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Exposure risk assessment to organic compounds based on their concentrations in return water from shale gas developments

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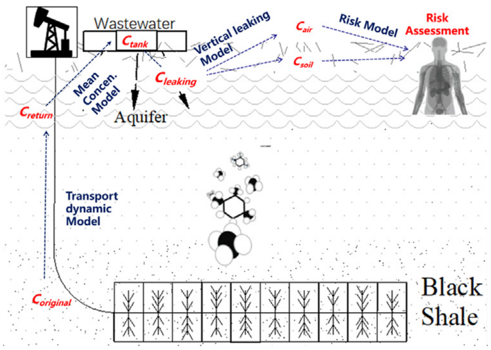
HIGHLIGHTS

- Benzene is the compound that generates the highest risks.
- Inhalation pathway is associated with the highest risks (Cancer and non-cancer).
- Hazard quotients <1 for all organic compounds based on soil pathway.
- Humid environments are the fastest to exceed risk limits.
- The model makes it possible to foresee the time required for action.

GRAPHICAL ABSTRACT



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ABSTRACT

Because of shale gas operations, significant amounts of return water from hydraulic fracturing are stored in tanks and/or ponds on the surface. These waters contain varying concentrations of toxic organic compounds; hence, there is reasonable concern about the occurrence of hypothetical leakages, which would cause adverse environmental effects and pose a risk to human health. In this study, the chronic and acute carcinogenic and non-carcinogenic risks from exposure to these pollutants by inhalation, ingestion and dermal contact have been assessed for an affected area. The first part of this study focused on estimating the concentrations of organic compounds in the water–soil–atmosphere system. These models are of a general nature and can be applied to any site. In this study, they are applied to the Marcellus shale formation. The analyses developed in this work show that the risks - both carcinogenic and non-carcinogenic - regarding the inhalation of volatile organic compounds (VOCs) increase rapidly and exceed the acceptable thresholds by several orders of magnitude in all scenarios, irrespective of the different recharge rates considered. Given that the hypothetical leakage under consideration occurs at a depth of 50 cm, in the buried part of a semi-buried tank-type reservoir, the direct contamination via wastewater of the most superficial parts of the soil is less likely, and soil particles are generally widely dispersed in air before inhaling. Moreover, the sensitivity analysis indicated that the variable contributing the most to the determined risk levels was the pollutant concentration, followed by the exposure time. Therefore, using appropriate technology to reduce pollutant concentrations in storage ponds is the best strategy to minimise the associated risk to human health.

1. Introduction

Given the current scenario of international energy crisis, as technological innovations in drilling and well stimulation techniques continue to advance, unconventional gas production from hydraulic fracturing are

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increasingly becoming a resource to be considered for a significant number of countries. In fact, these technologies are currently used to exploit low-permeability, organic-rich shale formations and 'tight sand' reservoirs in North America, North and South Africa, China, and Australia (Tan et al., 2019; Vengosh et al., 2014; Kargbo et al., 2010). During these operations, an average of 7500–19,000 m^3 (2–5 million gallons) of fluid is injected into the well, and on average 35% of this fracturing fluid comes again to the surface as return water, comprising flowback and produced waters (U.S. Environmental Protection Agency (EPA), 2011b). This is often stored in ponds or lined tanks prior to treatment and disposal or recycling, mainly depending on the applicable environmental regulations. It is necessary to carry out a proper use and management of these facilities as there is strong evidence supporting the conclusion that these fluids can lead to local environmental contamination (Wollin et al., 2020; Abualfaraj et al., 2018). This can be particularly relevant when they involve storage of return waters in uncovered containers at ground level. The handling of these facilities has implications for air quality due to the volatile compounds that are often mixed with the rest of the fluids, and for soil and groundwater quality in relation to leakage/overflow from these facilities (Colborn et al., 2011; Veiguela et al., 2016; DiGiulio et al., 2015).

Toxicity of the return waters is a key factor from an environmental point of view since it contains not only the chemicals needed for the advanced hydraulic fracturing techniques, but also, and depending on the geology. Compounds naturally occurring in the strata in which the gas being exploit is located, such as salts, chlorides, heavy metals (e.g. cadmium, lead, and arsenic), organic chemicals, bromide, and naturally occurring radioactive materials –NORM- (e.g. radium-226).

Among the compounds that can be found in these wastewaters, volatile organic compounds (VOCs, e.g., benzene, toluene, ethylbenzene, and xylene – normally known as BTEX) and polycyclic aromatic hydrocarbons (PAHs) are of particular concern due to their potential effects on human health and the environment (Holder et al., 2019; Zhou et al., 2021; Sun et al., 2019; Wollin et al., 2020). For instance, VOCs can produce health effects such as nausea, eye and throat irritation, induction of asthma attacks, fatigue, dizziness, and mental confusion, even at low concentrations. What is more, BTEX compounds are often associated with an increased risk of cancer or adverse effects on reproduction, especially with chronic exposure, even at low concentrations (McKenzie et al., 2012; Durmusoglu et al., 2010; Masekameni et al., 2018). In addition, PAHs have carcinogenic properties and long-term health effects even at low levels, such as cataracts, kidney and liver damage, and jaundice. The US EPA lists some PAHs as priority pollutants because they are persistent in the environment. They are highly lipophilic and readily adsorb onto particles in both water and aerosols, indicating that exposure to PAHs can occur through inhalation of atmospheric particles, ingestion of contaminated particles (e.g. soil), or dermal contact with contaminated material (e.g. soil, sediment, water) (Irvine et al., 2014; Zhang et al., 2009). Therefore, these chemicals are associated with health risks (carcinogenic and/or non-carcinogenic), and exposure to them can cause harm to both workers and the local population. Exposure to toxic compounds can occur through the contamination of air, soil, and/or water from discharge sites through physical and chemical transport processes (Wattenberg et al., 2015; Shonkoff et al., 2014; McKenzie et al., 2012) Furthermore, the mixing of these compounds can synergistically increase their toxicities (Ragas et al., 2011; Montero-Montoya et al., 2018). And these may result in additional risks, such as skin and eye irritation, neurological and nervous system damage, cancer, and endocrine disruption (Vengosh et al., 2014; Shonkoff et al., 2014; Webb et al., 2016).

With that in mind, well-designed studies are needed to assess the risk to human health from the initial phases of the operation with high certainty (Wollin et al., 2020).

Within this framework, in (Ma et al., 2018) a physicochemical model was established to estimate the expected concentrations of organic compounds present in the return waters of unconventional gas fields.

Subsequently, assuming a leak in a semi-buried surface storage pond, the evolution of the concentrations of these compounds in the different environmental compartments and for different environmental considerations was calculated (Ma et al., 2019).

Based on the above, this article aims to provide answers to questions regarding the risk that such concentrations may pose to human health. Thus, using the field data released by the Marcellus Shale Coalition (Hayes, 2009), to fit the physicochemical model cited above, the present study examines the chronic carcinogenic and non-carcinogenic risks posed to workers and the local community in the region of the Marcellus shale formation in terms of exposure to VOCs and PAHs.

In addition, a sensitivity analysis is performed to assess the effects of parameter variability and uncertainty on the exposure pathways, and to identify the factors that most significantly contribute to the carcinogenic and non-carcinogenic risks (Rasa et al., 2013).

2. Method and materials

2.1. Initial data

This study has made use of the available return water data from several horizontal wells (locations C, D, E, F, F, G, K, M, and O in Hayes (2009)) in the Marcellus shale region (Pennsylvania and West Virginia). These data include organic compound concentrations and return water volumes at different times (0, 1, 1, 5, 14 and 90 days after fracturing event).

Analyses conducted by the Marcellus Shale Coalition covered more than 212 organic compounds in the return water (Hayes, 2009). Therefore, considering the difficulty of individualised treatment, organic compounds were grouped into categories based on (1) their temporal behaviours in return flows (Ma et al., 2018), (2) their physicochemical properties (mainly solubilities and the soil organic carbon–water partition coefficient (K_{oc}) values), and (3) ecotoxicological properties. As a result of the above, the following eight categories were defined: acetophenone; benzene; phenol; TEX (toluene, ethylbenzene, and xylene); TMB (1,2,4-trimethylbenzene and 1,3,5-trimethylbenzene); R-benzene (isopropylbenzene, N-butylbenzene, N-propylbenzene, Sec-butylbenzene, and P-isopropyltoluene); naphthalene (NAPH); and PAHs (pyrene, benzo [a]pyrene) without considering NAPH (referred to hereafter as PAHs - NAPH). Because NAPH is the most volatile and water-soluble PAH, it was separated from PAHs with higher molecular weights, which are less volatile and less water-soluble (Hawthorne and Miller, 2003).

In order to estimate the evolution over time of the concentrations of the eight pollutant categories in a wastewater storage tank, two models are integrated.

- A model for determining the temporal evolution of concentrations in the return water. It is a physicochemical dual permeability model (Ma et al., 2018) fitted with data from Hayes (2009). In the temporary sampling carried out by Hayes (Hayes, 2009), it was not possible to satisfactorily perform the model adjustment for phenol and for R-Benzene to obtain the evolution of their concentrations in the return water (Ma et al., 2018). These two families of compounds have higher solubility and the sampling times are inadequate to fit the physicochemical model parameters (Ma, 2018), so these compounds are not considered in the present work.
- A model for estimating the temporal evolution of return water volumes. In this case, it is modeled through an empirical expression adjusted to the available data (Ma et al., 2019).

Note that, although the pollutant concentrations in the produced water are higher than in the flowback fluid, differences in the volume of the return water lead to reach the highest concentrations in the storage pond during the first 2 months after hydraulic fracturing.

2.2. Pollutant concentrations in environmental compartments

In order to carry out a health risk assessment, concentrations of contaminants in the different environmental compartments (soil, groundwater and air) are necessary. These concentrations are then associated with different exposure pathways for humans. By combining these predicted concentrations with their toxicity values, the risk to human health associated with each pollutant in the return water is determined. This will allow the development of a risk classification of the pollutants by assessing them with respect to their corresponding threshold values.

The study of Ma et al. (2019) provides the concentration data for this work under three environmental scenarios (arid, semi-arid and humid). In this, an analytical two-phase transport model assuming an unsaturated environment was used. The model can weigh the impact of different parameters (e.g. recharge rate or K_{oc} value) on the pollutant concentrations obtained. The source term for pollutants was set as a leak in the wastewater storage system. A semi-buried tank-type reservoir with a leak in the buried part at a depth of 50 cm was considered, which resulted in a uniform source term within the unsaturated zone.

The flux from the unsaturated zone to the soil surface provides the mass flux rate (F_A) of pollutants to the atmosphere. The evolution of organic compounds presents in the return water, as a function of the solubilities and volatilities of the organic compounds involved, provides the soil concentration profiles (C_S).

Several processes determine the distribution in the atmosphere of VOCs released through the soil interface (F_A), as shown in Fig. 1 (Waitz et al., 1996):

- Boundary flux: transport from the soil to the atmosphere may be restricted by the existence of a stationary air layer at the atmosphere–soil interface (Schlichting and Gersten, 2017; Waitz et al., 1996). Transport within this layer is described by Fick's first diffusion law and the concentration gradient is a function of boundary layer thickness, h, in this case, with a selected value of 0.01 m (Jiang et al., 2012):

$$Flux = D_{air} \times (C_A - C_a)/h \tag{1}$$

where *Flux* is the diffusion flux of the compound under consideration (acetophenone; benzene; TEX; TMB; R-benzene NAPH; and PAHs – NAPH) (mg/(m^2·s)), C_A is its concentration at the surface of the vadose zone (ppm), C_a is its concentration in the mixed atmosphere (ppm), h is the thickness of the boundary layer (m), and D_{air} is the diffusion coefficient of the compound under consideration in the gas phase (m^2/s).

- Flux to the atmosphere: once VOCs reach the atmosphere above the stationary layer, they mix and migrate with the wind (ASTM, 2015). In this scenario, VOCs are diluted in the atmosphere, which can be calculated assuming horizontal and vertical mixing for an inexhaustible source. The dilution rate is based on the wind speed and mixing height, which depend on the air dispersion and atmospheric stability (Waitz et al., 1996). Assuming that VOCs are completely diluted in the inhalation zone and that the concentration is uniform within a given volume, the flux is given by Eq. (2) (Chen and Wu, 2007):

$$Flux = (V_{air} \times H)/W \times C_a \tag{2}$$

where V_{air} is the wind speed (m/s) in the mixed atmosphere, H is the vertical thickness (m) of the mixed atmosphere (taken as the height for worker inhalation), and W is the width (m) of the pollution source in the downwind direction.

When stationary conditions are reached, the net flux is zero (Eq. (3)), and the atmospheric chemical concentrations (C_a) can be calculated using Eq. (4). The default parameters for the calculation of the inhalation concentrations are listed in Table S1.

$$Flux = \frac{V_{air} \times H}{W} \times C_a = D_{air} \times \frac{C_A - C_a}{h} \tag{3}$$

$$C_a = C_A \times \frac{D_{air} \times W}{V_{air} \times H \times d + D_{air} \times W} \tag{4}$$

With respect to the concentration of contaminants in the soil (C_S), the results of the organic pollutant concentrations in soil, groundwater, and air show that virtually all of them are adsorbed within the unsaturated zone after the initial discharge period (that is, the first 10 days) under arid, semi-arid, and humid conditions. As time increases, more than 95% of the non-volatile organic chemicals will remain absorbed in the solid phase for decades. In contrast, volatile compounds migrate in the soil gas phase; however, their associated impacts on soil contamination cannot be ignored.

The scope of this work does not include groundwater risks assessment. However, this methodology can be applied in order to study the risks arising in the groundwater to human health once the pollutants reach the water table.

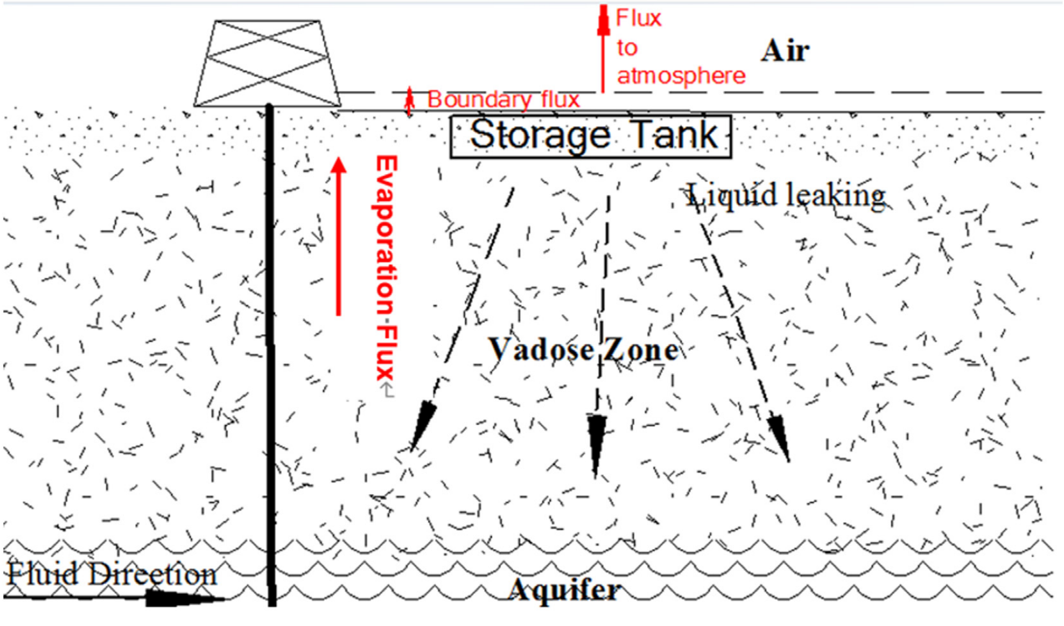

Fig. 1. Diagram of transport flows from the unsaturated zone to the atmosphere.

2.3. Probabilistic risk assessment

The main emphasis of our research is the identification of organic compounds in hydraulic fracturing wastewater that may pose human health risks through the atmosphere and soil. Environmental exposure pathways were taken as an analytical framework to describe, in general terms, the connections between contaminant sources and human health outcomes. This framework starts with the emission source, in this case a well pad and the associated infrastructure for storing return wastewater, which can lead to the leakage/emission of various pollutants to the surrounding soil, groundwater, and atmosphere. The pollutant concentrations in air, water, and soil resulting from these emissions determine the magnitude of human exposure through organs such as the nose, mouth, and skin, which specify the exposure pathways. Once these pathways are identified, it is possible to estimate the dose or amount of pollutants that enter the body in a given period. This dose, in turn, determines the health outcomes (Shonkoff et al., 2014).

Mathematical modelling for health risk assessment establishes the relationships between the pollutant source, exposure pathways, and potential risk. In this study, carcinogenic and non-carcinogenic risks associated with chronic exposure to VOCs and PAHs were considered for humid, semi-humid, and dry environmental scenarios (U.S. Environmental Protection Agency (EPA), 1996). Chronic toxicity via inhalation, ingestion, and dermal exposure routes is relevant for workers who may be exposed for several years while working in the shale gas exploration industry, and for the public living in the vicinity of the operation. The exposure pathways that can be considered for the public included (Wattenberg et al., 2015): (1) exposure via ingestion or inhalation of contaminated surface soil, or dermal contact with contaminated surface soil, (2) exposure via inhalation of airborne contamination, and (3) exposure via ingestion or inhalation of groundwater, or dermal contact with groundwater (U.S. Environmental Protection Agency (EPA), 2009, 2011a).

As mentioned in Section 2.2, only the pathways associated with surface soil and atmospheric contamination were considered in this study. The exposure models used to determine the amount of pollutant incorporated into an organism are shown in Table 1. Monte Carlo simulations were perform using 100,000 iterations to obtain the 50th and 95th percentile values for each risk distribution. The values of the input variables used in the Monte Carlo simulation are listed in Table S2.

Once the exposure to each pollutant had been estimated for each pathway, the associated carcinogenic and non-carcinogenic health risks were calculated using the Integrated Risk Information System (U.S. Environmental Protection Agency (EPA), 2021) to evaluate and understand the potential adverse effects. In this context, the IRIS provides toxicological indices for health effects resulting from chronic exposure to chemicals. The slope factor *(SF)* was used to determine the development of excess cancers in a receptor, while the chronic reference dose (*RfD*) and chronic reference concentration (*RfC*) for inhalation were used to determine the potential for a non-carcinogenic toxic effect. These values are listed in Table S3 for the different compounds considered. Subsequently, the hazard quotient (*HQ*, Eq. (5)) and carcinogenic risk (*CR*, Eq. (6)) were used to compare the risks associated with the assessed compounds. The *HQ* is defined as the ratio of exposure to the estimated daily exposure at which no adverse health effects are likely to occur (Durant et al., 2016), whereby a value of <1 indicates that the health risks are within safe limits. The *CR* value estimates the excess lifetime cancer risk, that is, the increased lifetime probability of developing cancer, and is calculated by multiplying the dose by a chemical-specific toxicity factor for each exposure pathway (*SF* in Eq. (6)). The US EPA standard risk threshold for a *CR* is $<10^{-6}$ (Durant et al., 2016; U.S. Environmental Protection Agency (EPA), 2015).

Table 1
Models for different exposure pathways.

Medium	Exposure pathway	Daily intake equation
Soil	Inhalation	$I_{soil-inhalation} = \frac{C_S \times IR \times ET \times EF \times ED}{BW \times AT \times PEF \times 365}$
	Dermal	$I_{soil-dermal} = \frac{C_S \times CF \times SA \times AF \times ABS \times ET \times EF \times ED}{BW \times AT \times 365}$
	Ingestion	$I_{soil-ingestion} = \frac{C_S \times IRS \times EF \times ED \times EF \times CF}{BW \times AT \times 365}$
	Total	$I_{soil} = I_{soil-inhalation} + I_{soil-dermal} + I_{soil-ingestion}$
Air	Inhalation	$I_{air-inhalation} = \frac{C_a \times IR \times ET \times EF \times ED}{BW \times AT \times 365}$

C_s – surface soil concentration; $C_{air\text{-}inhalation}$ – inhalation air concentration; *EF* – exposure frequency; *ED* – exposure duration; *AT* – average time; *BW* – body weight; *ET* – exploration time; *IR* – inhalation rate; *IRS* – ingestion rate; CF – unit conversion factor; *SA* – exposure skin surface area; *ABS* – dermal absorption factor; *PEF* – particle emission factor; $I_{soil\text{-}inhalation}$ – intake soil particle by inhalation; $I_{soil\text{-}dermal}$ – dermal absorb soil particle; $I_{soil\text{-}ingestion}$– intake soil particle by ingestion; $I_{soil\text{-}}$ – intake soil particle by all kinds of soil contact; $I_{air\text{-}inhalation}$ – air inhalation contamination.

As we dealt with the behaviours of chemical compounds grouped into eight categories (Ma et al., 2018, 2019), the mean *RfD*, *RfC,* and *SF* values for each category were considered. The chronic oral reference doses and *SFs* of the Risk Assessment Information System (RAIS; https://rais.ornl.gov) used for the risk assessment are shown in Table S3. The *RfC* values of toluene, ethylbenzene, and xylene are 5 mg/m^3, 1 mg/m^3, and 0.1 mg/m^3, respectively. This study used 0.1 mg/m^3 to ensure a conservative estimate of risk.

$$\text{Non-cancer } HQ = \frac{I}{RfD} \geq 1\ (oral)\ \ HQ = \frac{I}{RfC} \geq 1\ (inhalation) \tag{5}$$

$$\text{Cancer } CR = I \times SF \geq 10^{-6} \tag{6}$$

As data on the variation of the pollutant concentrations in the wastewater storage tank were available (Ma et al., 2019), the corresponding risks to human health could be obtained depending on the time of leakage. Accordingly, the cases in which the carcinogenic and non-carcinogenic risks exceeded the corresponding thresholds for the different exposure pathways could be determined. A sensitivity analysis (available from Supplementary Materials) was then carried out to determine the parameters with the greatest influence on the determined risks. The risk levels obtained for the different compounds were used along with information on exposure pathways and contaminant transport to define possible control and remediation measures to prevent carcinogenic and non-carcinogenic health risks.

Conservative criteria have been applied in this work from a risk management point of view. As is well known, the worst scenarios - from the point of view of oil spills in refineries and gas stations - are those associated with hidden leaks remaining for a long time. This is why the scenario considered is that of a hidden leak for a long period of time (maximum 30 years, associated with the definition of chronic risk). In this study, these assumptions lead to a source term that may produce contamination continuously, therefore using constant concentration value for human risk assessment.

In addition, processes than can lead to reductions in contaminant concentrations, such as biodegradation, photodegradation or other attenuation processes (Mallants et al., 2022) are not considered. Yet the goal of the study is placed within the context of risk management, from this point of view the non-consideration of this term introduces bias in a rational and feasible manner faced to improve safety. That is to say, an upper limit to the concentrations is being obtained within the limitations defined by the conservative risk regulations (Viscusi et al., 1997).

A sensitivity analysis was carried out to assess how the variability of each input parameters (e.g. pollutant concentration, exposure time, and inhalation rate) involved in the exposure pathways influenced the *HQ* calculations, and to determine the contribution of their uncertainties to the overall uncertainty. Hence, parameters contributing most significantly to the risk estimates and associated uncertainties could be detected, and data gaps could be assessed (Rasa et al., 2013; Lonati and Zanoni, 2013).

3. Results

For the exposure assessment, it was necessary to start with the pollutant concentrations in the soil (C_S) or air (C_a). The final C_a values (Table S4) were calculated using Eq. (3), which is based on the evolution of the surface concentration (C_A) in the gas phase (shown for different recharge rate conditions in Table S6) (Ma et al., 2018, 2019). Because the pollutant concentrations in the storage pond (C_A) change over time, Table S4 shows the results for C_a obtained for different leakage times. The pollutant concentrations in surface soil (C_S) are shown in Table S5 under different recharge rates and leakage times.

3.1. Air inhalation risks

The *HQ* and *CR* indicate the probability of non-carcinogenic and carcinogenic effects of pollutants, respectively. The exposure associated with a given organic compound depends on its behaviour in the unsaturated zone, which is linked to its physicochemical properties (e.g., solubility and volatility) (Ma et al., 2019). Therefore, the analysis of the *HQ* results for the inhalation route was separated according to whether the compounds are volatile or non-volatile (the latter including semi-volatile). The pollutant concentrations under different recharge rates and leakage times used to calculate the quantitative chronic exposure *HQ* are shown in Table S4.

3.1.1. Non-carcinogenic risks

3.1.1.1. Non-volatile and semi-volatile compounds. The inhalation *HQ* values associated with non-volatile compounds (see Fig. 2) were well below the permitted limits owing to their behaviours after the spill started in the vadose zone. Acetophenone is a good example of an organic compound with relatively high solubility and low volatility. The temporal variation of the acetophenone concentration in the unsaturated zone (Ma et al., 2019) indicates that it was almost entirely absorbed by soil organic matter during the initial phase. Over time, the acetophenone concentration would have moved towards the interfaces with the saturated zone and atmosphere. However, as its Henry's constant (K_H) value is very small; its diffusion into the atmosphere would have been very slow.

Compounds belonging to the semi-volatile group were PAHs, which comprise fused aromatic rings and have low solubilities that tend to decrease with an increase in the number of rings. We focused on NAPH, which has a Henry's constant (K_H) of 1.8×10^{-2} and is the most volatile PAH. The *RfC* of NAPH is 0.003, which means that low concentrations can cause health problems. In an arid vadose zone, a plume of NAPH contamination will reach the interface with the atmosphere in the long term, and for the maximum concentration values, the probability of exceeding the permissible limits is 95%. In the case of PAHs - NAPH (i.e. PAHs excluding NAPH), the risk due to inhalation was found to be negligible. This related to the fact that most of these compounds are initially absorbed in the solid phase, and then dissolve in groundwater over time and eventually migrate into the aquifer.

3.1.1.2. Volatile organic compounds. The *HQ* value characterises the potential non-carcinogenic risk associated with inhalation of VOCs. The results for benzene, TEX, and TMB are shown in Fig. 3, where the *HQ* values are shown for different times.

For VOCs, gaseous diffusion is usually the dominant transport mechanism in dry soils. In such cases, the migration rate is directly proportional to the recharge rate and inversely proportional to the volatility. Dissolved organic chemicals are preferentially adsorbed at the soil interface during the movement of a contaminant plume associated with wastewater discharge. They are then adsorbed/desorbed and/or volatilised to other phases depending on their volatilities until they reach the upper and lower limits of the vadose zone. Because the evaporation of VOCs in the gas phase is more efficient than their dissolution in water, there will be a higher leakage rate at the interface with the atmosphere.

In general, the *HQ*s of VOCs for the inhalation exposure route of contaminated air increased rapidly (Fig. 3) and exceeded the acceptable limit within a short time. Under arid conditions, the *HQ* values of benzene and TEX exceeded the threshold by a factor of 1000 and 500, respectively,

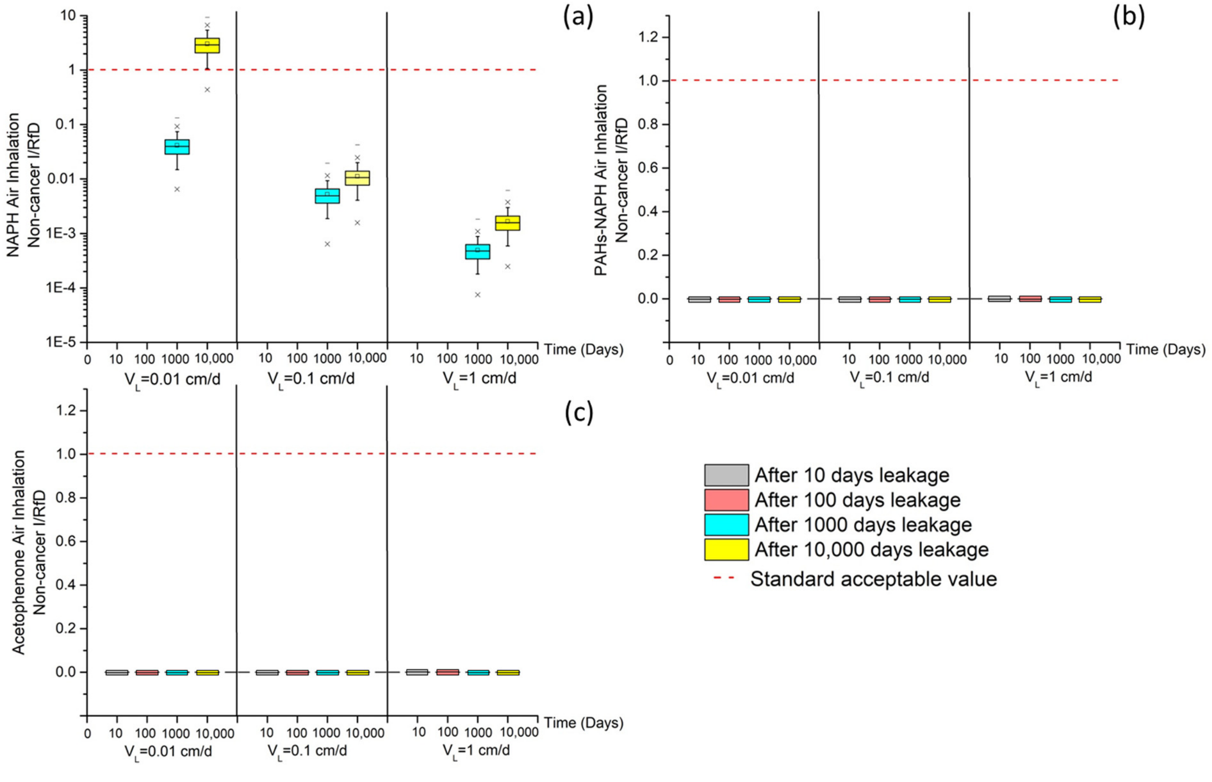

Fig. 2. Inhalation hazard quotient (non-cancer) results for non-volatile and semi-VOCs compounds. The HQ value for PAHs-NAPH (b) and Acetophenone (c) is below 10^{-5}. For NAPH (a) the grey, red, green and yellow boxes indicate the results 10-, 100-, 1000- and 10,000-days from the spill, respectively. Box range is from 25% to 75% and whistler range is from 5% to 95% of hazard quotient result. The "–" types represent the minimum or maximum percentile, and the 'x' types correspond to the 1% or 99% percentile. The red dashed line is the standard acceptable level.

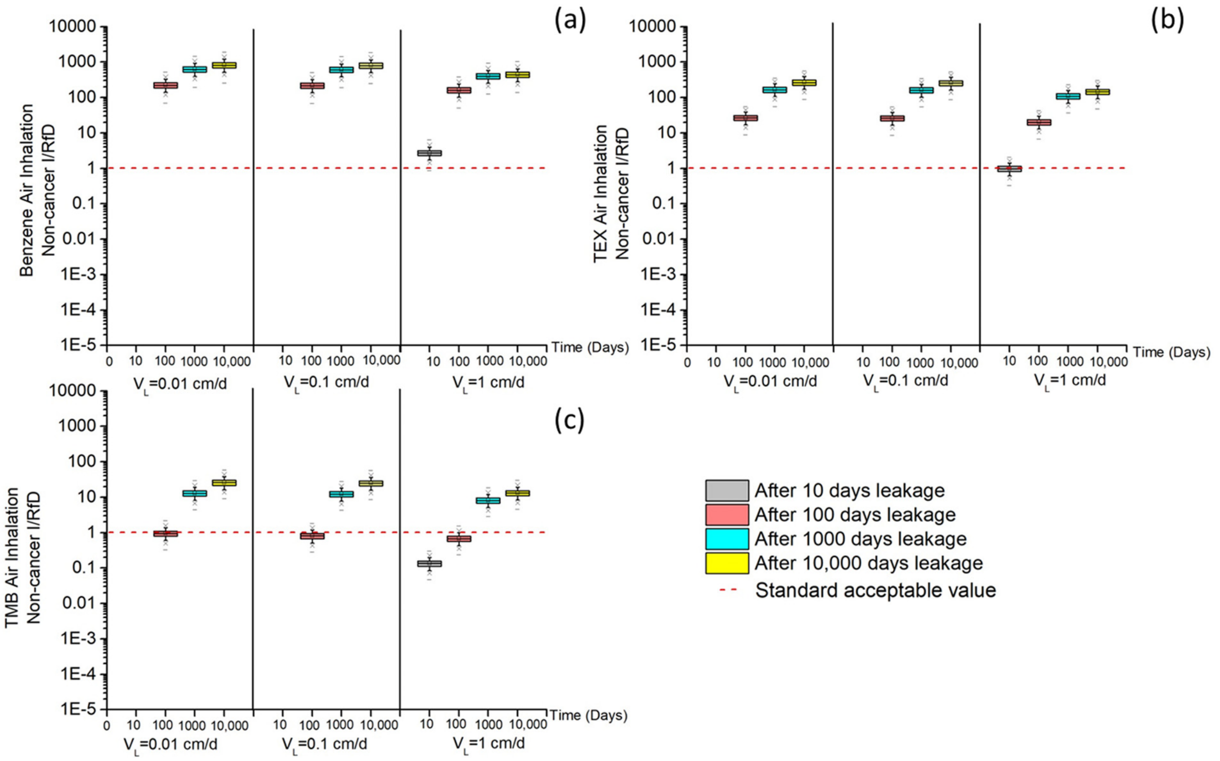

Fig. 3. Exposure by inhalation of pollutants in the atmosphere. Hazard quotient results for volatile organic compounds (Benzene (a), TEX (b) and TMB (c)). The grey, red, green and yellow boxes indicate the results 10-, 100-, 1000- and 10,000-days from the spill, respectively. Box range is from 25% to 75% and whistler range is from 5% to 95% of hazard quotient result. The "–" types represent the minimum or maximum percentile, and the 'x' types correspond to the 1% or 99% percentile. The red dashed line is the standard acceptable level.

thus leading to high toxicities and a potential risk to human health and the environment. The *HQ* of TMB was >1 after 100 days of seepage; however, different scenarios, such as increased precipitation, would affect the *HQ* value and decrease the probability of health damage.

The results of the sensitivity analysis are shown in Fig. S1 and indicate that the air pollutant concentration is the parameter that has the largest effect on the estimated risks.

3.1.2. Carcinogenic risks

The high *CR* values were mainly associated with the assessed VOCs, which have high volatilities in the atmosphere. For the inhalation of air, benzene had the highest *CR* values, which ranged from 10^{-4} to 10^{-1} depending on the recharge rate (Fig. 4), thus exceeding the threshold of 10^{-6} (US EPA, designated risk severity indicator) by several orders of magnitude. After a spill, the carcinogenic risk of benzene increased rapidly during the first 3 years and then tends to stabilize gradually according to the transport dynamics of the system. Ultimately, most of the benzene that was initially present in the spill water was transferred to the atmosphere. Therefore, the *CR* of benzene exhibited an increasing trend as the spill progressed. Although rainfall could slightly reduce the high benzene concentration in air, benzene was still the compound that posed the highest risk when considering the estimated maximum concentrations.

Compared with the other compounds considered here, TEX, TMB, and NAPH had lower *CR* values. In addition, some studies have reported limited or no carcinogenic potential for toluene and xylene (i.e. denoted by T and X in TEX) (Masekameni et al., 2018). Thus, we did not assess these substances in terms of carcinogenic risk.

Additionally, sensitivity analyses were performed to assess the relative contributions of individual *CR* values (i.e. of each compound) to the total *CR* and the influence of each model parameter on the variance of the estimated risk (Lonati and Zanoni, 2012). Fig. S2 shows the influence of each model parameter on the risk associated with the inhalation exposure route. As in the previous case of non-carcinogenic risk, the dominant parameter in the variance of the *CR* was the pollutant concentration in air, C_a, contributing 29.1% for benzene. Therefore, the use of appropriate technology to reduce the pollutant concentrations in the storage tank would be the best way to reduce the corresponding risks. For example, by emptying the storage tank and taking the water for treatment after the first 10–100 days when, as seen in the article by Ma (Ma et al., 2019), the highest concentration values are reached.

In addition, for working personnel, reducing the exposure time/frequency and introducing mandatory safety precautions would also be effective methods to reduce potential harm.

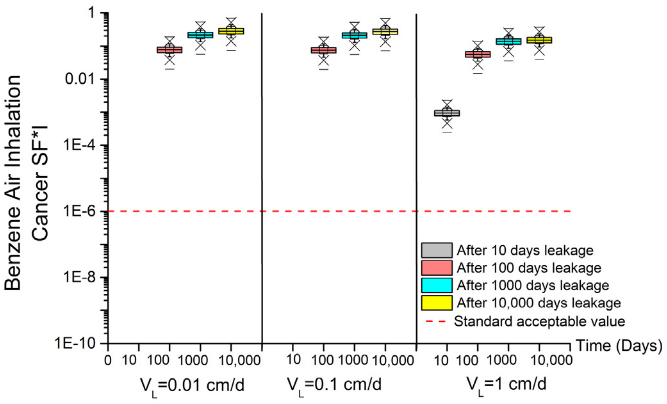

Fig. 4. Inhalation exposure carcinogenic risk results for Benzene. The grey, red, green and yellow boxes indicate the results 10-, 100-, 1000- and 10,000-days from the spill, respectively. Box range is from 25% to 75% and whistler range is from 5% to 95% of hazard quotient result. The "–" types represent the minimum or maximum percentile, and the 'x' types correspond to the 1% or 99% percentile. The red dashed line is the standard acceptable level (10^{-6}).

3.2. Surface soil exposure risks

Another possible route of exposure to contaminants is contact with surface soil. Pollutant concentrations in soil will determine the magnitude of human exposure through organs such as the nose, mouth, and skin. For the calculation of exposure, it was assumed that local residents were exposed to surface soil (0 cm depth) and that the contaminants present in the soil were absorbed through the skin and ingested/inhaled orally.

Thus, from the initial pollutant concentrations in soil, and depending on the route considered (inhalation, ingestion, or dermal contact with soil), the non-carcinogenic risks (*HQ*s) were estimated (see Fig. 5). The *HQ*s ranged from 10^{-6} to 10^{-3}, which were orders of magnitude below the acceptable threshold of 1. This is because most of the assessed chemicals tend to volatilise in the atmosphere, while only a minor percentage is absorbed by surface soil. The *HQ*s for benzene, TEX, and TMB for different exposure routes associated with soil contact are shown in Fig. 5 and Fig. 6. Because solid particles are widely dispersed in the atmosphere (the particulate emission factor value considered was 10^{-9} m^3/kg (U.S. Environmental Protection Agency (EPA), 2011a), the concentration available at the surface for the inhalation pathway was much lower than the concentration in soil, and the likelihood of inhaling pollutants was greatly reduced, thus minimising the risk associated with soil inhalation. If we compare the risks associated with the different exposure routes of the selected substances, the greatest concern in terms of potential harm was for dermal exposure. This is because, for company personnel, the entire skin surface is considered that can come into direct contact with contaminated soil.

For compounds with lower volatilities than VOCs (acetophenone, NAPH, and PAHs excluding NAPH), their concentrations can be considered negligible in the solid phase at the surface (Ma et al., 2019).

From the results obtained, the greatest health risk was found to be associated with air pollution rather than exposure to contaminated soil. Therefore, increasing ventilation in the affected area may be the most effective method for removing VOCs in the short term.

Organic compounds are also associated with cancer risk. In this study, the *CR* was estimated from the *SF*, which quantitatively defines the dose–response relationship. The *SF* is defined probabilistically and represents an upper bound, approximating to a 95% confidence limit, of the increased cancer risk from ingestion or inhalation of a carcinogen. A *CR* of $<10^{-6}$ is considered to be below the permissible limit. Similar to the non-cancer risk assessment, the *CR* values for benzene with respect to soil contact ranged from 10^{-10} to 10^{-7} (see Fig. 7); hence, they were below the acceptable *CR* threshold. As mentioned, this is because benzene tends to volatilise in the atmosphere, and only a minor percentage is absorbed by the soil surface.

4. Discussion

In this study, the *HQ* and *CR* are indicators of non-carcinogenic and carcinogenic risks, respectively. When used in a risk assessment, the *HQ* and *CR* values indicate how and when public health is most likely to be affected, and inform risk prevention strategies aimed at effectively reducing negative health effects (McKenzie et al., 2012). In this work, all parameters for the calculation of the *HQ* and *CR* were described using probability density functions. Uncertainties were propagated through the assessment model using Monte Carlo simulations, resulting in pollutant concentrations in air and surface soil and a health risk assessment through different exposure pathways expressed in terms of probability distributions.

Both non-carcinogenic and carcinogenic risks were estimated for inhalation exposure to air pollution. The results for VOCs showed that non-carcinogenic and carcinogenic risks both increased rapidly over time in

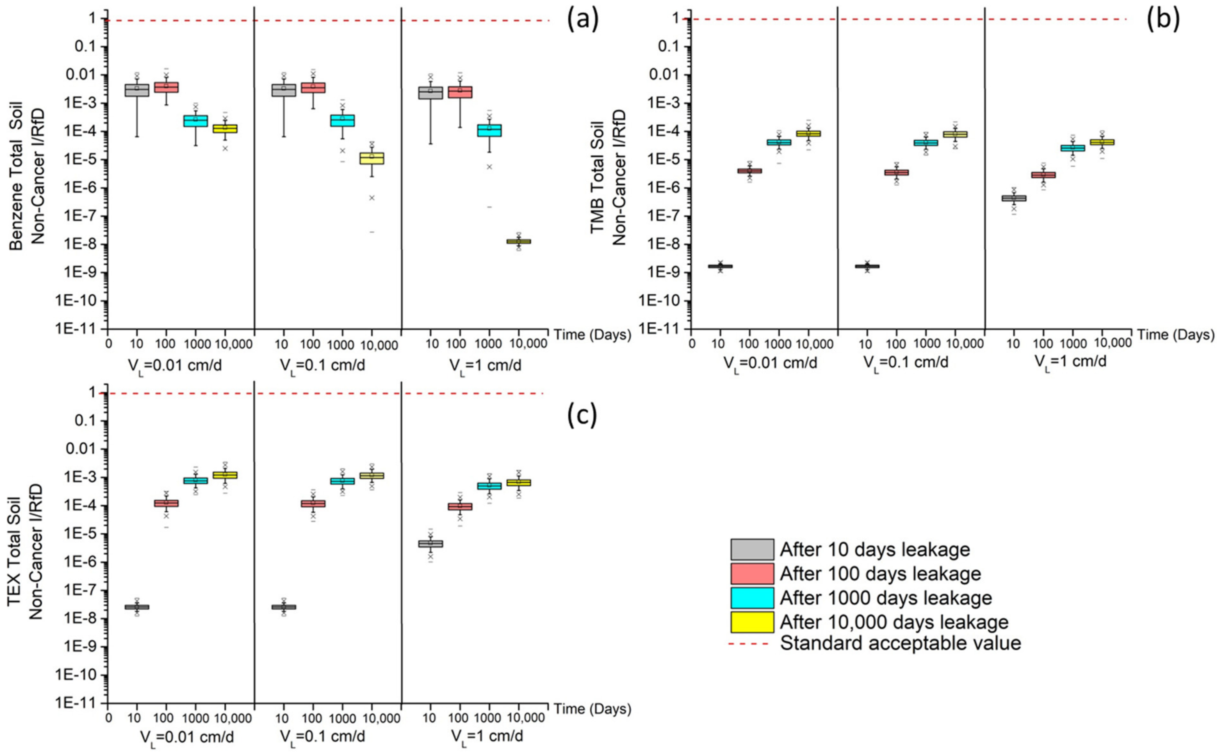

Fig. 5. Total soil exposure non-cancer risk results estimated for volatile organic compounds (Benzene (a), TEX (b) and TMB (c)). The black, blue and green lines indicate the results for the recharge rate conditions of 0.01 cm/d, 0.1 cm/d and 1 cm/d, respectively. The solid line represents the 50th percentile of the hazard quotient result and the dashed line the 95% percentile. The red line is the standard acceptable level and the value is 1.0. The grey, red, green and yellow boxes indicate the results after 10, 100, 1000 and 10,000 days from the spill, respectively. The boxes range from 25% to 75% and the whistles range from 5% to 95% of the hazard quotient result. The '-' types represent the minimum or maximum percentile and the 'x' types correspond to the 1% or 99% percentile. The red dashed line is the standard acceptable level.

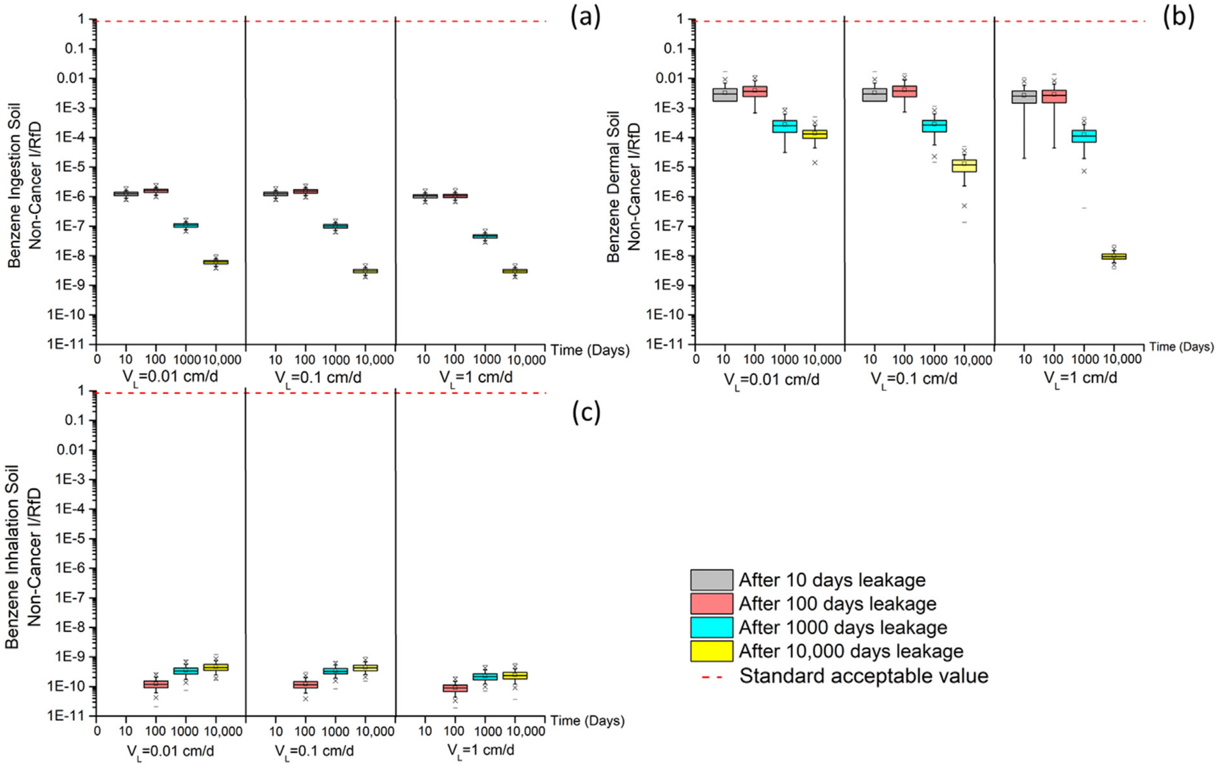

Fig. 6. Hazard quotient (non-cancer) of Benzene for different forms of soil exposure (Dermal (a), Ingestion (b) and inhalation (c)). The results are plotted for recharge rates of 0.01 cm/d, 0.1 cm/d and 1 cm/d, respectively. The grey, red, green and yellow boxes indicate the results 10-, 100-, 1000- and 10,000-days from the spill, respectively. The box range from 25% to 75% and the whistler range from 5% to 95% of hazard quotient result. The "–" types represent the minimum or maximum percentile, and the 'x' types correspond to the 1% or 99% percentile. The red dashed line is the standard acceptable level.

all scenarios, irrespective of the different recharge rates considered, leading to estimates that exceeded the stipulated thresholds by several orders of magnitude. These results indicate that this pathway may pose the highest risk to human health with respect to VOCs. The results of the sensitivity analysis revealed that in almost all cases, the parameter that contributed most to the *HQ* and *CR* was the pollutant concentration in air, followed by the exposure time. Therefore, the use of appropriate technology to reduce the pollutant concentrations in the storage tank is the best way to minimise health risks. In addition, for personnel working at the site, risks could be lowered by reducing the time/frequency of exposure and by introducing mandatory safety precautions. For NAPH, a semi-volatile compound, the *HQ* (non-carcinogenic risk) only exceeded 1 at the upper confidence limit of the 95th percentile. For acetophenone and PAHs - NAPH, the inhalation risks were negligible because these substances were mainly absorbed in the solid phase.

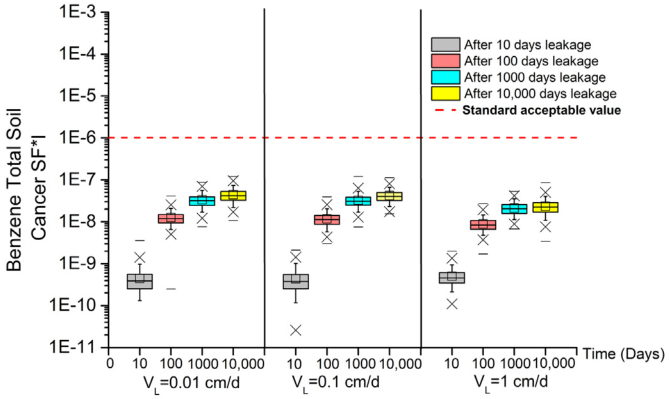

Fig. 7. Total soil exposure carcinogenic risk for benzene. The results are plotted for recharge rates of 0.01 cm/d, 0.1 cm/d and 1 cm/d, respectively. The grey, red, green and yellow boxes indicate the results 10-, 100-, 1000- and 10,000-days from the spill, respectively. The box range from 25% to 75% and the whistler range from 5% to 95% of hazard quotient result. The "–" types represent the minimum or maximum percentile, and the 'x' types correspond to the 1% or 99% percentile. The red dashed line is the standard acceptable level (10^{-6}).

Regarding the exposure pathway of surface soil, the results of the Monte Carlo simulations showed that even for the highest percentiles of the distributions, the *HQ* and *CR* values were several orders of magnitude below the threshold levels. A detailed analysis revealed the following. (1) Because the simulated leakage occurred underground and in the unsaturated zone, the dissolved organic compounds were adsorbed/desorbed and/or volatilised within the unsaturated zone of the soil until they reached the water table or surface. Thus, the solid particles at the surface could continuously adsorb contaminants from the gas phase of the vadose zone until the entire contamination plume disappeared. Studies (Ma et al., 2019) have shown that the concentrations of all of the studied VOCs (i.e. benzene, TEX, and TMB) tend to increase rapidly in the surface soil layer and peak after approximately 100 days. Subsequently, the concentrations decrease until a dynamic equilibrium between the solid and gas phases is reached because desorption to the atmosphere dominates. (2) Benzene has a higher dissolution capacity than other organic compounds present in return water; hence, surface soil in humid areas is associated with a higher risk with respect to benzene than other compounds (e.g. TEX and TMB) because precipitation prevents its volatilization to the atmosphere. (3) Of the different exposure pathways for soil, the risk from inhalation of soil particles is minimal because the particulate emission factor value of 10^9 m^3/kg causes solid particles on the surface to be widely dispersed in the atmosphere. This greatly reduces pollutant concentrations in the upper soil layer compared with those at depth. Comparing the results for the different compounds for the three exposure routes considered, dermal exposure presented the highest risk because some personnel come into direct contact with contaminated soil, while ingestion was ranked second and inhalation last.

In addition to the risks associated with pollutant concentrations in surface soil, risks also exist for the unsaturated zone of soil. Considering the vertical transport dynamics of organic compounds in the vadose zone (Ma et al., 2019), all the studied compounds would be preferentially adsorbed at the soil interface if a leak occurred, and would subsequently spread to deeper areas or evaporate into the gas phase. Therefore, the pollutant concentrations in the solid phase were significantly higher than those in other phases over a long period, and may therefore be associated with a higher level of risk in the surrounding environment.

Although the initial NAPH concentration in air was negligible, the NAPH present in the vadose zone moved into the atmosphere over time, such that the risk level exceeded the threshold after 1000–10,000 days. In the case of non-volatile or semi-volatile compounds, which diffuse very slowly into the atmosphere due to their K_H values, the risks were all at least one order of magnitude lower than the threshold values.

5. Conclusion

The application of the physicochemical models developed and implemented in this study allow estimating the temporal evolution of the different pollutants in the storage pond and, because of this, making and a prior analysis of the evolution of the risk over time.

The model fitted with the data from the Marcellus Formation shows that the carcinogenic and non-carcinogenic risks for the inhalation exposure route of VOCs increase rapidly over time and exceed the acceptable thresholds by several orders of magnitude in all scenarios, irrespective of the different recharge rates considered. In addition, sensitivity analysis reflects the importance of concentration and exposure time in risk estimation. Therefore, reducing the pollutant concentrations in the storage tank by emptying this and taking the water for treatment after the first 10–100 days, when the highest concentrations are reached, would be an appropriate way to reduce the corresponding risks.

In contrast, the inhalation risks associated with acetophenone and PAHs-NAPH are one order of magnitude lower than the threshold values. This is related to the fact that such compounds diffuse very slowly into the atmosphere because of both their K_H values and their low volatilization in the gas phase. As a compound that poses a high risk, the NAPH present in the vadose zone move into the atmosphere over time, increasing the initially low concentration in air after 1000–10,000 days to a level that exceeded the acceptable threshold.

With respect to the exposure pathways from surface soil particles, the results of the Monte Carlo simulations show that, even for the highest percentiles of the distributions, the carcinogenic and non-carcinogenic risks are several orders of magnitude below the threshold levels. This can be explained by the fact that the simulated leakage occurred 10 cm below the ground surface in the unsaturated zone. From this point on, the dissolved organic compounds are adsorbed/desorbed and/or volatilised to the different phases of the unsaturated zone of the soil until they reach the water table or surface.

Regarding the influence of environmental scenarios, the highest dissolution capacity of benzene compared with the other organic compounds present in the return water means that surface soil in humid scenarios are associated with the highest risks with respect to benzene.

Additionally, since all the studied compounds are adsorbed preferentially at the unsaturated soil interface following a leak, the pollutant concentrations in this phase are significantly higher than those in other phases over a long period, and therefore that means a higher level of risk in the surrounding environment.

From the point of view of risk management associated with the type of leaks considered in this study, the results show that the greatest risks are those due to inhalation and that, in arid and semi-arid environments, there are about 100 days to detect the leak and act before the carcinogenic and non-carcinogenic risk levels reach unacceptable values. This time period is reduced by an order of magnitude for humid environments.

The carcinogenic and non-carcinogenic risks associated with soil in any case reach unacceptable values within the scenarios analysed. However, the fact that benzene is the only one that decreases its risk in soil after 100 days, the more rapidly the more humid the environment, indicates that from this period onwards there would be a migration of benzene to adjacent environmental compartments.

In short, these studies represent a risk management tool for both pond storages and the different environmental compartments in the event of a leakage, since it allows a risk prioritization by estimating the times in which the different compounds will reach risk concentration to health and environment. That is why this approach can help in determining the precautions and preventive measures needed to successfully manage and regulate the environmental impacts of shale gas developments, and serve as a first approximation to guide subsequent efforts to prevent the materialization of risks and minimise the health risks to local residents and workers.

CRediT authorship contribution statement

Lanting Ma: Conceptualization, Formal analysis, Investigation, Writing – original draft. **Antonio Hurtado:** Methodology, Validation, Writing – review & editing. **Sonsoles Eguilior:** Methodology, Software, Writing – review & editing. **Juan F. Llamas Borrajo:** Supervision, Validation, Resources.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.scitotenv.2022.153586.

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