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System-dynamics modeling of source mass-depletion and risk-exposure evolution for natural attenuation processes in the vadose zone

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RUNNING HEAD TITLE: System-dynamics modeling in natural attenuation processes

Abstract Public health is potentially at risk after a contaminant of concern (COC) is released into the ecosphere. The extent of contamination depends on numerous factors; modeling a contaminant's dynamic behavior is challenging, given the multitude of relevant parameters and the fluid nature of processes involved. For example, weather events (e.g., wet or dry periods) may affect the mass depletion and the fate and transport of COCs, and hence, the risk assessment of current and potential future exposures. Thus, to give realistic estimates for potential risks, a contaminant's dynamic behavior must be taken into account in decision-making processes. In this paper, a system-dynamics framework for a dynamic-risk assessment is developed taking into consideration the mass-depletion processes in a natural attenuation environment. This framework rests on the premise that natural attenuation is a complex system involving a variety of source mass-depletion phenomena which evolve over time. Through cause-and-effect loops, a system-dynamics model connects the contaminant's physicochemical and biological mass-depletion processes with the potential risk for exposure by water ingestion and air inhalation. The model considers an idealistic approach involving a continuous average infiltration rate, and a realistic approach incorporating weather fluctuations into the system. To test the proposed model, a conceptual example of benzene contamination in the vadose zone is analyzed. Geological site specifications, contaminant characteristics, and fate-and-transport mechanisms contributing to source mass-depletion are considered, including water infiltration, volatilization, biodegradation, and groundwater recharge. Cancer risk is assessed in two exposure routes (ingestion, inhalation) for idealistic and realistic case scenarios.

Keywords System dynamics · Total Cancer Risk · Monitored Natural Attenuation (MNA) · Mass depletion

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1. Introduction

According to the latest reports by the U.S. Environmental Protection Agency, approximately 51 per cent of the total U.S. population lives within three miles of a Superfund site (US EPA OSWER 2013), which may pose risks to human health. Numerous environmental-health studies suggest that a variety of human health problems, including cancer (US EPA 1987), correlate strongly with the degree of exposure of the local community to contaminated sites by air inhalation, water and food ingestion, or direct contact. Public awareness and concerns about possible adverse effects of hazardous-waste sites on human health became prominent in the late 1970s (Swartjes 2011).

Remedial actions are often undertaken in order to mitigate or eliminate the adverse effects of contamination. Formulated remediation objectives commonly focus on mass reduction of contaminants of concern (COCs) using cost-effective treatment methods that serve the ultimate goal of protecting human health and the environment (Havranek 1999; Fjeld et al. 2007). The extent of contamination depends on dynamic and stochastic phenomena, including contaminant properties and amount released, transport and transformation mechanisms, site hydrogeological characteristics, prevailing environmental factors, and meteorological conditions (Corbitt 1990; Huntley and Beckett 2002). Contamination of natural ecosystems and resources often places a high burden on land use planning, hence a risk assessment investigation is necessitated. Thus, a long-term estimation of the dissolution, fate and transport of COCs considering all system components, and their interaction over time, is needed (Karapanagioti et al. 2003). This dynamic behavior needs to be taken into account in the decision-making process, in order to provide better estimations for potential risks.

In recent years, various environmental tools have been developed to support the decision-making process concerning the land use of contaminated areas. Comprehensive reviews can be found in the literature (Sullivan 2004; Rizzoli and Young 1997). These decision-supporting tools rely on a multitude of input parameters, commonly grouped into four major categories: (a) COC characteristics and extent of contamination; (b) applicable remediation schemes for the specific site and COC; (c) potential human and ecological risks (carcinogenic and/or hazardous); (d) cost/benefit analysis, including cost estimation or other benefits (i.e., risk reduction) resulting from remedial interventions. Thus, complexity and data intensiveness may limit the effectiveness of these tools (SADA 2005), particularly during the initial stages of the investigation, when data are scarce. Another limitation is that natural-attenuation alternatives are assumed to act linearly without the consideration of any externalities (i.e., meteorological events) that could affect the COCs' fate and transport mechanisms and consequently the receptor exposure levels.

This research argues that it is important to develop a holistic tool capable of integrating the dynamic behavior of a COC fate and transport, and the uncertainty of externalities, in assessing receptor exposure and resulting health risks. From this standpoint, a system-dynamics (SD) framework is developed, considering all system components and their interaction over time. A demonstration of this framework is presented in the form of a case study in which natural attenuation is the selected remedial option for a vadose zone site contaminated by a semi-volatile contaminant (e.g., benzene). The natural-attenuation mechanisms considered include volatilization, biodegradation, and contaminant migration towards the groundwater table as a result of water infiltration. These mechanisms are considered while factoring-in meteorological externalities (i.e., dry and wet events). The model allows the dynamic determination of the contaminant exposure levels in the air and groundwater, and assesses the cancer risk for two exposure routes, namely air inhalation and water ingestion.

2. Analysis

2.1. Scope and Definition of the System/ Research Goals and Objectives

The objectives of this research work are: (1) to develop a holistic model that integrates the contaminant depletion processes considering weather fluctuations; (2) to determine the actual exposure duration (ED) for different exposure routes; and (3) to estimate the cancer risk considering all these factors.

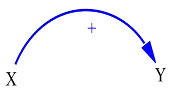
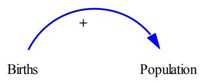
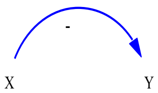
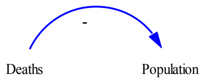
The developed model is applied to a case study. The case study system consists of a contaminated vadose zone area (soil, groundwater, and air), the target contaminant and affected parties (humans living nearby). The system also includes contaminant fate-and-transport mechanisms due to volatilization, groundwater (GW) infiltration and GW advection, biodegradation, and adsorption. The effects of weather externalities (wet/dry events) are also considered. Exposure to contaminant and cancer risk is assessed considering average weather effects (common approach) and weather fluctuations (research approach). Depending on the risk assessment results, the need for human intervention will be evaluated and a possible course of action will be suggested.

2.2. System Analysis and System Dynamics

The American Cybernetics Society defines System Analysis as: "*An approach that applies systems principles to aid a decision-maker with problems of identifying, reconstructing, optimizing, and managing a system, while taking into account multiple objectives, constraints, and resources.*" (Mostashari 2011)

Systems thinking, an integral part of system-dynamics (SD), is the analysis toward a holistic approach that takes into consideration the interactions between the components of a system, in contrast with a narrowed analysis that focuses only on specific parts of the system in an isolated environment. SD provides a better insight into a system's behavior by using casual loop diagrams (CLDs) that illustrate and provide a qualitative interpretation of the feedback structure of the system (Table 1 and Figure 1)(Sterman 2000). SD provides a better insight into the system's behavior while using the stock and flow structures, time delays, and nonlinearities (Figure 1) and determining the dynamic and complex behavior of a system, regardless of the degree of complexity (Bossel 2007; Chang 2011). Limited research work has been done in the environmental field using the system-dynamics approach, especially in the water-management field (Khan et al. 2009; Simonovic 2002, 2009; Winz et al. 2009).
Analysing contaminated sites and their effects by using systems thinking, allows decision-makers to understand the key elements and their interconnections at different spatial levels (local, regional, global) and, from different perspectives (social, economic, environmental), while taking into consideration all the stakeholders' needs and concerns (Kalomoiri and Braida 2013; Kalomoiri et al. 2016; Kalomoiri 2016). In this research work, the system-dynamics model developed using systems thinking principles, aims at a better insight into a system's behavior by using CLDs (Table 1) (Sterman 2000).

Table 1 Links between polarity, definitions and examples (Sterman 2000).

Symbol	Interpretation	Mathematics	Example
	If X increases or decreases, then Y increases or decreases, respectively. In the case of accumulations, X adds to Y.	$\frac{dy}{dx} > 0$	
	If X increases or decreases, then Y decreases or increases, respectively. In the case of accumulations, X is subtracted from Y.	$\frac{dy}{dx} < 0$	

Stocks and flows, together with CLDs, the central concepts of systems dynamic theory (Sterman 2000; Ford 1999), are also used to model the system, while simulations are utilized to study the behavior of the system. The SD software used in this analysis is Vensim DSS 6.4 (Ventana Systems Inc. 2006).

Figure 1 Stock and flow model.

2.3. Case Study

A SD model is used to analyze natural attenuation phenomena governing the fate and transport of a light non-aqueous phase liquid (LNAPL) contaminating vadose zone soils and the groundwater of an adjacent unconfined aquifer. This case study considers a pure compound (benzene) in order to establish a simpler conceptual model (Figure 2). The mass of the benzene at $t_o = 0$ (initial conditions), is set at 8×10^5 g. The average thickness of the benzene layer is 40 cm and it expands to an area of 9×10^5 cm^2. The contamination resides in the vadose zone, which is assumed to be homogenous with an average porosity of 0.35. The unconfined aquifer is located 1000 cm below the spill area and the direction of the groundwater flow is toward the location of the receptor's well. The soil is assumed to be homogenous with no impermeable materials present. Consequently, the aquifer is directly influenced by climatic factors (precipitation, temperature) and human interventions such as irrigation.
Depending upon the fate of the LNAPL, several receptor exposure scenarios may be possible, including surface water exposure due to recharge of surface streams, inhalation due to vapor intrusion in basements, and exposure to dissolved species in groundwater via contaminated wells (Fetter 1993). In this case study, it is assumed that the receptor is exposed to benzene by two different pathways: (1) via groundwater ingestion from consumption of benzene-contaminated well water; and (2) via inhalation of benzene vapor that intrudes into the house from the subsurface. The distance between the

contaminated subsurface area and the receptor's house is assumed to be 1500 cm (X_R) and the distance to the surface area is 1000 cm (L_R).

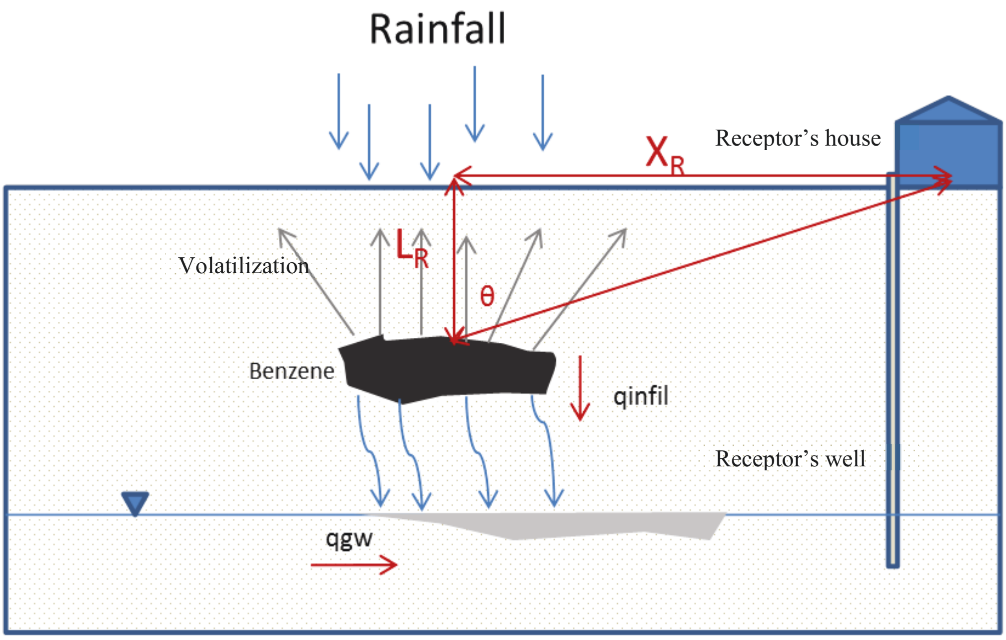


Figure 2 Conceptual model of contaminant transport, and transport mechanisms
(X_R = horizontal distance between plume and receptor's house, L_R = vertical distance between plume and surface, q_{infil} = Infiltration flow rate, q_{gw} = groundwater flow rate)

The LNAPL substance(s), once in the vadose zone, can partition into the dissolved, sorbed, and vapor phases depending upon composition characteristics (Sara 2003). Partitioning depends on the substance's water solubility, soil organic carbon partition coefficient, soil organic carbon content, and contaminant volatility. Upon release, various transport mechanisms may contribute toward the mass depletion of the contaminant. Specifically, in this case study, the following mass fluxes are considered: a gaseous mass flux resulting from direct volatilization of the LNAPL (benzene) into the gas phase; and a dissolved mass flux resulting from water infiltration in the vadose due to weather processes (precipitation), or human interventions (irrigation). In addition, two transformation mechanisms may contribute to contaminant mass depletion and are taken into consideration in this exercise: biodegradation and adsorption, quantified by the retardation factor which evaluates transport delays.
System dynamics allows for the incorporation of environmental parameters, such as temperature, pH, etc., and their changes over time; however, for simplicity reasons they are not considered here.

2.4. Governing Equations

2.4.1. Mass depletion Equations

The processes mentioned above are modeled using the following equations:

Contaminant Volatilization. The mass flux that occurs due to volatilization Eq.(1) is based on Huntley and Beckett (2002):

$$J_{vol}^{i} = C_{air,i}^{sat} \frac{D_{eff}^{i}}{z} H_s \times L_s \tag{1}$$

where i = i-th component of a mixture of different compounds, and in this case study is equal to 1, as benzene is the sole compound considered in the analysis;
z = distance between the benzene source and the surface (cm);
H_s = width of the source (cm);
L_s = length of the source (cm);
D_{eff}^{i} = effective diffusivity ($cm^2 \cdot month^{-1}$).

The latter is calculated by Eq. (2) (Bartelt-Hunt and Smith 2002; Millington 1959):

$$D_{eff}^{i} = D_a \times \frac{\theta_a^{3.33}}{n^2} \quad (2)$$

where D_a = free air diffusion coefficient ($cm^2 \cdot month^{-1}$);

θ_a = air-filled porosity;

n = soil porosity.

Based on Raoult's law, the air saturation concentration $C_{air,i}^{sat}$ is given by Eq. (3):

$$C_{air,i}^{sat} = x_i \frac{P_i \times MW_i}{R \times T} \quad (3)$$

where x_i = mole fraction of the i-th component;

P_i = vapor pressure above the pure phase of benzene (kPa);

MW_i = molar mass of benzene (78.11 $g \cdot mole^{-1}$);

R = universal gas constant, 8.3×10^{-3} ($kPa \cdot cm^{-3} \cdot moles^{-1} \cdot K^{-1}$);

T = absolute temperature (K).

Air intrusion concentration. The vapor concentration that reaches the soil under the receptor's house is estimated using Eq. (4) (Thibodeaux and Hwang 1982):

$$C_{air}^{rec} = C_{air,i}^{sat} - \frac{X_R \times J_{vol} \times \cos\theta}{D_{eff} \times A_s} \quad (4)$$

where X_R = distance between the source and the receptor's house;

J_{vol} = volatilization mass flux on the y axis.

Contaminant transport to groundwater. Assuming a completely mixed reactor, the mass flux for groundwater infiltration, $J_{gw,}$ is given by Eq. (5):

$$J_{in}^{i} = C_{w,i}^{sat} \left(1 - e^{-\frac{t}{\tau}}\right) \mathrm{A}_s \times q_{in} \times f \quad (5)$$

where $C_{w,i}^{sat}$ is the water saturation concentration ($g \cdot cm^{-3}$), given by Eq. (6):

$$C_{w,i}^{sat} = x_i \times C_s \quad (6)$$

where C_s = aqueous solubility of benzene;

q_{in} = groundwater infiltration rate ($cm \cdot month^{-1}$);

A_s = area occupied by the contaminant (cm^2);

V_s = volume of the contaminant (cm^3);

n = porosity;

f = factor giving the percentage of the permeable surface area, taking values on the interval [0, 1];

τ = residence time (months), defined by Eq. (7):

$$\tau = \frac{V_s \times n}{q_{in} \times A_s} \quad (7)$$

This factor can influence all three main processes involved in mass depletion. In this case study, it is assumed that there is no impermeable surface and that all the processes are dependent on the environmental conditions, such as rain or snow, or any human interventions, such as irrigation.

Based on field experience, $C_{w,i}^{sat}$ rarely reaches contaminant aquatic solubility levels, and it commonly assumes values of less than 30 % of C_s. For the purposes of this study, $C_{w,i}^{sat}$ is assumed to be 30 % of C_s.

A mass-balance approach was utilized in order to estimate the benzene concentration at the lower floor of the receptor's house. This is a conservative approach, but it is a safe assumption, as it quantifies the highest carcinogenic health risk to which the receptor is exposed (Eq. (8)):

$$C_{air}^{bas} = \frac{C_{air}^{rec} \times Q_{soil}}{Q_b} \quad (8)$$

where Q_b = building ventilation rate ($cm^3 \cdot month^{-1}$).

The building ventilation rate is given by Eq. (9) (Johnson and Ettinger 1991; US EPA 1997):

$$Q_b = \frac{A \times ER \times H_b}{3600} \tag{9}$$

where A_h = area of the receptor's house (cm^2);
H_b = first floor height (cm);
ER = air exchange rate ($hour^{-1}$) and
Q_{soil} = volumetric flow rate of soil vapor entering the building ($cm^3 \cdot month^{-1}$)
3600 is a conversion factor for hours to seconds.

Table 2 Values used to estimate the vapor concentration at receptor's house

List of Symbols		Default value/Citation	Values	Units
A_h	Receptor's house area		3×10^6	cm^2
ER	Air exchange rate	Parker et al. (1995); Koontz and Rector (1995)	0.45/h	h^{-1}
H_b	First floor height		400	cm
Q_{soil}	Soil vapor volumetric flow rate	US EPA (1997)	2.19×10^8	$cm^3 \cdot month^{-1}$
X_R	Distance between source and receptor's house		1500	cm

Contaminant concentration reaching receptor's well. To estimate the benzene concentration reaching the receptor's well, advection-is considered as the dominant groundwater transport mechanism, while diffusion that contributes toward the concentration reduction is left out of the analysis, thereby giving a more conservative estimation. Eq. (10) is used to estimate the concentration at the receptor's well is the following:

$$C_{rec}^{well} = \frac{J_{gw}^{i}}{Vf_{gw}} \tag{10}$$

where J_{gw}^{i} = mass flux of the dissolved benzene that recharges the groundwater ($g \cdot month^{-1}$);
Vf_{gw} = groundwater volumetric flow ($cm^3 \cdot month^{-1}$)

The groundwater volumetric flow is given by Eq. (11):

$$Vf_{gw} = q_{gw} \times A_{aq} \tag{11}$$

where q_{gw} = groundwater flow rate ($cm \cdot month^{-1}$);
A_{aq} = aquifer cross-sectional area (cm^2).

Contaminant biodegradation. The amount of mass biodegraded over time is given by Eq. (12):

$$J_b = C_{w,i}^{sat} \times k \times V_w \tag{12}$$

where k = biodegradation rate constant ($month^{-1}$);
V_w = pore volume occupied by water (cm^3), given in turn by Eq. (13):

$$V_w = \theta_w \times A_s \times T_s \tag{13}$$

where θ_w = water-filled porosity;
A_s = source area (cm^2);
T_s = contaminant's source thickness (cm).

Finally, the retardation factor is estimated by Eq. (14):

$$R = 1 + \frac{\rho_b}{n} \times K_d \tag{14}$$

where ρ_b = soil bulk density (g·cm^{-3});

K_d = distribution coefficient (g·cm^3).

The values used for running simulations for this exercise are summarized in Table 3.

Table 3 Values used to estimate benzene's mass depletion through natural attenuation processes

List of Symbols		**Values**	**Units**
A_s	Source area	9×10^5	cm^2
C_s	Water solubility	1.7×10^{-3}	g·cm^{-3}
D_a	Free air diffusivity	2.44×10^4	cm^2·month^{-1}
K_d	Distribution coefficient	0.01178	g^{-1}·cm^3
K	Rate constant	1.05	month^{-1}
MW_i	Molar mass	78.11	g·mole^{-1}
N	Porosity	0.35	-
P_i	Benzene vapor pressure	12.7	kPa
q_{in}	Infiltration rate	108	cm·year^{-1}
T_s	Source thickness	40	cm
T	Absolute temperature	297	K
x_i	Mole fraction	1	-
L_R	Source-to-surface distance	1000	cm
θ_w	Water-filled porosity	0.07	-
θ_a	Air-filled porosity	0.28	-
ρ_b	Soils bulk density	1.65	g·cm^{-3}

2.4.2. Cancer Risk Equations

The governing equations used to assess the carcinogenic risk for the two applicable pathways (vapor inhalation, water ingestion) are presented in Table 4, and the values used for model simulations for this exercise are given in Table 5 (Fjeld et al. 2007; US EPA 2005; Theodore and Dupont 2012).

Table 4 Cancer risk equations due to vapor inhalation and water ingestion

Cancer risk equations
Cancer risk due to vapor inhalation
$CR_{inh}^{i} = LADD_{inh} \times CSF_{inh}^{i}$
Exposure concentration
$LADD_{inh} = \dfrac{C_{air}^{bas} \times EF \times ED \times I_{inh}R}{AT \times BW}$
Cancer risk due to water ingestion
$CR_{ing}^{i} = LADD_{ing} \times CSF_{ing}^{i}$
$LADD_{ing} = \dfrac{C_{well}^{rec} \times EF \times ED \times I_{ing}R}{AT \times BW}$

Table 5 Values used to estimate the cancer risk due to benzene vapor inhalation and water ingestion

List of Symbols		Values	Units
$I_{inh}R$	Air inhalation rate	12	$m^3 \cdot d^{-1}$
$I_{ing}R$	Fraction of contaminated drinking water	670	$cm^3 \cdot d^{-1}$
BW	Body weight	15	kg
EF	Exposure frequency	29	$Days \cdot month^{-1}$
ED	Exposure duration (highest)	Actual event duration or 30 years if chronic	years
CSF^i_{inh}	Cancer slope factor for inhalation	1.5×10^{-3}	$kg \cdot d \cdot g^{-1}$
AT	Averaging time	70	year
CSF^i_{ing}	Cancer slope factor for ingestion	2.5×10^{-3}	$kg \cdot d \cdot g^{-1}$

These values are site-specific and for this particular analysis, one of the most vulnerable receptor categories is considered: a child between 6 to 12 years of age. If the cancer risk is not found to be substantial, then no further remediation actions need to be considered.

3. Results

3.1. Modeling Natural Attenuation (NA) with SD

The above-mentioned processes contributing to COC mass depletion are modeled using system dynamics, as illustrated in Figure 3. The model is operated in a monthly time step with the end of the simulation signaled by the complete depletion of the mass of benzene. The presented model has not been calibrated with any observed data.

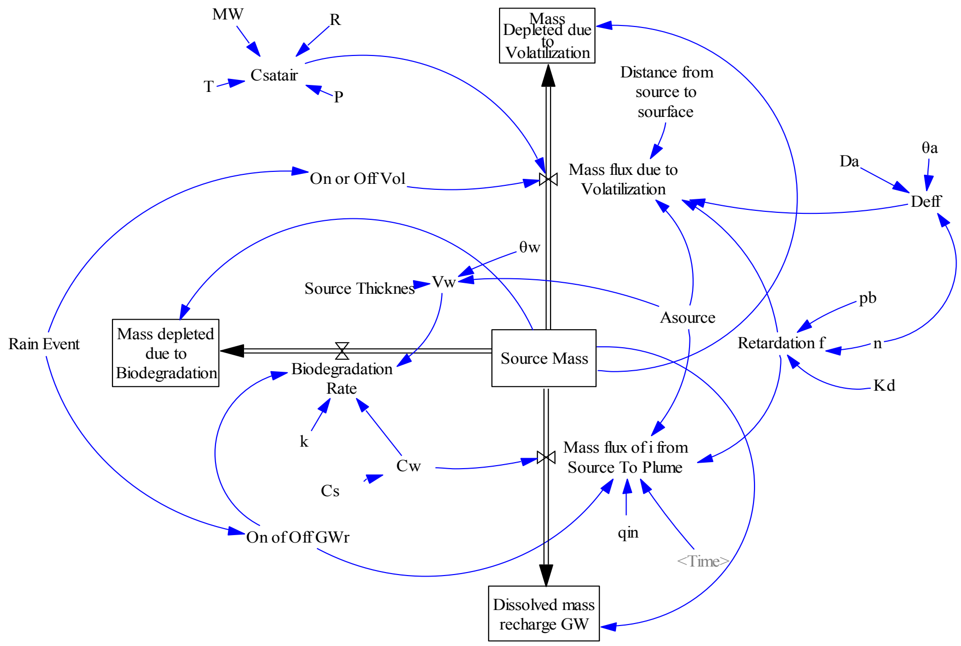
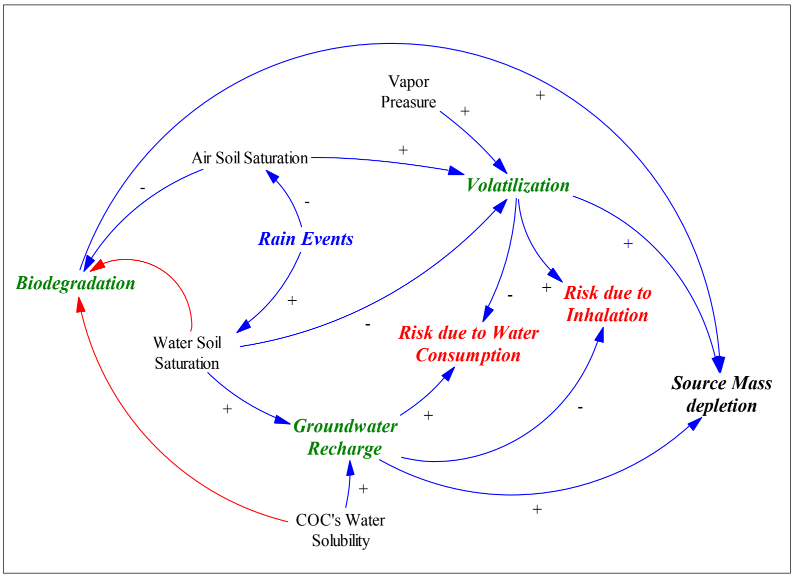


Figure 3 SD model of natural attenuation processes.

The initial simulation of the model considers that all the processes evolve through time, and takes into account an average annual value of the infiltration rate, resulting from an average precipitation rate. This is a common approach used especially in the initial stages of a site investigation to determine the COC mass-depletion rates due to the physical and biological processes that evolve through time. This research approach contends with the above-mentioned approach, showing that dry and wet events can alter the evolution of the transport processes. The causes and effects between the dry-wet events and the physical-biological processes are shown in Figure 4.

Figure 4 Casualty behaviour between the mass-depletion due to the physical, chemical and biological processes and the rain events, and the causes and effects between the processes and the carcinogenic risk.



The rain-event variable can take two values (Table 6): (a) 0 (Yes), when rain events occur and the vadose zone is saturated with water; and (b) 1 (No), when rain events do not occur (dry seasons) and the vadose zone has very low water content. It is important to state that the rain-dry event fluctuations, presented in Table 6, are assumed; more realistic data that correspond to a specific geographic region where a contaminated site is located can be used, to give more realistic outcomes of the model.

Table 6 Rain Events: When Yes, rain events occur; when No, rain events do not occur

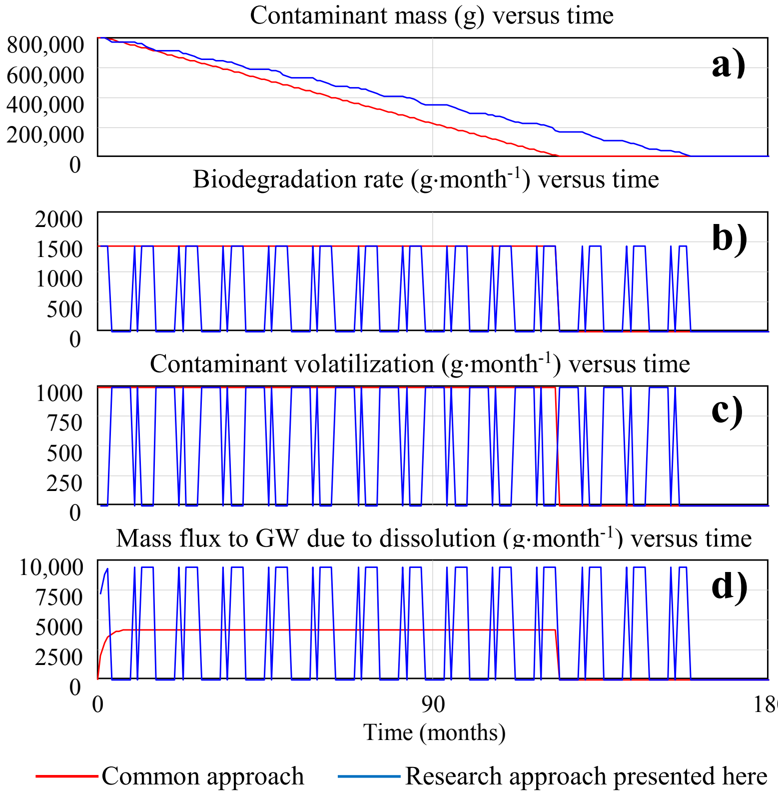
Time/Months	1	2	3	3.7	4	5	6	7
Events	Yes	Yes	Yes	Yes	No	No	No	No
Time/Months	8	8.7	9	9.5	10	10.5	11	12
Events	No	Yes	No	No	Yes	Yes	No	Yes

The On/Off Vol variable is the causal relation between the volatilization process and the wet-dry events. When a rain event occurs, the volatilization process stops as the soil pore space is flooded with water. In contrast, when dry seasons prevail, the water content in the pore space of the vadose zone is low, air filled porosity increases, and volatilization becomes the dominant contaminant depletion mechanism. Similarly, the On/Off GW variable describes the causal relation between the wet-dry events, biodegradation, and groundwater recharging. The On/Off GW variable signifies that both processes benefit from wet conditions, when the soil pore space is filled with water. Conversely, during dry periods, biodegradation and groundwater become less significant. The above discussion clearly indicates that weather- related externalities influence the water-air ratio in the vadose pore space and consequently the dynamic processes that govern contaminant depletion.

3.2. Simulation of NA Processes

Figure 5 shows the mass depletion of benzene considering both scenarios that have been described above.

Figure 5 Mass-depletion rates considering a common approach and that in the present work:
(a) Source mass depletion;
(b) Mass depletion due to biodegradation;
(c) Mass depletion due to volatilization;
(d) Mass depletion due to dissolution and GW infiltration



It is apparent that the second scenario gives a more conservative mass-depletion time, approximately thirteen and a half years, than the first scenario, which shows that the mass is depleted within ten and a half years. Additionally, Figure 5 shows how the mass-depletion rates due to (a) volatilization, (b) groundwater infiltration, and (c) biodegradation respond to the integration of dry and wet events into the system analysis. When volatilization is at a maximum, the other two processes are negligible and vice versa.

3.3. Modeling and Simulation of Cancer Risk

Considering that all the processes evolve through time as described previously, the system-dynamics model integrates and simulates the carcinogenic risk due to two different exposure pathways (air inlahaltion and water ingestion), as shown in Figure 6.

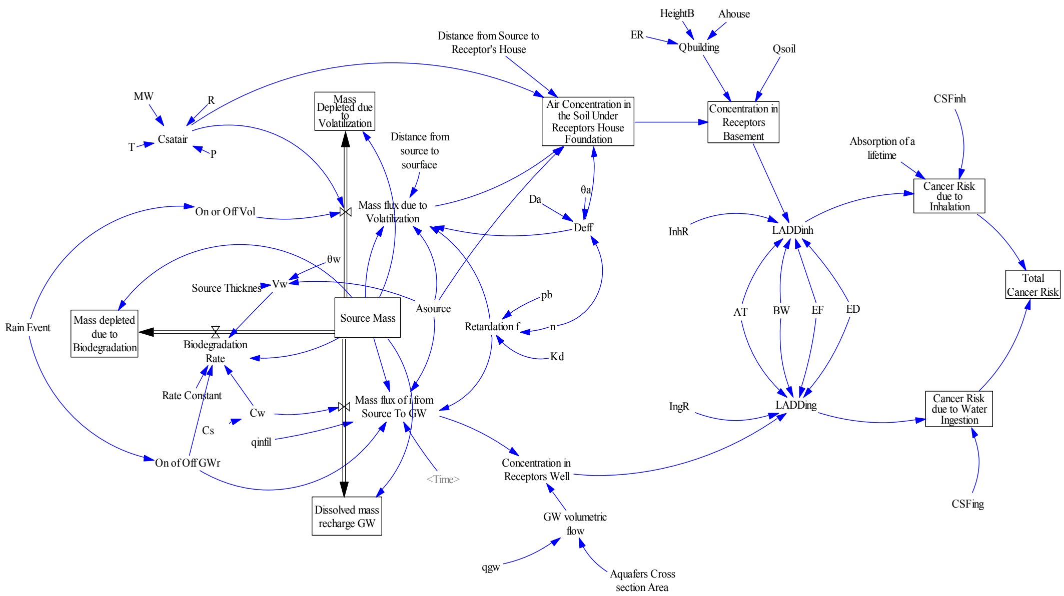


Figure 6 MNA and risk-assesment system-dynamics model

Figures 7 and 8 show the concentration of benzene at the receptor location by the two different pathways considered.

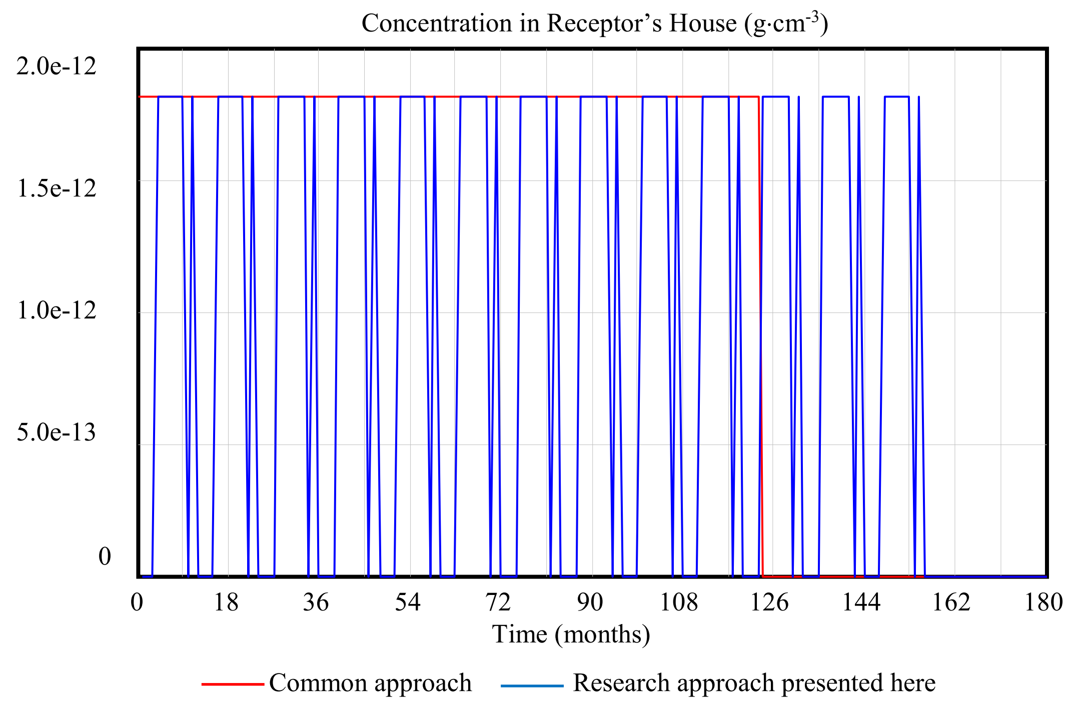


Figure 7 Concentration in receptor's house

Considering the common approach, Figure 7 shows that the concentration in the receptor's house is 1.8×10^{-12} g·cm^{-3}, remaining constant thereafter until the mass of benzene is completely depleted. Conversely, when the wet-dry fluctuations are considered, the concentration at the receptor's house fluctuates between zero (for the wet events) and the maximum value of 1.8×10^{-12} g·cm^{-3} (for the dry events).

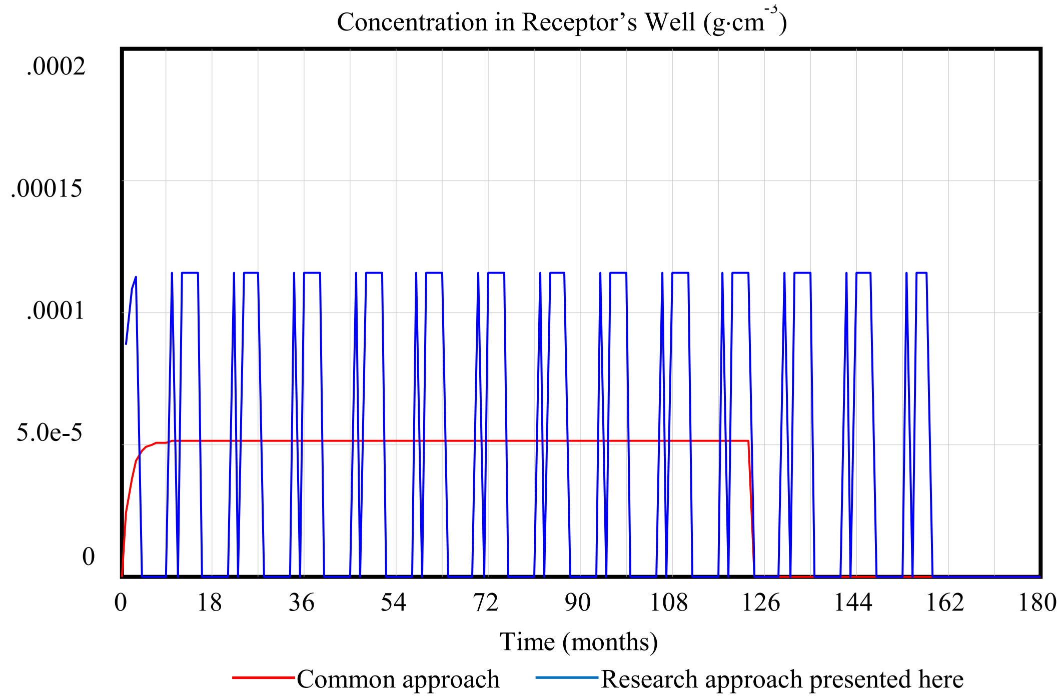


Figure 8 Concentration in receptor's well

Figure 8 shows the contaminant concentration in the receptor well. Accordingly, the concentration gradually reaches a maximum value of 5.1×10^{-5} g·cm^{-3} and sustains it until the mass of benzene is depleted completely. On the other hand, considering wet-dry event fluctuations, the concentration at the receptor's well fluctuates similarly between zero (for dry events), and the maximum value of 1.1×10^{-4} g·cm^{-3} (for wet events). The maximum concentration is greater than the common approach, as the estimated monthly infiltration is greater.

According to the *Guidelines for carcinogen risk assessment* (US EPA 2005), the threshold risk of benzene is 10^{-6} indicating a 1:1,000,000 risk of cancer. The total carcinogenic risk is derived from the summation of the risk for each of the exposure pathways (inhalation and water ingestion considered in this study). The most important parameters that affect the carcinogenic risk are the concentration of COC at the receptor's location and the contaminant exposure duration (ED). As it is shown in Figures 7 and 8, the COC mass depletion time is estimated to be 127 months and 159 months for the common and present research approaches, respectively. This estimation establishes the total ED to the COC at 127 and 159 months, as well. The common approach considers that this ED is constant for both water ingestion and air inhalation.

This SD research argues that the ED should be considered differently for air inhalation and water ingestion for the following two reasons: (a) the benzene concentration in the air is zero when the vadose zone is saturated, and reaches the maximum value when dry weather conditions prevail. Thus, during wet events when the contaminant concentration in the air is zero, the receptor is not exposed to the air contaminant, and thus, the ED for the air inhalation is null; (b) conversely, the ED for water ingestion is zero when there are no events that promote water infiltration and groundwater recharge. Accounting for the above, the SD model estimates that the actual total exposure duration periods for air inhalation and water ingestion are 91 and 68 months, respectively.

Based on these ED values, the cancer risks (air inhalation, water ingestion and total risk) can be estimated. The estimated values for both approaches are given on Table 7. Accordingly, the risk values estimated by the research approach are about one order of magnitude smaller than those estimated by the common approach. Evidently, the conservative risk estimates generated by the common approach are due to an overestimation of the actual ED.

Table 7 Cancer risk estimations considering 127 and 159 months depletion time under common and research approaches.

Air Inhalation Cancer Risk	$3\text{x}10^{-6}$	Common Approach
	$9.9\text{x}10^{-7}$	Research approach
Water Ingestion Cancer Risk	$1.7\text{x}10^{-2}$	Common Approach
	$4.1\text{x}10^{-3}$	Research approach
Total Cancer Risk	$1.7\text{x}10^{-2}$	Common Approach
	$4.1\text{x}10^{-3}$	Research approach

The cancer risk due to air inhalation as estimated using the present research approach is less than the benzene threshold risk in contrast with the values estimated by the common approach. On the other hand, in both approaches, both water ingestion and total cancer risk are above the benzene threshold risk. In order to mitigate the receptor's potential adverse health risk, soil and/or groundwater remediation actions are necessary.

4. Conclusions

The integration of weather-event fluctuations (dry-wet events) in the analysis of the monitored natural attenuation (MNA), the SD model gave a less conservative estimation of benzene depletion time. Moreover, the SD model proved that those fluctuations affect the physical-biological processes dynamically and in different directions. This alteration in the mass-depletion processes, depending on externalities (dry-wet events), can similarly feed different pathways, in which a receptor is exposed to carcinogenic adverse effects.

Contaminated sites are very sensitive to weather conditions. In recent years, the uncertainty related to weather events has increased due to climate change, and many extreme events (extreme rain-dry periods) occur globally. Therefore, it is necessary to take into consideration these extremes into all stages of soil and groundwater remediation, including initial site investigation, remediation method selection, and design and implementation. More specifically, modeling tools are necessary to provide a better estimation of time depletion rates and potential risks of adverse health effects. This work provides an exercise that demonstrates how systems thinking along with system dynamics can be used effectively to model remedial and natural attenuation schemes.

From the analysis presented herein, it can be concluded that a system-dynamics framework can provide more realistic estimations of the remediation time, contaminant concentration, and overall adverse health effect risk for a receptor. This tool can be particularly useful during the initial stages of investigation, when information is limited. It is important to know the potential pathways by which the COC reaches the receptor, as well as the associated risk of exposure to contaminants, in order to avoid adverse health effects.

Evidently system dynamics can be an effective tool in the hands of engineers that can aid the decision-making process when comparing remediation or natural attenuation alternative schemes and their associated exposure risks.

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