes sorption, dissolution, oxidation, and biodegradation

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Table 1. Comparative properties relevant to migration in soil

Parameter	Methane	Methanethiol	Technical significance
Chemical formula	CH_4	CH_3SH	Structural differences indicate distinct chemical classes, not just different sizes.
Molecular mass	16.043 g/mol [1]	48.11 g/mol [2]	The model odorant is heavier, but this aspect alone does not explain behavior in soil.
Functional role	major component of natural gas [3]	example of thiol / mercaptan; in practice, TBM, THT, mixtures are also used [4, 5, 6]	The pedagogical molecule must be separated from real commercial odorization formulations.
Attenuation in porous media	lower compared to odorant, unless microbial oxidation and particular conditions intervene [7, 8]	higher through sorption, dissolution, and oxidation [9, 10]	This is where the technical explanation of odor fade appears.

Table 2. Factors that differentially modify methane migration and the olfactory signal

Factor	Effect on methane	Effect on sulfur odorant
High humidity	reduces diffusivity and may divert migration towards more permeable pathways	favors dissolution/absorption and increases attenuation
Clay and fine fraction	decreases permeability and slows propagation	increases sorption and olfactory retention
Iron oxides/hydroxides, rust	limited direct effect on methane	can catalyze mercaptan oxidation and reduce odor intensity
Concrete and porous materials	can redirect migration through joints and voids	can contribute to odor fade in contact with gas
High pressure at source	increases the advective component and extends the plume	may initially transport the odorant as well, but does not cancel reactive attenuation

1. Introduction

In the case of an underground leak from a distribution pipe, the released gas no longer circulates in a controlled system of pipes and equipment, but enters a complex, heterogeneous, and multi-phase porous medium, composed of mineral particles, organic matter, interstitial water, and pore air. From this moment on, the mixture's composition and the trajectory of each component depend on the medium's properties and local flow conditions. Therefore, a significant difference may arise between the composition of the gas leaving the pipe and the composition of the gas reaching the surface.

The popular explanation that the soil acts as an osmotic filter is incorrect for two fundamental reasons. Firstly, osmosis is a process defined for the transfer of a solvent through a semipermeable membrane, under the action of a chemical potential gradient, usually between liquid solutions. Secondly, underground gas leaks develop in natural porous media, without an actual semipermeable membrane and without the classical conditions of the osmotic phenomenon. The appropriate conceptual framework is that of gas transport in soil and reactive attenuation in the porous medium.

The relevant technical problem is, therefore, the following: why can methane be detected at the surface, while the odor of the sulfur odorant is much diminished or even absent? The answer requires a clear separation of several mechanisms: advective flow near the source, diffusion at greater distances, selective sorption of odorant compounds, their dissolution in pore water, oxidation on reactive surfaces, and sometimes biological transformation.

It is important to note that natural gas distribution pipelines are typically buried at depths of 0.9–1.5 m, in accordance with regulatory standards [11]. Consequently, the vertical distance that leaking gas must travel to reach the ground surface is relatively short, usually not exceeding 2 m. However, lateral migration through permeable backfill, utility trenches, or soil layers can extend the total travel distance to several meters. Therefore, while the primary path is vertical, the overall transport distance can vary. The following analysis considers both vertical and lateral components, with an emphasis on the fact that significant odorant attenuation can already occur over the short vertical segment due to strong interactions with soil and construction material.

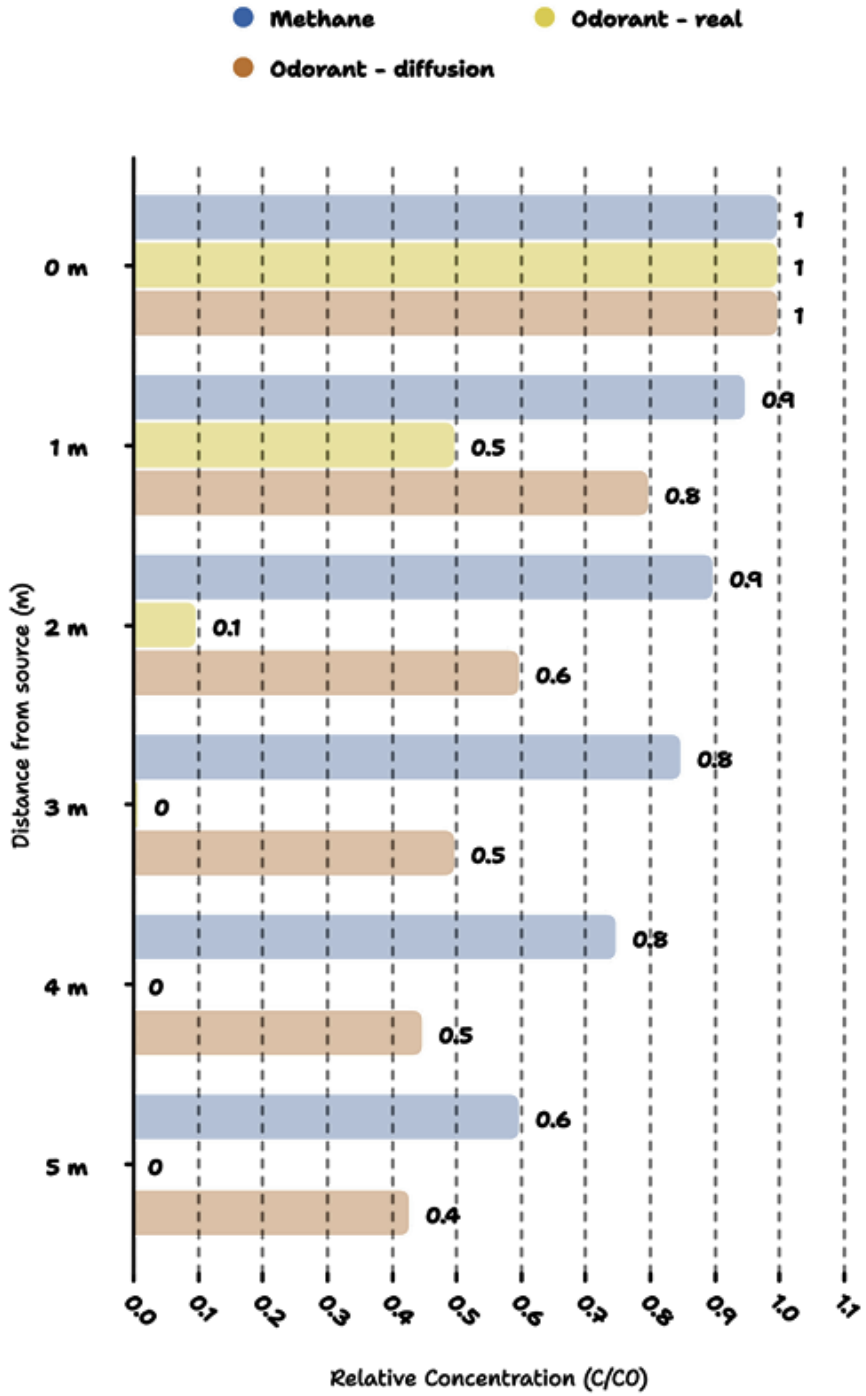

Fig. 1. Conceptual diagram illustrating the differential migration of methane and selective attenuation of sulfur odorant in soil. Methane (blue arrows) migrates preferentially through connected gas-filled pores, while the odorant (red arrows) is retained by adsorption on clay particles, oxidation on rust, and dissolution in pore water. Preferential pathways (trenches, backfill, utility ducts) can redirect gas flow. The surface expression shows methane detected instrumentally but odor absent due to attenuation.

2. Composition of natural gas and nature of odorants

Natural gas distributed through pipeline networks is composed predominantly of methane, which is intrinsically odorless. For operational safety, the distributed gas is therefore intentionally odorized so that leaks can be recognized by smell before hazardous concentrations are reached [3]. This safety function is essential, but it does not imply that the odorant will migrate through soil with the same persistence as methane. Once gas escapes from a buried pipe into an unsaturated porous medium, methane and the added odorant are carried by the same macroscopic gas flow field, yet they do not experience the same attenuation mechanisms. As a result, the gas reaching the ground surface may remain methane-rich while the sulfur odor becomes weak or even absent [9, 10].

In common language, "mercaptan" is often used for the entire odorization system, but this simplification hides a more nuanced technical reality. Commercial odorization of natural gas relies on organosulfur compounds such as methanethiol, tert-butyl mercaptan (TBM), tetrahydrothiophene (THT), or formulated mixtures selected for recognizability, stability, and compatibility with gas infrastructure [4]. The literature shows that TBM and THT are treated as distinct odorant species with different sorption and removal behavior [5, 6], which confirms that a scientific discussion should use the broader term **sulfur odorant** unless a specific compound is meant.

For conceptual comparison, it is useful to relate methane to a simple mercaptan, such as methanethiol. Methane has a molecular mass of 16.043 g/mol [1], while methanethiol has a molecular mass of 48.11 g/mol [2]. The difference is real and significant, but it cannot be elevated to the rank of a unique explanation. In transport through porous media, molecular mass intervenes together with a host of other properties: volatility, affinity for surfaces, relative solubility in water, reactivity to oxidation, and compatibility with organic materials and corrosion products.

From the standpoint of leak behavior in soil, methane and sulfur odorants must be treated as chemically distinct species with different attenuation pathways. Methane is the dominant constituent of natural gas and the primary hazard indicator, whereas the odorant is an added warning signal. This distinction is central to the logic of the article: the hazard is controlled by methane concentration, but olfactory detection depends on whether enough odorant survives migration through the porous medium to reach a receptor location.

Representative sulfur odorants used in practice include:

- **Methanethiol (CH_3SH)** – often useful as a model thiol in conceptual discussion;
- **tert-Butyl mercaptan (TBM)** – a common network odorant;
- **tetrahydrothiophene (THT)** – also widely used in gas odorization systems;
- **commercial mixtures** – combine sulfur compounds for olfactory performance and operational robustness [4, 5, 6].

These compounds should not be treated as interchangeable. Existing research shows that TBM and THT differ in adsorption and removal behavior on sorbent materials [5], while broader odorization research emphasizes that different odorants interact differently with system materials and operating conditions [6]. For that reason, the manuscript refers to **organosulfur odorants** in general, while acknowledging that methanethiol is mainly a useful model compound rather than a universal surrogate for all practical odorants.

Key physicochemical contrasts controlling differential migration

The critical issue is not whether methane and sulfur odorants obey different transport laws, but whether they experience different **sink terms** once they enter soil.

First, *gas-phase diffusivity* differs among species, and heavier odorant molecules generally diffuse more slowly than methane. However, molecular mass alone cannot explain strong field-scale odor depletion. In porous media, effective mobility depends on air-filled porosity, tortuosity, pore connectivity, and water saturation.

Second, *gas–water partitioning* is far more consequential for sulfur odorants than for methane. Once an odorant partitions into pore water or wet surface films, it is removed from the mobile gas phase and becomes subject to slower aqueous transport, sorption, and degradation.

Third, *sorption and interfacial retention* can selectively delay or deplete sulfur odorants. Studies confirm that TBM and THT can be strongly retained by reactive or sorptive materials [5], and that odorant performance depends on interactions with materials rather than on simple volatility alone [6].

Fourth, **c***hemical transformation* may further reduce odor intensity. Organosulfur compounds can be oxidized, chemisorbed, or transformed on reactive surfaces such as corrosion products, mineral oxides, or infrastructure materials. This matters because such processes remove not only mass from the gas phase but also olfactory potency [4, 9].

Fifth, *sensory detection and analytical detection are not equivalent*. A human observer responds to the concentration of odorant that survives transport, whereas methane hazard must be evaluated instrumentally. Therefore, weak odor does not prove weak methane migration, and odor absence does not prove methane absence [10, 12].

Minimal transport framing

At the Darcy scale, the transport of gaseous species i may be represented by:

$$\mathbf{N}_i = C_i \mathbf{q}_g - D_{\text{eff},i} \nabla C_i \tag{1}$$

with the corresponding local mass balance:

$$\frac{\partial(\varepsilon_g C_i)}{\partial t} + \nabla \cdot \mathbf{N}_i = -R_i \quad (2)$$

where C_i is the gas-phase concentration, $\mathbf{q}_g$ the bulk gas velocity, $D_{\text{eff},i}$ the effective diffusion coefficient, ε_g the air-filled porosity, and R_i a net sink term that may include partitioning, sorption, interfacial retention, chemical reaction, and biodegradation.

This formulation expresses the central asymmetry directly: methane and sulfur odorants may share the same advective field $\mathbf{q}_g$, but the odorant generally experiences a much larger sink term:

$$R_{\text{odorant}} \gg R_{\text{CH}_4} \quad (3)$$

under many subsurface conditions. That asymmetry is exactly what produces differential transport and explains why methane can remain instrumentally detectable while the odor signal fades along the migration path [9, 10, 13].

3. Fundamentals of gas transport in porous media

Immediately after the leak occurs, the advective regime usually dominates in the vicinity of the pipe. The pressure gradient between the source and the surrounding environment causes the rapid displacement of the gas phase through better-connected pores, through areas with higher permeability, and through possible preferential pathways created by backfills, joints, technical ducts, or other discontinuities. Recent literature on underground natural gas migration shows that transport is predominantly pressure-driven near the leak and progressively becomes diffusion-controlled as the gas moves away from the source [7, 14].

In a simplified formulation, the diffusive flux of a species can be expressed by Fick's first law adapted for porous media: $\mathbf{J}_{d,i} = -D_{\text{eff},i}\nabla C_i$. Unlike diffusion in free gas, $D_{\text{eff},i}$ depends on porosity, tortuosity, gas phase connectivity, and the degree of water saturation. When pores are partially occupied by water, the available cross-section for gas transport decreases, and the effective path becomes more sinuous; consequently, the mobility of all gases decreases, but not identically for all species.

The total flux of a component is not only diffusive: $\mathbf{N}_i = C_i\mathbf{q}_g + \mathbf{J}_{d,i}$. Additionally, for a sulfur odorant, an attenuation term R_i must be introduced, so that the local mass balance reflects the loss from the gas phase through sorption, dissolution, and reaction. From this perspective, the comparison between methane and odorant is not a comparison between two particles trying to cross a filter, but between two species with very different attenuation terms.

Role of moisture and water saturation

Moisture exerts first-order control over gas transport in the vadose zone because it regulates the fraction of pore space available to the gas phase and the continuity of gas-filled pathways. As water saturation increases, air-filled porosity decreases, tortuosity increases, and gas-phase connectivity becomes more fragmented. The direct consequence is a reduction in effective gas diffusivity and, therefore, a slower propagation of volatile species through the porous matrix [8, 15].

Yet moisture does more than reduce mobility. Under unsaturated conditions, the air–water interface becomes an active retention domain. Modeling studies of transport in unsaturated media show that species interacting with interfaces may be retained more strongly at air–liquid interfaces than at the solid matrix alone, and that this interfacial effect becomes increasingly important as moisture conditions alter interfacial area and accessibility [16, 17]. For sulfur odorants, this means that rising water saturation not only suppresses gas-phase migration but also enhances opportunities for gas–water transfer and interfacial loss. Methane is affected by the same structural change in pore geometry, but it is generally penalized less by partitioning and sorption than sulfur-bearing odorants.

This distinction is crucial for interpreting methane–odorant decoupling in soil. A relatively dry and coarse medium may preserve enough gas connectivity for both methane and odorant to migrate detectably, whereas a wetter or finer-textured medium may still allow methane to reach the near-surface zone while preferentially attenuating the odorant through dissolution, retention, and subsequent transformation. Experimental work on methane transport in variably saturated porous media further confirms that saturation significantly changes gas transport behavior by restricting diffusive movement and modifying breakthrough characteristics [18, 19].

Mathematical formulation of gas transport in porous media

To describe the migration of gaseous components through soil quantitatively, it is necessary to introduce the fundamental equations governing mass transport in porous media. These equations separate the contributions of advection, diffusion, and reactive attenuation [13].

The diffusive flux of a gaseous species i in a porous medium is given by Fick's first law adapted for porous media [7, 12]:

$$\mathbf{J}_{d,i} = -D_{\text{eff},i}\nabla C_i \tag{4}$$

where:

- $\mathbf{J}_{d,i}$ = diffusive flux of species i (mol·m^{-2}·s^{-1})
- $D_{\text{eff},i}$ = effective diffusion coefficient of species i in the porous medium (m^2·s^{-1})
- ∇C_i = concentration gradient of species i (mol·m^{-4})

The effective diffusion coefficient $D_{\text{eff},i}$ is always smaller than the molecular diffusion coefficient in free air $D_{0,i}$, due to the porous structure and the presence of water. A commonly used empirical relationship is [15, 20]:

$$D_{\text{eff},i} = D_{0,i} \cdot \frac{\varepsilon_g^{\beta}}{\tau} \cdot f(S_w) \tag{5}$$

where:

- ε_g = air-filled porosity (volume fraction of pores occupied by gas)
- τ = tortuosity factor (>1), accounting for the longer path length through pores [15, 21]
- β = empirical exponent (typically between 1 and 2)
- $f(S_w)$ = a reduction factor that depends on water saturation S_w (usually $f(S_w) = (1 - S_w)^{\gamma}$, with γ between 2 and 3) [20, 22]

The tortuosity factor τ typically ranges from 0.4 to 0.8 in natural soils, with a commonly used empirical value of 0.5 established by Carman. Alternative formulations, such as the Millington-Quirk model, estimate tortuosity directly from porosity and saturation [20, 22].

Equation (5) shows that *increasing soil moisture* (higher S_w) *reduces the effective diffusivity* of all gases, but this reduction is purely physical and affects methane and odorants similarly.

The *total flux* $\mathbf{N}_i$ of a species includes both advective and diffusive components [7, 13]:

$$\mathbf{N}_i = C_i\mathbf{q}_g + \mathbf{J}_{d,i} \tag{6}$$

where:

- $\mathbf{q}_g$ = apparent (Darcy) velocity of the gas phase (m·s^{-1}), driven by the pressure gradient
- $C_i\mathbf{q}_g$ = advective flux

The *mass balance* for a species i in a representative elementary volume of soil, including attenuation processes, is expressed by the continuity equation [13, 14]:

$$\frac{\partial(\varepsilon_g C_i)}{\partial t} = -\nabla \cdot \mathbf{N}_i - R_i \tag{7}$$

where:

- R_i = attenuation term (mol·m^{-3}·s^{-1}), representing all processes that remove the species from the gas phase: sorption onto solid surfaces, dissolution into pore water, chemical oxidation, and biodegradation [13].

Minimal two-species model

To make the methane–odorant contrast explicit, a minimal model can be formulated for methane (M) and a representative sulfur odorant (S):

$$\frac{\partial(\varepsilon_g C_M)}{\partial t} + \nabla \cdot (C_M\mathbf{q}_g - D_{\text{eff},M}\nabla C_M) = -R_M \tag{8}$$

$$\frac{\partial(\varepsilon_g C_S)}{\partial t} + \nabla \cdot (C_S\mathbf{q}_g - D_{\text{eff},S}\nabla C_S) = -R_S \tag{9}$$

The formal symmetry of these equations is important: both species are transported by the same porous medium and can be exposed to the same bulk gas flow field. The divergence appears in the sink terms and, in practice, also in the effective transport coefficients.

For methane, a minimal attenuation term may be written as:

$$R_M = k_{\text{bio},M} C_M \tag{10}$$

where $k_{\text{bio},M}$ is an effective first-order rate coefficient that primarily represents biological oxidation when oxygen is available. Methane oxidation in unsaturated porous media is well established and can materially affect concentration profiles, but its magnitude depends on environmental conditions and residence time [16, 18].

For the sulfur odorant, the sink term must generally be broader:

$$R_S = (k_{\text{pw}} + k_{\text{sorp}} + k_{\text{chem}} + k_{\text{bio},S})C_S \tag{11}$$

where k_{pw} represents gas–water transfer and associated depletion, k_{sorp} represents sorption and interfacial retention, k_{chem} accounts for abiotic transformation on reactive surfaces, and $k_{\text{bio},S}$ denotes biodegradation. This decomposition highlights that odorants are subject to several parallel attenuation pathways that are either absent, weaker, or less effective for methane [9, 10, 13].

A further advantage of the two-species model is interpretive clarity. If methane remains detectable while odor is strongly diminished, the explanation can emerge naturally from the inequality $R_S \gg R_M$, or from a combination of larger R_S and lower effective mobility for the odorant. In other words, the same leak can generate a methane plume that persists farther than the olfactory signature because the odorant is selectively removed during transport.

Characteristic time analysis and orders of magnitude

The competition between transport and attenuation can be summarized through characteristic times. For a characteristic travel distance L, one may define a diffusive timescale:

$$t_D \sim \frac{L^2}{D_{\text{eff}}}, \tag{12}$$

an advective timescale:

$$t_A \sim \frac{L}{q_g}, \tag{13}$$

and a reactive timescale:

$$t_R \sim \frac{1}{k_{\text{eff}}}, \tag{14}$$

where k_{eff} is the effective first-order attenuation constant for the species considered. This timescale framework is standard in reactive transport analysis because it expresses, in physically transparent form, whether a compound is more likely to be transported or consumed over the distance of interest [13, 16].

For methane, if $t_{R,M} \gg t_D$ and $t_{R,M} \gg t_A$, then transport occurs faster than attenuation and methane can migrate appreciable distances before substantial depletion. For the odorant, however, if $t_{R,S} \lesssim t_D$ or $t_{R,S} \lesssim t_A$, then attenuation becomes competitive with, or faster than, transport. Under those conditions, odor loss is expected before the gas reaches the surface.

Moisture shifts these inequalities in a direction that usually favors selective odor attenuation. By reducing D_{eff}, water saturation lengthens diffusive transport times for all gaseous species. But because it also promotes gas–water exchange and interfacial retention, it can simultaneously shorten the effective attenuation timescale for sulfur odorants. Hence, the same hydrological change may increase t_D while decreasing $t_{R,S}$, a combination that strongly enhances odor fade [17, 19].

This characteristic-time perspective also clarifies why direct methane monitoring is operationally indispensable. Human odor perception reflects only the residual odorant concentration after all transport and attenuation processes have acted; it does not directly track the methane concentration field.

Non-idealities, heterogeneity, and rate-limited transfer

Although the advection–diffusion–reaction framework is a useful starting point, field behavior in porous media often deviates from ideal Fickian transport. Heterogeneity in grain size, structure, air-filled porosity, and moisture distribution can generate preferential flow paths, dead-end pores, and variable residence times. Under such conditions, apparent plume spreading and attenuation may no longer be captured fully by constant effective coefficients [23, 24].

Rate-limited transfer introduces an additional source of non-ideality. If gas–water partitioning, sorption, or desorption is not instantaneous relative to transport, then local nonequilibrium may arise between the mobile gas phase and less mobile retention domains. Conceptually, sulfur odorants are more vulnerable than methane to this behavior because they interact more strongly with interfaces and surfaces. In such cases, the observed signal can show delayed breakthrough, long concentration tails, or strong local depletion even when bulk gas flow remains active [17, 25].

Biological effects may also alter transport beyond simple first-order consumption. More generally, biological growth in porous media can modify dispersion and produce anomalous transport behavior, showing

that reactive and structural evolution of the medium may feedback on migration dynamics [26]. Even if such complexity is not modeled explicitly, acknowledging it is important because real buried infrastructure environments are rarely homogeneous laboratory systems.

The practical implication is that selective odor attenuation may occur in localized "hotspots" controlled by wet zones, fine-textured layers, corrosion products, concrete interfaces, or organic-rich patches. These local features can disproportionately suppress odorant breakthrough while still allowing methane to migrate through connected gas pathways.

Practical modeling recommendations

For subsequent modeling and interpretation, the following parameters should be treated as species-specific whenever possible:

1. Effective diffusivity $D_{\mathrm{eff},i}$
2. Gas-phase Darcy flux $\mathbf{q}_g$
3. Air-filled porosity ε_g
4. Water saturation S_w
5. Gas–water partitioning parameters
6. Sorption and interfacial retention coefficients
7. Kinetic constants for abiotic transformation and biodegradation
8. Spatial heterogeneity, including buried structures, textural contrasts, and reactive materials

These recommendations are consistent with the broader reactive-transport literature, which shows that predictive accuracy depends not only on the governing equation but also on an appropriate representation of species-specific reactions and heterogeneous parameter fields [13, 16, 23].

Quantitative comparison (Table 3)

A comparative order-of-magnitude summary is useful for separating processes that affect methane and sulfur odorants similarly from those that selectively attenuate the odorant signal. The quantitative contrasts between methane and a model sulfur compound, methanethiol, based on Eqs. (4)–(11), representative parameter choices, and literature-based ranges, are summarized in Table 3. The values are intentionally presented as illustrative order-of-magnitude estimates for mechanistic comparison, not as universal defaults for field prediction or quantitative risk assessment.

Table 3. Comparative order-of-magnitude parameters for methane (CH_4) and a model sulfur compound (methanethiol, CH_3SH) relevant to subsurface migration and attenuation in soil

Parameter	Symbol (unit)	Methane (CH_4)	Methanethiol (CH_3SH)	Observations / justification
Molecular diffusion coefficient in air	D_0 ($cm^2\ s^{-1}$)	0.22	0.18	Based on kinetic correlations; the difference is modest, so molecular size alone cannot explain strong odor loss.
Effective diffusion coefficient in dry sandy soil	D_{eff} ($cm^2\ s^{-1}$)	~ 0.10	~ 0.08	Calculated illustratively from Eq. (5) using representative unsaturated conditions: $\varepsilon_g = 0.3$, $\tau = 2$, $\beta = 1.3$.
Effective diffusion coefficient in moist clay soil	D_{eff} ($cm^2\ s^{-1}$)	~ 0.02	~ 0.015	Illustrative values for reduced gas-filled porosity and stronger moisture limitation: $\varepsilon_g = 0.1$, $\tau = 3$, $f(S_w) = 0.3$.
Soil–gas partition / sorption coefficient	K_d ($cm^3\ g^{-1}$)	<0.1	50–100	Sulfur compounds are expected to sorb much more strongly to clay minerals and organic matter than methane.
Indicative oxidation rate on rust / Fe oxides	k_{ox} (s^{-1})	negligible	$\sim 10^{-3}$–10^{-2}	Illustrative first-order range under reactive-surface conditions; sulfur compounds are much more susceptible to abiotic surface oxidation than methane.
Combined attenuation indicator (relative magnitude)	R_i/R_{CH_4} (–)	1	50–1000	Conceptual aggregated comparison including sorption, gas–water transfer, oxidation, and biodegradation; shown only as an order-of-magnitude contrast.

Note to Table 3. The values reported here are order-of-magnitude estimates intended for illustrative and comparative purposes only. They combine literature-based ranges, simple calculations from Eq. (5), and representative parameter choices for typical soils. Actual field values may vary substantially with soil texture,

mineralogy, organic matter, moisture, temperature, pressure, redox conditions, and the composition of the commercial odorant mixture. The ranges proposed for K_d and k_{ox} should therefore not be extrapolated without site-specific validation. Likewise, the ratio R_i/R_{CH_4} is not a directly measured constant but a conceptual aggregate used to illustrate the likely scale of selective attenuation of sulfur odorants relative to methane under unsaturated heterogeneous conditions. These values are not intended as universal defaults for quantitative risk assessment.

Interpretation. Table 3 supports the central mechanistic point of this section: the contrast between methane detectability and loss of odor signal is not controlled primarily by molecular diffusion, because the difference in gas-phase diffusivity between CH_4 and CH_3SH is relatively small. Instead, the dominant difference arises from selective attenuation processes represented by R_i, including stronger sorption, partitioning into pore water, oxidation on reactive surfaces, and biological transformation. As a result, methane may remain instrumentally detectable even when the sulfur odor signal has been substantially weakened along the migration path. Methanethiol is used here as a model sulfur compound for mechanistic comparison; commercial odorants such as TBM, THT, or blends may exhibit quantitatively different partitioning, sorption, and reactivity.

4. Comparative properties of methane and a model mercaptan

From a physico-chemical point of view, methane is a small, non-polar molecule with weak interactions with most mineral surfaces under ordinary conditions. Its low molecular mass and sub-unity vapor density facilitate its dispersion in air after emergence, but in the subsurface, its behavior is still governed by porosity, saturation, pressure gradient, and preferential pathways. Methane is not absolutely inert, as it can be biologically oxidized in the unsaturated zone, but this attenuation usually has a different spatio-temporal scale compared to the rapid loss of odorant intensity.

Methanethiol, used here as a representative species for the thiol family, has a molecular mass approximately three times greater than that of methane [1, 2]. However, its major relevance derives not only from its mass but from the chemical nature of the sulfhydryl group and the higher polarizability of the molecule. These characteristics increase the probability of interaction with solid surfaces, the liquid phase, and oxidative species present in soil, concrete, or corrosion products.

Industrial reports and safety documents consistently describe that the odorant can be lost through adsorption, absorption, and oxidation, and the degree of the phenomenon depends on the pipe material, the presence of rust, the soil, and concrete [9, 10]. Thus, what practically distinguishes the odorant from methane is not only molecular size, but a much greater susceptibility to processes that remove it from the free gas phase or alter its olfactory signal.

A quantitative look at the differences

To rigorously evaluate the dimensional hypothesis, a quantitative comparison is useful. In air, the molecular diffusion coefficient of methane is approximately 0.22 cm²/s, while that of methanethiol is approximately 0.18 cm²/s, based on kinetic correlations. The difference is only ~18%. This means that in a purely diffusive regime, methanethiol would be only marginally slower.

In contrast, the adsorption capacity on clay can be orders of magnitude higher for mercaptans than for methane. Adsorption constants (e.g., the soil-gas partition coefficient K_d) for organosulfur compounds can be 50 to 100 times higher than those for methane under the same conditions of humidity and mineralogy [5, 13]. This massive difference clearly shows that chemical interaction with the solid surface overwhelmingly dominates the purely physical effect of molecular size.

5. Dominant mechanisms of sulfur odorant attenuation

The phenomenon known in the industry as "odor fade" designates the diminution of the olfactory perception of odorized gas, without this necessarily meaning a proportional reduction of the combustible fraction. PG&E and NIOSH documents explicitly indicate three families of processes involved: adsorption, absorption, and oxidation [9, 10]. In a more general scientific language, these processes can be grouped into sorption onto the solid phase, transfer into the liquid phase, and transformation reactions.

Adsorption is relevant because organosulfur compounds interact more strongly with mineral surfaces, the fine clay fraction, and organic matter than methane does. Soils rich in clay or active metal compounds can retain the odorant more efficiently, reducing the fraction that continues to migrate in the gas phase. Even in the absence of an explicit isotherm model, this selective retention is sufficient to explain why the olfactory signal decreases faster than the methane concentration.

Absorption and dissolution in pore water become important when the soil is moist or when the gas traverses porous materials containing capillary water. The sulfur component can be partially transferred into this phase, where it becomes less available for free gas transport. High humidity thus acts in a dual manner: it reduces the connectivity of the gas phase and increases the probability of odorant attenuation.

Chemical oxidation is perhaps the most important mechanism for understanding why the odor does not faithfully follow methane. Safety literature and PHMSA projects discuss the transformation of mercaptans into disulfides or other products with different olfactory intensity, a process favored in the presence of oxygen, rust, and other reactive surfaces [4, 9]. A molecule that has been oxidized no longer contributes to the olfactory signal in the same way, even if the total sulfur mass remained in the system.

Finally, biological attenuation can be added to these mechanisms. In aerated zones of the soil, microorganisms can oxidize methane and transform organosulfur compounds. However, from the perspective of the immediate manifestation observed in a leak, sorption and oxidation of the odorant are usually the mechanisms that most directly explain the disappearance of the odor before the disappearance of methane.

Speed of attenuation processes (kinetics) and spatial heterogeneity

To understand why in some situations the odor disappears after only a few meters of soil, while in others it persists over long distances, it is necessary to introduce the concept of **kinetics** of attenuation processes. In other words, it matters not only whether the odorant can be retained or transformed, but also how quickly this happens relative to the gas migration speed.

Different mechanisms have very different speeds:

- **Chemical oxidation on reactive surfaces** (e.g., on rust – hydrated iron oxides) can be a relatively rapid process. When odorized gas comes into contact with a rusty surface of a pipe or with an environment rich in oxides, the transformation of mercaptan into disulfides (with a weaker odor) can occur in minutes or hours. This explains the sudden disappearance of odor near old metallic infrastructure [9, 10].
- **Adsorption on clays and organic matter** is, as a rule, a slower process, controlled by the diffusion of the molecule into the particle's micropores. Therefore, a clay soil can retain the odorant over a greater distance, functioning as a kind of slow "chromatograph" that gradually separates the odorous component from the gas phase [5, 13].
- **Dissolution in pore water** has an intermediate speed and depends strongly on the contact surface between the gas phase and the liquid phase. In moist but well-aerated soils, transfer can be efficient; in saturated soils, where the gas phase is discontinuous, the process can be much slower [17, 19].

This difference in speed explains field observations: a leak that crosses a thin layer of sandy soil and then enters a technical duct with fresh concrete surfaces may lose its odor almost instantaneously (due to oxidation/sorption on concrete), while the same leak, migrating exclusively through moist clay soil, may retain a weak but persistent odor at the surface.

Odorant mobility in the liquid phase – a secondary transport pathway

An often-neglected aspect is that, once dissolved in pore water, the sulfur odorant is not permanently immobilized. It can be further transported, this time by the movement of groundwater or infiltration water. This mechanism introduces a possible spatial separation between the two components:

- **Methane**, insoluble and non-adherent, continues to migrate almost exclusively in the gas phase, following paths of least resistance (high permeability, dry zones).
- **The odorant**, partially dissolved, can be entrained by the slow water flow towards completely different areas, such as deeper soil layers, or can be brought back to the surface at another point, through capillarity or evaporation, as the water recedes.

This phenomenon can generate seemingly paradoxical situations in the field, such as:

- Detection of a strong mercaptan odor in a low-lying area after rain, without high methane concentrations being present there.
- The presence of methane in a dry basement, while the odor is perceived in the yard, a few meters away, where the soil is moister and the odorant has been "washed" from the gas phase.

This biphasic mobility (gas and liquid) confirms once again that a simple comparison of molecular size is insufficient to describe the complex trajectory of the odorant in the subsurface.

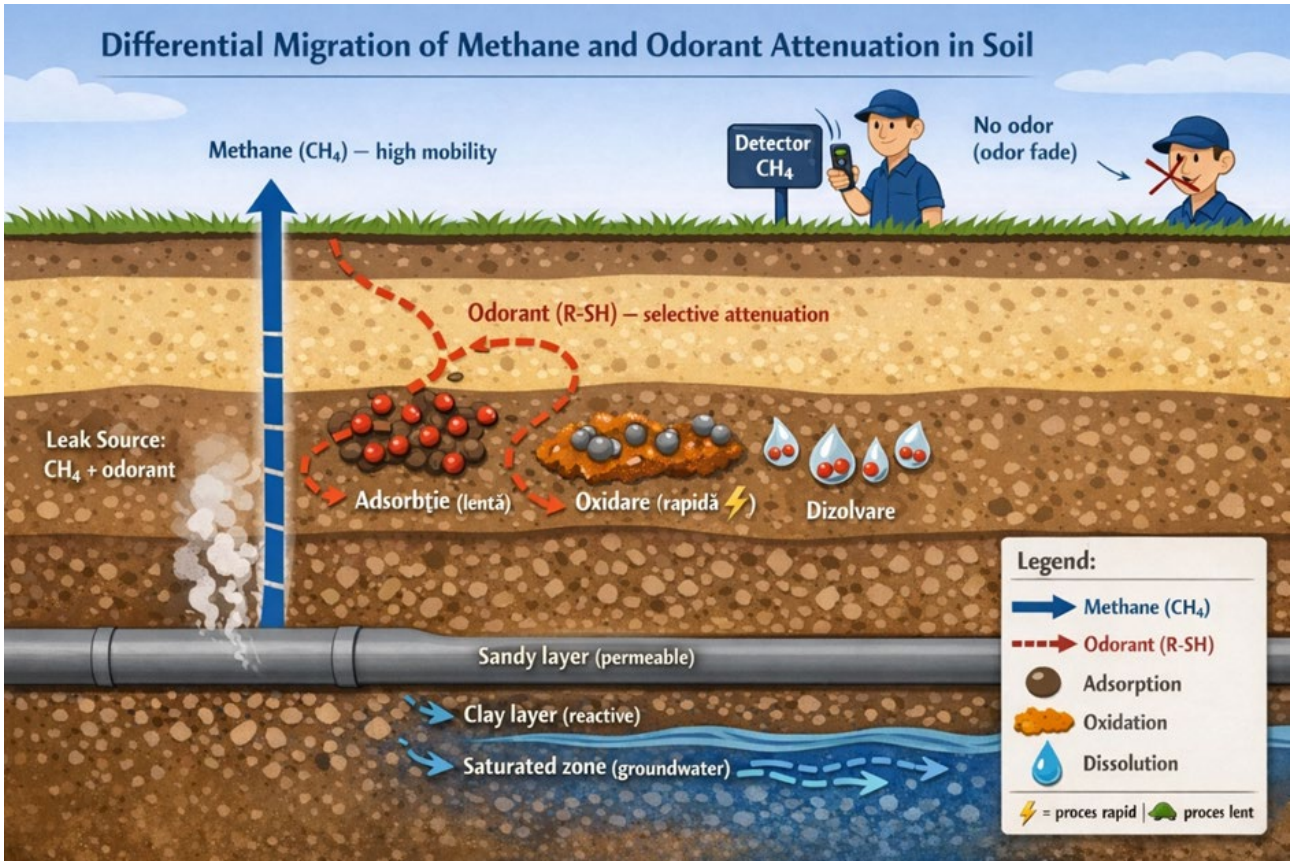

Fig. 2. Comparative concentration profiles for methane and a sulfur odorant (e.g., methanethiol) as a function of distance from the leak source. The x-axis represents the total migration distance, which for vertical transport is limited to 1–2 m (typical burial depth), but may extend laterally through preferential pathways. The y-axis shows relative concentration on a logarithmic scale. The blue solid line represents methane, which declines slowly. The red solid line represents the odorant under realistic conditions, showing rapid decline due to sorption, dissolution, and oxidation. The red dashed line shows the hypothetical odorant concentration if only diffusion (no reactive attenuation) occurred. The light red shading indicates the contribution of reactive attenuation. The light yellow shading marks the hazard zone where methane remains above hazardous levels while the odorant is below olfactory detection thresholds. Methanethiol is used as a model compound; commercial odorants (TBM, THT, blends) may exhibit quantitatively different behavior [5, 6]

6. Monitoring, detection and interpretation for underground gas leaks

Objectives of monitoring

Monitoring of underground natural gas leaks must be organized around three complementary objectives: *safety, diagnosis, and mechanistic interpretation*. The primary safety objective is the rapid detection and assessment of methane accumulation in the subsurface, at the ground surface, and within accessible confined spaces such as basements, manholes, ducts, and utility vaults. This priority is justified by the fact that methane is the flammable component of concern and may remain present even when odor perception is weak or absent due to odor fade. Field and experimental studies show that underground methane migration is strongly influenced by soil moisture, texture, and leak rate, with advection dominating close to the source and diffusion becoming increasingly important farther away [7, 8].

The second objective is *source diagnosis*. Monitoring should not merely confirm that gas is present; it should also help identify the approximate leak location, the geometry of the migrating plume, and the preferential pathways that connect the buried source to the atmosphere or to underground structures. Preferential migration can occur through backfill, pipe corridors, cracks, utility trenches, soil–structure interfaces, and permeable anthropogenic layers, meaning that the point of surface detection is not necessarily the point vertically above the leak source [14].

The third objective is *investigative interpretation*, especially in cases where instrumental methane readings and odor observations appear inconsistent. A weak olfactory signal does not demonstrate the absence of methane. Rather, it may indicate selective attenuation of sulfur odorants by sorption, dissolution, interfacial retention, or chemical transformation in soil and construction materials [9, 10].

Detection principles and instrument selection

A technically sound monitoring program must distinguish between the **hazard indicator** (methane) and the **warning indicator** (odorant). Methane must be measured instrumentally. Sulfur odorants are auxiliary indicators that may support interpretation but cannot replace methane measurements.

For methane detection, preferred instruments depend on campaign purpose and required sensitivity: portable methane detectors for rapid field screening, catalytic bead sensors for flammability-oriented screening, flame ionization detectors and laser-based analyzers for sensitive concentration measurements, and gas chromatography for confirmatory laboratory analysis [7, 27].

Sulfur odorants require more selective analytical methods because they occur at much lower concentrations and are more chemically reactive. Depending on the investigation, these may include electrochemical sensors for sulfur compounds, laboratory gas chromatography, or GC–MS for speciated analysis of odorants such as methanethiol, TBM, and THT [5, 6]. However, such measurements should be interpreted cautiously because odorants can be selectively lost during underground migration.

Method selection should be matched to the operational goal:

- **Screening:** mobile surveys, walking surveys, rapid-response methane detectors
- **Point validation:** portable methane analyzers, shallow soil-gas measurements
- **Quantification:** flux chambers, stationary analyzers, dispersion-based methods
- **Detailed characterization:** depth-resolved soil-gas sampling with laboratory analysis
- **Performance testing:** controlled releases to evaluate method sensitivity and detection probability [28]

Recommended field strategy and protocols

Stage 1 – Rapid screening

The first operational stage should be a rapid spatial survey to identify methane anomalies and prioritize locations for follow-up. This stage may be conducted on foot or by vehicle-mounted instrumentation. Each observation should include metadata: geographic coordinates, date/time, instrument type, sampling height, meteorological conditions, and visible site conditions.

Stage 2 – Local validation

Once a methane anomaly is identified, local validation should be performed using multipoint methane measurements at short radial distances. Shallow soil-gas probes are valuable for investigating vertical and lateral concentration gradients. This step is essential because single-point confirmation is rarely sufficient for reliable interpretation [7, 18].

Stage 3 – Quantification campaign

If release magnitude estimation is required, a dedicated quantification campaign should follow. Appropriate approaches include stationary monitoring, flux chambers, and dispersion-based methods. Multi-hour monitoring windows (e.g., ~6 hours) are recommended to obtain representative estimates, as short-duration snapshots are often unreliable [27].

6.3.4. Stage 4 – Targeted soil-gas sampling

Targeted soil-gas sampling should be performed at key locations to collect paired samples for methane and sulfur odorant analysis. This is particularly informative where field personnel report a mismatch between odor intensity and methane readings, supporting interpretation of odor fade [9, 10].

6.3.5. Stage 5 – Controlled releases and calibration

Controlled-release experiments should be incorporated into method evaluation, training, or validation programs. They provide known release rates and source locations against which detection and quantification methods can be tested [28].

Quantification methods and uncertainties

Emission quantification from underground leaks is substantially more uncertain than anomaly detection. Methane may emerge diffusely over an area, intermittently through preferential vents, or shift spatially with changing conditions. Principal uncertainty sources include temporal intermittency, imperfect knowledge of source geometry, variable atmospheric stability, heterogeneous soil permeability and moisture, preferential pathways, and mismatch between subsurface plume location and surface expression [7, 27].

Odorant detection versus methane detection – practical recommendations

The most important operational principle: *olfactory observations must never substitute for instrumental methane measurements*. The absence of odor does not imply the absence of methane.

This distinction has direct consequences:

- Methane must be measured instrumentally at every suspected leak location
- Sulfur odorant analysis should be used only when investigating odor fade
- Odor presence may indicate strong local interaction, not necessarily the location of maximum methane concentration
- A high methane reading without strong odor is entirely plausible and should be treated as a serious safety condition [10, 12]

Data interpretation and modeling integration

Field interpretation should be supported, where appropriate, by transport modeling that treats methane and odorants as distinct species. Even simplified models can help test hypotheses about moisture, soil texture, source strength, and preferential pathways. However, models are interpretive tools, not substitutes for measurement [16, 23].

Safety protocols and reporting

All monitoring programs must prioritize methane measurements in accessible enclosed or semi-enclosed spaces (basements, manholes, ducts, valve boxes, vaults). If methane concentrations exceed action thresholds, immediate response should include access restriction, ignition source isolation, ventilation where safe, and escalation according to procedures.

Reports must state explicitly that *absence of odor is not evidence of absence of methane*, particularly in underground leak investigations where odor fade is plausible.

Summary operational checklist

1. Perform rapid methane screening
2. Validate anomalies through multipoint measurements
3. Use stationary monitoring, chambers, or dispersion methods for quantification
4. Collect paired methane–odorant soil-gas samples if investigating odor fade
5. Prefer multi-hour measurement windows for emission estimation [27]
6. Use controlled releases to calibrate detection probability [28]
7. Interpret data within a species-specific framework
8. Treat methane instrumental measurement as the primary safety metric

7. Controls on migration and odorant attenuation

Soil texture and permeability

Soil texture exerts first-order control on gas migration. Coarse-grained soils (sands, gravels) provide more continuous pathways, favoring higher effective permeability and more rapid migration. Fine-grained soils (clays) restrict gas mobility due to smaller pores, increased tortuosity, and water retention. Pore-scale modeling confirms that water in narrow pore spaces can sharply reduce methane pathway connectivity, potentially approaching a percolation threshold under water-wet conditions [24]. Clayey or compacted soils may strongly distort leak footprints, delay breakthrough, and increase odorant attenuation.

Water saturation and air–water interfaces

Water saturation is one of the most important state variables. As saturation increases, air-filled porosity decreases, effective diffusivity is reduced, and gas–water contact increases. This dual effect limits methane mobility and enhances selective odorant removal. Partially saturated media exhibit strong coupling between vapor diffusion, capillary geometry, and liquid-phase connectivity [17]. Moist soils create conditions favoring *selective odor fade*, explaining field observations after rainfall or in poorly drained ground.

Sorption, surface reactivity, and construction materials

Mineral grains, soil organic matter, clay surfaces, corrosion products, concrete, masonry, and porous backfill can act as sinks for sulfur odorants. Even when gas follows the same flow path, methane and odorant do not experience the same boundary interactions. Heterogeneous sorption fields can retard some constituents far more strongly [23]. Reactive surfaces such as rusted steel, iron oxides, alkaline concrete, or aged porous materials may remove odorant mass or reduce olfactory potency without equivalent methane loss. This is especially relevant in urban settings where plumes interact with vaults, ducts, utility corridors, and cementitious materials.

Preferential pathways and underground infrastructure

Gas plumes rarely move through homogeneous soil alone. Excavation backfill, pipe trenches, bedding layers, utility ducts, drainage corridors, foundation interfaces, cracks, and service conduits create preferential pathways with conductivity much higher than surrounding soil. These structures redirect gas laterally, toward confined spaces, or allow emergence far from the vertical above-source position. A pathway lined with inert coarse backfill permits efficient gas transmission, whereas a pathway intersecting concrete walls, corroded metal, wet fines, or stagnant water films may produce strong odorant attenuation. Thus, the place of odor perception may reflect a local interaction zone rather than the place of highest methane concentration.

Biphasic transport and secondary aqueous mobility

Once sulfur odorants transfer into pore water, they may undergo slower aqueous transport, local storage, delayed release back into the gas phase, or degradation. This creates biphasic transport: methane remains predominantly gas-phase, while odorant partitions between gas and liquid. In partially saturated media, the geometry of liquid bridges, water films, and capillary-connected regions strongly influences mass transfer [17]. Odorant movement can become temporally and spatially decoupled from methane movement, generating non-intuitive outcomes: odor offset from methane maximum, delayed odor release after wetting, persistent smell in wet depressions, or weak odor at the surface despite continuing methane migration below.

Implications for field detection and interpretation

Because soil properties, moisture, and infrastructure vary strongly, no single field indicator is sufficient. Odor should not be treated as a conservative surrogate for methane. A defensible field strategy includes:

- Multipoint methane measurements
- Depth-resolved soil-gas sampling
- Paired methane–odorant analysis when investigating selective attenuation
- Documentation of soil texture, moisture, and hydrologic conditions [7, 24]
- Inspection of preferential pathways and reactive contact zones
- Species-specific interpretation, recognizing heterogeneous sorption and reactivity [23]

The practical lesson: methane is the hazard indicator; odor is only an auxiliary warning signal whose persistence depends on the pathway.

8. Evaluation of the molecular size hypothesis

The initial statement – "mercaptan is larger than methane, therefore it remains in the soil" – contains a partially true element but erroneously transforms it into a sufficient cause. It is true that a simple mercaptan has a larger molecular mass and, generally, slightly lower diffusive mobility than methane. However, a simple difference in molecular size alone cannot produce the field contrast observed between the presence of methane and the sudden diminution of odor.

The decisive argument is the following: if the sole mechanism were a kind of geometric sieving, then operational factors such as rust, concrete, the mineral composition of the soil, or the presence of water would have reduced importance. Yet technical documents on odor fade precisely underline the role of these factors [4, 9, 10]. This indicates that the dominant process is not a purely geometric one, but a physico-chemical one of selective interaction and transformation.

In scientific terms, the corrected hypothesis must be formulated as follows: the larger molecular mass and kinetic size of the sulfur odorant may contribute marginally to reducing its diffusion speed, but the difference in behavior compared to methane is mainly controlled by sorption, transfer into the liquid phase, and oxidation. Therefore, molecular size is a contributory factor, not the main explanatory mechanism.

9. Operational implications for detection and risk assessment

The most important practical consequence is that the assessment of an underground leak should not be based exclusively on odor. Operators and safety documents explicitly recommend the use of instrumental detection, precisely because odor fade can mask the presence of gas [10, 12]. An area without a strong odor may still contain methane in relevant concentrations, especially if the gas has migrated towards poorly ventilated underground volumes or technical voids.

The correct interpretation of field evidence requires separating the source indicator from the hazard indicator. A persistent sulfur odor from soil or backfill may indicate strong interaction of the odorant with the environment, but does not by itself locate the methane maximum. Conversely, a high methane reading at an emergence point may occur even in the absence of a strong odor, precisely due to the differential attenuation of the odorant along the path.

In terms of risk management, this distinction justifies an integrated approach: measurements at multiple points, correlation with data on soil type and moisture, identification of preferential pathways, and interpretation of the materials with which the gas has come into contact. Without this framework, intuitive expressions like "gas is smelled" or "gas is not smelled" can lead to assessment errors.

10. Conclusions

This study demonstrates that the apparent discrepancy between instrumentally detected methane and the intensity of sulfur odor perceived at the ground surface is best explained by **differential transport and selective attenuation in porous media**, rather than by a simple molecular-size or so-called "osmotic filter" effect. Methane generally behaves as the more mobile and comparatively conservative gas-phase component, whereas sulfur odorants are significantly more susceptible to **sorption on mineral and organic surfaces, partial dissolution into pore water, interfacial retention, and chemical or biological transformation** during subsurface migration [9, 10, 13]. Methanethiol is used here as a representative model for mechanistic analysis, while recognizing that commercial odorants such as TBM and THT may exhibit quantitative differences [5, 6].

A first major conclusion is therefore that **weak or absent odor does not imply the absence of hazard**. Methane may continue to migrate efficiently through connected air-filled pores or along preferential subsurface pathways even when the odorant concentration has already been substantially reduced by interactions with soil, pore water, concrete, corrosion products, or other reactive materials. For this reason, odor cannot be treated as a reliable stand-alone indicator of underground gas presence or safety [10, 12].

A second major conclusion is that **soil texture, water saturation, and subsurface heterogeneity exert first-order control** on the observed behavior. Dry, coarse, and well-connected materials tend to preserve gas-phase mobility and favor methane transmission, whereas wetter and finer-grained soils increase tortuosity, reduce gas-filled connectivity, and enhance gas–water partitioning and retention of sulfur compounds [7, 8, 24]. Under such conditions, odorants may be selectively attenuated even when methane remains detectable in the gas phase.

A third conclusion concerns the role of **preferential migration pathways and reactive infrastructure materials**. Gas does not migrate only through the soil matrix, but may also follow trenches, backfill zones, cracks, basements, ducts, and soil–structure interfaces. In addition, concrete, masonry, rust, and other reactive underground materials may intensify odor fade through sorption, chemisorption, or transformation of sulfur compounds [9, 10]. Consequently, the point of strongest odor is not necessarily the point of highest methane concentration.

From an operational and safety perspective, the main implication is clear: **odor must not be used as the primary criterion for leak assessment**. Reliable investigation of underground natural gas leaks should prioritize **instrumental methane detection**, ideally through multi-point and, where feasible, depth-resolved measurements. Odor observations remain useful, but only as supplementary evidence that must be interpreted together with soil type, moisture conditions, likely preferential pathways, and contact with reactive materials.

Limitations and uncertainties

While the conceptual and mathematical framework presented in this paper provides a robust explanation for the differential migration of methane and sulfur odorants in soil, several limitations and uncertainties must be acknowledged.

First, **quantitative data for commercial odorant mixtures** under realistic field conditions remain scarce. Although studies on TBM and THT sorption exist [5, 6], the behavior of complex odorant formulations in heterogeneous, variably saturated soils is not fully characterized. Partition coefficients, sorption isotherms, and reaction kinetics for these compounds are often extrapolated from laboratory experiments that may not capture the full range of field conditions.

Second, **soil heterogeneity** at multiple scales (pore, local, and site) introduces significant variability in transport parameters. Effective diffusivity, tortuosity, and gas-phase connectivity can vary by orders of magnitude over short distances, depending on texture, structure, organic matter content, and preferential pathways [23, 24]. This heterogeneity limits the predictive power of any simplified model and underscores the need for site-specific characterization.

Third, **transient moisture conditions** (e.g., rainfall, evaporation, water table fluctuations) dynamically alter air-filled porosity, gas connectivity, and gas–water interfacial area [17, 19]. These changes can temporarily enhance or suppress odorant attenuation, making short-term olfactory observations unreliable indicators of long-term methane migration.

Fourth, the **reactive attenuation mechanisms** for sulfur odorants—particularly oxidation on rust and concrete, and biodegradation—are represented here by lumped first-order rate constants. In reality, these processes are often nonlinear, substrate-limited, and dependent on microbial community dynamics, which are beyond the scope of this paper.

Fifth, the **two-species model** (Eqs. 8–11) is a minimal representation that captures the essential asymmetry between methane and odorants but does not account for coupled processes such as competitive sorption, temperature effects, or barometric pumping, which may influence field observations.

Finally, it must be emphasized that **conceptual and numerical models are interpretive tools, not substitutes for direct measurement**. The values in Table 3 are illustrative and should not be used as universal defaults for risk assessment without validation against local soil and site conditions.

These limitations do not invalidate the central thesis—that selective attenuation of sulfur odorants relative to methane is the dominant mechanism behind odor fade—but they highlight the need for further experimental research and the importance of integrating site-specific data into any operational interpretation. Consequently, the framework presented here is best understood as a conceptual and mechanistic explanation for odor fade, supported by order-of-magnitude estimates, rather than a quantitative predictive model. Its primary value lies in guiding interpretation, identifying key controlling factors, and informing the design of field investigations and experimental studies.

In summary, the technically correct interpretation of underground natural-gas leakage is that the subsurface produces **preferential attenuation of sulfur odorants relative to methane**. Methane may therefore remain detectable and hazardous even where odor is weak, delayed, displaced, or absent. Safe practice requires instrumental detection, contextual geotechnical interpretation, and explicit recognition of odor-fade mechanisms in leak assessment.

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