

Article

Time-Evolution of Vapor Intrusion Risk from Gasoline-Derived Multiphase and Multicomponent Sources in Soil

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Abstract

Human health risk assessment of vapor intrusion caused by organic pollutants is commonly based on steady-state predictions of partition and vapor migration in the subsoil. This study develops a pseudo-dynamic, process-based Partition–Diffusion Risk Model (PDRM) using a one-dimensional numerical model for organic mixtures to assess the time evolution of cancer and non-cancer risks, indoor air concentrations, and non-aqueous phase liquid (NAPL) formation. The model has been applied to a low-carbon sandy soil without microbial degradation, which might be a worst-case scenario. Six simulation scenarios combined two source concentrations (1000 and 3000 mg/kg) and three source depths (1, 3, and 5 m) over 30 years. Results show that source depth governs exposure dynamics: shallow contamination poses unacceptable risks rapidly but declines quickly, whereas at greater depths, unacceptable levels appear later and persist throughout the exposure period. NAPL formation may act as a secondary source, sustaining vapor release and extending indoor exposure under high-loading conditions. Multicomponent partitioning induces nonlinear, compound-specific behavior, with the first 3–5 years representing a critical period for rapid risk changes. Conventional models show that neglecting NAPL formation and time variability may lead to an underestimation of cancer risk by up to an order of magnitude. These findings highlight the importance of incorporating depth and time-dependent characterization to reduce uncertainty in vapor intrusion risk assessments.

Keywords: NAPL; partitioning; human health risk

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1. Introduction

Human exposure to air contaminants is largely shaped by indoor environments, where individuals typically spend the majority of their time—often up to about 80% of the time. This makes the concentration of indoor pollutants a critical component of environmental health assessments [1,2]. Within this context, contamination of subsurface soils by volatile organic compounds (VOCs) represents a persistent concern due to their mobility, toxicity, and long-term effects on human exposure [3].

A major source of such contamination is associated with fuel storage in tanks and pipelines. Facilities such as petrol stations often contribute to subsurface hydrocarbon

pollution. This happens through leaks from underground storage tanks (USTs), accidental spills, and emissions related to their infrastructure [4]. These processes result in the presence of gasoline and other petroleum compounds in soils, creating conditions that favor subsequent vapor migration into overlying structures [5].

The significance of VOCs in vapor intrusion (VI) scenarios arises from their physico-chemical properties. Their volatility and partial solubility enable partition across multiple environmental phases, including air, water, and soil, and non-aqueous phase liquid (NAPL) in soil [6–8]. This multiphase behavior enhances their capacity for migration while also influencing their persistence and availability for transfer into the vapor phase. From a toxicological perspective, even low-level exposure has been linked to adverse health outcomes, including carcinogenic and neurological effects [9–11]. Importantly, VOCs rarely occur as single compounds and are usually found as complex mixtures. This creates additional uncertainty due to potential interactions among different components.

Among the various pathways contributing to indoor contamination, vapor intrusion has emerged as a critical but not well-understood subsurface time-dependent process that can lead to inhalation exposure. This process involves the migration of volatile compounds from subsurface sources through the vadose zone into indoor environments in buildings [12]. Transport is primarily driven by vapor diffusion through soil pores, followed by entry into buildings via structural openings such as cracks and utility penetrations [13]. Given its relevance at sites impacted by petroleum hydrocarbons and chlorinated solvents, vapor intrusion represents a key exposure pathway that must be accurately quantified for reliable risk assessment [14].

To address this need, numerous modeling approaches have been developed to estimate indoor air concentrations based on subsurface conditions. These models are especially useful when indoor measurements are limited or not possible. They can be used as screening tools to estimate exposure levels [15]. Within these frameworks, VOCs are commonly grouped into chlorinated compounds and petroleum hydrocarbons. The second group is often linked to non-aqueous phase liquids (NAPLs), such as gasoline mixtures that contain benzene, toluene, ethylbenzene, and xylenes (BTEX) compounds [16] between others.

The behavior of petroleum-derived NAPLs is inherently complex due to the wide range of properties found in their different compounds [6]. Differences in solubility and volatility govern how individual chemicals partition among coexisting phases, thereby influencing their availability for vapor transport [5]. This emphasizes the importance of more accurately representing phase partitioning to capture the release of contaminants into the soil gas phase [8]. Once volatilized, these compounds migrate upward, establishing a direct link between subsurface contamination and indoor air in a building [10,17,18].

In such multiphase systems, the partition of contaminants is controlled by thermodynamic equilibrium relationships. A common approach relies on Raoult's Law, which relates the effective solubility of individual components to their mole fraction in the liquid phase and their pure-component properties [8,19]. This relationship provides a mechanistic basis for estimating vapor-phase concentrations originating from NAPL mixtures, thereby linking subsurface phase behavior to soil gas composition [20]. At the same time, the partition of contaminants across phases is guided by mass conservation principles, which ensure that the total amount of each compound remains constant throughout the system [8,21].

Although diffusion is generally considered the dominant transport mechanism in vapor intrusion scenarios, many existing models fail to adequately couple diffusive transport with time-varying phase interactions. This limitation is particularly relevant in multicomponent systems, where partitioning processes continuously modify contaminant availability in the soil gas phase [22,23]. As a result, simplified models may fail to

capture critical processes that determine indoor air concentrations and the resulting health risks. Indoor air concentrations link subsurface transport to human exposure in vapor intrusion scenarios, requiring models that capture interactions among transport processes and evolving subsurface conditions [24].

Over the past decades, widely used models such as the Johnson–Ettinger (J&E) model and risk-based corrective action (RBCA) approaches have provided practical tools for vapor intrusion assessment [24]. These models typically do not account for partitioning processes that occur dynamically with diffusion. As a result, samples and analytical determination of Chemicals of Concern (COCs) taken at a single point in time may not capture the pseudo-dynamic time evolution of risk driven by changing subsurface processes. While computationally efficient, such simplifications limit their ability to represent dynamic processes and evolving subsurface conditions [18,25,26]. Also, the common assumption of single-component behavior neglects the complexity of real-world contaminant mixtures (like NAPL formation in the soil profile), introducing additional uncertainty into risk estimates [10,27]. A key limitation of existing approaches is their inability to simultaneously capture multicomponent partitioning, dynamic NAPL behavior, and pseudo-dynamic vapor transport. In reality, these processes occur concurrently and interact in a nonlinear manner, influencing both the magnitude of indoor exposure during time [11,28–32]. Failure to represent these interactions may lead to incomplete or biased assessments of human health risk. Although one-dimensional analytical models are widely used for screening due to their simplicity, they generally do not capture the time-varying behavior of vapor intrusion and related subsurface processes [14,33–35]. In contrast, one-dimensional numerical models can represent these dynamic subsurface processes, remaining relatively simple, flexible, and computationally efficient for site-specific applications [10].

In response to these gaps, the objective of this work is to develop a mechanistic framework to assess the pseudo-dynamic behavior of vapor intrusion risks from multicomponent VOC mixtures in contaminated soils. The proposed approach combines equilibrium phase partitioning and the formation of NAPLs coupled with vapor transport processes within a one-dimensional numerical model, linking these calculations directly to time-varying indoor concentrations and associated risks.

2. Materials and Methods

2.1. Conceptual Representation of the Model

To systematically evaluate vapor intrusion, an integrated conceptual framework was established that links subsurface contamination, transport mechanisms within the vadose zone, and indoor air exposure. Rather than handling these elements independently, the model interprets them as interdependent components of a unified system.

The contamination source is conceptualized as a long-lasting subsurface multicomponent non-aqueous phase liquid (NAPL), representative of gasoline-derived hydrocarbons. A schematic overview of the model and associated processes is presented in Figure 1.

Transport is represented within a one-dimensional vertical domain, reflecting the dominant upward migration pathway of vapors in the absence of significant lateral gradients [10,36]. This simplified approach allows focus on the main mechanisms that control vertical vapor movement, while keeping the calculations manageable. The subsurface medium is treated as homogeneous in structure; however, depth-dependent variations in environmental conditions, such as temperature and moisture, are incorporated due to their influence on vapor diffusion behavior [37].

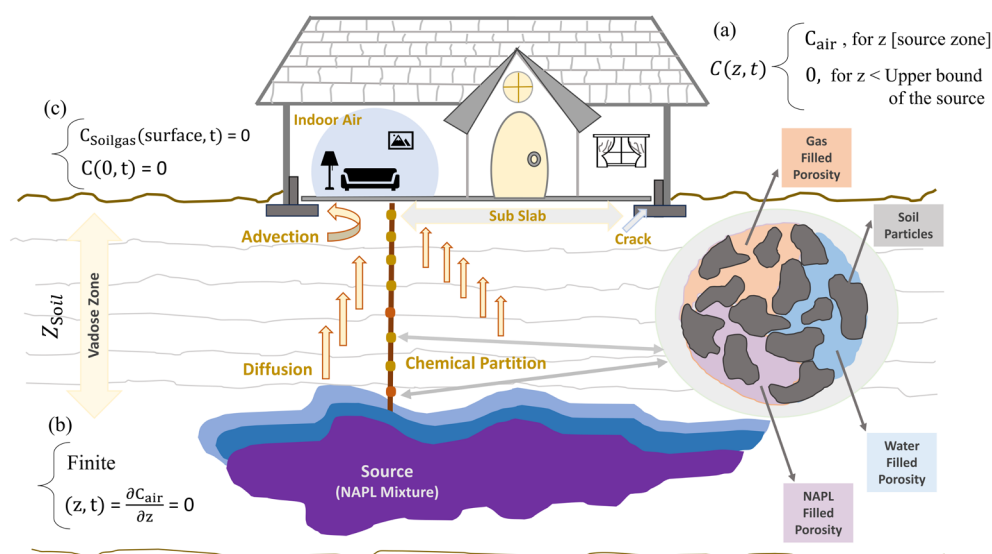


Figure 1. Conceptual model of vapor transport from a subsurface NAPL source to indoor air, including key pathways and boundary conditions. (a) Initial condition; (b) Source boundary condition; (c) Surface boundary condition.

The overlying structure is modeled as a slab-on-grade building positioned directly above the contamination zone at a defined separation distance. Vapor entry is assumed to occur through cracks in the foundation, enabling the transfer of contaminated vapor from the sub-slab region into indoor air. Importantly, the interface between the soil and the building is clearly included, allowing the model to capture sub-slab accumulation, entry through cracks, and subsequent indoor mixing.

This conceptualization keeps a good balance between representation of key physical processes and model simplicity. A key implication is that the framework preserves the dominant processes governing vapor intrusion while still being practical for screening-level applications.

2.2. Mathematical Formulation and Process Coupling

The conceptual model was developed into a coupled mathematical framework to simulate contaminated vapor transport across multiple phases and along the vertical domain.

In the present framework, individual transport and partitioning processes are formulated using steady-state relationships; however, system evolution over time is represented through sequential iterative updates of concentration across computational time steps. Therefore, the model should be interpreted as a pseudo-dynamic sequential framework rather than a fully transient transport solver.

The resulting model, referred to as NAPL_PDRM (Partition–Diffusion–Risk Model), integrates phase partitioning, vapor transport, building entry, and exposure assessment within a single building.

A distinguishing feature of this formulation is the explicit coupling between multi-component partitioning and vapor-phase diffusion. Unlike conventional approaches that separate or ignore these processes, the present model represents phase partition as a time-varying input to transport calculations.

Chemical partitioning of VOCs from the NAPL mixture into gas, aqueous, and solid phases is governed by thermodynamic equilibrium relationships, primarily based on Raoult's law (Equation (A5), Appendix A) [20,38]. The resulting phase concentrations are

constrained by mass conservation principles, ensuring consistent allocation of each component across all phases Equations (A12)–(A20) (Appendix A) [8,21]. The aqueous-phase concentration (C_{wi}) is determined using a phase-selection criterion based on thermodynamic equilibrium constraints. Specifically, when the condition ($IC_{wi} \geq S_i^F$) is satisfied, the effective solubility limit (S_i^F) is used as the governing soil pore-water concentration; otherwise, (IC_{wi}) is retained. This criterion is in line with a Raoult's-law-based phase partitioning approach, ensuring that dissolved concentrations do not exceed the effective solubility limit and providing a clear thermodynamic threshold for phase transition in accordance with mass conservation principles. Among these resulting concentrations, the vapor-phase concentrations obtained from equilibrium serve as the driving force for subsequent transport.

Vapor migration in the vadose zone is modeled as a diffusion-dominated process. Although individual governing equations are formulated under steady-state conditions, changes along the vertical direction are fully represented. These steady-state transport calculations are subsequently embedded within the iterative updating framework described below to represent progressive time-dependent redistribution of vapor concentrations. Diffusion is described using Fick's second law (Equation (A22), Appendix A) [39], with the effective diffusion coefficient adjusted to account for compound properties and soil characteristics such as porosity, tortuosity, moisture content, and temperature [37,40–42]. The series of these modification calculations is presented in Equations (A28)–(A30) (Appendix A), based on the correlations in Equations (A23)–(A27) (Appendix A), following the temperature and diffusion correction relationships adopted from Holmes et al. [43] and Barrio-Parra et al. [37].

Despite the steady-state formulation of individual processes, the model exhibits inherent temporal variability. This arises from iterative updates of the vapor concentration profile along the vertical domain, where local equilibrium and interphase mass exchange continuously modify vapor availability. This suggests that system evolution is governed by process interactions rather than explicit transient equations, resulting in a pseudo-dynamic representation of vapor intrusion. This behavior emerges because the vapor concentration field is repeatedly updated through successive equilibrium partitioning and interphase mass-transfer calculations along the vertical domain, resulting in an iterative pseudo-dynamic representation of vapor intrusion. As a result, the system evolution reflects cumulative process interactions and progressive redistribution of vapor concentrations across computational steps, even though the governing equations themselves are solved under steady-state assumptions rather than as fully transient transport equations.

At the soil–building interface, transport converted from diffusion-dominated behavior to advective entry driven by pressure gradients across foundation cracks. Indoor air concentrations are subsequently estimated using a continuous stirred tank reactor (CSTR) formulation presented in Equations (A35)–(A42) (Appendix A), which accounts for vapor entry, air exchange, and mixing within the building [44,45]. Under this formulation, the indoor environment is represented as a single well-mixed control volume with a constant indoor air exchange rate and spatially uniform contaminant concentration. The sub-slab vapor concentration adjacent to the contaminant source is used as the input boundary condition for vapor entry calculations, in agreement with commonly applied vapor intrusion modelling approaches based on the Johnson and Ettinger conceptual framework [44,45]. Finally, risk is calculated based on the Equations (A43)–(A46) (Appendix A) [46,47].

Collectively, the framework integrates partitioning, diffusion, mass balance, and exposure within an integrated, process-based structure, enabling a mechanistic evaluation of vapor intrusion.

2.3. Model Configuration and Input Parameters

To represent more realistic subsurface conditions, sandy loam soil was selected as the reference medium due to its intermediate permeability and balanced air–water interactions [48,49]. Low carbon contents of 0.3% and a clay-silt-sand distributions of 10%, 22%, 68% was assumed, leading to a total porosity of 38.7%. The contamination source was defined as a gasoline-derived multicomponent NAPL, composed of compounds with varying volatility and partitioning characteristics [4,30,50]. This mixture includes various volatile organic compounds (VOCs), such as BTEX and other light hydrocarbons. The physicochemical properties and composition of the selected compounds representing the composition of the contamination source are summarized in Table 1.

Three source depths (1 m, 3 m, and 5 m) were considered to capture a range of soil contamination scenarios, from shallow to relatively deep conditions commonly reported in vapor intrusion studies [51–53].

Exposure assessment was conducted based on a residential scenario involving an adult receptor exposed via inhalation within a single-family house, consistent with widely adopted United States Environmental Protection Agency (U.S. EPA) vapor intrusion frameworks and risk assessment practices [12,24,54]. Residential settings are of particular importance in vapor intrusion studies due to the potential for continuous, long-term indoor exposure and associated chronic health risks. An exposure duration of 30 years was assumed to represent long-term residential occupancy, aligned with earlier EPA guidance and commonly applied assumptions in risk assessment [55]. Although more recent exposure factor values suggest a combined exposure duration of approximately 26 years [56], a 30-years duration was retained for the simulation timeframe to enable explicit evaluation of long-term system behavior. This extended duration is particularly important for petroleum-contaminated sites, where multiphase processes and NAPL formation, which are represented through equilibrium partitioning and mass-balance criteria, may sustain long-term vapor release [28]. Capturing the time evolution of vapor intrusion under these conditions, along with monitoring NAPL dynamics, is therefore important for interpreting both peak and long-term indoor exposure risks. All exposure factors presented in Table 2 were applied consistently across both RBCA and PDRM simulations to ensure comparability between modeling approaches.

To facilitate implementation, several simplifying assumptions were introduced. The system was assumed to operate under steady-state transport conditions with a limited source mass of organic pollutants. The composition and properties of gasoline are presented in Table 1. The soil domain was represented as physically homogeneous, while environmental parameters influencing vapor transport, such as moisture content and temperature, were allowed to vary with depth. Lateral diffusion was neglected, in keeping with the widespread use of one-dimensional representations in vapor intrusion modeling, where vertical transport is assumed to dominate, and lateral spreading is often simplified. Biodegradation was also not included, as many established vapor intrusion models are formulated without explicitly accounting for degradation processes, particularly in screening-level or transport-focused analyses, where inclusion of biodegradation introduces additional complexity and uncertainty [16].

In addition, biodegradation in vadose-zone systems is strongly influenced by site-specific factors such as oxygen availability, microbial activity, and depth-dependent environmental conditions controlling aerobic and anaerobic degradation processes [57]. Explicit representation of these coupled reactive processes would require a fully coupled reactive transport framework beyond the scope of the present transport-focused model. Consequently, the current formulation provides a conservative representation of vapor migration and associated exposure potential, while allowing the individual effects of transport and partitioning processes to be evaluated more clearly.

Table 1. Gasoline Composition and Chemical Properties Used in RBCA and PDRM Simulations [50,58–60].

Component	Relative Mass Fractions in Gasoline (%)	Diffusivity Coefficient in Air D_{air} ($m^2 s^{-1}$)	Diffusivity Coefficient in Water D_{water} ($m^2 s^{-1}$)	Solubility Limit S ($mg L^{-1}$)	Henry's Law Constant H (-)	Organic Carbon Coefficient Koc ($L kg^{-1}$)	Density d ($kg L^{-1}$)	Inhalation Unit Risk Factor URF ($m^3 \mu g^{-1}$)	Inhalation Reference Concentration RFC ($mg m^{-3}$)
Benzene	5	8.95×10^{-6}	1.03×10^{-9}	1.79×10^3	2.27×10^{-1}	66.07	0.88	7.8×10^{-6}	0.03
Toluene	25	7.78×10^{-6}	9.20×10^{-10}	5.26×10^2	2.72×10^{-1}	140	0.87	-	5
Ethyl Benzene	3	6.85×10^{-6}	8.46×10^{-10}	1.69×10^2	3.45×10^{-1}	239.88	0.87	2.5×10^{-6}	1
Xylene	15	6.84×10^{-6}	8.44×10^{-10}	1.61×10^2	2.94×10^{-1}	196	0.88	-	0.1
n-Hexane	3	2.00×10^{-5}	7.77×10^{-10}	1.30×10^1	4.65×10	478.63	0.66	-	0.67
n-Heptane	1.5	6.50×10^{-6}	7.00×10^{-10}	2.66×10^0	8.37×10	6896	0.68	-	18
Naphthalene	1	5.90×10^{-6}	7.50×10^{-10}	3.14×10^1	2.00×10^{-2}	1548.8	1.14	-	0.003
MTBE	1	7.90×10^{-6}	9.41×10^{-9}	4.80×10^4	2.44×10^{-2}	14.12	0.74	2.6×10^{-7}	3

Table 2. Exposure Factors Applied in the Simulations [61].

Parameter	Symbol	Unit	Value
Exposure Duration	ED	years	30
Exposure Frequency	EF	days/year	350
Average Time for Carcinogens	AT_c	years	70
Target Cancer Risk Level	TR	-	10^{-5}
Average Time for non-Carcinogens	AT_{nc}	years	30
Target Hazard Quotient	THQ	-	1

Six simulation scenarios were defined by combining two source concentrations with three depths. Two representative source concentrations (1000 and 3000 mg/kg) and three source depths (1 m, 3 m, and 5 m) were considered, resulting in the following cases; scenario 1:1000 mg/kg at 1 m, scenario 2:1000 mg/kg at 3 m, scenario 3:1000 mg/kg at 5 m, scenario 4:3000 mg/kg at 1 m, scenario 5:3000 mg/kg at 3 m, and scenario 6:3000 mg/kg at 5 m. This simulation design enables a clear evaluation of sensitivity to both source strength and depth. The same scenarios were also simulated using the RBCA framework to enable direct comparison.

Input parameters presented in Table 3 were categorized into contaminant properties, soil characteristics, and building parameters. These values were compiled from published literature and established databases.

Table 3. Soil and Building Parameters Used in RBCA and PDRM Simulations [45,49,62–65].

		Unit	Value
Soil Parameters	Soil texture	-	Sandy Loam
	Porosity (total)	θ_T	% 38.7
	Gas-filled porosity	θ_a	% 28.4
	Water-filled porosity	θ_w	% 10.3
	Residual water	θ_r	$cm^3 cm^{-3}$ 0.0102
	Saturated water	θ_s	$cm^3 cm^{-3}$ 0.419
	Alpha retention parameter	α	cm^{-1} 0.0113
	n retention parameter	nn	- 1.546
	Fraction of Organic Carbon	f_{oc}	- 0.003
	Soil Density	D_s	$kg L^{-1}$ 2.65
	Soil Air Permeability	K_a	m^2 6.09×10^{-13}
Building Parameters	Foundation area in contact with soil	A_b	m^2 100

Depth of foundation below ground surface	d_f	m	0.25
Thickness of foundation	t_{ck}	m	0.1
Width of crack	w_{ck}	m	0.001
Foundation perimeter	L_{ck}	m	40
Height of building at which contaminant mixing occurs	L_{mix}	m	3
Building air exchange rate	ER	h^{-1}	0.5
Pressure difference between building and soil	ΔP	Pa	5

The organic carbon fraction ($f_{oc} = 0.003$) was selected to represent a low-organic-carbon sandy loam soil condition based on literature-reported soil characteristics [59]. The selected value was used consistently throughout the simulations as a representative input parameter for the conceptual modelling framework.

2.4. Numerical Implementation

The model was implemented in MATLAB (R2021a) using an object-oriented programming (OOP) approach to facilitate modular design and couple different processes. Each component—partitioning, diffusion, and exposure—was represented as an independent module with clear connections between them.

The governing diffusion equation was discretized using the finite difference method (FDM), employing a central difference scheme to ensure numerical stability and efficiency which is presented in Equations (A31)–(A34) (Appendix A). The subsurface domain was divided into a one-dimensional grid, with a spatial resolution chosen to capture concentration gradients accurately.

The vertical soil profile was discretized using a one-dimensional nodal mesh, with spatial and temporal resolutions (Δz and Δt) selected to ensure numerical stability and accuracy; detailed values are provided in Table A2 (Appendix B).

The computational framework was organized into four interconnected modules representing: (i) phase partitioning defines vapor concentrations in four phases (NAPL, soil, water, and gas phases), (ii) vapor-phase diffusion governs transport through the vadose zone, (iii) mass balance calculations across discretized soil layers, (iv) advective entry controls transfer into the building, indoor air concentrations are calculated using the CSTR approach and finally risk estimation. Risk metrics are subsequently derived based on these indoor concentrations.

A key feature of the implementation is the iterative updating of vapor phase concentrations and free-phase NAPL formation across both depth steps and time steps of the simulation. This coupling enables the model to capture evolving subsurface conditions without explicit transient equations and only with concentrations updated at each point in time and depth, which is a pseudo-dynamic process. NAPL formation in the present framework is represented through equilibrium partitioning and mass balance, rather than explicit multiphase flow simulation. The complete model workflow follows a sequential process: partitioning, mass balance, diffusion, NAPL Formation, advective entry, indoor air concentration, and risk estimation, as illustrated in Figure 2.

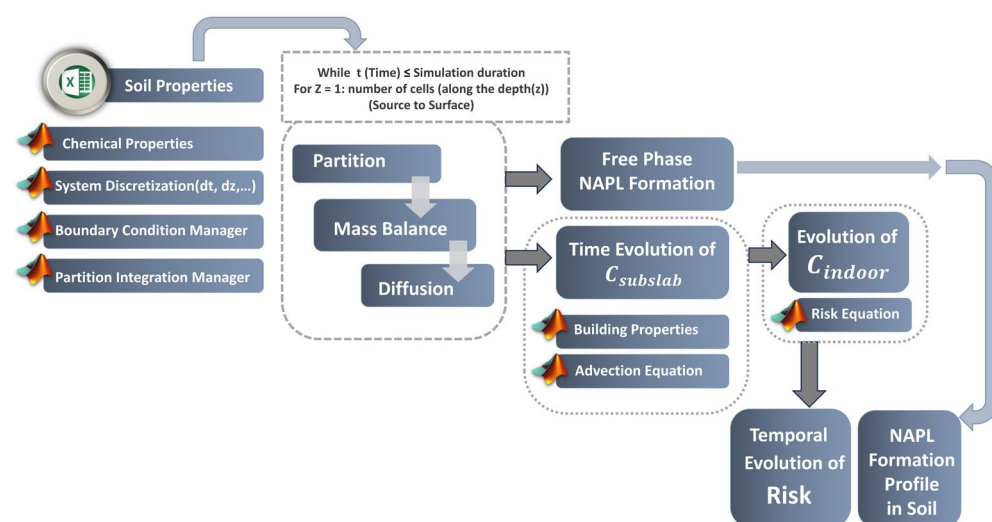


Figure 2. Sequential workflow of NAPL-PDRM; iterative vapor intrusion modeling: partitioning, mass balance, diffusion, NAPL formation, advective entry, and indoor air concentration and risk estimation.

2.5. Boundary and Initial Conditions

Boundary conditions were defined to ensure physically consistent transport behavior. A no-flux (Neumann) condition ($\frac{\partial C_{air}}{\partial z} = 0$) was applied at the source to represent finite contaminant mass, while the ground surface was assigned a zero-concentration (Dirichlet) boundary ($C_{soilgas}(surface, t) = 0$) to reflect atmospheric dilution.

Initial conditions assume contamination is limited to the NAPL source zone, with the overlying soil initially free of contaminants. The boundary conditions and initial conditions are illustrated in Figure 1.

Vapor entry into the building was represented as an advective process driven by pressure differentials across foundation cracks. In the soil–building interface, the sub-slab concentrations ($C_{subslab}$) are used to determine crack entry concentrations (C_{crack}), which are subsequently used to estimate indoor air concentrations (C_{indoor}) inside the building.

2.6. Model Verification

Model performance was evaluated through comparison with established methods and literature benchmarks. The partitioning module showed consistency with the NAPLator approach [20], while diffusion results aligned with published concentration profiles [66]. Indoor air predictions were also aligned with the reported magnitude of values in advective transport models [45].

This agreement indicates that the coupled processes are implemented consistently and that the model provides a representation of vapor intrusion behavior consistent with the compared literature cases. Additional verification details are provided in Table A3 (Appendix B).

3. Results

3.1. Indoor Air Concentration Dynamics

Indoor air concentrations exhibit highly nonlinear and compound-specific trends over the 30 years (Figure 3), reflecting the combined effects of transport processes and phase interactions. Pseudo-dynamic concentration changes reflect the modeled time-dependent vapor intrusion and compound-specific behavior in indoor environments. A

detailed breakdown for indoor air concentration of Benzene (for six scenarios) is provided in Appendix C.

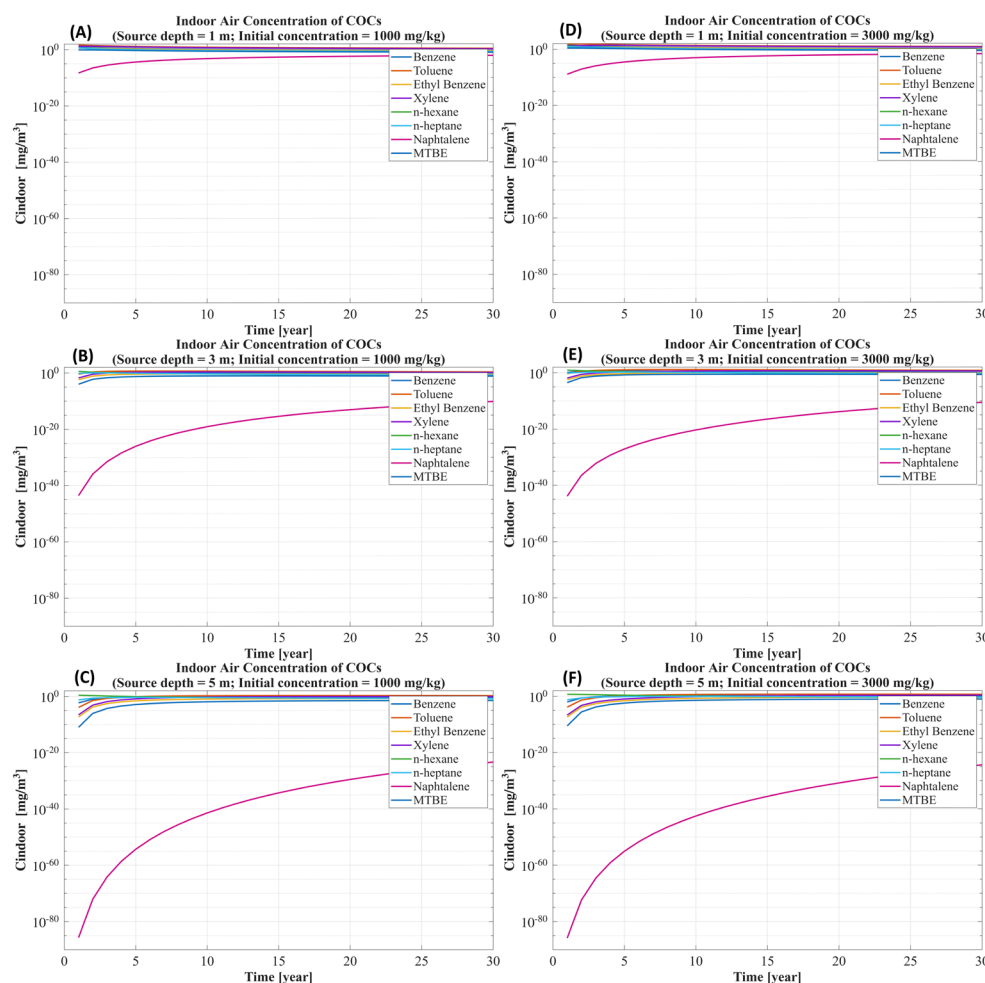


Figure 3. Time evolution of Indoor Air Concentration for six scenarios varying source concentration and depth. (A) Scenario 1: 1 m, 1000 mg/kg; (B) Scenario 2: 3 m, 1000 mg/kg; (C) Scenario 3: 5 m, 1000 mg/kg; (D) Scenario 4: 1 m, 3000 mg/kg; (E) Scenario 5: 3 m, 3000 mg/kg; (F) Scenario 6: 5 m, 3000 mg/kg.

A key finding is that, under modeled scenarios, source depth has a stronger influence than source concentration, particularly during early exposure stages. Increasing depth results in substantial attenuation, reducing concentrations by several orders of magnitude. In contrast, increasing source concentration primarily amplifies values without significantly changing temporal patterns, suggesting that depth plays a more dominant role in shaping exposure over time.

Compound behavior varies considerably. Toluene persistently exhibits the highest concentrations, whereas naphthalene remains orders of magnitude lower but shows gradual increases over time. This suggests that volatility and partitioning properties strongly influence indoor air composition. These differences are also influenced by the initial composition of the source mixture, including the initial concentrations and molar fractions of individual compounds.

For shallow sources, concentration remains relatively stable, except for naphthalene, which increases dramatically during the early years, likely due to its lower volatility, lower solubility, partitioning characteristics, and initial concentration in the mixture. At intermediate pollution-source depths, concentrations evolve more gradually and exhibit

complex early-stage variability, indicating competing effects of transport delay and accumulation.

Notably, the observed decrease in naphthalene at higher concentrations simulated in this framework may be attributed to its relatively low vapor pressure and limited solubility compared to other mixture components, as well as to its partitioning behavior and initial concentration and mole fraction within the multicomponent system, demonstrating non-linear system responses. This reflects that some compounds may behave differently under varying conditions.

In deep-source scenarios, indoor air concentrations remain low and increase slowly, reflecting diffusion-limited transport. Even after 30 years, values remain significantly attenuated compared to shallower conditions. These patterns suggest that indoor air concentrations may not be fully characterized using single-time-point estimations or measurements.

3.2. Evolution of Cancer and Non-Cancer Risk over Time

Rather than exhibiting uniform behavior, cancer risk changes over time in clearly different patterns depending on source depth and concentration, indicating that exposure is strongly time dependent. Across all simulated conditions (Figure 4), the time-varying trend of cumulative lifetime cancer risk (LCR) reflects the interactions among contaminated vapor availability, transport delay, and attenuation mechanisms. This suggests that risk management strategies may be considered under similar conditions, accounting for source depth and temporal dynamics, rather than relying solely on threshold exposure levels.

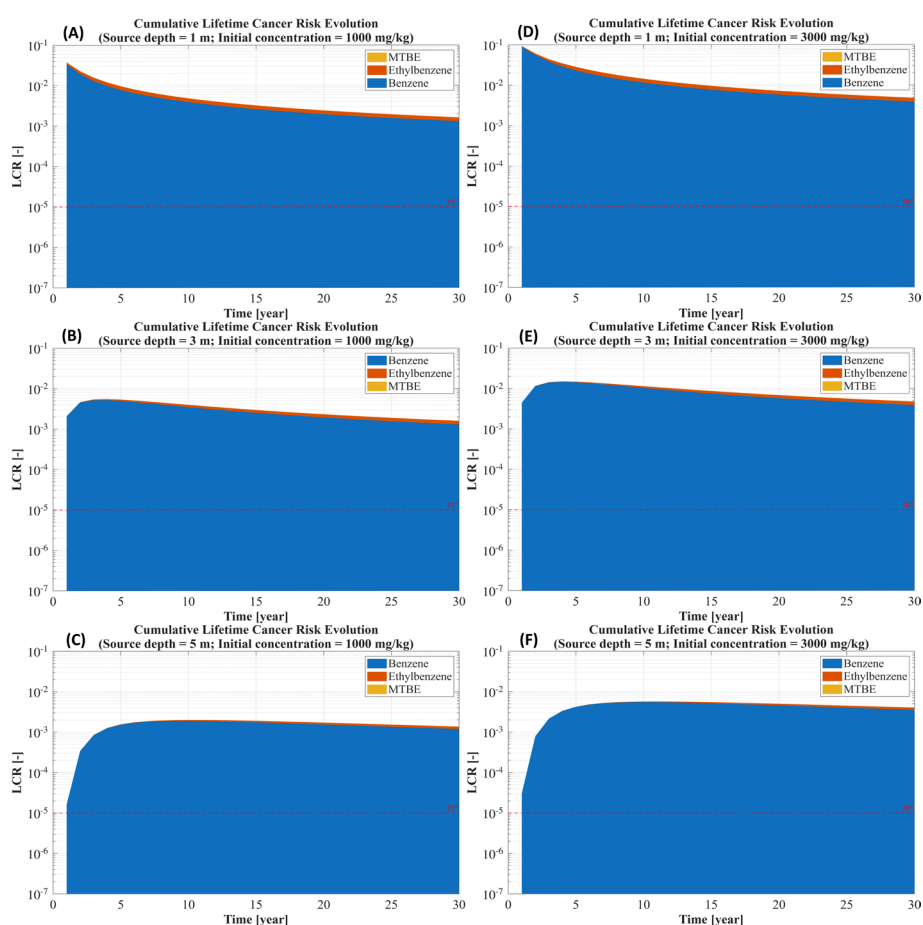


Figure 4. Time evolution of cumulative lifetime cancer risk (LCR) for six scenarios varying source concentration and depth. (A) Scenario 1: 1 m, 1000 mg/kg; (B) Scenario 2: 3 m, 1000 mg/kg; (C)

Scenario 3: 5 m, 1000 mg/kg; (D) Scenario 4: 1 m, 3000 mg/kg; (E) Scenario 5: 3 m, 3000 mg/kg; (F) Scenario 6: 5 m, 3000 mg/kg.

A key observation is that benzene persistently dominates the cumulative cancer risk throughout the exposure period under the considered scenarios, reflecting its higher toxicity and sustained indoor air concentrations over time. Ethylbenzene shows a lower but time-persistent contribution, indicating a smaller contribution compared to benzene but higher persistence than MTBE over time. MTBE remains negligible throughout the entire simulation period due to its low concentration in the mixture and limited time-varying accumulation. This consistency in cancer risk ranking over time supports that differences in risk behavior among compounds are associated with both toxicity differences and time-dependent concentration trends.

For shallow contamination (1 m), risk is initially high but declines continuously over time. For example, under lower concentration conditions (scenario 1, Panel A in Figure 4), LCR decreases from 0.037 in the first year to 0.0016 after 30 years. A similar pattern is observed at higher concentrations (scenario 4, panel D in Figure 4), although at a greater magnitude. This rapid early decrease shows strong initial vapor release followed by progressive source depletion, reflecting the critical importance of early exposure periods in risk assessment.

In contrast, intermediate depths (3 m) introduce a fundamentally different behavior. Instead of an immediate decline, risk increases during the early years before reaching a peak and subsequently decreases. In scenario 2, LCR rises by approximately 150% within the first few years, reaching a maximum near year 4. An increase is observed in scenario 5, where the peak increase exceeds 300%. This behavior suggests that delayed transport allows contaminant accumulation beneath the structure before significant indoor exposure occurs. Delayed peaks underscore the need to consider early accumulation even when initial risk appears low.

For deeper sources (5 m), the time-varying response shifts further toward delayed and sustained exposure. Risk increases gradually over a longer period before reaching a broad peak. In scenario 3 (panel C in Figure 4), LCR increases by several orders of magnitude before stabilizing and declining slightly, while scenario 6 exhibits a similar but more amplified pattern. This extended growth phase reflects diffusion-limited transport and sustained availability of contaminated vapor, emphasizing that deep contamination can pose long-term exposure risks even when early-year impacts remain limited.

The Hazard Index (HI) follows trends broadly consistent with cancer risk but shows additional insights into exposure dynamics (Figure 5). Similar to LCR, depth controls the time-varying pattern of HI, while initial concentration mainly changes the magnitude. This behavior reflects the influence of compound-specific properties and mixture interactions, where partitioning governed by molar fraction and pure-component solubility (Raoult's Law) controls the time evolution of vapor-phase concentration in soil and, consequently, indoor exposure and risk. Compounds such as benzene, toluene, ethylbenzene, xylene, and hexane, characterized by relatively higher solubility within the mixture, exhibit more pronounced time variability and contributions to the Hazard Index, as observed across the evaluated exposure period. By explicitly accounting for these pseudo-dynamic subsurface processes in multicomponent systems such as BTEX and hexane, the model captures how subsurface partitioning behavior carries over to indoor environments, providing additional insight into risk evolution under the NAPL mixture conditions considered in this study.

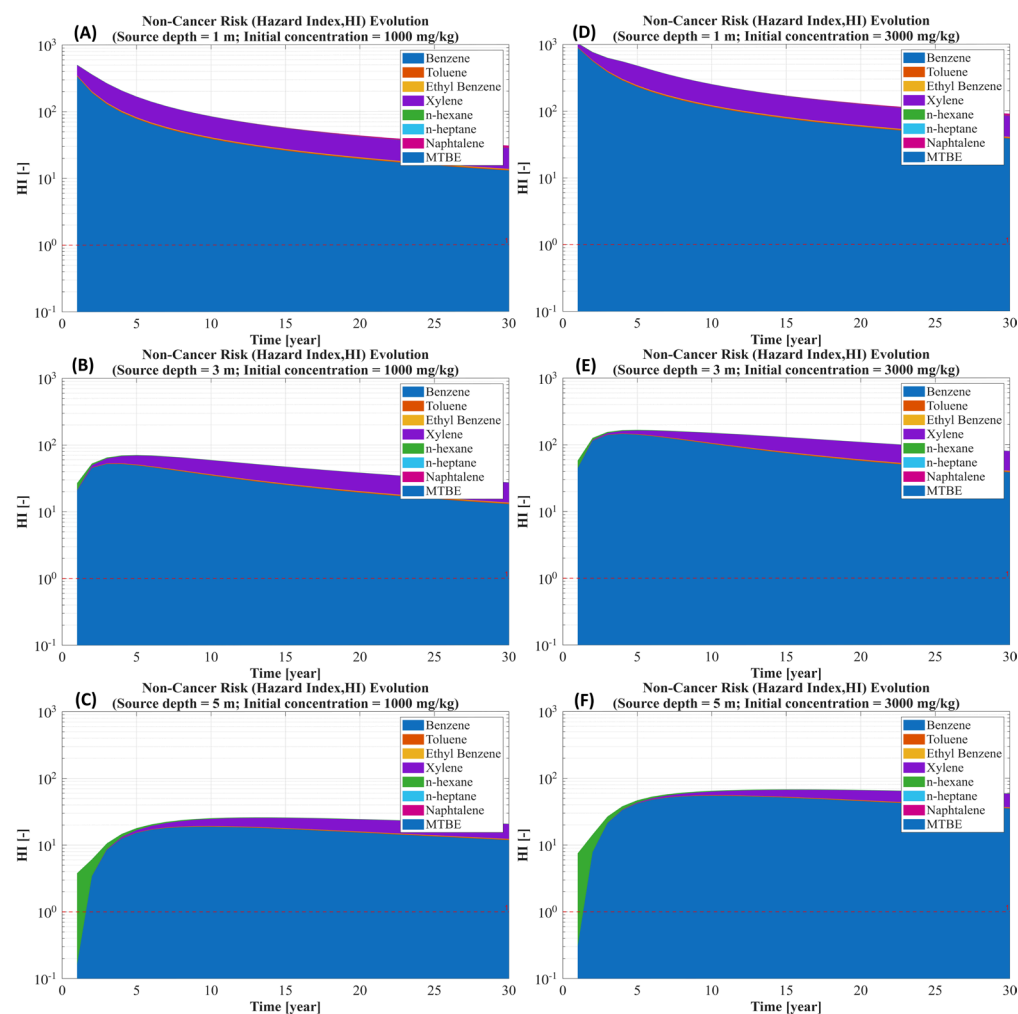


Figure 5. Time evolution of non-cancer Hazard (HI) for six scenarios varying source concentration and depth. (A) Scenario 1: 1 m, 1000 mg/kg; (B) Scenario 2: 3 m, 1000 mg/kg; (C) Scenario 3: 5 m, 1000 mg/kg; (D) Scenario 4: 1 m, 3000 mg/kg; (E) Scenario 5: 3 m, 3000 mg/kg; (F) Scenario 6: 5 m, 3000 mg/kg.

For shallow sources simulated in this study, HI decreases continuously over time. At lower concentrations, values declined sharply during the first half of the simulation period, followed by a slower reduction. Increasing the source concentration results in proportionally higher HI values, but the general temporal pattern remains unchanged. This reveals that early exposure dominates in shallow systems, illustrating the strong influence of initial conditions on risk during the exposure period.

At intermediate depths, however, HI exhibits an increasing trend over time. It means that HI increases for a short period of time and then starts to decrease, rather than staying high or changing continuously in a single trend. In the case of lower concentration, values increase significantly during the first few years, reaching a peak before gradually declining. Interestingly, the similarity between initial and final HI values suggests a balance between early accumulation and long-term attenuation. At higher concentrations, this increase becomes stronger, with peak values substantially exceeding initial levels. This emphasizes that short-term buildup may play an important role before long-term reduction begins.

For the deepest source zone scenarios, HI increases gradually and then stabilizes, forming a plateau-like profile. This behavior emphasizes that transport limitations delay exposure, while sustained vapor supply maintains elevated risk over extended periods. The relatively small decline after the peak further suggests that attenuation processes are less effective at greater depths under similar conditions considered in this study.

Across all cases, benzene remains the dominant contributor, while compounds such as hexane show greater influence during early stages in deeper scenarios, reflecting differences in volatility, initial concentration within the mixture, and phase partitioning behavior that appears to influence their time-varying contribution to indoor air concentrations.

Collectively, these results suggest that source depth primarily governs the timing and evolution pattern of both cancer and non-cancer risks, whereas source concentration controls their overall magnitude. While cancer risk exhibits smoother time-varying behavior dominated by persistent exposure, non-cancer risk reveals more complex dynamics, including early-time dominance, varying increase, and delayed stabilization depending on source depth. These differences may arise from the interplay between transport processes, chemical-specific properties, and initial mixture composition, which together regulate the time-varying contribution of individual compounds to indoor exposure. A key insight is that the complexity of risk evolution may not be fully captured under static, single-time assessments. Instead, time-varying scenario analyses are useful to better characterize both cumulative exposure and time variations in exposure, thereby improving risk assessment by providing additional insights under the modeled scenarios.

3.3. Dynamics of NAPL Formation and Persistence

The formation and evolution of free-phase NAPL may introduce an additional layer of complexity to vapor intrusion behavior (Figure 6). Rather than acting as a static source, NAPL evolves dynamically in response to subsurface conditions.

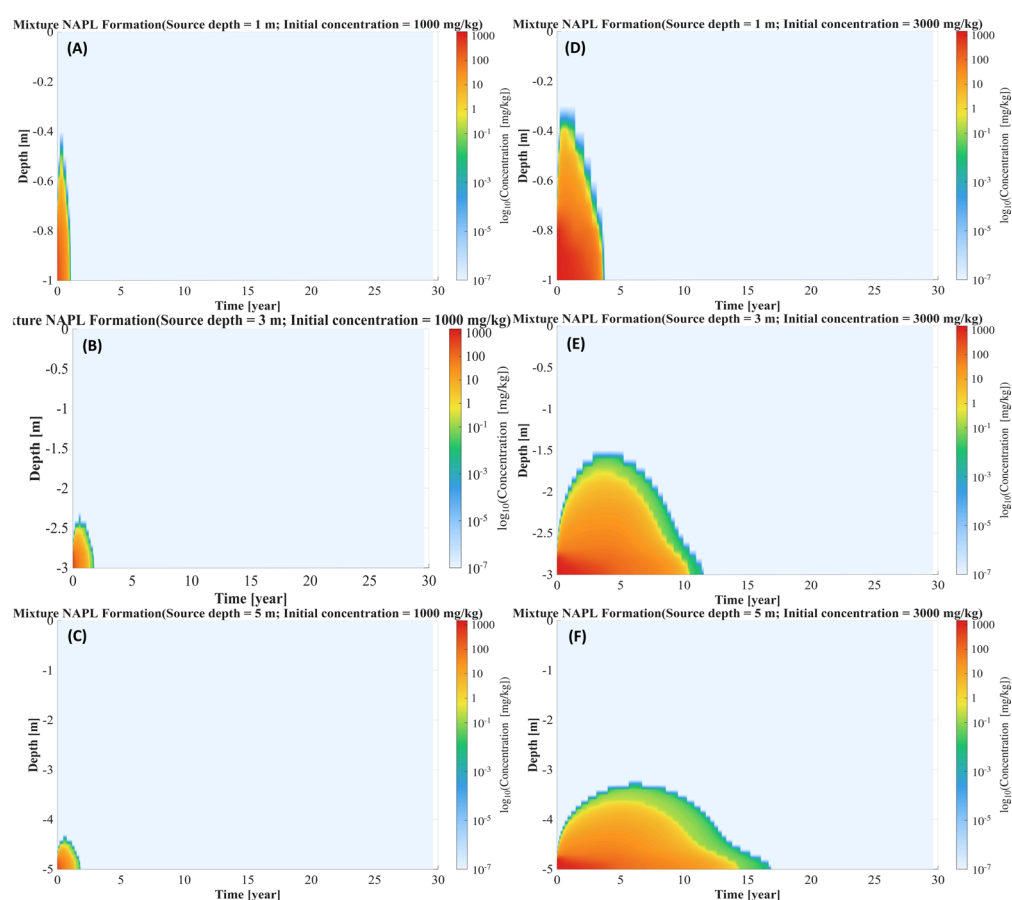


Figure 6. Mixture NAPL Formation in Soil for six scenarios varying source concentration and depth. (A) Scenario 1: 1 m, 1000 mg/kg; (B) Scenario 2: 3 m, 1000 mg/kg; (C) Scenario 3: 5 m, 1000 mg/kg; (D) Scenario 4: 1 m, 3000 mg/kg; (E) Scenario 5: 3 m, 3000 mg/kg; (F) Scenario 6: 5 m, 3000 mg/kg.

A key observation from the simulated scenarios is that source concentration may primarily influence the spread and longevity of the formed NAPL during vapor transport in soil, while depth appears to influence the timing of its formation. At lower concentrations, free-phase NAPL formed for a short time and remains spatially limited. In contrast, higher concentrations may lead to sustained and greater vertical expansion. This suggests that concentration may control how much NAPL forms and how long it continues to actively spread in the subsurface.

Depth-dependent differences are also observed. Shallow sources generate NAPL rapidly, followed by a relatively quick decline. Deeper sources, however, exhibit delayed formation but significantly extended persistence. In the deepest, high-concentration scenario considered in this study, NAPL remains active for more than a decade, reaching peak extent several years after initial formation. This may characterize the strong role of depth in delaying but extending NAPL behavior.

Intermediate depths display quasi-steady behavior, suggesting a balance between vapor generation and phase repartition. This suggests that NAPL acts as a dynamic reservoir, sustaining vapor release over time.

The observation of results suggests that NAPL is represented as a secondary source within the equilibrium partitioning and mass-balance framework, which influences vapor flux and exposure. The formation and subsequent depletion of NAPL are associated with distinct temporal patterns in subsurface vapor flux, which are reflected in corresponding variations in sub-slab and indoor air concentrations. Periods of NAPL presence occur simultaneously with sustained or raised vapor concentrations, whereas declining NAPL mass corresponds to a reduction in vapor flux and indoor concentrations over time. These patterns indicate a clear time-varying linkage between NAPL dynamics and the evolution of vapor intrusion, which may reflect the effect of equilibrium partitioning and mass balance.

3.4. Model Comparison with RBCA

A comparison between the proposed framework and conventional RBCA estimates reveals clear systematic differences in predicted risk (Table 4). Both models are applied uniformly over the same 30-year exposure period, and both report cumulative risk values based on time-averaged indoor air concentrations. Incorporating multicomponent partitioning leads to consistently higher risk estimates, indicating that simplified approaches may yield lower exposure estimates under the conditions evaluated here. This means the simplified VI tools may not fully reflect real exposure conditions.

Specifically, under the scenarios considered in this study, RBCA-based predictions are approximately one order of magnitude lower than those obtained using the partitioning-based framework (PDRM), while non-cancer risk estimates are 5–6 times lower. This difference reflects the importance of representing multiphase interactions in vapor intrusion modeling. This shows the need to include key subsurface processes for more reliable predictions.

Table 4. Cancer and Non-Cancer Risk Estimates for Different Exposure Scenarios Using RBCA and PDRM.

Scenarios			Cumulative Cancer Risk			Non-Cancer Hazard (HQ)		
Number	Source Concentration (mg kg ⁻¹)	Depth (m)	PDRM with Partition	PDRM Without Partition	RBCA Software	PDRM with Partition	PDRM Without Partition	RBCA Software
1	1000	1	1.6×10^{-3}	1.8×10^{-4}	1.6×10^{-4}	30.63	2.11	4.97
2	1000	3	1.59×10^{-3}	1.8×10^{-4}	1.6×10^{-4}	27.37	2.11	4.57
3	1000	5	1.36×10^{-3}	1.8×10^{-4}	1.6×10^{-4}	20.82	2.11	4.17
4	3000	1	4.8×10^{-3}	2.2×10^{-4}	4.7×10^{-4}	90.45	2.44	14.95

5	3000	3	4.7×10^{-3}	2.2×10^{-4}	4.7×10^{-4}	80.50	2.44	13.95
6	3000	5	4×10^{-3}	2.2×10^{-4}	4.7×10^{-4}	59.15	2.44	12.65

The highest risk levels occur under conditions combining shallow depth and high concentration, whereas deeper, lower-concentration scenarios yield the lowest values. Notably, the non-partitioning model produces results similar to RBCA, suggesting that both approaches may not explicitly represent some of the subsurface processes considered in the present framework.

Differences between models are more evident in shallow systems, where rapid transport and strong phase interactions may play a major role. This suggests that conventional single-time-point assessment tools appear to be less representative under conditions where dynamic processes are most influential. This indicates that varying subsurface processes require more detailed modelling approaches.

Collectively, the RBCA comparison results show that neglecting dynamic behavior and multicomponent partitioning may lead to substantially lower vapor intrusion risk estimates under the scenarios evaluated in this study. In contrast, the proposed PDRM framework provides an alternative pseudo-dynamic process-based representation of exposure dynamics under the assumptions considered in this study, while also capturing the temporal linkage between NAPL formation and depletion and the corresponding evolution of vapor intrusion risk.

4. Discussion

4.1. Reinterpreting the Role of Source Depth in Exposure Dynamics

The results collectively suggest a shift in how vapor intrusion risk may be conceptualized: rather than being primarily concentration-driven, exposure is largely shaped by subsurface transport restrictions, with source depth emerging as the dominant governing variable. This suggests that depth plays a more central role than typically assumed in risk assessment.

A key insight is that the vadose zone not only attenuates flow of contaminated vapor but actively reshapes the time-varying exposure profile. As depth increases, diffusion limitations and phase interactions introduce a lag between contaminated vapor release and indoor impact. This delay may alter risk trends, transforming what would otherwise be immediate exposure into a temporally distributed process [55,67] under the modeled conditions. These results suggest timing effects may be as important as concentration levels under the scenarios evaluated in this study.

In shallow systems, the absence of significant transport resistance results in rapid vapor migration, producing high initial indoor concentrations followed by a decline driven by source depletion. By contrast, deeper contamination leads to a separation between source release and indoor exposure. Contaminated vapor is temporarily retained within the soil column, resulting in delayed peaks and extended exposure durations.

This indicates that depth primarily governs when exposure occurs, whereas concentration influences how much exposure ultimately develops. Such differentiation is not captured in conventional frameworks, where depth is often considered a less influential parameter. This may lead to underestimating the role of depth in real conditions, which are close to the modeled conditions considered here.

An additional layer of complexity may arise from the formation of free-phase NAPL. Rather than being a passive side effect, NAPL introduces a feedback mechanism that may sustain vapor flux over time. This effect becomes increasingly important at greater depths, where delayed NAPL formation prolongs the release of contaminated vapor and extends the duration of risk. By representing these interactions, the PDRM framework provides

insight into processes—such as pseudo-dynamic accumulation and delayed transport—that remain unresolved in single-time-point risk assessment models [18,68].

4.2. Multicomponent Interactions as a Driver of Nonlinear Risk

The behavior observed in both cancer and non-cancer metrics reflects that vapor intrusion may not be fully represented using single-compound or simplified assumptions. Instead, the system operates as a coupled multiphase and multicomponent network in which interactions among compounds redefine transport and exposure patterns.

An important observation from the modeled scenarios is that partitioning processes cause more redistribution of mass, potentially influencing the timing and persistence of vapor release. Through continuous exchange among liquid, vapor, and solid phases, the system produces concentrations that vary over time and space. These patterns reflect the combined effects of multiple compounds. Each compound contributes differently to transport and persistence across soil depth. The results suggest that single-compound representations may not fully capture exposure and risk behavior in multicomponent systems such as those evaluated in this study. It also shows the potential importance of interactions among co-occurring VOCs in shaping vapor intrusion dynamics.

Within the assumptions of the present framework, NAPL may play an important role in the VI context. Acting as an active secondary source medium within the framework, it may regulate fluctuations in vapor concentration while maintaining a sustained source of emissions. This moderating feature of the NAPL phase in VI becomes more pronounced at higher contaminant loads, where increased mass availability enhances both the longevity and spatial spread of the NAPL phase. The modeled scenarios suggest that higher contaminant loads may increase both the persistence and spatial influence of subsurface sources.

The varying increase in non-cancer risk observed in intermediate-depth scenarios provides a clear example of this behavior. The delayed rise in the Hazard Index suggests that exposure is not necessarily highest immediately after the soil becomes contaminated but may instead peak after a period of subsurface accumulation. This pattern may reflect the combined effects of transport delay, interphase mass redistribution, and gradual vapor release from NAPL.

Such observations indicate that neglecting multicomponent interactions may obscure both early-stage peaks and long-term exposure persistence, especially in systems where NAPL formation is significant [6,67,69,70]. The timing of risk appears to be influenced by subsurface dynamics, in addition to source concentration alone. NAPL may play a key role in regulating both initial and prolonged exposure patterns within the present framework. These dynamics also explain why single-compound models may produce lower risk estimates under the conditions examined in this study, during both early and late stages. Ignoring these pseudo-dynamic subsurface processes and multicomponent interactions may lead to a lower estimation of risks over both short and extended time periods within the scope of the scenarios evaluated in this study.

4.3. Time as a Governing Dimension of Vapor Intrusion

An important outcome of this study is the recognition that time appears to be an important factor influencing vapor intrusion behavior in the modeled scenarios. Exposure patterns evolve continuously, and their interpretation depends strongly on the time scale of observation.

The results of this study further reinforce that indoor air concentrations represent an important link between subsurface transport processes and human exposure. However, this linkage is not static and can be interpreted as inherently evolving over time. The observed time variability arises from evolving subsurface mechanisms, including diffusion

processes, multicomponent partitioning, and iterative pseudo-dynamic mass transfer behavior driven by coupling processes and time-stepped updating, which collectively govern the evolution of vapor-phase concentrations over time. This perspective emphasizes that single-time-point or steady-state assumptions may not adequately represent the actual exposure dynamics and therefore supports the potential usefulness of modeling approaches in vapor intrusion assessment frameworks.

The early phase of exposure may represent an important period, typically within the first few years, that emerges as a critical window in which rapid changes in concentration and risk occur. For shallow and intermediate depths, this period captures either the initial peak or the buildup that precedes it. Conventional monitoring strategies or sampling campaigns, which often rely on infrequent or single-time measurements, may be insufficient to capture these dynamics. These results suggest that repeated, time-distributed monitoring or sampling of sub-slab and indoor conditions may be beneficial for better characterizing changing exposure conditions, especially in the early stages of vapor intrusion.

For deeper contamination, the temporal structure shifts toward delayed maxima and long-lasting plateaus. The modeled scenarios suggest that peak exposure may occur well after the initial contamination occurrence, challenging the assumption that early measurements are representative of long-term conditions.

The results suggest that, for the scenarios considered in this study, exposure assessment may benefit from moving beyond static snapshots to time-varying or continuous characterization. Under the modeled conditions examined here, neglecting time variability may contribute to the underestimation of peak exposure or misinterpretation of exposure duration [28,71]. Incorporating periodic measurements is therefore useful for characterizing both the magnitude and duration of risk to human health.

4.4. NAPL as a Regulator of Vapor Flux

The simulations highlight that NAPL formation may introduce a regulating effect on contaminant availability, potentially influencing the long-term evolution of vapor intrusion and indoor air levels.

Rather than functioning only as a primary source, NAPL may operate as a mass reservoir that influences phase partitioning and modulates interphase mass transfer. Its persistence is strongly linked to contaminant loading, while its initiation and distribution are influenced by depth-dependent transport processes. This suggests that vapor intrusion models can be used to represent NAPL as a dynamic, phase-regulating source, rather than a static contaminant reservoir.

In high-concentration scenarios, NAPL remains active over extended periods, continuously supplying additional contaminated vapor to the vapors already undergoing diffusive transport through the soil. This sustained release prolongs indoor exposure even as the main first source gradually declines. The effect is particularly significant in deeper systems, where delayed formation aligns with extended exposure periods.

A key implication is that, within the present framework, NAPL may influence not only the duration but also the composition of the mixture of contaminants presents in indoor air during human exposure. Over time, compounds with lower volatility may become relatively more important as more volatile components are depleted. This evolving composition may not be fully represented without explicitly representing multiphase interactions.

These observations suggest potential limitations of models that ignore NAPL formation dynamics, as they may not reproduce either the persistence or the temporal variability of contaminant flux [7,68,72].

4.5. Structural Limitations of Single-Time-Estimation Risk Models

The comparison with RBCA Toolkit indicates that differences between the modeling approaches appear to be both quantitative and conceptual. Commercial RBCA software (version 2.6) is generally designed to represent vapor intrusion using some simplified screening-level assumptions, representing it as a largely non-evolving phenomenon. Specifically, it estimates risk based on representative steady-state indoor air concentrations over the exposure period, rather than explicitly resolving time variations. This approach relies on volatilization factors defined as steady-state ratios between indoor air and source concentrations, assuming constant source conditions throughout the exposure duration, even when finite source adjustments are applied [73]. Consequently, simultaneous chemical partitioning among multiple contaminants, such as those in gasoline mixtures, during subsurface vapor transport is not explicitly represented. This simplification may approximate near-equilibrium conditions, which may overlook key dynamic interactions and exposure variability over time.

In contrast, the PDRM framework represents exposure as a pseudo-dynamic process-based system. Within the present framework, risk evolution is represented through the combined effects of transport, partitioning, and phase dynamics over time. This approach can represent both early-stage peaks and long-term persistence, which may contribute to differences compared with RBCA predictions under the scenarios considered in this study. Recognizing these dynamics is particularly important when assessing complex multicomponent contaminant mixtures, like gasoline.

For the scenarios considered in this study, RBCA estimations were approximately one order of magnitude lower for cancer risk and several-fold lower for non-cancer effects than those obtained using the proposed framework. These differences may reflect the limited representation of temporal peaks and delayed exposure patterns within the assumptions applied here. These discrepancies are most significant in scenarios with rapid transport or strong multiphase interactions, where steady-state assumptions break down.

In contrast to the assumptions considered in this study, RBCA does not incorporate NAPL dynamics, which may limit its ability to represent sustained vapor release and long-term contaminant persistence. As a result, differences in the estimated timing and magnitude of exposure may arise under some modeled conditions.

The model obtained results suggest that relying solely on simplified screening tools may be limited for evaluating complex subsurface conditions involving hydrocarbon contamination similar to those considered here. Incorporating process-based, pseudo-dynamic modeling may provide an alternative process-based assessment of vapor intrusion risk [11,24,27]. The conclusions should be interpreted within the assumptions of the present pseudo-dynamic framework.

4.6. Implications for Monitoring Strategies and Risk Management

The mechanistic insights obtained from this study may have implications for the monitoring and management of vapor intrusion sites under the modeled conditions. Importantly, these insights reflect conceptual differences within the modeling framework, rather than purely numerical variations.

The results suggest that monitoring strategies may benefit from being aligned with the time-varying behavior of the subsurface that may influence risk to human health under the modeled conditions. For shallow contamination, short-term, high-frequency measurements may be useful under the modeled conditions in this study to capture rapid early exposure. In contrast, deeper sources require extended monitoring programs to identify delayed peaks and long-term trends. This also indicates the importance of designing sub-slab sampling campaigns that capture variability over time, rather than relying on snapshot measurements. Broadly consistent with EPA vapor intrusion guidance

monitoring frequency may need to be adapted to the temporal behavior of the subsurface system [24]. In shallow contamination scenarios, where rapid changes in exposure conditions are expected, higher-frequency monitoring (e.g., quarterly or more frequent sampling) may help capture short-term variability. In contrast, deeper contamination sources typically exhibit delayed and attenuated responses and therefore may be characterized through lower-frequency, long-term monitoring programs. These patterns are consistent with the time-dependent response patterns observed in this study, where shallow and deep source configurations exhibit distinctly different characteristic time scales.

From a practical risk assessment perspective, the results suggest that monitoring may be extended until concentration trends approach stabilization, which may help better capture early-stage exposure peaks or long-term risk conditions. Consequently, the present findings may have implications for monitoring frequency and for the duration of sampling programs used to characterize vapor intrusion behavior over time. This may also help identify both early-stage peaks and delayed exposure patterns.

In addition, seasonal variability associated with environmental factors such as temperature, atmospheric pressure, and soil moisture conditions may be considered during monitoring design, as these factors may influence vapor transport dynamics and measured indoor or sub-slab concentrations.

The presence of NAPL further complicates monitoring, because it introduces temporal variability that is not readily captured through single sampling or measurement instances. Repeated or continuous measurements are likely to be important for more accurately characterizing exposure conditions, including indoor air concentrations.

From the risk regulatory perspective, these findings challenge the widespread use of static estimates based on one or a few points in risk assessment. Under the conditions considered in this study, integrating pseudo-dynamic modeling frameworks such as PDRM provides a more detailed representation of exposure under the modeling framework, supporting better-informed decision-making, and potentially improved mitigation strategies and time-based sampling designs [14,27].

4.7. Study Constraints and Future Directions

While the proposed framework captures key mechanisms governing vapor intrusion and its influence on the evolution of human health risk over time, several simplifying assumptions need to be acknowledged.

The analysis assumes homogeneous soil conditions and does not explicitly account for heterogeneity, preferential flow pathways, or three-dimensional transport. Processes such as biodegradation and building-specific variability are also not incorporated. In addition, uncertainties in input parameters (which are not site-specific data) and partitioning relationships may influence quantitative predictions. A formal uncertainty analysis was beyond the scope of this study.

Specifically, the assumption of homogeneous soil conditions and the neglect of preferential flow and three-dimensional effects may lead to an oversimplification of vapor transport pathways, potentially smoothing local concentration peaks and underestimating spatial variability. The exclusion of biodegradation introduces a conservative bias in concentration and risk estimates, as biodegradation processes that may reduce vapor-phase mass [74] are not represented. In addition, uncertainties in input parameters and partitioning relationships may propagate through the model and could affect the absolute magnitude of predicted concentrations, although the relative trends between scenarios are expected to remain generally consistent. Because a formal sensitivity analysis was not performed, the ranking and magnitude of predicted risks may vary under alternative parameter selections and site conditions. Taken together, these assumptions primarily may

affect the quantitative magnitude of predictions, while the conceptual trends and comparative interpretations are generally consistent within the modeling conditions.

The primary objective of the proposed framework is not strict site-specific quantitative prediction, but rather the investigation of pseudo-dynamic vapor intrusion risk evolution within a multi-component and multi-phase system. The model is intended to evaluate how diffusive transport, phase partitioning, and potential NAPL formation during subsurface migration influence long-term concentration behavior and associated risk trends. From a practical standpoint, the framework is particularly relevant for interpreting soil-gas sampling strategies and vapor intrusion risk assessments, where time variability and phase interactions may affect measured concentrations and exposure estimates. Therefore, the preliminary qualitative verification presented here is intended to suggest consistency with general system behavior and concentration scales relative to previous studies, while comprehensive field-scale quantitative validation remains a subject for future work.

Future developments may focus on extending the model to incorporate spatial heterogeneity and transient boundary conditions, on validating it against field-scale observations, and on investigating the sensitivity of the proposed framework to key environmental and building-related parameters, including soil moisture, organic carbon content, air exchange rates, pressure gradients, and crack characteristics, in order to better quantify parameter uncertainty and model robustness. In addition, field-scale monitoring and validation efforts incorporating temporal and seasonal variability would be valuable for evaluating the modeled evolution of contaminant behavior and associated risk trends under site-specific conditions. Incorporating these elements may improve the applicability of the framework in practical assessment conditions. This could support its potential application in field-based risk assessment following further validation.

5. Conclusions

This study reframes vapor intrusion as a pseudo-dynamic process-controlled phenomenon rather than a simplified exposure condition. By integrating multicomponent partitioning, dynamic NAPL formation, and depth-dependent transport within the PDRM framework, the analysis provides a mechanistic interpretation of how subsurface conditions shape both cancer and non-cancer risks to human health over extended time scales.

A central outcome is that source depth acts as the primary regulator of exposure dynamics. Instead of simply attenuating contaminated vapor flux, the vadose zone continuously shapes how exposure evolves over time, shifting shallow sources tend to produce immediate but short-lived exposure impacts, while deeper sources generate delayed yet persistent risk profiles. This suggests that risk characterization may benefit from explicit consideration of both the timing and magnitude of exposure, as well as the underlying subsurface processes and their time evolution. This perspective shifts the focus from static concentration thresholds to time-dependent exposure behavior.

The results further indicate that free-phase NAPL formation in soil should be interpreted within the equilibrium partitioning and mass-balance framework, as a potential secondary source that may contribute to sustained vapor release. By acting as a potential secondary source, it sustains vapor release and extends exposure duration, particularly under high contaminant loading and at greater depths. A key implication is that long-lasting risk may not be fully represented without accounting for NAPL-mediated mass transfer.

In addition, multicomponent partitioning introduces nonlinear and compound-specific behavior. This results in distinct time-dependent patterns in indoor air concentrations and associated risk metrics, driven by interactions among multiple compounds. These

effects are especially important in multicomponent mixtures such as gasoline, where differences in volatility and partitioning behavior may strongly influence exposure dynamics. This is especially relevant for petroleum-contaminated sites, where the NAPL mixture can alter exposure timing and magnitude.

These interactions are especially critical during the early stages of exposure, when rapid changes and peak conditions may occur within a limited time window. This shows the usefulness of accurately representing short-term dynamics alongside long-term trends.

The comparison with conventional approaches shows that, for the high-concentration scenarios considered in this study, single or average time-point risk assessment frameworks, such as RBCA, produced lower estimates of both the magnitude and timing of vapor intrusion risk in the high-concentration scenarios considered here, where concentrations were sufficiently high to allow NAPL formation. By neglecting peaks during temporal variations, delayed transport, and multiphase interactions under consideration of chemical partitioning and mass balance during vapor transport in subsurface soil, such models may overlook capturing critical exposure situations, under the modeled conditions considered in this study. In contrast, the process-based structure of PDRM enables a more comprehensive process-based representation of subsurface-to-indoor transport pathways.

From a practical perspective, these findings have direct implications for site assessment and risk management. Monitoring strategies and sampling campaigns may benefit from both time variability and depth-dependent behavior. Reliance on single-time or snapshot measurements may lead to significant mischaracterization of exposure. Instead, time-distributed and repeated sampling may be incorporated into monitoring programs.

Incorporating pseudo-dynamic modeling tools can improve decision-making and support more effective remediation planning. It is particularly important for managing sites affected by vapor intrusion, such as buildings located near petroleum release sources (e.g., fuel stations), to enhance the protection of human health.

In summary, this work shows that bridging the gap between simplified regulatory models and the complexity of real subsurface systems requires explicit integration of pseudo-dynamic processes, depth effects, and multiphase subsurface interactions. Such an approach not only improves consistency of model predictions but also provides a useful framework for process-based interpretation of vapor intrusion behavior under the modeled conditions considered in this study, although field-scale validation remains necessary. Ultimately, considering time-varying behavior may contribute to improved protection of human health in contaminated sites with complex subsurface environments. Despite these advances, the present study relies on simplifying assumptions, including homogeneous subsurface conditions and limited system representation. Because biodegradation was not included in the present framework, the reported concentrations and risks may be interpreted as conservative estimates. In addition, because a formal sensitivity analysis was beyond the scope of this study, the ranking and magnitude of predicted risks may vary under alternative parameter selections. Future work should incorporate site heterogeneity, biodegradation, exposure variability across different receptors, and parameter uncertainty. Field-scale validation remains necessary to further evaluate the applicability of the framework under real-site conditions.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/soilsystems10070076/s1>, including MATLAB codes, detailed descriptions of the simulation procedures, and corresponding results.

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Abbreviations

The following abbreviations are used in this manuscript:

PDRM	Partition–Diffusion Risk Model
NAPL	Non-Aqueous Phase Liquid
RBCA	Risk-Based Corrective Action
VOC	Volatile Organic Compound
UST	Underground Storage Tank
VI	Vapor Intrusion
J&E	Johnson–Ettinger
BTEX	Benzene, Toluene, Ethylbenzene, and Xylenes
U.S. EPA	United States Environmental Protection Agency
OOP	Object-Oriented Programming
FDM	Finite Difference Method
CSTR	Continuous Stirred-Tank Reactor
LCR	Lifetime Cancer Risk
MTBE	Methyl Tertiary-Butyl Ether
HI	Hazard Index

Appendix A. Mathematical Formulations of the NAPL_PDRM

Appendix A.1. Governing Equations (Vapor Transport to Risk Calculations)

Table A1. Definition and units of parameters used in this model calculations.

Parameter	Symbol	Unit
Air-filled soil porosity	θ_a	%
Amplitude of temperature oscillations at ground level	T_{10}	°C
Angular seasonal or diurnal frequency	ω	$\frac{1}{s}$
Average soil temperature	T_0	°C
Averaging time for carcinogens	AT_C	yr
Averaging time for noncarcinogens	AT_{NC}	yr
Bulk density of soil	P_b	kg/L
Cancer risk associated with contaminant i	CR_i	-

Concentration in soil pore water for compound i	M_{wi}	mg/kg
Concentration in soil pore-air for compound i	M_{ai}	mg/kg
Concentration sorbed to soil for compound i	M_{si}	mg/kg
Conversion factor	CF	mg/L
Cumulative cancer risk	CCR	-
Density for compound i	d_i	kg/L
Density of air	d_a	kg/L
Density of NAPL	$d_{naplmix}$	kg/L
Density of soil	d_s	kg/L
Density of the mixture	$d_{naplmix}$	kg/L
Density of the NAPL mixture	d_{napl}	mg/L
Density of water	d_w	kg/L
effective diffusion coefficient	D	$\frac{m^2}{s}$
Effective Diffusion Coefficient	$D_{eff}(z)$	$\frac{m^2}{s}$
Effective Solubility for compound i in mixture	S_i^E	mg/L
Exposure duration	ED	yr
Exposure frequency	EF	$(\frac{days}{yr})$
Fraction Organic Carbon	f_{oc}	-
Gas-filled porosity	θ_g	%
Hazard Index (Cumulative hazard quotient)	HI	-
Hazard quotient for contaminant i	HQ_i	-
Henry's Law Constant for compound i	H_i	-
Indoor Air Concentration	$C_{building}$	$\frac{mg}{m^3}$
Indoor Air Concentration for Carcinogens	C_{indoor}	$\frac{\mu g}{m^3}$
Mass for compound i	W_{ti}	mg/mg
Measured soil contaminant concentration for compound i	C_{ti}	mg/kg
Molar Mass or Moles/Gram for compound i	M_{ci}	mol/g
Mole Fraction for compound i	X_i	%
Molecular Weight for compound i	MW_i	g/mol
Pressure	P	Pa
Pure-Phase Aqueous Phase Solubility for compound i at 20 °C	S_i	mg/L
Reference Concentration	RfC	$\frac{mg}{m^3}$
Residual NAPL saturation in soils	S_r	%, L/L
residual water contents	θ_{wr}	-
retention parameter	α	m^{-1}
retention parameter	n	-
retention parameter	m	-
saturated water contents	θ_{ws}	-
Soil Air Concentration	C	$\frac{mg}{L}$
Soil organic carbon/water partitioning coefficient	K_{oc}	L/kg
Soil pore-vapor concentration for compound i	C_{ai}	mg/L
Soil Pore-Water Concentration	C_{wi}	mg/L
Soil Saturation Limit for compound i	C_{sati}	mg/kg
Soil sorbed concentration for compound i	C_{si}	mg/kg
Soil volumetric heat capacity	C_{soil}	$J \cdot m^3 \cdot ^\circ C^{-1}$
Soil-water partitioning coefficient	K_{di}	L/kg
Solubility of the Mixture	S_t	mg/L

Sum of contaminant masses for all compounds in the sample	M_t	mg/kg
Temperature	T	K
The building air exchange rate	ER	$\frac{1}{\text{hour}}$
The convective soil vapor entry rate into the building	Q_s	$\frac{\text{m}^3}{\text{s}}$
The crack radius	r_{ck}	m
The depth of foundation below the ground surface	d_f	m
The diffusion coefficient of the contaminant in air	D_{air}	$\frac{\text{m}^2}{\text{s}}$
The distance	z	m
The distance of the foundation cracks from the edge of the contaminant plume	d_s	m
The Effective Diffusion Coefficient	D_e	$\frac{\text{m}^2}{\text{s}}$
The foundation area in contact with the soil	A_b	m^2
the foundation crack fraction	η	-
The foundation perimeter	l_{ck}	m
The height of the building at which contaminant mixing occurs	L_{mix}	m
The molecular diffusion coefficient in phase i	D^*_i	$\frac{\text{m}^2}{\text{s}}$
The pressure difference between the building and the soil	Δp	Pa
The soil air permeability	K_a	m^2
The soil gas viscosity	μ	Pa·s
The thickness of the foundation	t_{ck}	m
The time	t	s
The tortuosity	τ_i	-
The width of the crack	w_{ck}	m
Theoretical Soil Pore-Water Concentration for compound i	IC_{wi}	mg/L
Thermal soil conductivity	k	$\text{J} \cdot \text{m}^{-1} \cdot \text{s}^{-1}$
Total contaminant Concentration of compound i	M_{ti}	mg/kg
Total mass of NAPL in soil sample	$NAPL_t$	mg/kg
Total porosity	θ_t	%
Total soil porosity	n_t	%
Unit risk factor	URF	$(\frac{\mu\text{g}}{\text{m}^3})^{-1}$
Universal Gas Constant	R	$\text{Pa} \cdot \text{m}^3 / (\text{K} \cdot \text{mole})$
Volume NAPL	N_V	%, L/L
Volume of soil	S_V	%, L/L
Volume of soil pore-air volume	A_V	%, L/L
Volume of soil pore-water	W_V	%, L/L
Volumetric Soil Saturation Limit	C_{coni}	mg/L
Water-filled soil porosity	θ_w	%
Wet Bulk Density	P_b	kg/L

Appendix A.1.1. Chemical Partitioning Equations

$$W_{ti} = \frac{C_{ti}}{M_t} \quad (A1)$$

where

W_{ti} = % Mass for compound i (mg/mg)

C_{ti} = Measured soil contaminant concentration for compound i (mg/kg)

M_t = $\sum C_{ti}$, Sum of contaminant masses for all compounds in the sample (mg/kg)

$$M_{ci} = \frac{W_{ti}}{MW_i} \quad (A2)$$

where:

M_{ci} = Molar Mass or Moles/Gram for compound i (mol/g)

MW_i = Molecular Weight for compound i (g/mol)

$$X_i = \frac{M_{ci}}{\sum M_{ci}} \quad (A3)$$

where:

X_i = Mole Fraction for compound i (%)

$$d_{naplmix} = \sum (X_i \times d_i) \quad (A4)$$

where:

$d_{naplmix}$ = Density of the mixture (kg/L)

d_i = Density for compound i (kg/L)

$$S_i^E = X_i \times S_i \quad (A5)$$

where:

S_i^E = Effective Solubility for compound i in mixture (mg/L)

S_i = Pure-Phase Aqueous Phase Solubility for compound i at 20 °C (mg/L)

$$S_t = \sum S_i^E \quad (A6)$$

where:

S_t = Solubility of the Mixture (mg/L)

$$K_{di} = f_{oc} \times K_{oc} \quad (A7)$$

where:

K_{di} = Soil-water partitioning coefficient (L/kg)

f_{oc} = Fraction Organic Carbon (f_{oc} , %)

K_{oc} = Soil organic carbon/water partitioning coefficient (L/kg)

$$P_b = (W_v \times d_w) + (A_v \times d_a) + (S_v \times d_s) + (N_v \times d_{naplmix}) \quad (A8)$$

where:

P_b = Wet Bulk Density (kg/L)

W_v = Volume of soil pore-water (% , L/L)

d_w = Density of water (1.0 kg/L)

A_v = Volume of soil pore-air volume (% , L/L)

d_a = Density of air (0.0013 kg/L)

S_v = Volume of soil (% , L/L)

d_s = Density of soil (2.65 kg/L)

N_v = Volume NAPL (% , L/L)

$d_{naplmix}$ = Density of NAPL (kg/L)

$$IC_{wi} = \frac{(C_{ti} \times P_b)}{(K_{di} \times P_b + \theta_w + H_i \times \theta_a)} \quad (A9)$$

where:

IC_{wi} = Theoretical Soil Pore-Water Concentration for compound i (mg/L)

C_{ti} = Mass of contaminant i in soil sample (mg/kg)

θ_w = Water-filled soil porosity (%)

θ_a = Air-filled soil porosity (%)

H_i = Henry's Law Constant for compound i (dimensionless)

$$C_{sati} = \left(\frac{S_i^E}{P_b} \right) \times (K_{di} \times P_b + \theta_w + H_i \times \theta_a) \quad (A10)$$

where:

C_{sati} = Soil Saturation Limit for compound i (mg/kg)

$$C_{coni} = C_{sati} \times P_b \quad (A11)$$

where:

C_{coni} = Volumetric Soil Saturation Limit (mg/L)

$$C_{wi} = IC_{wi} \text{ or } S_i \text{ or } S_i^E \quad (A12)$$

where:

C_{wi} = Soil Pore-Water Concentration (mg/L)

C_{wi} is determined from logic tests. For example if $X_i = 1$, S_i will be selected as the soil por-water concentration. If $IC_{wi} \geq S_i^E$ then S_i^E will be selected as the soil por-water concentration, otherwise, (IC_{wi}) will be selected.

$$C_{ai} = C_{wi} \times H_i \quad (A13)$$

where:

C_{ai} = Soil pore-vapor concentration for compound i (mg/L)

$$C_{avi} = \frac{C_{ai} \times R \times CF \times T}{P \times M_{wi}} \quad (A14)$$

where:

C_{avi} = Volumetric soil pore-air concentration for compound i (ppmv)

R = Universal Gas Constant (8.31451 Pa·m³/(K·mole))

CF = Conversion factor (10⁶ mg/L)

T = Temperature (293.15 K)

P = Pressure (101,325 Pa)

$$C_{si} = K_{di} \times C_{wi} \quad (A15)$$

where:

C_{si} = Soil sorbed concentration for compound i (mg/kg)

$$M_{wi} = \frac{C_{wi} \times \theta_w}{P_b} \quad (A16)$$

$$M_{ai} = \frac{C_{wi} \times \theta_a \times H_i}{P_b} \quad (A17)$$

$$M_{si} = C_{wi} \times K_{di} \quad (A18)$$

$$M_{NAPLi} = C_{ti} - C_{sati}, \text{ if } C_{ti} > C_{sati} / \text{if not, } M_{NAPLi} = 0 \quad (A19)$$

Appendix A.1.2. Mass Balance Equation

$$M_{ti} = M_{ai} + M_{wi} + M_{si} + M_{NAPLi} \quad (A20)$$

where:

M_{wi} = Concentration in soil pore water for compound i (mg/kg)

M_{ai} = Concentration in soil pore-air for compound i (mg/kg)

M_{si} = Concentration sorbed to soil for compound i (mg/kg)

M_{ti} = Total contaminant Concentration of compound i (mg/kg)

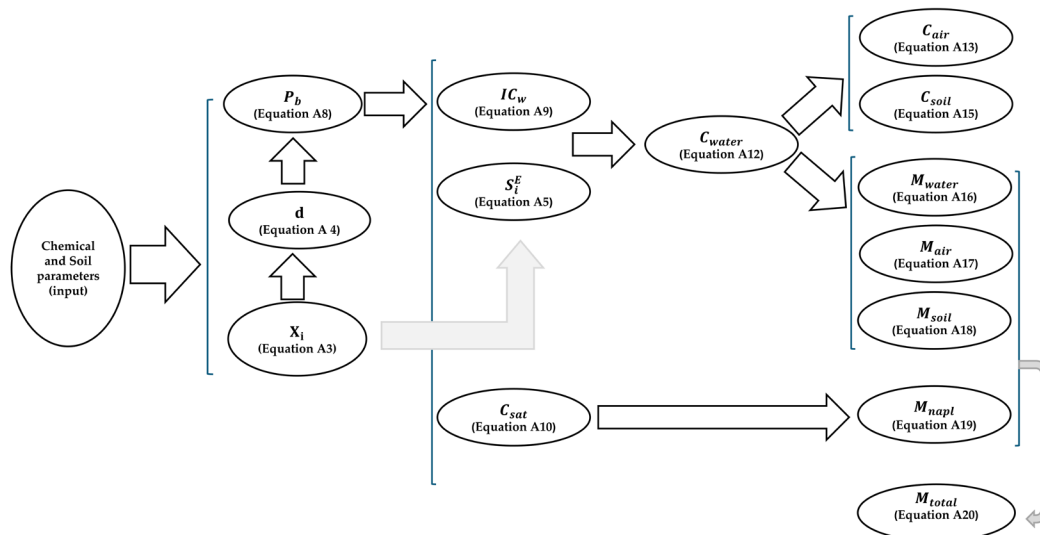


Figure A1. Computational Workflow for Solving the Mass Balance Equations (A12–A20).

Appendix A.1.3. Residual NAPL Saturation Equation

$$S_r = (\text{NAPL}_t \times \frac{P_b}{d_{\text{napl mix}}}) / n_t \quad (\text{A21})$$

where:

S_r = Residual NAPL saturation in soils (% , L/L)

NAPL_t = Total mass of NAPL in soil sample (mg/kg)

d_{napl} = Density of the NAPL mixture (mg/L)

P_b = Bulk density of soil (kg/L)

n_t = Total soil porosity (%)

Appendix A.1.4. Vapor Transport (Diffusion Equation)

Fick's Second Law:

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial z^2} \quad (\text{A22})$$

where:

D : effective diffusion coefficient ($\frac{\text{m}^2}{\text{s}}$)

C : Soil Air Concentration ($\frac{\text{mg}}{\text{L}}$)

z : The distance (m)

t : The time (s)

Appendix A.1.5. Soil Temperature Equation

$$T(x, t) = T_0 + T_{10} \times \exp(-\alpha \cdot x) \cos(\omega \cdot t - \alpha x) \quad (\text{A23})$$

where:

T_0 : Average soil temperature 16 °C, adopted consistently with the formulations reported by Holmes et al. [43], and subsequently applied by Barrio-Parra et al. [37].

T_{10} : Amplitude of temperature oscillations at ground level. Considering the meteorological data on the site, a value of 13 °C was used in this work.

ω = Angular seasonal or diurnal frequency ($7.27 \times 10^{-5} \left(\frac{1}{\text{s}}\right)$).

$$\alpha = \sqrt{\frac{C_{\text{soil}} \cdot \omega}{2 \cdot k}} \quad (\text{A24})$$

where:

C_{soil} : Soil volumetric heat capacity ($2 \cdot 10^6 \text{ J} \cdot \text{m}^3 \cdot ^\circ\text{C}^{-1}$)

k : Thermal soil conductivity = $1.2 \text{ J} \cdot \text{m}^{-1} \cdot \text{s}^{-1}$ [75].

In the present study, the same temperature formulation and parameterization adopted in previous studies were retained to maintain consistency with the original modelling framework.

Appendix A.1.6. Soil Moisture Equation

$$\theta_w(x) = \theta_{wr} + (\theta_{ws} - \theta_{wr})[1 + (\alpha \cdot x)^n]^{-m} \quad (\text{A25})$$

$$m = 1 - \frac{1}{n} \quad (\text{A26})$$

where θ_{wr} [-] and θ_{ws} [-] corresponds to the residual and saturated water contents (respectively), α [m^{-1}], n [-], and m [-] are the dimensionless retention parameters that depend on the type of soil [76] and x [m] is the pressure head, equal to the elevation above the static groundwater level.

Appendix A.1.7. Soil Tortuosity Equation

$$\tau_i(x) = \frac{\theta_g^{10/3}}{\theta_t^2} \quad (\text{A27})$$

where:

θ_g : Gas-filled porosity (%)

θ_t : Total porosity (%)

Appendix A.1.8. Effective Diffusion Coefficient Modification Equations

Diffusion Coefficient Correction (relative to soil turbidity, moisture, and temperature, respectively)

$$D_i = \tau_i D_i^* \quad (\text{A28})$$

where:

τ_i : The tortuosity [-]

D_i^* : The molecular diffusion coefficient ($\frac{\text{m}^2}{\text{s}}$) in phase i.

$$D_e(m, \epsilon) = D_{\text{air}} \cdot \epsilon \cdot e^{(-6m\epsilon - 6m^{14}\epsilon)} \quad (\text{A29})$$

where:

D_{air} : The diffusion coefficient of the contaminant in air ($\frac{\text{m}^2}{\text{s}}$)

$$D_{\text{eff}}(z) = D_{\text{air}} \cdot \tau(x) \cdot \left(\frac{T}{273}\right)^{3/2} \quad (\text{A30})$$

where:

$D_{\text{eff}}(z)$: Effective Diffusion Coefficient ($\frac{\text{m}^2}{\text{s}}$)

D_{air} : The diffusion coefficient of the contaminant in air ($\frac{\text{m}^2}{\text{s}}$)

T : The temperature along the soil profile (K)

Appendix A.1.9. Numerical Implementation

Finite Difference Discretization of Diffusion Equation:

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} \quad (\text{A31})$$

$$C_i^{n+1} = C_i^n + \frac{D \times \Delta t}{(\Delta z)^2} (C_{i+1}^n - (2C_i^n) + C_{i-1}^n) \quad (\text{A32})$$

$$\text{Define: } \lambda = \frac{D \times \Delta t}{(\Delta z)^2} \quad (\text{A33})$$

$$C_i^{n+1} = C_i^n + \lambda (C_{i+1}^n - (2C_i^n) + C_{i-1}^n) \quad (\text{A34})$$

Appendix A.1.10. Vapor Entry to Building (Indoor Air Concentration Calculations)

Crack Concentration:

Advection:

$$C_{ck} = \frac{\pi \cdot D_e(d_s) \cdot t_{ck}}{D_a w_{ck}} \cdot C_{\text{subslab}} \quad (\text{A35})$$

where:

t_{ck} : The thickness of the foundation (m)

w_{ck} : The width of the crack (m)

$D_e(d_s)$: The Effective Diffusion Coefficient ($\frac{m^2}{s}$)

d_s : The distance of the foundation cracks from the edge of the contaminant plume (m)

D_a : The Air Diffusion Coefficient ($\frac{m^2}{s}$)

Indoor Air Concentration:

$$C_{in} = C_{ck} \left(\frac{R_{mix}}{R_{crack} + R_{mix}} \right) \quad (\text{A36})$$

where:

C_{ck} : The sub-slab crack concentration

$$R_{mix} = \frac{1}{L_{mix} \cdot ER} \quad (\text{A37})$$

$$R_{crack} = (R_{mix} \frac{A_b}{Q_s})(e^{-\varepsilon} - 1) \quad (\text{A38})$$

$$\varepsilon = \frac{A_b t_{ck}}{Q_s D_a \cdot \eta} \quad (\text{A39})$$

$$\eta = \frac{w_{ck} l_{ck}}{A_b} \quad (\text{A40})$$

$$Q_s = \frac{2\pi K_a \Delta p l_{ck}}{\mu \ln \left(\frac{2d_f}{r_{ck}} \right)} \quad (\text{A41})$$

$$r_{ck} = \frac{\eta A_b}{l_{ck}} \quad (\text{A42})$$

where:

r_{ck} : The crack radius (m)

η : the foundation crack fraction (-)

A_b : The foundation area in contact with the soil (m^2)

l_{ck} : The foundation perimeter (m)

Q_s : The convective soil vapor entry rate into the building ($\frac{m^3}{s}$)

K_a : The soil air permeability (m^2)

Δp : The pressure difference between the building and the soil (Pa)

μ : The soil gas viscosity (Pa·s)

d_f : The depth of foundation below the ground surface (m)

L_{mix} : The height of the building at which contaminant mixing occurs (m)

ER: The building air exchange rate ($\frac{1}{\text{hour}}$)

Appendix A.1.11. Risk Calculation (Cancer and Non-Cancer)

Cancer Risk:

$$\text{Risk} = \frac{\text{URF} \cdot \text{EF} \cdot \text{ED} \cdot C_{\text{indoor}}}{\text{AT}_C \cdot 365 \text{ days/year}} \quad (\text{A43})$$

where:

URF: Unit risk factor $(\frac{\mu\text{g}}{\text{m}^3})^{-1}$

EF: Exposure frequency $(\frac{\text{days}}{\text{yr}})$

ED: Exposure duration (yr)

C_{indoor} : Indoor Air Concentration for Carcinogens $(\frac{\mu\text{g}}{\text{m}^3})$

AT_C : Averaging time for carcinogens (yr)

As indicated by Equation (A43), the estimated lifetime cancer risk is directly proportional to the indoor air concentration of carcinogenic compounds (e.g., benzene) when exposure duration, exposure frequency, and toxicity parameters remain constant. Consequently, increases in indoor vapor concentration lead to corresponding increases in predicted cancer risk within the adopted exposure assessment framework. The risk estimates presented in this study are based on a conservative residential exposure scenario; therefore, alternative exposure settings (e.g., occupational scenarios with reduced exposure duration or frequency) would generally be expected to result in lower overall risk estimates.

Non-Cancer Risk:

$$\text{HQ} = \frac{\text{EF} \cdot \text{ED} \cdot \frac{1}{\text{RFC}} \cdot C_{\text{building}}}{\text{AT}_{\text{NC}} \cdot 365 \text{ days/year}} \quad (\text{A44})$$

where:

C_{building} : Indoor Air Concentration $(\frac{\text{mg}}{\text{m}^3})$

RfC: Reference Concentration $(\frac{\text{mg}}{\text{m}^3})$

AT_{NC} : Averaging time for noncarcinogens (yr)

Cumulative Hazards:

$$\text{CCR} = \sum_{i=1}^n C R_i \quad (\text{A45})$$

where:

CCR: Cumulative cancer risk [-]

CR_i : Cancer risk associated with contaminant i [-]

n : Number of carcinogenic contaminants

$$\text{HI} = \sum_{i=1}^n H Q_i \quad (\text{A46})$$

where:

HI: Hazard Index (Cumulative hazard quotient) [-]

HQ_i : Hazard quotient for contaminant i [-]

n : Number of non-carcinogenic contaminants

Appendix B. Model Verification and Numerical Implementation Details

Appendix B.1. Numerical Solution Parameters for Soil Diffusion

Table A2. Numerical Solution Parameters for Soil Diffusion.

Parameter		Value	Unit
Vertical discretization	Δz	0.1	m
Time step	Δt	2	hour

The selected time step (2 h) was determined based on numerical stability and convergence testing. Additional sensitivity checks confirmed that smaller time steps did not significantly affect model outputs. The total simulation period considered in this study was 30 years, consistent with the residential exposure scenario adopted in the human health risk assessment framework.

Appendix B.2. Model Verification Summary

Table A3. Model Verification Summary.

Process Verified	Reference	Quantity Compared	Reference Values	NAPL_PDRM Results	Agreement Assessment
Multi-Phase Chemical Partitioning	NAPLator (Rucker, 2003) [20]	Phase concentrations	Identical values reported	Identical values obtained	Exact numerical agreement
Diffusion- Driven Soil Gas Transport	Yao et al. (2017) [66]	Soil gas concentration at depth	Reported concentration ranges	Predicted values within reported ranges	Consistent with reported ranges
Advection Soil Gas Transport and Indoor Air Entry	Unnithan et al. (2023) [45]	Sub-slab concentration (g/m ³)	0.025	0.021	Agreement in order of magnitude with literature-reported ranges
		Indoor air concentration (g/m ³)	3.86×10^{-5}	1.29×10^{-5}	

Appendix C. Detailed Results

Indoor Air Concentration for Benzene for Six Scenarios Related to Figure 3

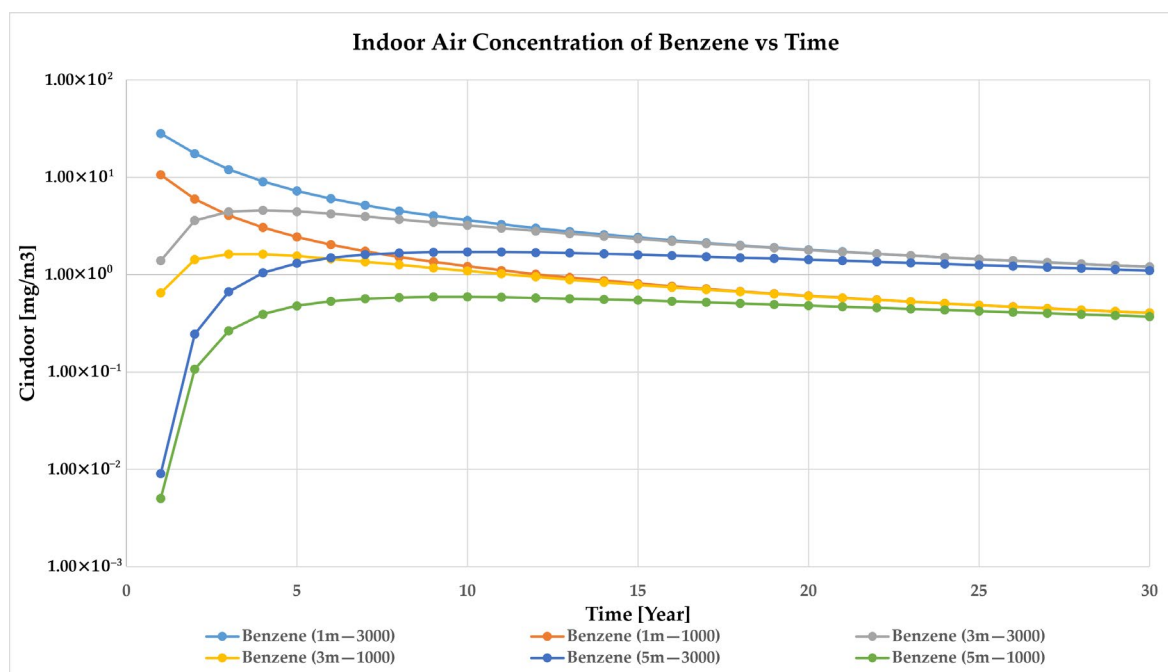


Figure A2. Comparing Indoor Air concentration for benzene for six scenarios.

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